Chemisches Recycling von Polyestern, Polycarbonaten und Polyamiden mit homogenen Katalysatoren

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List of abbreviations

Bmim	1-butyl-3-methyl-1H-imidazol-3-ium
BPA	bisphenol A
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DMAP	4-(dimethylamino)pyridine
DMC	dimethyl carbonate
DMSO	dimethyl sulfoxide
DMT	dimethyl benzene-1,4-dicarboxylate
DPC	diphenyl carbonate
DSC	differential scanning calorimetry
EG	ethylene glycol
ESI	electro-spray ionization
GC	gas chromatography
GPC	gel permeation chromatography
HMF	5-(hydroxymethyl)furan-2-carbaldehyde
3HB	3-hydroxybutyrate
3HV	3-hydroxyvalerate
Im	imidazole
MALDI	matrix-assisted laser desorption/ionization
MIMPS	3-methyl-1-(3-sulfopropyl)-1H-imidazol-3-ium
MS	mass spectrometry
NHC	*N*-heterocyclic carbene
Oct	2-ethyl hexanoate
PA	polyamide
PBAC	poly(bisphenol A carbonate)
PBS	poly(butylene succinate)
PCL	poly(ε-caprolactone)
PEF	poly(ethylene furanoate)
PEG	poly(ethylene glycol)
PET	poly(ethylene terephthalate)
PHA	poly(hydroxy alkanoate)
PLA	poly(lactide)
PMMA	poly(methyl methacrylate)
POM	poly(oxymethylene)
PP	poly(propylene)

PS	poly(styrene)
PTFE	poly(1,1,2,2-tetrafluoroethylene)
PUR	polyurethane
PVC	poly(vinyl chloride)
RCD	ring closing depolymerization
ROP	ring opening polymerization
SBA-15	Santa Barbara Amorphous-15
TBA	tetrabutylammonium
TBD	1,5,7-triazabicyclo(4.4.0)dec-5-en
TOF	turnover frequency
TPA	benzene-1,4-dicarboxylic acid

1. Zusammenfassung

Im Rahmen der Arbeit wurden Methoden zum chemischen Recycling mit Hilfe von Depolymerisation-Polymerisation-Prozessen von industriell relevanten Polymeren untersucht. Hierbei lag der Fokus insbesondere auf den Depolymerisationsreaktionen. Für die Polymere Poly(bisphenol A carbonat), Poly(propylencarbonat), Poly(lactid), Poly(ethylenterephthalat), Poly(3-hydroxybuttersäure), Poly(ethylenfuranoat), Poly(ε-caprolacton) und Nylon 6 wurden verschiedenste Reaktionsparameter, wie beispielsweise Katalysatoren, Katalysatorbeladung, Depolymerisationsreagenz und deren Einfluss auf die Depolymerisationsreaktion untersucht. Außerdem wurden die Reaktionen, sofern vorhanden, an Alltagsgegenständen getestet.

Zur Depolymerisation von **Poly(bisphenol A carbonat)** wurden als Reagenzien Ac_2O, MeOH, PhOH und H_2 eingesetzt. Ac_2O in Kombination mit katalytischen Mengen 4-(Dimethylamino)pyridin führten zu hohen Ausbeuten an Bisphenol A Diacetat. 4-(Dimethylamino)pyridin zeigte zudem gute Ergebnisse für die Depolymerisation mit MeOH (TOF von 1164 h^{-1}). Interessanterweise offenbarte KF (TOF von 1844 h^{-1}) eine ähnliche Aktivität wie das vergleichsweise teure 4-(Dimethylamino)pyridin. Darauf aufbauend war es möglich, zum ersten Mal durch Phenolyse Poly(bisphenol A carbonat) mithilfe von KF oder 4-(Dimethylamino)pyridin abzubauen und daraus direkt die Monomere für die industrielle Polymerisation zu erhalten. Die katalytische Hydrierung der Carbonatfunktion in Poly(bisphenol A carbonat) zu Methanol wurde anhand von verschiedenen Katalysatorsystemen basierend auf Ruthenium und Eisen untersucht. Die Verwendung des Milstein-Katalysators erforderte zwar hohe Katalysatorbeladungen (2.5-5 mol-%), aber die Reaktion lief auch bei geringem H_2-Druck (10 bar) noch ab. Unter Verwendung des Katalysatorsystems $[RuClH(CO)(PPh_3)_3]/H_2NCH_2CH_2P\textit{i}Pr_2/KO\textit{t}Bu$, das keine aufwendige Katalysatorsynthese erfordert, konnten hohe Ausbeuten unter Verwendung von mindestens 1 mol-% nach 24 h erzielt werden. Es wurden jedoch deutlich verminderte Ausbeuten beobachtet, wenn Alltagsgegenstände depolymerisiert wurden. Der Ru-MACHO-BH Präkatalysator konnte bereits bei einem Wasserstoffdruck von 2 bar Poly(bisphenol A carbonat) abbauen und es waren nur maximal 0.5 mol-% erforderlich. Außerdem wurde die Ausbeute nicht maßgeblich durch Additive in Alltagsgegenständen beeinflusst. Die Hydrierung mittels eines strukturell ähnlichen Eisen-Präkatalysators erforderte jedoch verglichen mit dem Ru-MACHO-System höhere Katalysatorbeladungen, um vergleichbare Ausbeute zu erzielen.

Das aliphatische **Poly(propylencarbonat)** konnte selektiv entweder mittels NaOAc-katalysierter Methanolyse zu 1,2-Propandiol und Dimethylcarbonat oder durch $Zn(OAc)_2$-katalysierter ringschließender Depolymerization zu 1,2-Propylencarbonat abgebaut werden.

Zudem konnte die Hydrierung zu 1,2-Propandiol und Methanol mithilfe eines Eisen-Präkatalysators gezeigt werden.

Poly(lactid) wurde mithilfe von der Reagenzien MeOH oder H_2 depolymerisiert. Zudem wurde die ringschließende Depolymerisation zu L-Lactid untersucht. Analog zu Poly(bisphenol A carbonat) konnte für die Methanolyse von Poly(lactid) eine erhöhte Aktivität für KF (TOF von 816 h^{-1}) gegenüber 4-(Dimethylamino)pyridin (TOF von 187 h^{-1}) erzielt werden. Als weitaus aktivere Katalysatoren stellten sich Bi(subsalicylat) und $Sn(Oct)_2$ heraus. Letzteres ist mit einer hervorragenden TOF von bis zu 39600 h^{-1} der bislang aktivste literaturbekannte Katalysator für diese Anwendung. Desweiteren ergab die Hydrierung von Poly(lactid) katalysiert durch den Ru-MACHO-BH Präkatalysator hohe Ausbeuten an 1,2-Propandiol. In Abwesenheit von Reagenzien konnte aus Poly(lactid) mittels RCD direkt L-Lactid mit hohen Ausbeuten erhalten werden, wobei Zn(II)-Salze bei Temperaturen über 180 °C eingesetzt wurden. Allerdings konnte eine Racemisierung nicht vollständig verhindert werden.

Poly(ethylenterephthalat), Poly(ethylenfuranoat), Poly(3-hydroxybuttersäure) und **Poly(ε-caprolacton)** wurden ebenfalls mittels Methanolyse unter Zn(II)-Katalyse abgebaut. Aufgrund der schlechten Löslichkeit von Poly(ethylenterephthalat)in MeOH, war CH_2Cl_2 als zusätzliches Lösungsmittel erforderlich, wohingegen Poly(ethylenfuranoat), Poly(3-hydroxybuttersäure) und Poly(ε-caprolacton) ohne CH_2Cl_2 abgebaut werden konnten.

Im Rahmen einer Untersuchung der ringschließenden Depolymerisation von **Nylon 6** in Ac_2O zu *N*-Acetylcaprolactam in hohen Ausbeuten, konnten mithilfe der Nebenprodukte eine plausible Reaktionssequenz ermittelt werden. Zudem wurde das erhaltene Produkt als mildes Acetylierungsreagenz für ein Amin eingesetzt.

2. Abstract

Within this thesis methods for the chemical recycling using a depolymerization-polymerization processes. The focus here was particularly on the depolymerization reactions. For the polymers poly(bisphenol A carbonate), poly(propylene carbonate), poly(lactide), poly(ethylene terephthalat), poly(3-hydroxybutyrate), poly(ethylene 2,5-furandicarboxylate), poly(ε-caprolactone) and Nylon 6 different reaction parameters, for instance catalysts, catalyst loading, depolymerization reagent and their influence on the depolymerization were investigated. Furthermore, if available, plastic commodities were subjected to depolymerization.

For the depolymerization of **poly(bisphenol A carbonate)** the reagents Ac_2O, MeOH, PhOH und H_2 were successfully applied. Ac_2O in combination with catalytic amounts of 4-(dimethylamino)pyridin allowed for high yields of the monomer bisphenol A diacetate. 4-(dimethylamino)pyridin showed good results for the depolymerization with MeOH (TOF von 1164 h^{-1}). Interestingly, KF (TOF von 1844 h^{-1}) revealed a comparable activity than the more expensive 4-(dimethylamino)pyridine. Consecutively, the polymer could be degraded by phenolysis with the aid of KF or 4-(dimethylamino)pyridine as catalysts to obtain the monomers for industrial polymerization in a straightforward fashion. The catalytic hydrogenation of the carbonate function in poly(bisphenol A carbonate) was investigated by means of different catalyst systems based on ruthenium and iron. The application of the Milstein-catalyst required required high catalyst loadings (2.5-5 mol%), but the reaction could be accomplished at low hydrogen pressure (10 bar). Applying the catalyst system $[RuClH(CO)(PPh_3)_3]/H_2NCH_2CH_2P\textit{i}Pr_2/KO\textit{t}Bu$, which does not necessitate an extensive synthesis, high yields of bisphenol A were realized with only 1 mol% after 24 h. However, diminished yields were observed when this system was applied to commodity goods. As an alternative, the Ru-MACHO-BH precatalyst readily depolymerizes poly(bisphenol A carbonate) at 2 bar hydrogen pressure using a low loading of 0.5 mol%. The yield was not significantly affected when commodity goods were depolymerized. The hydrogenation with a structurally similar iron precatalyst required higher catalyst loading compared to the Ru-MACHO-BH precatalyst to obtain comparable yields.

The aliphatic **poly(propylene carbonate)** was selectively converted either by NaOAc-catalyzed methanolysis to 1,2-propanediol and dimethyl carbonate or by $Zn(OAc)_2$-catalyzed ring closing depolymerization to 1,2-propylene carbonate. In addition, its hydrogenation with an iron precatalyst was demonstrated.

Poly(lactide) was depolymerized with the reagents MeOH, H_2 or by ring closing depolymerization. As observed for poly(bisphenol A carbonate), KF (TOF of 816 h^{-1}) was more active than 4-(dimethylamino)pyridin (TOF of 187 h^{-1}) in the methanolysis. By far more active catalyst were displayed by Bi(subsalicylat) and $Sn(Oct)_2$. The latter is with an excellent TOF of 39600 h^{-1} the to date most active catalyst for this application. Furthermore, the hydrogenation of poly(lactide) was accomplished by the robust Ru-MACHO-BH precatalyst to furnish high yields of 1,2-propanediol. In the absence of reagents, lactide could by obtained directly from poly(lactide) using Zn(II)-salts as catalysts above 180 °C. However, racemization could not be fully prevented.

Poly(ethylene terephthalate), poly(ethylene furanoate), poly(3-hydroxybutyrate) and **poly(ε-caprolacton)** were depolymerized with MeOH using Zn(II) catalysis. Due to the poor solubility of poly(ethylene terephthalate) in MeOH, CH_2Cl_2 was required as additional solvent, whereas poly(ethylene furanoate), poly(3-hydroxybutyrate) and poly(ε-caprolacton) were depolymerized without CH_2Cl_2.

An investigation of the ring closing depolymerization of **Nylon 6** in Ac_2O led to high yields of *N*-acetylcaprolactam. Based on the observed side products a plausible underlying reaction sequence could be identified. Moreover, the obtained product was used as a mild acetylation reagent for an amine.

3. Introduction

3.1 Plastics

The history and development of humankind has been mainly affected by the resources and materials which were accessible in the time periods. For instance, the historical importance of materials is underlined by the naming of time periods (e.g. stone age, iron age) with the current one being plausibly referred to as plastic age.[1] The first reported synthetic polymer is poly(styrene) (PS) which was first prepared in 1839 by polymerization of styrene in air.[2] However, the first commercially available synthetic polymer (Bakelite) was patented in 1909.[3] A deeper understanding of the concept of polymerization can be assigned to Staudinger's introduction of the word "macromolecule" in 1920[4] which defined this new class of substance as large covalently bond molecules.[5] The work of Staudinger, who received the Nobel Prize in 1953, paved the way for more sophisticated approaches towards synthetic polymers. Later, their unique physical and chemical properties, that are in stark contrast to their corresponding monomers, led to applications as materials. Driven by the urge of the military for high performance materials during World War II a variety of plastics have been commercialized (e.g. poly(isoprene) for tires, polyamides (PA) for parachutes, poly(methyl methacrylate) (PMMA) for synthetic glas). Until now, a steady increase in production volume can be observed (Figure 1) and it was estimated that an overall amount of 8300 Mt plastics have been fabricated until 2015.[6]

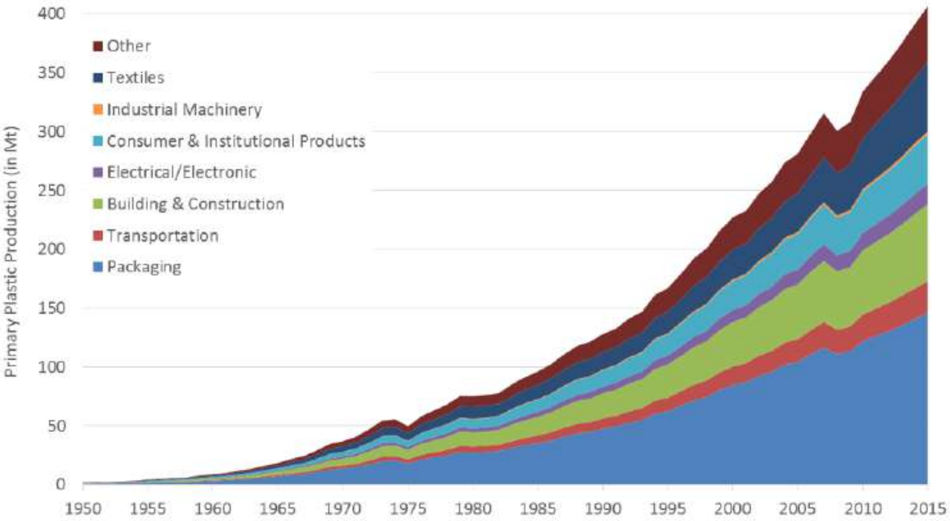


Figure 1: Progress of annual global plastic production (produced from virgin materials) from 1950-2015.[6]

Thereby, it has substituted other materials, due to its adjustable and versatile properties, low price and durability. Importantly, the plastic properties do not only depend on the chemical nature of the polymer but also on additives (e.g. fillers, plasticizers, dyes, stabilizers and flame retardants) and on the processing (e.g. injection molding, extrusion, foaming, 3D-printing). Unlike any other material it has a broad spectrum of applications including packaging, textiles, automotive, construction or electrical insulators, artificial organs, dental filling or drug delivery.[6-7] The striking benefits for society have made them inalienable for the future.[8]

Despite the aforementioned versatility of plastic goods, 80% of the total plastic demand in the EU (2019) can be covered by only seven polymers and approximately two-thirds of the demand are polyolefins (Figure 2).[9]

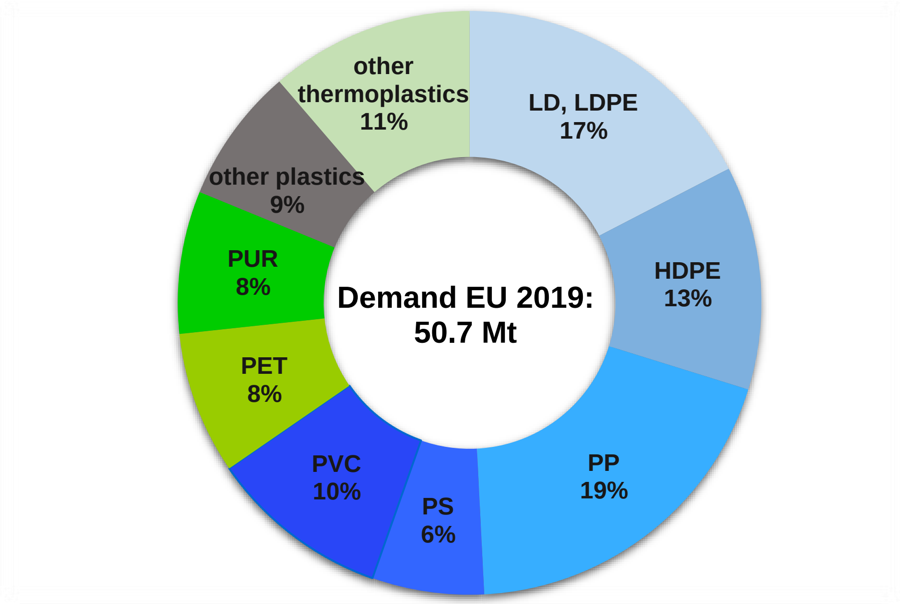


Figure 2: Share of polymer sorts on the total plastic demand in the EU28 + Norway and Switzerland in 2019.[9]

The large quantities of unrecycled plastic waste contribute to two main problems that result from the current plastic economy. First, the continuous consumption of fossil resources[10] and second, the continuous leaching of plastic parts into the biosphere.[6] Nearly all plastics are derived from fossil resources. The current annual plastic production requires approximately 8% of the annual oil production volume.[10] To save resources and reduce the environmental impact of plastics, some attempts have been made. In this regard, an alternative to conventional plastic production can be the production of polymer substitutes derived from renewable feedstocks. Therefore, biomass is enabled as a renewable feedstock for monomers. This strategy was transferred to an environmental-friendly remake of the established commodity polymers, (e.g. *bio*-polyethylene (PE), *bio*-PA or *bio*-poly(ethylene terephthalate) (PET)) as well as novel bio-derived polymers of which some reveal biodegradability (e.g. poly(butylene succinate) (PBS) or poly(hydroxyalkanoate)s (PHA)s).[11-12] Due to comparably higher energy demand and, due to their more extensive preparation, the environmental-friendly substitutes have a to some extent unfavorable CO_2-footprints compared to mass polymers.[7,13] As a consequence, the global production volume for bioplastics did not exceed 2.2 Mt in 2020. However, the production volume is expected to rapidly increase within the next years (2.87 Mt in 2025).[14] Overall, fossil resources are saved at the price of agricultural surface and, to date, higher production costs.

One of the advantages of polymers, the high chemical persistence towards degradation, is also a crucial drawback. Personal misuse of plastics and insufficient waste management systems are responsible for an accumulation of plastics debris in the environment.[15,16] The effects of this are multi-facetted and differ, depending on marine or terrestrial environment. Notable biological impact arises from contaminations, like microplastics and additives. The latter, for instance phthalates (plasticizers) or bisphenol A (BPA) (additive) are considered as endocrine disruptors and were found in several organisms, negatively affecting their reproduction.[17,18] On the other hand, microplastics have gained increasing interest in the last years. Being formed by mechanical abrasion they are spread as small particles in the environment by air, water or organisms. The particles were even found in high concentrations (2 million particles/m^3) in outlying areas like the arctic.[19] Aside from that, recent research has led to the conclusion that microplastic accumulates potentially toxic chemicals from water, soil or air that can be released after uptake by organisms.[20] Nevertheless, the overall environmental impact of microplastic is not fully clear, as the question of how their shape, size and chemical identity influences its toxicity has not yet been answered. On the macroscopic scale, plastic parts influence the fishery[21] and cause unnatural migration of organisms into foreign biospheres[22] Additionally, for instance plastic bags or old fishing nets can cause death to animals by entanglement or ingestion.[16,23] The degree of contamination by plastics becomes visible by an exemplification. Of 8300 Mt of plastics ever made between 1950 and 2015, estimated 4900 Mt have not been sufficiently disposed, this implies uncontrolled release to environment but also “storing” in landfills.[6] If the current developments proceed for the next 30 years, additional 21000 Mt plastic will be produced of which 7100 Mt will be discarded.[6] Although plastic pollution in its entirety is only barely quantified and the environmental impact is hitherto not fully understood,[24] a rethinking is taking place regarding the current production, usage and end-of-life options of plastics.

3.2 Plastics and the question of sustainability

In nature, resources are managed in a circular fashion. No wastes are created, moreover, end-of-life biomass serves as a resource for new biomass.[25] In 1989, this concept was first discussed as a model for a future-proof and fully sustainable anthropogenic economy.[26] Dated back to the time of the Industrial Revolution, when resources seemed to be non-depleting and unlimited, the linear economy was born (Type I ecology). The current linear economy is increasingly turned into an economy with circular elements[27] which still results in substantial waste generation but also contains circular elements. Recycling can be seen as a step towards a sustainable ecology, as it can turn materials in circular fashion in analogy to nature. Therefore, different approaches have been established to increase sustainability. All of them convert the end-of-life product to a good in an earlier stage of the value chain or even upgrading of waste to higher-value-goods.[28] A drastically shift to a circular economy could lead to a reduction in greenhouse-gas emission by approximately 70%.[28] As depicted in Figure 3 this can be used to classify different types of recycling. From primary to tertiary recycling the outcome can be fed into the value chain. Landfill storage and quaternary recycling convert the material to either greenhouse gases or pollutants with environmental impact.

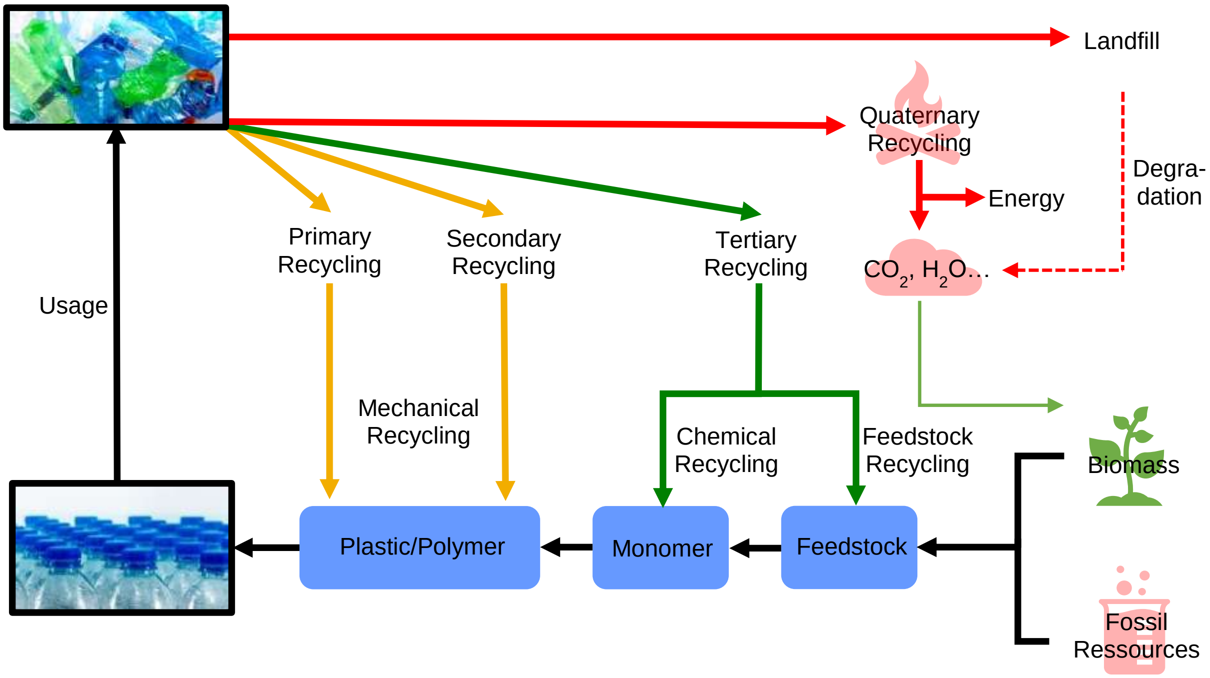


Figure 3: Overview on recycling pathways and their connection to the value chain of plastic goods.[29-31]

3.2.1 Primary recycling

Plastic parts designed for a single use have a short life span and are rapidly subjected to the waste management system after production. As a consequence, light induced degradation of the polymer can be neglected and the polymer chains are of comparable quality than the virgin material. If the waste stream contains one polymer type and low amounts of contamination, it becomes suitable for primary recycling. The plastics can either be directly reused or melted and reprocessed into a good with comparable or lower quality, which is called mechanical recycling. For colorless PET bottles from take-back systems or pre-consumer waste in industry, primary recycling works in a highly efficient fashion.[32] When the recycled material is reused for the same purpose as its virgin counterpart, then the process is called closed-loop recycling.[33] Often, primary recycling is executed during the production of plastic goods, e.g. with shreds originating from shaping processes.[33] Compared to other recycling technologies, recycled materials derived from primary recycling require the lowest amount of energy and investments. Nevertheless, it is rarely applied as the typical plastic waste often does not fulfill the required properties.[34] However, plastic portions that have been repeatedly shredded, melted and re-extruded lose quality. Shear forces, thermal stress and the presence of oxygen can cause radical or peroxide formation via different mechanisms. This results in follow-up chemistry causing crosslinking of chains and/or chain scission and impacting the mechanical, physical and optical properties.[35-39] Therefore, in some cases, recyclates have diminished qualities and are mixed with virgin material prior to extrusion. Recyclates with lower quality have been successfully implemented in so called secondary applications, for instance, in packaging as a layer between two layers of virgin material.[40]

3.2.2 Secondary recycling

The majority of collected plastic waste is contaminated with e. g. colors, fillers or food remnants. A direct mechanical recycling of mixed polymers is seldom carried out. In general, before mechanical recycling becomes viable, sorting and cleaning of the waste stream is necessary. The sorting process itself is very complex and different techniques are employed. Initially, metal and glass parts are removed by a rotating drum washer.[33] Then, after washing, the sorting begins by density using a float-sink separation, where low density polymers like PE and PP (polypropylene) are separated off. Some plastics contain fillers that “decouple” the polymer type from density which causes errors in this separation step. Next, a wind sifter or ballistic separator can be used to remove “light” parts like foils, paper and foams from “hard” parts.[33] The heavier fraction is further separated by melt filtration to remove fillers (wood, talcum) and non-melting plastics. Spectroscopic techniques are commonly applied thereafter. Fourier transform near-infrared (FT-NIR) is the most important technique in automated sorting as it can directly identify polymer types.[32] However, errors occur when copolymers or blends are used or contaminations alter the reflection of the near NIR beams. Especially in packaging, where multi-layer composites are used, this method lacks in accuracy.[33] Further separation techniques include electrostatic separation.[41] Froth flotation is a step where the hydrophobicity of the plastic surface is exploited. Therefore, the parts are placed in a water bath and treated with air bubbles. Hydrophobic parts bind air bubbles more frequently and drift upwards, thereby causing a separation.[42] After the automated separation, manual sorting can correct errors of the automatic system and increase the purity. Finally, cameras are used to separate the parts of one polymer by color.[33] During the sorting process, significant losses occur since black parts, copolymers, blends, heavily contaminated parts are not recyclable and have to be disposed by landfill storage or incineration.[33] If they remain in the sorted stream, they hamper the quality of the recyclate. Overall, in 2020, 65% of the total plastic waste, that was submitted to recycling facilities in Germany, was converted to recyclates.[43] Nevertheless, due to low efficiency during sorting and the aforementioned decomposition of plastics mainly downcycled materials are obtained. They have reduced properties in terms of elasticity, tensile strength, clarity or unaesthetic odor or homogeneity. As a consequence, the application of these materials may entail additional costs in product development since their performance has to be critically evaluated before application (material tests, mixing with additives, modified production lines, passive costs by toxic contaminations).[25] To achieve higher efficiency in mechanical recycling, the sorting process itself can be further optimized. Techniques of the future might be NMR spectroscopy, X-Ray diffraction and UV-Vis.[44,45] Also, the selective dissolution/precipitation purification using solvents has gained increasing attention. This process can be coupled with mechanical recycling and achieves high selectivity. Remarkably, it allows close for quantitative recycling of multi-layer composites that are commonly used for packaging.[46-48] In addition, the perceptibility of plastics during sorting can be increased during the stage of the product development. As an example, different fluorescent markers can be added to the virgin polymer. During sorting, the fluorescence could be assigned to the polymer type and serve as an additional sorting criterium. It would also allow a sorting of black parts.[49] Despite several efforts to increase sorting efficiency, the recycled material is not sustainable per definition due to degradation and remaining impurities, therefore, the lifespan of the plastic is prolonged before it finally must be discarded. In conclusion, mechanical recycled materials are not capable to equivalently replace primary plastic production.[25]

3.2.3 Feedstock recycling

In this class of recycling, the material is converted to low molecular weight chemicals. A distinction is drawn between chemical and feedstock recycling. This depends on the outcome of the transformation. Chemical recycling is more selective, leading to specific monomers that can be used for polymerization. Although there is a dependence on the chemical identity of the end-of-life plastic, the products from feedstock recycling are strongly influenced by the temperature and reaction conditions. Feedstock recycling operates at relatively high temperatures (>300 °C) and can be carried out under oxygen or air, hydrogen or inert atmosphere (pyrolysis). As the degradation is mechanistically diverse at high temperatures, the selectivity of the processes is lower than for chemical recycling. The products of feedstock recycling are often not suitable for a straight repolymerization but can be used to regenerate the monomers by chemical conversion.[31,51]

The gasification process was originally developed for the conversion of coal with water and oxygen to syngas, a mixture of CO and H_2. It has later been applied for biomass[51] and mixed plastic waste[52] It is typically carried out between 700-1200 °C and is robust towards contaminations.[53] However, poly(vinyl chloride) (PVC) interferes with the process due to formation of HCl or Cl_2 gas and chlorinated hydrocarbons as side products.[54] Removing of contaminations from the gas stream is effortful. Surprisingly, the co-gasification of coal, biomass and plastics was demonstrated, showing that existing plants for coal gasification can be used for this purpose.[55]

Thermal treatment of plastics in the presence of hydrogen is an alternative to the gasification process. Here, the product distribution depends on the composition of the feedstock polymers.[56] Those processes are carried out in the presence of catalysts and sometimes solvents at 300-500 °C using high H_2 pressures.[31] As products, light alkanes, waxes, oils and gases are formed.[56] During the 1980s, a plant for coal gasification with capacities of 80 kt/y was put into operation by VEBA AG in Germany. It was later modified with a depolymerization unit to convert mixed plastic waste streams. However, it was dismounted, probably due to lack of competitiveness.[31]

Among the three feedstock recycling techniques, pyrolysis is most thoroughly studied and finds notable industrial application, e.g. by BASF or Quantafuel. It is carried out at variable conditions, pressures and temperatures, in the absence or presence of solvents, catalyst, but mostly at ambient pressure or reduced pressure. The products of the thermal degradation are highly depending on the polymer feed. In some cases, high selectivities for the corresponding monomers were achieved e.g. for PMMA, PS, poly(tetrafluoroethylene) (PTFE) or Nylon

6.[50,57] For PE or PP statistical radical chain scission occurs. In case of PE pyrolysis, the application of heterogeneous acidic catalysts allowed for a control of the product spectrum. Depending on the catalyst, either more linear alkanes or 1-olefins are formed.[50] Herein, the linear C_6-C_{12} hydrocarbons are the main products at 450 °C with silica-alumina catalyst.[58] These products are suitable Diesel substituents or, in case of 1-olefins, interesting co-monomers. In contrast, for PP the products show increased amount of branching. It was also demonstrated that at higher temperatures the selectivity for the monomers ethylene and propene can be raised, e.g. ca. 70 wt% ethylene/propene at 700-800 °C for mixed polyolefin waste.[50]

When PVC is pyrolyzed, in an initial stage HCl is eliminated at 300 °C under formation of polyenes. These undergo crosslinking to form alkylated aromatics, (poly)aromatics and substantial amounts of chars. In addition, incomplete elimination of HCl then leads to formation of carcinogenic polychlorinated aromatics or chlorinated hydrocarbons hence it is essential to scavenge HCl by suitable additives. Overall, PVC pyrolysis is challenging and can cause additional costs when mixed plastics are used, however the obtained oil can be successfully added to natural oil and be submitted to steam cracking.[50] Step growth polymers like polyesters, polyamides and polycarbonates can also be submitted to feedstock recycling. Pyrolysis of polyesters like PET is accompanied by significant amount of CO_2 formation. In addition, PET β–scission leads to the generation of benzoic acid and vinyl ester functions among others. Due to the high melting point of these species, they often cause clogging in the reactor, blocking valves and inlets[50] In conclusion, polyolefins are suitable feedstocks for pyrolysis yielding valuable basic chemicals. There is a direct competition with fossil resources and therefore, the economic feasibility is coupled to the availability and price of raw oil.

Some of the products from feedstock recycling may reenter the value chain towards plastic at an earlier stage. However, a variety of the basic chemicals are not suitable to regenerate the polymer and are more likely to be repurposed (e.g. CO/H_2, benzene, alkanes) such as solvents, reagents or fuels. In conclusion, it is of limited applicability to promote a fully circular economy, but it provides a good alternative to combustion or landfill storage.

3.2.4 Chemical recycling

For polymers with functionalized backbones bearing e.g. carbon-heteroatom bonds or C-C double bonds, it seems more efficient to selectively cleave the polymer with suitable reagents to obtain monomers. Consequently, after repolymerization of the monomers, the properties are decoupled from those of the virgin material displaying its major advantage over mechanical recycling. In chemical recycling, the monomeric structure remains widely intact, so that in contrast to feedstock recycling, less chemical transformations are required to regenerate the polymer. As depicted in Figure 4 end-of-life polymers are converted to their monomers.

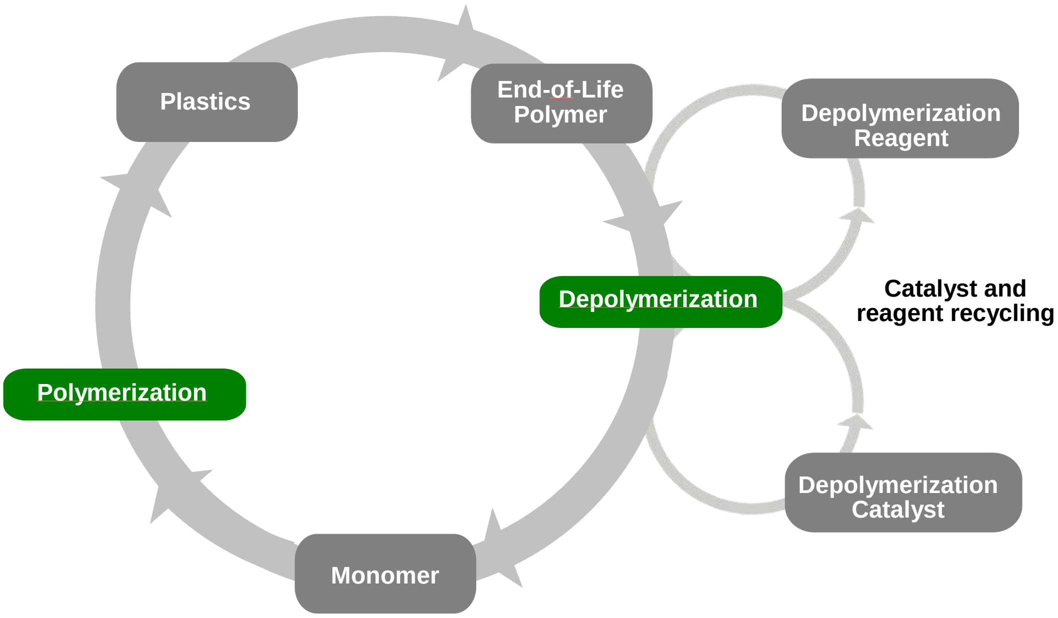


Figure 4: Schematic overview on chemical recycling.

This step is often promoted by reagents and catalysts. Both should fulfill complete recyclability, so if wastes or side products from catalysts or reagents arise, these should be recovered to be reused. In addition, guidelines for the development, choice of catalysts and reagents for depolymerization processes can be expressed by the “12 Principles of Green Chemistry”.[59]

1. Prevention of waste
2. Atom Economy
3./4. Low Toxicity
5. Avoiding or Use of Safer Solvents
6. Energy Efficiency
7. Cheap and Recyclable Reagents
8. Reduce Derivatives
9. Catalysis
10. Benign by Design
11. Real-Time Analysis of Pollution
12. Inherently Safer Chemistry

As chemical recycling does not typically deal with pure starting materials, the process should also tolerate impurities as discussed in chapter 3.2.2. Depolymerizations are classified by reagents, some examples are hydrogenolysis, hydrolysis, alcoholysis, aminolysis or aminoalcoholysis. The overall choice of the process is dependent on a careful life-cycle assessment, taking emissions, wastes, capital expenditure and energy consumption into account. In addition, for chemical processes, also the work-up, solvents, waste treatment and the reactor type are important for the overall costs and environmental impact.[60]

3.3 Depolymerization reagents for polymers

Transesterification reactions can be carried out under mild reaction conditions applying inexpensive catalysts. The established polymerization catalysts provide an excellent platform for suitable depolymerization catalysts. It is of interest to apply the same catalyst for both, polymerization and depolymerization to simplify the chemical recycling process.[61] In several cases, which are polymers that are prepared by ring opening polymerization (ROP), no reagent is necessary. However, the majority of polycondensation or polyaddition derived polymers requires a reagent. This should either be recovered during polymerization or be recyclable in a second circle, as shown in Figure 5.

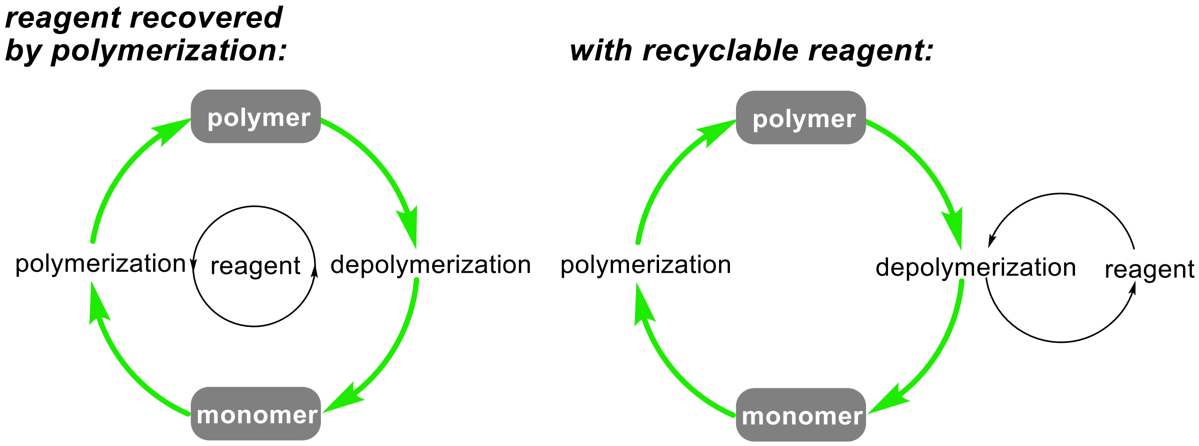


Figure 5: Recycling of reagents during the chemical recycling.

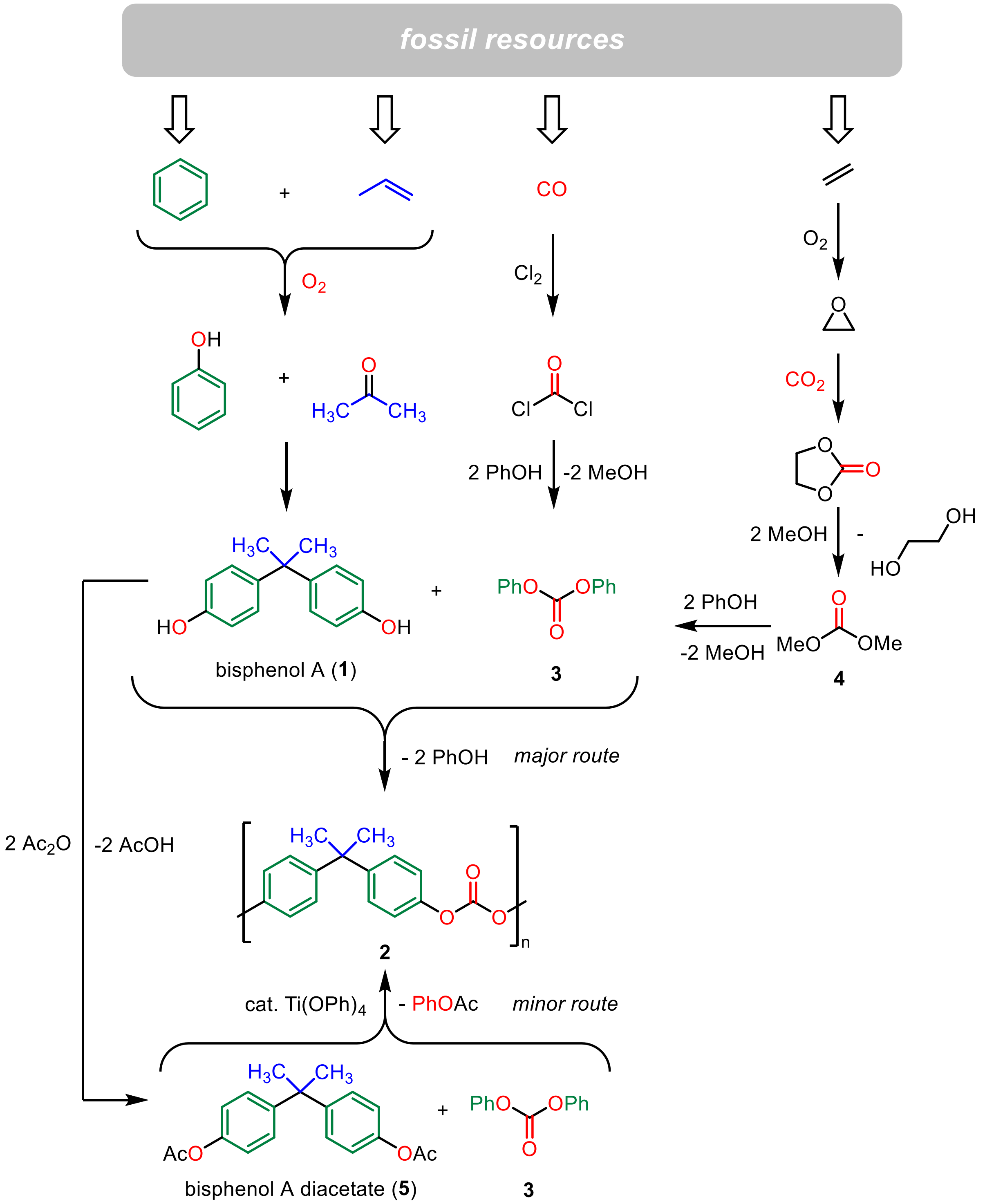
Moreover, using one depolymerization reagent for all polycarbonates and polyesters could turn down the overall sorting efforts and mixtures could be degraded in one pot. Methanol is an interesting degradation reagent due to its low cost and high abundance. Owed to its low steric demand it reveals the highest reactivity among all aliphatic alcohols.[62] In turn, the methyl esters of the corresponding monomers can be efficiently purified and repolymerized.

In addition, the polycondensation of methyl esters is in many cases well investigated and part of the industrial route to polyesters.

Another very abundant and cost efficient depolymerization reagent is H_2. It is straightforwardly accessible by the electrolysis of water. All polymers with heteroatoms in their backbone (polyesters, polyamides, polyether, polyurea, polyurethanes) can be potentially hydrogenated to form the corresponding reduced monomers. However, to date the literature reports regarding this recycling approach are scarce.

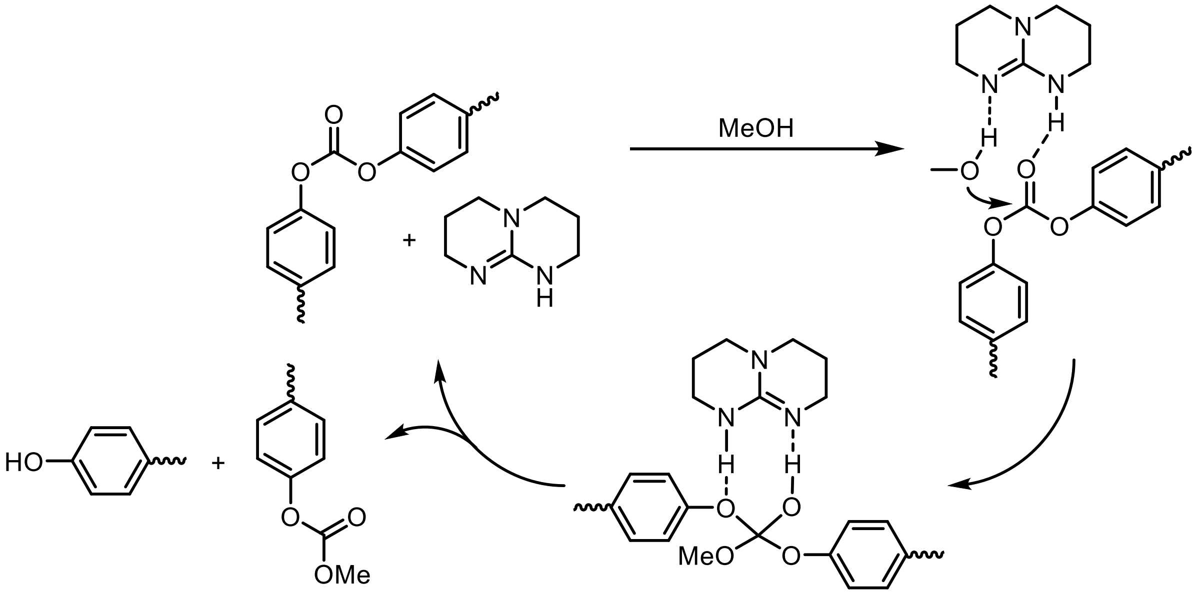
3.3.1 Poly(bisphenol A carbonate)

The only polycarbonate with a noteworthy demand of 0.73 Mt in 2020 (EU27 + 3)[63] is based on BPA (**1**) as diol component. Poly(bisphenol A carbonate) (PBAC) (**2**) is often found in optical storage media or artificial glasses due to its high transparency. Aside from that, it exhibits high tensile strength and stability and is therefore found in e.g. suitcases or safety helmets.[64] BPA (**1**) is obtained exclusively from fossil resources, namely propylene and benzene. The important intermediates phenol and acetone are obtained from Hook’s phenol synthesis and in turn are condensed in presence of acidic catalysts to give BPA (**1**). Thus, around 30% of the total phenol production is subjected to the BPA (**1**) production. To achieve high selectivity for substitution in *para*-position thiols are often applied as co-catalysts.[65,66] For the polymerization to PBAC (**2**), a variety of processes have been established. In the initial process, the BPA sodium salt is converted with phosgene. Due to the high toxicity accounted to phosgene, it has been replaced by diphenyl carbonate (DPC) (**3**) in modern processes. This chemical is obtained by different routes that all have a dialkyl carbonate as last intermediate in common. Asahi Chemical for instance prepares dimethyl carbonate (DMC) (**4**) via ethylene carbonate that is again transesterified with MeOH. Alternatively, Mitsubishi converts abundant urea with *n*-butanol to the corresponding carbonate which is in turn converted with phenol.[67] An essentially different approach is patented by Dow Chemicals Co. In their process, both monomeric units are present as esters. In more detail, BPA diacetate (**5**) is polymerized with DPC (**3**) under condensation of phenyl acetate.[68,69]



Scheme 1: Overview on the syntheses of PBAC (**2**) and its chemical value chain. For clarity, only the syntheses of PBAC (**2**) with transesterification reactions are shown.

Considering preparation processes, several approaches exist to achieve chemical recycling. All of them regenerate BPA (**1**), while the carbonate function is converted depending on the depolymerization reagent. These are in more detail glycolysis, methanolysis and phenolysis. The glycolysis is only limitedly applicable. For instance, the chemoselectivity of glycolysis is highly affected by the catalyst. Inorganic bases (NaOH or Na_2CO_3) were demonstrated to catalyze the degradation to give high yields for the ethers mono- or bis (2-hydroxyethyl)-BPA.[70,71] The organic carbonate is decomposed by decarboxylation. In the absence of catalyst, no ethoxylation of BPA (**1**) was observed, but due to higher operating temperatures (180-220 °C), detected yields for the carbonate were mediocre.[70,71] This was overcome when 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was applied in combination with glycerol or 1,2-propanediol. High yields for the corresponding carbonates and BPA (**1**) were realized.[72] Hence, organic bases like 1,5,7-triazabicyclo(4.4.0)dec-5-en (TBD), DBU or 4-(dimethylamino)pyridine (DMAP) were also found to efficiently catalyze the alcoholysis of PBAC (**2**).[73] With an additional solvent (2-MeTHF) it was possible to carry out the depolymerization at room temperature. It was found that in case of highly active catalysts, the reaction rate is still reduced due to the limited solubility of PBAC (**2**).[74] It is assumed that the high activity of especially TBD in transesterification reactions originates from the bifunctional nature and ability to stabilize the tetrahedral intermediate (Scheme 2).[74,75]



Scheme 2: A plausible mechanism for the cleavage of the carbonate bond with methanol. The organocatalyst increases the nucleophilicity of methanol and the electrophilicity of the carbonate function by its dual role as hydrogen bond donator and acceptor.[74]

Surprisingly, if an additional, less polar solvent is present, the methanolysis can be selectively carried out at 60 °C using NaOH as catalyst.[76,77] In addition, ionic liquids were reported to serve as solvent and catalyze the transesterification.[78-80] Another report deals with the application of a recyclable heterogeneous catalyst, namely CaO(SrO,BaO)/SBA-15, which required higher temperatures and larger catalyst loadings compared to the homogeneous systems[81] based on ionic liquids[78-80] or NaOH.[76,77] Furthermore, ZnO-nanoparticles in combination with tetrabutylammonium chloride (TBACl) were found to convert PBAC (**2**) with a number of alcohols or amines, forming the corresponding carbonate or urea and BPA (**1**)[82] Especially interesting for chemical recycling is the depolymerization with PhOH, to access DPC (**3**) as it can be directly converted to PBAC (**2**). Concerning this straightforward resynthesis of the monomers, only one patent is available, that enables NaOH as catalyst.[83]

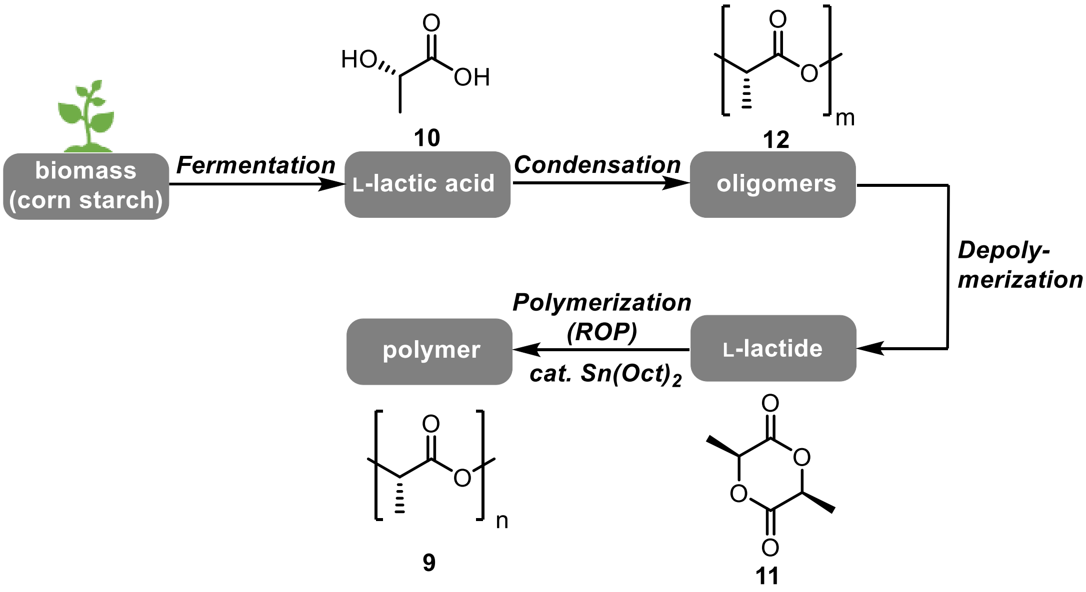
3.3.2 Poly(1,2-propylene carbonate)

Poly(1,2-propylene carbonate) (PPC) (**6**) is a polycarbonate that can be prepared from CO_2 and 1,2-propylene oxide.[84-86] As a less practical alternative, CO_2 can be copolymerized with 1,2-propanediol (**7**).[87] In another process, 1,2-propylene carbonate (**8**) is reacted to PPC (**6**) via ROP, which is accompanied by partial loss of CO_2 to form ether groups in the polymer backbone.[88] CO_2 is a very abundant chemical and can be taken from the atmosphere or combustion processes. On the other hand, 1,2-propylene oxide may be derived from propylene. A less common alternative is the dehydration of 1,2-propanediol (**7**).[89-92] The latter is potentially obtained from hydrogenation of biomass derived glycerol. However, these approaches have not made it to a widespread application.

Currently there are no studies addressing the chemical recycling of PPC (**6**). Nevertheless, some studies describe its thermal decomposition to 1,2-propanediol (**7**) and 1,2-propylene carbonate (**8**).[93-107] Moreover, the ring closing depolymerization (RCD) was accelerated by bases and decelerated by residual metal catalysts from the copolymerization.[108,109]

3.3.3 Poly(lactide)

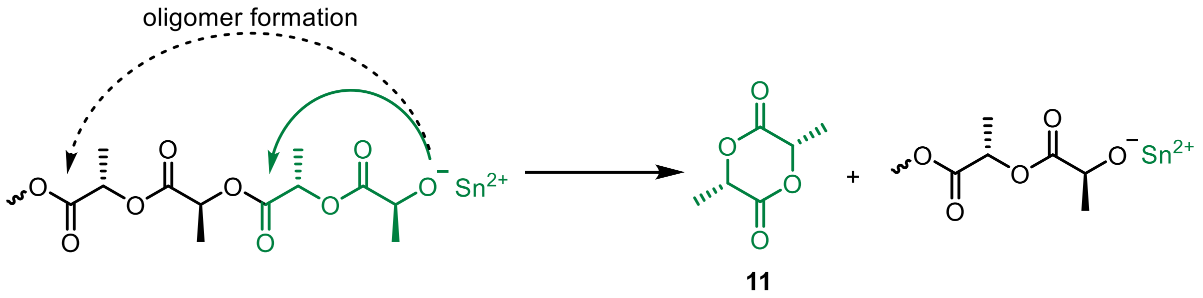
In 2020, poly(lactide) (PLA) is with an annual global production volume of 1.2 Mt the bioplastic with the largest global production 2020. As a biodegradable plastic with versatile properties, it is mainly used in packaging but also in textiles or as coating material.[110,111] Hence, its production volume is estimated to grow continuously, replacing fossil derived plastics. Although a shift towards biomass derived polymers is highly desirable, the demand for cultivable acreage grows, thus, creating a problematic competition with food production. The value chain for PLA (**9**) begins with the production of L-lactic acid (**10**) via microbial fermentation of starch rich biomass. Typically, L-lactic acid (**10**) is generated in a 10-20 wt% aqueous solution.[110] Attempts to obtain high molecular weight PLA (**9**) from the direct polycondensation of L-lactic acid (**10**) did not result in PLA with sufficient properties. Either the molecular weight did not exceed 33,000 g/mol[112] or the polymer properties were diminished due to racemization, high dispersities and uncontrollable molecular weights.[113] The industrial route towards high molecular weight PLA enables L-lactide (**11**) as monomer allowing for controllable and narrow molecular weight distribution. L-lactide (**11**) is obtained from the L-lactic acid (**10**) solution via initial removal of water. Thereupon, the formed PLA oligomers (**12**) are depolymerized in vacuum in the presence of catalysts like $SnHPO_3$, $Sn(Oct)_2$ or elemental Zn or Sn.[114-116] During the depolymerization, it comes to some extent to racemization, especially above 200 °C.[110,117] Therefore, commercial PLA (**9**) often contains 80-90% ee of the L enantiomer. Lower values cause the polymer to be less crystalline, thereby lowering its melting point and mechanical stability.[110] Remarkably, in 1932 Carothers *et al.* already described the ring-opening polymerization of L-lactide (**11**) and its reversibility.[118] Nowadays, the majority of PLA (**9**) is obtained using $Sn(Oct)_2$ as catalyst.[119]



Scheme 3: Preparation of PLA (**9**) starting from biomass.[114-116,119.]

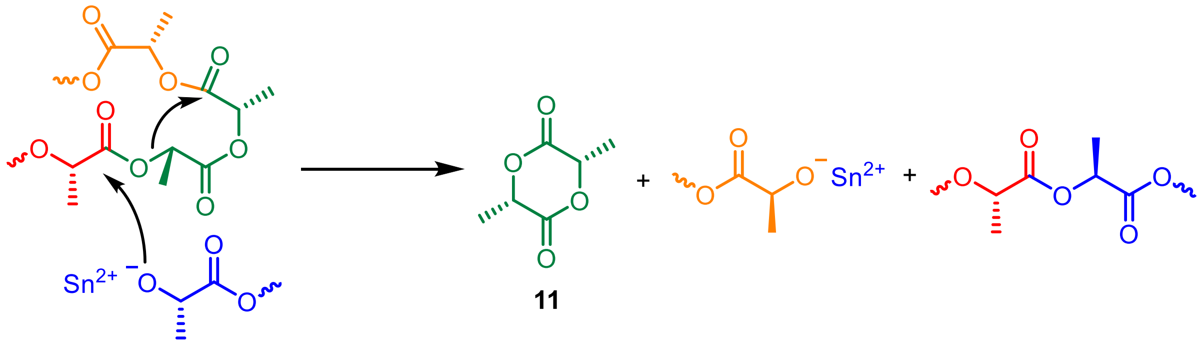
When it comes to chemical recycling, the straightforward regeneration of L-lactide (**11**) can be observed, when PLA (**9**) samples are subjected to pyrolysis. The thermal depolymerization of PLA was studied by means of pyrolysis-GC/MS (gas chromatography/mass spectrometry), TGA (thermogravimetric analysis), DSC (differential scanning calorimetry) and GPC (gel permeation chromatography).[120,121] Thus, the data indicate that the thermal stability depends on the residual amount of $Sn(Oct)_2$ present in the sample.[121]

In general, the transesterification can be enabled by alcohol end groups or by random inter- or intramolecular transesterification, leading to L-lactide (**11**) or cyclic oligomers. On the other hand, at higher temperature (>230 °C) gaseous products like CO_2, CO, acetaldehyde or ketene are observed as main products. Furthermore, the authors found that the degradation kinetics are affected by residual metal catalysts, moisture and molecular weight.[120,122] Later, Nishida *et al*. investigated the influence of residual $Sn(Oct)_2$ from the polymerization on the thermal stability and degradation kinetics using TGA measurements.[121] For OH-terminated and metal free PLA (M_n = 100 kg/mol), they found some degradation at 300 °C. The activation energy increased from 125 kJ/mol at 90% weight to 180 kJ/mol at 20% weight, underlining the effect of the molecular weight on the degradation kinetics. In the presence of 200-600 ppm of residual $Sn(Oct)_2$ the observed activation energy decreases significantly to 100-120 kJ/mol and the degradation starts at 260 °C.[121,123] The main degradation pathway is a backbiting mechanism leading to L-lactide (**11**), mediated by tin(II)-alkoxide end-groups. Notably, random transesterification between the chain ends and peripheral lactate units can occur, thus forming cyclic oligomers (Scheme 4). With less tin(II) present, this degradation process becomes dominant.[121]



Scheme 4: Unzipping depolymerization at the chain end via intramolecular transesterification.[121]

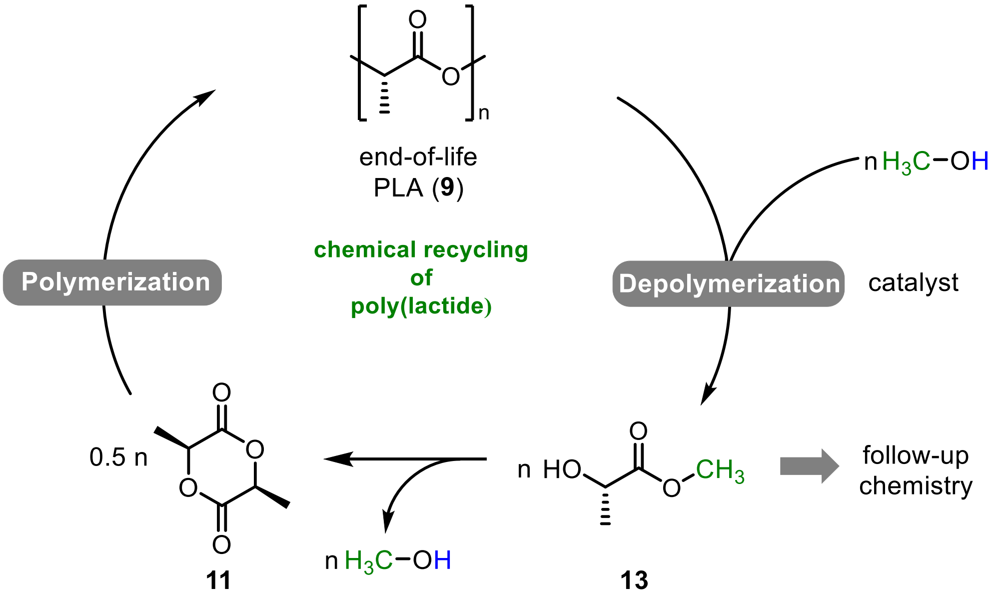
In addition, lactide units from the middle of the chain can be formed. Therefore, a transesterification at a random position of the chain induces the L-lactide (**11**) elimination.



Scheme 5: Random lactide (**11**) elimination initiated by intermolecular transesterification mechanism during the degradation of PLA (**9**).[121]

As a major drawback, during the depolymerization, lactic acid units undergo racemization, depending on the catalyst, this typically occurs above 200 °C. As mechanism, either a substitution reaction at C-2 was reasoned or deprotonation at C-2 with subsequent protonation.[124,125] As a consequence, repeating this process several times in the context of chemical recycling, will lead to insufficient enantiomeric purity to achieve the desired properties.

Alternatively, the chemical recycling can be carried out by methanolysis. As product, methyl lactate (**13**) is obtained from which methanol and L-lactide (**11**) can be recovered to close the cycle.[126-128] An overall recycling scheme is depicted in Scheme 6. The obtained ester **13** can alternatively be used as solvent.[129]



Scheme 6: Chemical recycling of PLA (**9**) by methanolysis and dimerization to L-lactide (**11**).

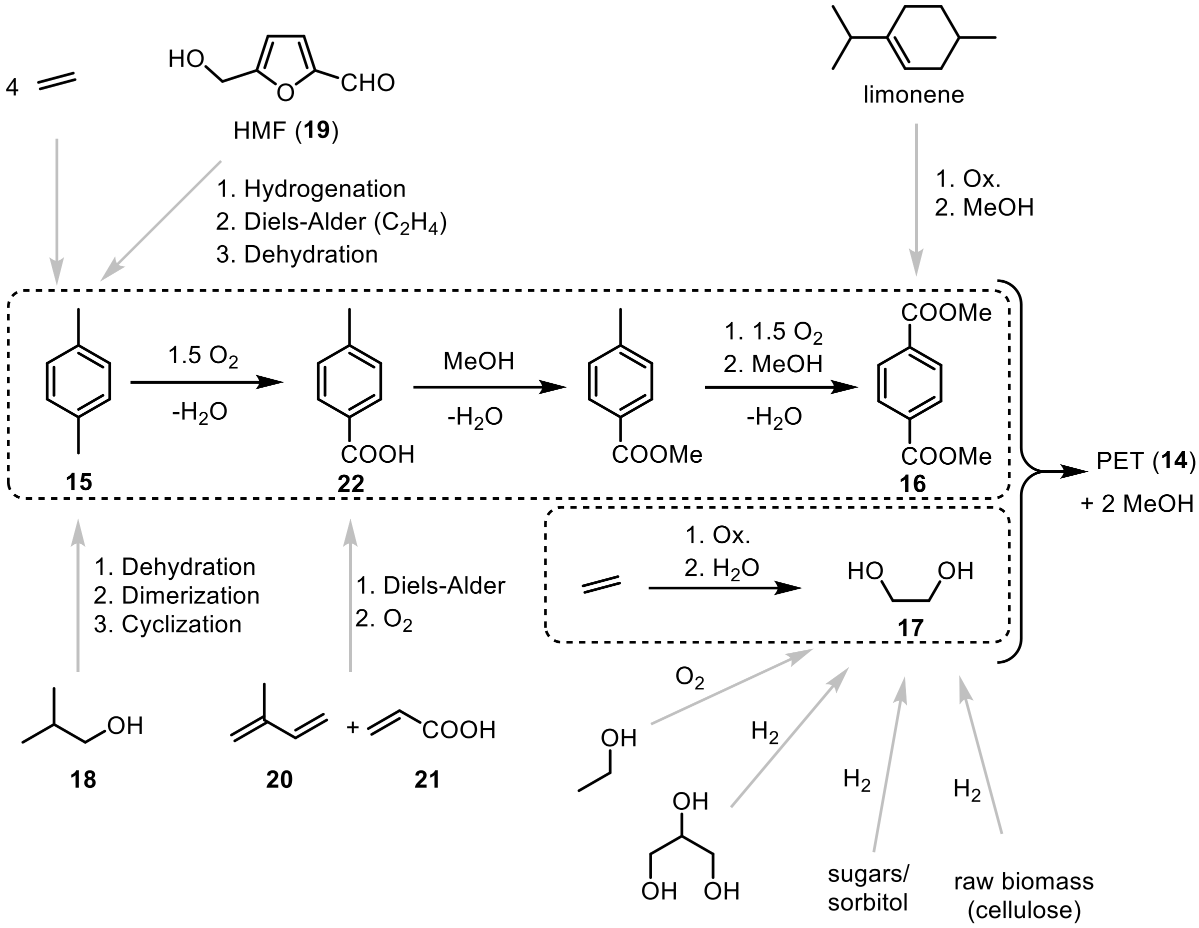
For the methanolysis of PLA (**9**) waste, a variety of catalysts have been applied. Some reports describe the catalytic activity of mineral acids in refluxing MeOH[130] or at 130 °C metal salts like NaOH, NaOMe, $Zn(OAc)_2$, $FeCl_3$ in neat MeOH of which $FeCl_3$ exhibited the highest activity.[131] They observed an activation energy of 32.4 kJ/mol for $FeCl_3$.[131] Zinc salts were investigated as catalysts in more detail, e.g. $Zn(OAc)_2 \cdot 2\ H_2O$, $Zn(stearate)_2$ and $ZnSO_4$. Refluxing PLA (**9**) waste in 5.3 equiv. of MeOH in the presence of 1.4 mol% $Zn(OAc)_2 \cdot 2\ H_2O$ for 15 h gave yields of up to 70%.[132] Using alkaline earth metal alkoxides (1 mol%) and excesses of different aliphatic alcohols, Petrus *et al*. degraded PLA (**9**) at 160-200 °C for 1.5-10 h obtaining a variety of alkyl lactates in excellent yields.[133] Liu *et al*. showed in another report, that only 0.25 mol% of the ionic liquid [Bmim]$FeCl_4$ can promote the depolymerization of PLA (**9**) in MeOH at 120 °C after 3 h. It was demonstrated that the valuable ionic liquid can be recovered and reused multiple times without loss of catalytic activity. They also found a lower activation energy for 100 °C - 125 °C of 21.28 kJ/mol in the absence of solvent. The authors reasoned, that the presence of a basic moiety reduces activation energy by increasing the nucleophilicity of MeOH.[134] The cooperative effect of the anion and the cation was underlined by a study, wherein the catalytic activity of ionic liquids based on $[Bmim]^+$ as cation was investigated. Together with a weakly basic or acidic counter anion no promising catalytic activities were observed. The investigated anions revealed activities in the following order: $Cl^- = PF_6^- < HSO_4^- << OAc^-$.[135] Another study by Song *et al*. investigates the influence of the counter cation in the presence of HSO_4^-. They found that organic sulfonic acids cations revealed superior properties compared to the imidazolium derivative.[136] Moreover, PLA (**9**) was fully depolymerized with 10 mol% [HDBU][Im] in MeOH at 70 °C and high yields up to 90% were realized.[79] A screening of different anions revealed increased activity for the strongly basic anions[137] in accordance to the observations of Song *et al*.[135] Recently, some organocatalysts have been introduced to methanolysis of PLA (**9**). For instance, Leibfarth *et al.* applied TBD, which is also a highly active catalyst for L-lactide (**11**) polymerization, with different solvents at room temperature or in neat MeOH at 100 °C.[138]

More recently, a couple of highly active metal complexes bearing pincer ligands were developed. The evaluated examples base on group 4 metals[139], Zn[140-144] coordinated by NHC or Schiff base ligands. In all cases, the complexes were also active in the repolymerization of L-lactide (**11**). The methanolytic downbreak readily operates at room temperature when a suitable solvent is present.

Moreover, the methanolysis was characterized by kinetic measurements. It was found that, the reaction rates observed under microwave heating were significantly higher than for conventional heating. The pre-exponential factor A under microwave conditions was increased while the activation energy remained constant.[62]

3.3.4 Poly(ethylene terephthalate)

With a global production of 70 Mt in 2016 and an annual growth of 4%,[145] PET (**14**) is by far the most important polyester. Its main applications are plastic bottles and textile fibers. Carpets, for instance, are a common application of mechanically recycled PET (**14**).[146] The feedstock chemical for the aromatic part of the polymer is *p*-xylene (**15**). It is collected during steam reforming in the C_8 fraction of the distillate together with its isomers and requires purification from its isomers by catalytic isomerization and distillation. Then, the pure *p*-xylene (**15**) is step wisely oxidized and optionally esterified with MeOH to dimethyl benzene-1,4-dicarboxylate (**16**, DMT).[67] As an alternative to DMT (**16**), terephthalic acid can be subjected to polymerization with ethylene glycol (EG) (**17**). Fossil derived *p*-xylene (**15**) serves as the major industrial feedstock for PET (**14**) production. However, in the last two decades, novel biomass derived feedstocks were implemented to generate *bio*-PET (**14**).



Scheme 7: Potential routes for the preparation of PET (**14**) via ethylene glycol (EG) (**17**) and DMT (**16**).[148-154]

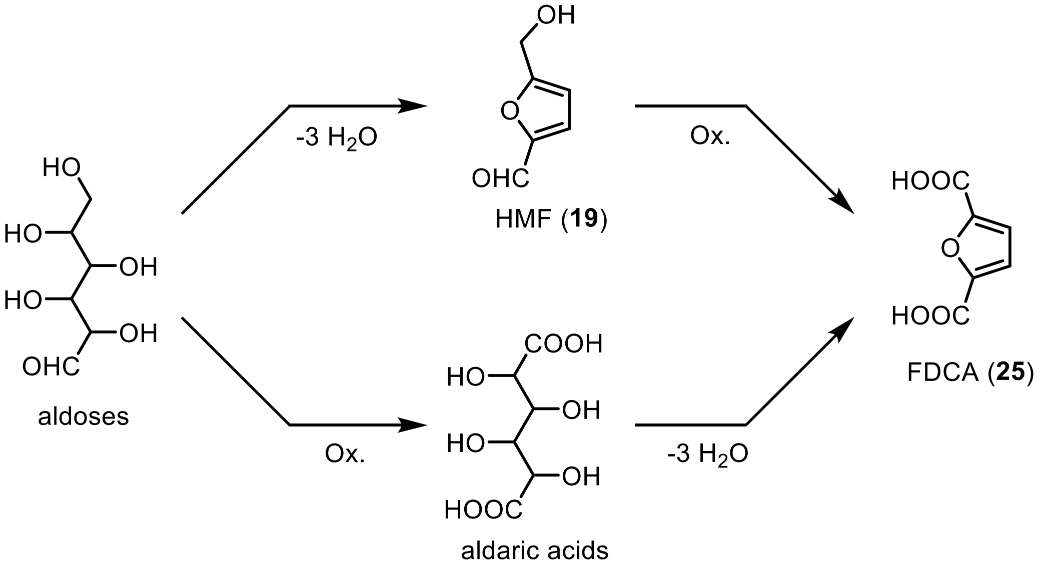
As depicted in Scheme 7, the *p*-xylene (**15**) can alternatively be prepared by tetramerization of *bio*-ethylene[147] or dimerization of *bio*-*iso*-butanol (**18**) which gives an overall yield of only 18.7%. However, this route was commercialized by Gevo Inc. and Coca-Cola Company.[148] In addition, carbohydrate derived 5-(hydroxymethyl)furan-2-carbaldehyde (**19**, HMF) was successfully enabled as feedstock in a scale of 20 t/year.[149] Another approach uses a Diels Alder reaction of isoprene (**20**) and acrylic acid (**21**) with subsequent oxidation to achieve excellent yields of *p*-toluic acid (**22**) of 83-100%.[150-152] A very efficient synthesis is based on limonene (**23**) giving high yields. However, the availability of limonene is too limited to satisfy the demand of PET (**14**).[153] For the EG (**17**) production, the oxidation of ethylene and subsequent hydrolysis is conveniently applied. In addition, some alternatives have been developed. Here, especially glycerol or higher sugars and their corresponding alcohols are inexpensive feedstocks of interest. Hydrocracking then affords EG (**17**) in low yields (20-30%) together with by-products like 1,2-propanediol (**7**) or 1,3-dihydroxyacetone.[149]

For chemical recycling of PET (**14**), glycolysis, hydrolysis and methanolysis have been studied.[154] The products can be directly submitted to repolymerization. The earliest report regarding the methanolysis of PET (**14**) originates from 1967 and describes a batch process where finely powdered PET (**14**) is dispersed as an aerosol and reacts with gaseous MeOH. Depending on the catalyst (zinc salts or gaseous HCl) the depolymerization is carried out at 250-300 °C under atmospheric pressure.[155] Another patent describes the use of 2 mol% of aromatic sulfonic acids at 200 °C in neat MeOH.[156] In a patent by DuPont, the methanolysis is carried out in solution without a catalyst at 230 °C at up to 15 bar. The yields of EG (**17**) and DMT (**16**) varied between 75% and 95%.[157] The yield was improved by converting the main side product methyl 2-hydroxyethyl terephthalate, that arises from incomplete methanolysis. This remains in solution and was separated from **16** by filtration and converted in a second reactor to DMT (**16**) in 90% yield. They used Na_2CO_3, NaOH or $Zn(OAc)_2$ as catalysts.[158] A more recent article introduced $Al(O\mathit{i}Pr)_3$ as catalyst to obtain up to 88% yield for DMT (**16**) and EG (**17**). The reaction temperature and yields were increased by the addition of 20 vol% $PhCH_3$.[159] Another publication first introduced microwave irradiation to reduce the energy consumption compared to conventional heating. As catalyst, $Zn(OAc)_2$ was applied and 1,2-propanediol (**7**) or PEG400 were used as co-solvent. The reaction was run to completeness within only 4 min, but no reaction temperature was reported. It was noticed, that the presence of a magnetic stir bar drastically increased heating of the reaction mixture due to its high absorbance of the microwave irradiation[160] In another publication, the reaction was carried out under microwave irradiation at 160-200 °C with $Zn(OAc)_2 \cdot 2\,H_2O$ as catalyst.[161] The depolymerization was also carried out in a continuous flow process between 240-260 °C, which requires extensive equipment.[162,163] In the process patented by Eastman-Kodak Co., the PET (**14**) is partially depolymerized to oligomers as main products. The small amounts of **16** and **17** are continuously removed by the methanol vapor and then purified by distillation.[164,165] A non-catalyzed degradation of **14** in supercritical methanol was reported by Mitsubishi to achieve high yield of both **16** and **17**. Their process was further implemented in a pilot plant.[166-168] Moreover, a protocol was reported in which in a first step glycolysis to oligomers is carried out. Subsequently, the oligomers are converted to DMT (**16**) by methanolysis leading to a total reduction of energy consumption compared to conventional methanolysis.[169] In contrast to glycolysis and hydrolysis, the obtained DMT (**16**) is of high purity and separation from potential impurities is easily accomplished.[170] Interestingly, due to its excellent thermal stability and crystallization, it is in some patents further converted with water to TPA, which is more often the starting material for the PET (**14**) production.[171] Recently, using a combination of 20 mol% K_2CO_3 and 50 equiv. of MeOH and CH_2Cl_2, it was possible to achieve yields above 90% of DMT (**16**). The reaction was carried out under mild conditions between 20-35 °C for 24 h. In this reaction K_2CO_3 serves as a heterogeneous catalyst that is decomposed in the presence of water, causing the formation of hydrolysis products and loss of catalytic activity.[172] Chlorinated solvents show high capability to dissolve PET, allowing it to be converted even at low temperatures. A combination of MeOH and CH_2Cl_2 was used to degrade PET in the presence of 15 mol% NaOMe. The reaction was performed within 2-3 h at 20-50 °C. Other solvents revealing similar effects in the swelling of PET (**14**) were claimed, including DMSO, DMF, acetone, nitrobenzene, benzyl alcohol and benzaldehyde.[173] In a different approach, wherein **16** is obtained from **14**, the polymer is first degraded by glycolysis to diglycol terephthalate, using $Mg(OAc)_2 \cdot 4\ H_2O$ as catalyst. Overall, the reaction pressure in the depolymerization step is lower than in conventional methanolytic degradation, as the depolymerization can be carried out in neat glycol. The obtained solution is then mixed with methanol and 0.5 mol% $Mg(OMe)_2$ as catalyst and heated to 70 °C for 2 h to obtain **16** and **17**.[174] In contrast to the products of glycolysis and hydrolysis, the purification of DMT (**16**) is easy to accomplish, e.g. by distillation or recrystallization and results in high puritiy monomers.[171] Interestingly, due to its excellent thermal stability and crystallization, it is in some patents further converted with water to TPA, which is more often the starting material for the PET production.[171]

3.3.5 Poly(ethylene 2,5-furandicarboxylate)

Although currently there are no commercial applications of poly(ethylene 2,5-furandicarboxylate) (**24**, PEF), it has the potential to replace PET (**14**) in the future. Based on this, first industrial plants have been installed.[175] Due to its structural similarity, it displays comparable and sometimes enhanced material properties than PET (**14**).[176] For instance, PEF (**24**) exhibits a highly enhanced CO_2 barrier compared to PEF (**24**), which could lead to substantial material savings in plastic bottle manufacturing.[177] Additionally, PEF (**24**) is fully bio-derived as in addition to EG (**17**) the aromatic building block can be obtained from C-6 sugars (Scheme 8). Some efforts have been made to establish cost efficient routes towards furane-2,5-dicarboxylic acid (FDCA, **25**), starting from sugars. Two main routes are present in the literature. In the first step, the sugar molecule is dehydrated to (**19**).[178,179] The HMF (**19**), serving as a versatile platform chemical is in turn oxidized to 2,5-furandicarboxylic acid (FDCA)

(**25**), which is the monomer for the production of **24**.[180] Using this route, Avantium will start the first industrial plant in 2023.[175] In the other route, the sugars are first oxidized at C-1 and C-6 to their corresponding aldaric acids, e.g. with HNO_3 or O_2 in the presence of solid Pt.[181-183]



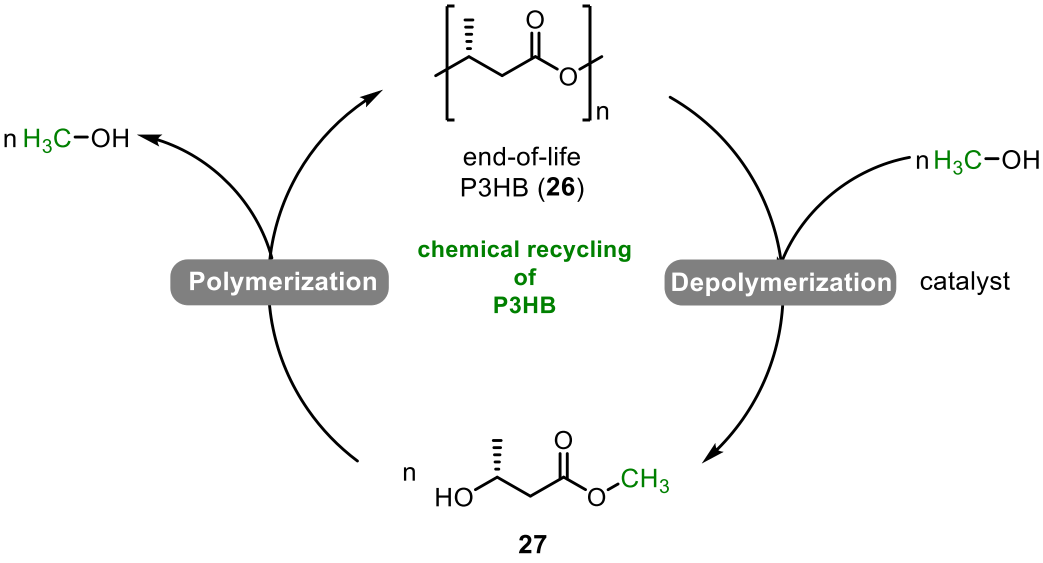
Scheme 8: Production of FDCA (**25**) from C6-aldoses via two feasible routes.[178-183]

As a novel polymer, to date only few studies address the depolymerization of PEF (**24**). Among them are reports on enzymatic hydrolysis using PET-hydrolyzing enzymes (PETase)[184-186] and glycolysis using a ionic liquid as catalyst.[187] Only one patent from 2015 exists, describing the methanolysis in neat MeOH.[188] Herein, NaOMe or TBD were used as catalysts at 90 °C to degrade **24**.

3.3.6 Poly(3-hydroxybutyrate)

Since its first discovery in the blue-green alga *Chlorogloea fritschii* in 1966[189] efforts have been made to enable this fully bioderived polymer as a thermoplastic with commercial relevance. Pure and stereoregular poly(3-hydroxybutyrate) (**26**, P3HB) shows thermal and mechanical properties comparable to isotactic PP, however, it is far more brittle (by elongation at break value). P3HB (**26**) is efficiently obtained by fermentation of e.g. sugars, acetate or citrate with some strains of cyanobacteria to obtain P3HB (**26**) or P(3HB-*co*-3HV), depending on the supplement given to the bacteria.[190] After fermentation, an extraction of the polymer is required to separate the polymer from side products and residual bacteria. This leads to the high production cost being approximately 18-times higher than for PP.[191] Therefore, the polymer from microbiological synthesis might not find broad application as commodity polymer but rather in specialized applications where biodegradability is required.[192] Recently, a promising chemical route was established, that, analogously to PLA production, enables a ring-opening polymerization of the bio-derived cyclic dimer of 3-HB.[193]

Regarding the chemical recycling by methanolysis according to the Scheme 9, both the degradation of the polymer and its repolymerization were investigated to some extent.



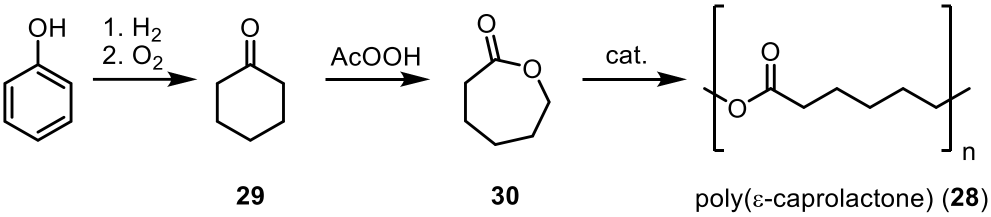
Scheme 9: Chemical recycling of P3HB (**26**) by methanolysis.

For the depolymerization, for instance Brønsted-acids, were found to catalyze the methanolysis.[194] With $FeCl_3$ or $Zn(OAc)_2$, satisfying conversions and high selectivities for methyl 3-hydroxybutyrate (**27**) were realized at 130-150 °C.[195] Additionally, ionic liquids are good co-solvents with catalytic activity. As for PBAC (**2**) or PET (**14**), it was found that the depolymerization is best carried out in the presence of ionic liquids bearing a basic counter ion (Im^-)[137] or a metallate ion ($[FeCl_4]^-$ or $[ZnCl_3]^-$). It was found that the metallate ions outperform their corresponding metal salts ($FeCl_3$, $ZnCl_2$).[196,197] Combining these Lewis-basic metallates with Brønsted-acidic cations ([MIMPS]), that contains a sulfonic acid group, had an accelerating effect on the reaction, leading to the highest catalytic activity. Using 5 equiv. of MeOH, a yield of 87.4% for **27** was obtained with 5 mol% $[MIMPS][FeCl_4]$ at 140 °C after 3 h.[196] A more recent study introduced $(Me_4N)F$ as catalyst to achieve full conversion at up to 100 °C in less than 1 h.[198]

The cycle can be closed by polycondensation of the obtained methyl ester **27**. Therefore, Ti(IV)-alcoholates typically serve as transesterification catalyst to reach a M_w in the range of 10-20 kg/mol.[199-201]

3.3.7 Poly(ε-caprolactone)

Poly(ε-caprolactone) (**28**, PCL) is a polymer derived from fossil resources. However, many microbial organisms are capable to completely degrade **28**. This led to its application in medicine, e.g. in drug delivery systems[202] However, it exhibits insufficient material properties for large scale applications like packaging. Especially its low melting point of only 60 °C limits its wide spread applicability. Advantageously, it shows high miscibility with polar and non-polar polymers that have led to its application in blends, e.g. with PLA (**9**)[203] or as co-polymer.[204] The majority of literature reports focuses on the ring-opening polymerization of ε-caprolactone (**30**) rather than the polycondensation of the corresponding hydroxyacid.[205] As depicted in Scheme 10, the feedstock for PCL (**28**) production is phenol, which is first hydrogenated to cyclohexanol, then oxidized to cyclohexanone **29** and subsequently oxidized in a Baeyer-Villiger oxidation with peracetic acid yielding ε-caprolactone **30**.[205]



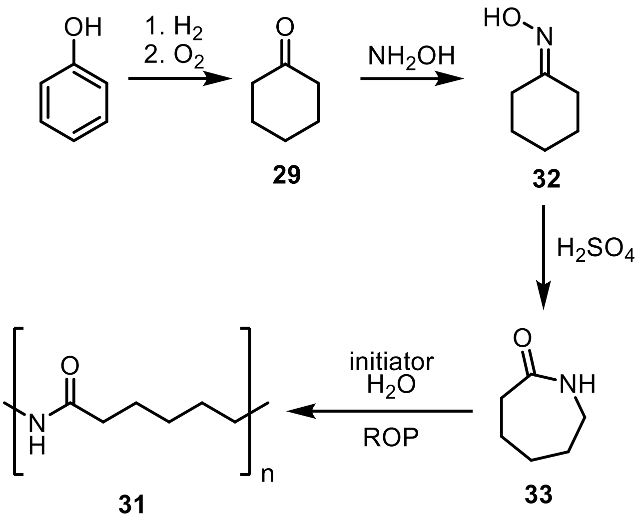
Scheme 10: Preparation of **28** from starting from phenol.[67]

The monomer is a liquid compound and is mainly polymerized in substance by either anionic, cationic or coordination-insertion polymerization. For **28** the most active catalyst system is $Sn(Oct)_2$. The living nature of the polymerization comprising $Sn(Oct)_2$ and an alcohol as initiator allows for an accurate control of the molecular weight. As active species, tin(II)-alkoxide as chain end was revealed by MS-MALDI[204], which is formed by protolysis of the tin(II)-carboxylate with the alcohol.[205] For medical applications, catalyst systems based on biocompatible metals like zinc[206] or magnesium[207] are preferred over Sn(II)-systems.

Surprisingly, to date no studies exist in which the methanolytic degradation is described. Instead, some studies describe the ring-closing depolymerization. Pyrolytic conditions in the absence of catalyst have been investigated. However, the unzipping degradation, occurring approximately above 250 °C, is accompanied by random chain scission (β-scission) which diminishes the yield for monomers.[208] Alternatively, treatment of **28** with a transesterification catalyst like $Bu_2Sn(OMe)_2$ in solution led to a complex mixture of cyclic oligomers, that is, in the equilibrium state, determined by the Jacobson-Stockmayer theory. As a consequence, at higher temperatures, **28** can be obtained in good yields by vacuum distillation.[209] In a more recent study, the ring closing depolymerization was catalyzed by lipase enzymes to yield the cyclic dimer of **28** which was repolymerized by the same enzyme.[210-212]

3.3.8 Nylon 6

Nylon 6 (**31**) is a polymer with high tensile strength and high melting point, for which reason it is found in materials where high rigidity and stability is required. Furthermore, it exhibits high thermal and chemical stability and is insoluble in common organic solvents. On an industrial scale, **31** is derived from fossil derived cyclohexanone (**29**) which is converted to its oxime **31** and then converted to the lactam **33** by a Beckmann rearrangement.[67]



Scheme 11: Industrial production of **31** from phenol.

The ROP of the readily obtained ε-caprolactam **33** is by far less studied than for e.g. lactone **28**, which is reasoned by the poor solubility and high melting point of Nylon 6 (**31**). Therefore, (**31**) is prepared exclusively by melt polymerization at temperatures above 240 °C with a small amount of water as initiator[213] or an anionic polymerization with sodium-ε-caprolactamate as initiator and an activator, e.g. *N*-acetyl caprolactam.[214]

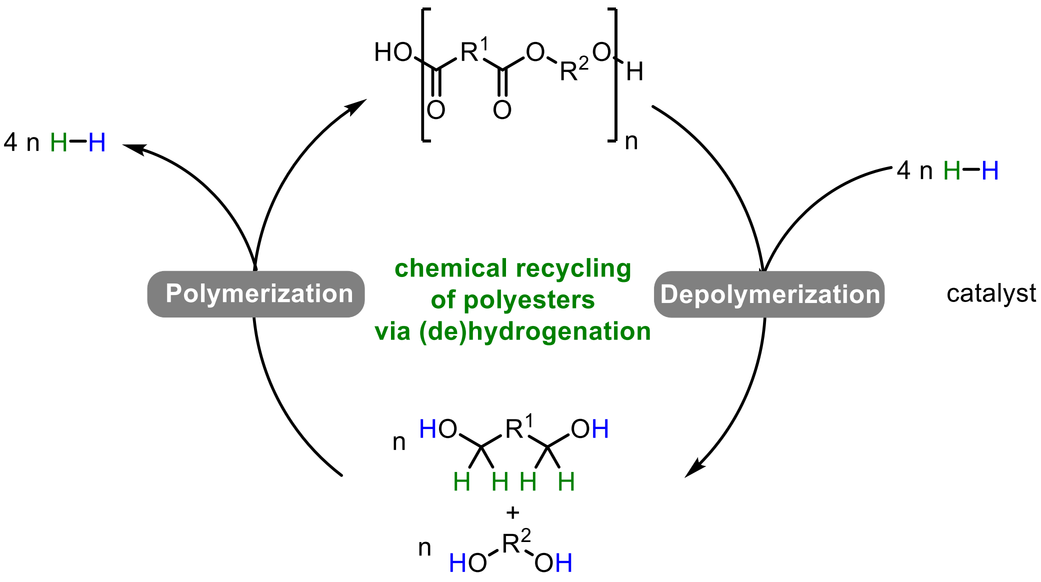
In several studies, Nylon 6 (**31**) was degraded by hydrolysis. As catalyst, mineral acids were applied under reflux conditions for up to 8 h. The crude 6-aminohexanoic acid had to be separated from residual oligomers by ion exchange chromatography[215] or reversed phase chromatography.[216] Carboxylic acids showed a higher activity compared to the investigated mineral acids and also other polyamides, e.g. PA11 were successfully degraded in a study from 2014. Interestingly, the reaction rate depended both on the pKs value of the acid as well as its solubility in the polymer.[217]

The straightforward regeneration of the lactam **33** is accomplished by pyrolysis at 410 °C in vacuo and isolated yields up to 92% were realized.[218] More recent investigation led to the application of supercritical alcohols as reaction medium. Thereby, after 1.5 h at 350 °C, the authors achieved yields above 90% for **33**.[219] The same group later introduced ionic liquids to further reduce the reaction temperature. Although **31** can be readily degraded at 300 °C in the ionic liquid *N*-methyl-*N*-propylpiperidinium bistriflimide the addition of catalytic amounts of DMAP further accelerated the reaction. The ionic liquid could be recovered and reused without notable loss of activity for at least 5 times.[220-222]

3.4 Polymer recycling by catalytic hydrogenation and dehydrogenation

Reduction reactions display an elemental, but multi-facetted organic reaction, being applicable to a variety of functional groups. Traditional reducing reagents like $LiAlH_4$ or $NaBH_4$ are often applied in lab- and industrial scale. However, their major drawbacks, the stoichiometric generation of wastes and their pyrophoric nature come in conflict with the 12 Principles of Green Chemistry. In recent times, based on the work of Noyori and Knowles (Nobel Prize in 2001) on the hydrogenation of carbonyl functions, a novel field of chemistry has been explored. Efficient catalysts for hydrogenations of a variety of functionalities were demonstrated. As reducing agents, either straightforward H_2 can be applied or sacrificial hydrogen donors (e.g. *i*PrOH, HCOOH, Hantzsch ester or silanes)[223,224] Important pioneering studies were published by the group of Milstein who developed a series of Ru-based catalysts bearing pincer ligands for the hydrogenation of carboxylic acid esters[225], amides[226] as well as organic carbonates and carbamates.[227] Since then, more earth abundant and inexpensive 3d metals have been enabled in numerous catalysts.[228-232]

However, the majority of homogeneous catalysts for hydrogenation was established for the hydrogenation and dehydrogenation for small molecules. Transferring this type of reactions to polyesters would allow for a chemical recycling according to Scheme 12.



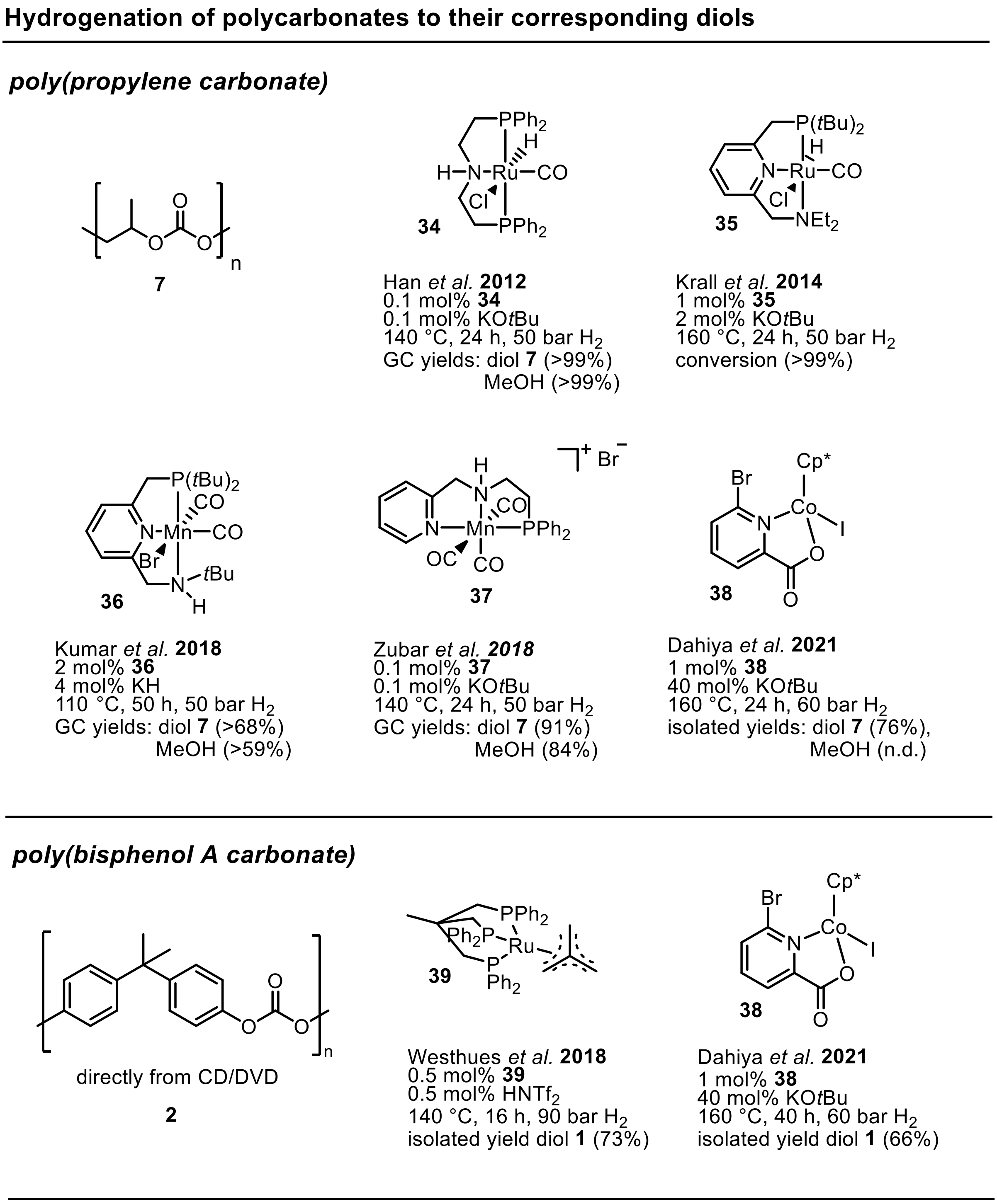
Scheme 12: Chemical recycling of polyesters via (de)hydrogenation catalysis.

In more detailed studies on the hydrogenations of polyesters/polycarbonates, Krall *et al.*[233] and Westhues *et al.*[234] demonstrated the hydrogenation of several polyesters and polycarbonates to their corresponding alcohols and methanol applying Ruthenium catalysis. Recently, also polyamides[235] and polyurethanes[236-238] were reductively depolymerized by Ru catalysts and hydrogen.

3.4.1 Hydrogenation of polycarbonates

Surprisingly, the first hydrogenative depolymerization by molecular catalyst was described in an article by Han *et al*. wherein PPC (**7**) was hydrogenated to 1,2-propanediol (**7**) and methanol.[239] As catalyst, they applied the Ru-MACHO complex (**34**), which was developed by the Takasago company for ester hydrogenation.[240] Only 0.1 mol% of the precatalyst was required to achieve excellent yields. In the publication by Krall *et al*., excellent yields were achieved using the Milstein precatalyst (**35**) under comparable conditions, however requiring a higher catalyst loading.[233] In 2018, two publications made use of more earth abundant manganese as inexpensive 3d metal for the hydrogenation. In the example by Kumar *et al*. with complex **36** as catalyst[241] a significantly lower reaction temperature of 110 °C was required while Zubar *et al*.[242] only applied 0.1 mol% of an air-stable precatalyst (**37**) at 140 °C. In all aforementioned reports, no isolation of the monomer 1,2-propanediol (**7**) was demonstrated. Recently, Dahiya *et al*. also include the purification of the monomer. However, their system based on **38** operates under relatively harsh conditions and high loadings of KO*t*Bu.[243] On the other hand, reports on the catalytic hydrogenation of the mass polymer

PBAC (**2**) are scarce. The reaction conditions stated again require either high pressures of hydrogen, as reported by Westhues *et al.* for catalyst **39**, or large quantities of precatalyst **38** and additive. Notably, the corresponding monomer BPA (**1**) could be obtained via simple recrystallization in good yields, while the yields for MeOH were not reported.[234]



Han *et al.* **2012**
0.1 mol% **34**
0.1 mol% KO*t*Bu
140 °C, 24 h, 50 bar H_2
GC yields: diol **7** (>99%)
MeOH (>99%)

Krall *et al.* **2014**
1 mol% **35**
2 mol% KO*t*Bu
160 °C, 24 h, 50 bar H_2
conversion (>99%)

Kumar *et al.* **2018**
2 mol% **36**
4 mol% KH
110 °C, 50 h, 50 bar H_2
GC yields: diol **7** (>68%)
MeOH (>59%)

Zubar *et al.* ***2018***
0.1 mol% **37**
0.1 mol% KO*t*Bu
140 °C, 24 h, 50 bar H_2
GC yields: diol **7** (91%)
MeOH (84%)

Dahiya *et al.* **2021**
1 mol% **38**
40 mol% KO*t*Bu
160 °C, 24 h, 60 bar H_2
isolated yields: diol **7** (76%),
MeOH (n.d.)

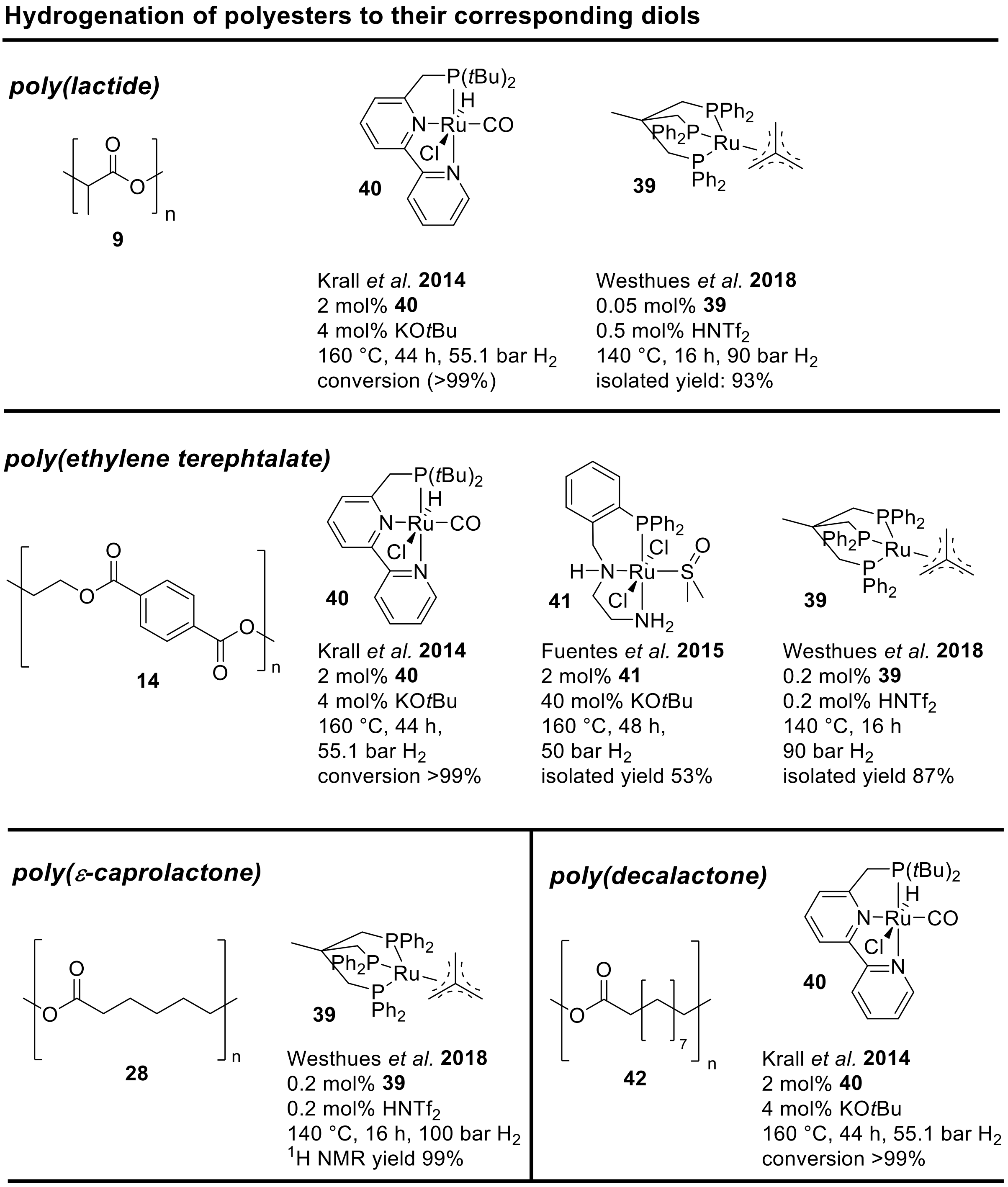
Westhues *et al.* **2018**
0.5 mol% **39**
0.5 mol% $HNTf_2$
140 °C, 16 h, 90 bar H_2
isolated yield diol **1** (73%)

Dahiya *et al.* **2021**
1 mol% **38**
40 mol% KO*t*Bu
160 °C, 40 h, 60 bar H_2
isolated yield diol **1** (66%)

Scheme 13: Overview of published catalysts and reaction conditions for the homogeneously catalyzed hydrogenation of polycarbonates.[233,234,239,242,243]

3.4.2 Hydrogenation of polyesters

On the other hand, the hydrogenation of polyesters was reported in three publications. The publication of Krall *et al.* from 2014 describes as suitable reaction conditions relatively high temperatures, reaction times and loadings of catalyst **40** for PLA (**9**), PET (**14**) and poly(decalactone) (**42**). Also, the formation of the diols was only qualitatively detected and the isolation was not reported. However, they found complete depolymerization for a variety of important polyesters (Scheme 14).[233] Later, Fuentes *et al.* hydrogenated PET (**14**) using complex **41** and described a purification of the monomers by column chromatography to achieve mediocre yields.[244] In 2018, Westhues *et al*. showed in a study, that low loadings of a Ru(triphos)tmm (**39**)/$HNTf_2$ system (0.05-0.2 mol%) can be used to achieve excellent isolated or ^1H NMR yields. Interestingly, they also demonstrated the selective hydrogenation of a mixture of PLA (**9**) and PET (**14**). The, PLA (**9**) is already reduced to 1,2-propanediol (**7**) at 45 °C while PET (**14**) requires temperatures of at least 80 °C to observe notable conversion. Overall, with regards to technical application, this approach is interesting as the catalyst loadings are very low. In addition, also a mixture of PLA (**9**) and PET (**14**) was successfully hydrogenated and a strategy to separate the monomers was presented.[234]



Hydrogenation of polyesters to their corresponding diols

poly(lactide)

9

40

39

Krall *et al.* **2014**
2 mol% **40**
4 mol% KO*t*Bu
160 °C, 44 h, 55.1 bar H_2
conversion (>99%)

Westhues *et al.* **2018**
0.05 mol% **39**
0.5 mol% $HNTf_2$
140 °C, 16 h, 90 bar H_2
isolated yield: 93%

poly(ethylene terephtalate)

14

40

41

39

Krall *et al.* **2014**
2 mol% **40**
4 mol% KO*t*Bu
160 °C, 44 h,
55.1 bar H_2
conversion >99%

Fuentes *et al.* **2015**
2 mol% **41**
40 mol% KO*t*Bu
160 °C, 48 h,
50 bar H_2
isolated yield 53%

Westhues *et al.* **2018**
0.2 mol% **39**
0.2 mol% $HNTf_2$
140 °C, 16 h
90 bar H_2
isolated yield 87%

poly(ε-caprolactone)

28

39

Westhues *et al.* **2018**
0.2 mol% **39**
0.2 mol% $HNTf_2$
140 °C, 16 h, 100 bar H_2
^1H NMR yield 99%

poly(decalactone)

42

40

Krall *et al.* **2014**
2 mol% **40**
4 mol% KO*t*Bu
160 °C, 44 h, 55.1 bar H_2
conversion >99%

Scheme 14: Overview of published catalysts and reaction conditions for the homogeneously catalyzed hydrogenation of polyesters.[233,234]

4. Aim of the work

The literature presented above provides a variety of different approaches to chemical recycling. However, in order to provide a good basis to establish chemical recycling on an industrial scale, further investigations are required. For all consisting chemical recycling strategies, more efficient catalysts should be established. These should be tolerant towards impurities like additives, food residues and other polymers. A practical purification of the corresponding monomer should be found which is then repolymerized ideally with the same catalyst. In addition, for the degradation optimized reaction conditions (solvent free, low-temperature, catalyst loading) should be evaluated and applied to contaminated “realistic” plastic waste. This should reveal potential catalyst poisons originating from impurities.

Furthermore, due to limitations of the pre-sorting technology, different sorts of polyesters might not be separable from each other. In this regard, information should be collected on how mixed polyesters and non-polyesters influence the depolymerization. This can be used for the development of a reaction sequence that is suitable to degrade mixtures of polyesters (Figure 6).

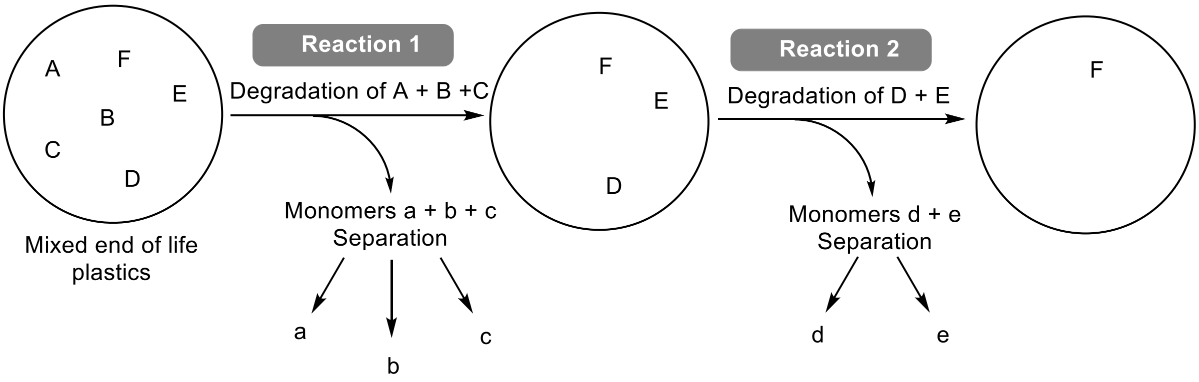


Figure 6: Exemplary reaction scheme for the degradation of complex polymer mixtures. Polymers A, B, C degrade readily under the conditions from reaction 1. Polymer D and E require higher temperature, different catalyst or additional solvents.

Herein, the catalysts that are capable to degrade many polymers at once are interesting. Ideally, a catalyst that is capable to degrade all polyesters at once should be found, that can also be reused multiple times.

For hydrogenative depolymerization, the practicability should be enhanced within this thesis. Therefore, more efficient catalysts that allow for less forcing reaction conditions (e.g. hydrogen pressure, catalyst loading, temperature) should be found. In this regard, also the ligand motif or central metal should be varied to enable easier accessible catalyst. Also, the scope of polymers should be extended and more efficient catalysts should be found.

5. Results and discussion

5.1 Depolymerization of polycarbonates

In the following article PBAC (**2**) was depolymerized with Ac_2O or AcOH in the presence of DMAP.[245] As valuable product BPA diacetate (**5**) was obtained in excellent yields. Therefore, either both microwave or conventional heating with elongated reaction times were feasible. Using AcOH, this reaction is less selective, thus giving BPA (**1**) and BPA diacetate (**5**) as byproduct. As second building block, CO_2 is obtained, that can be chemically captured with a suitable diamine in aqueous solution. As PBAC (**2**) source CDs were enable. If the PBAC (**2**) was extracted from the CD to filter off other materials (e.g. aluminium foil), the yield for BPA diacetate (**5**) was notably increased from 57% to 82%. Finally, it was possible to regenerate PBAC (**2**) with low molecular weight using the recycled BPA diacetate (**5**) and fresh DPC (**3**).

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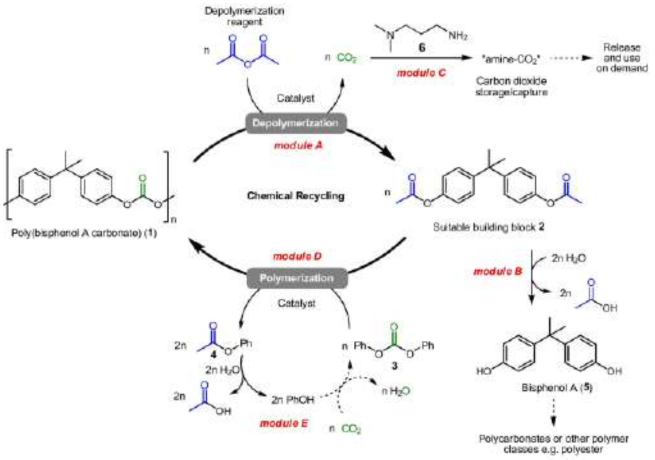
Sustainable Chemistry

Depolymerization of End-of-Life Poly(bisphenol A carbonate) via Transesterification with Acetic Anhydride as Depolymerization Reagent

Christoph Alberti,[a] Felix Scheliga,[b] and Stephan Enthaler*[a]

The chemical recycling, a combination of depolymerization and polymerization processes, of end-of-life plastics/polymers can contribute to a more sustainable, resource-conserving and environmental-benign society. In this regard, we have set up a capable procedure for the chemical recycling of the bisphenol A unit of poly(bisphenol A carbonate). In more detail, acetic acid or acetic anhydride were used as depolymerization reagent in the DMAP-catalyzed conversion of end-of-life poly (bisphenol A carbonate) to obtain bisphenol A diacetate as well-defined product. Moreover, it was demonstrated that bisphenol A diacetate in combination with diphenyl carbonate can be applied in the potassium *tert*-butoxide catalyzed synthesis of new poly(bisphenol A carbonate). In consequence a recycling of poly(bisphenol A carbonate) is feasible.

Every year, a steadily increasing amount of end-of-life plastics[1] based on fossil resources is manufactured on a multiton scale.[2] The state-of-the-art treatment for collected end-of-life plastic streams is based on energy recovery, mechanical recycling, downcycling and (landfill storage).[3,4,5] Disadvantageously, the major method, the energy recovery, converts the chemical functionalities of the polymers into greenhouse gases (e.g. carbon dioxide), hence for new plastics the steadily decreasing fossil resources will be consumed.[6,7] A better resource-conserving and environmental-benign method represents the chemical recycling.[8] In more detail, the end-of-life polymer is initially converted to low-molecular weight substances by depolymerization process. In a subsequent polymerization process the substances are used as feedstock for new polymers and therefore a recycling of polymers is feasible. Importantly, the quality of the product is not connected to the quality of the end-of-life polymer as observed in the case of mechanical recycling and downcycling. However, high energy demand, copolymers, additives, selectivity, and the current low price for fossil resources for the production of new polymers etc. hamper the successful implementation of chemical recycling.[9] Therefore, the development of new methods is of importance for reaching the goal of a more resource-conserving and environmental-benign society.[10,11] In the modern society, polycarbonates, e.g. bisphenol A based polymers are a widely applied class of polymers e.g. optical storage (CD, DVD, Blu-ray) or as artificial glass.[12] For the recycling of poly(bisphenol A carbonate) (**1**) several protocols have been reported so far including mechanical recycling, blending with other materials, pyrolysis (feedstock recycling), biochemical degradation and chemical recycling (e.g. hydrolysis, (hydro)glycolysis, alcoholysis and aminolysis).[13]



Scheme 1. Concept for the chemical recycling of poly(bisphenol A carbonate).

We report herein our investigations on a new concept for the chemical recycling of end-of-life **1** (Scheme 1). In more detail, the concept bases on a depolymerization composed of a transesterification of end-of-life **1** supported by a straigthforward catalyst and cheap and abundant acetic acid or acetic anhydride as depolymerization reagents. On the one hand carbon dioxide is formed originated from the carbonate function of the polymer, which can be captured by an amine to produce carbamic acid as liquid and high density carbon dioxide storage.[14,15] Noteworthy, the carbon dioxide can be easily released by temperature control and may be used for follow up reactions (e.g. polycarbonate synthesis).[16] On the

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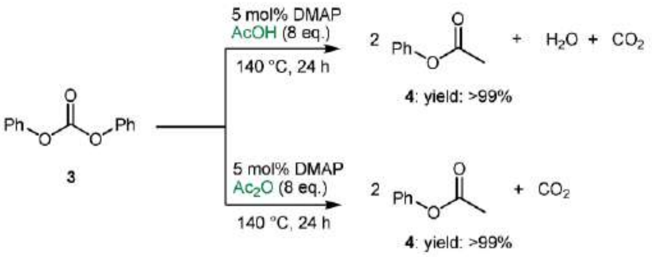
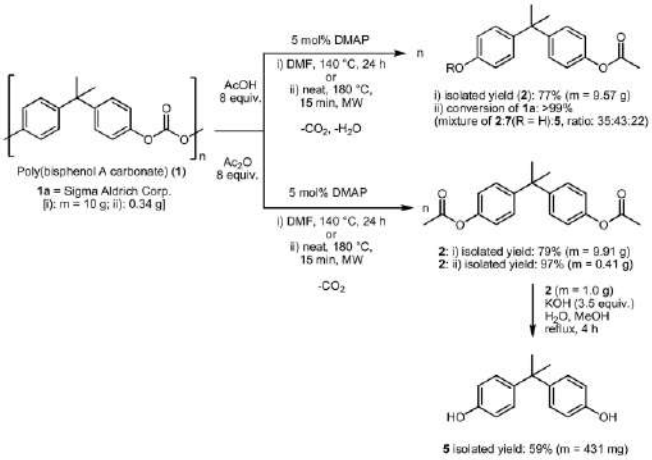
other hand, the low molecular weight compound bisphenol A diacetate (**2**) is formed during depolymerization. Chemical **2** can be used in combination with the industrial relevant diphenyl carbonate (**3**) for the polymerization of new **1** to close the cycle. Moreover, **2** can be applied for the synthesis of other bisphenol A based polymers as well as give access to bisphenol A (**5**), which also allows access to numerous types of polymers.[17,18]During the polymerization reaction of **2** and **3** phenyl acetate is formed, which can be hydrolyzed to acetic acid and phenol, which can be reacted with carbon dioxide to reproduce **3**.[19]

Initially, as model reaction for the depolymerization of bisphenol A based polycarbonates the conversion of diphenyl carbonate **3** was studied as motif for the repeating unit (Scheme 2). In more detail, diphenyl carbonate **3** was reacted with an excess of acetic acid (8 equiv.) and catalytic amount of 4-dimethylaminopyridine (DMAP, 5.0 mol%) under solvent-free conditions.[20] The mixture was stirred for 24 hours at 140 °C, meanwhile **3** and DMAP dissolve in the acetic acid.[21] Afterwards, chloroform-*d*1 was added and the mixture was analyzed by[1]H NMR. In the aliphatic range of the ^{1}H NMR a new signal was observed with a chemical shift of 2.29 ppm, which is assigned to the transesterification product phenyl acetate **4** and revealing the split of the carbonate unit.[22] Moreover, the presence of **4** was verified by ^{13}C{^{1}H} NMR (δ = 21.2 ppm). Phenyl acetate **4** was also detected as main product in high yields if acetic acid was replaced by acetic anhydride under identical reaction conditions (Scheme 2). The formation of carbon dioxide, in case of acetic acid and acetic anhydride, was detected by a positive probe based on an aqueous $Ba(OH)_2$-solution in a fermentation lock connected to the reaction system.[23]



Scheme 2. Reactions of diphenyl carbonate as model for polycarbonate with acetic acid and acetic anhydride [Reaction conditions: **3** (2.0 mmol), acetic acid or acetic anhydride (16.0 mmol), 4-dimethylaminopyridine (5.0 mol%, 0.1 mmol), 140 °C, 24 h, yield determined by ^{1}H NMR].

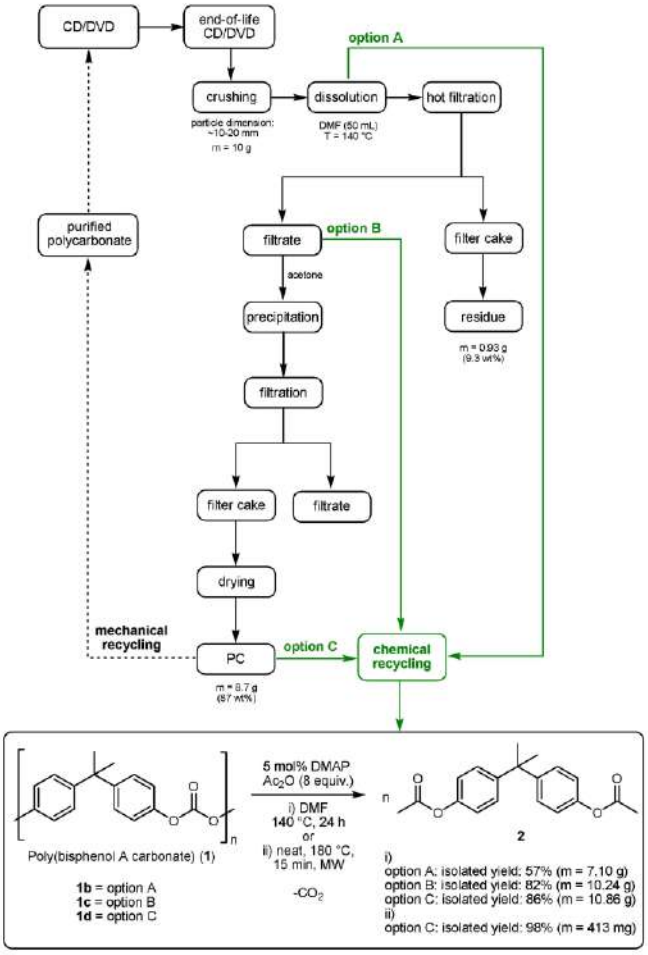


Scheme 3. Depolymerization of commercially available pure poly(bisphenol A carbonate) [Reaction conditions: a) depolymerization: *conventional heating*: **1 a** (40 mmol, based on the monomeric unit), acetic acid (320 mmol) or acetic anhydride (320 mmol), DMAP (5 mol%, 2 mmol), 140 °C, 24 h, work-up; *microwave heating*: **1 a** (1.35 mmol, based on the monomeric unit), acetic acid (10.8 mmol) or acetic anhydride (10.8 mmol), DMAP (5 mol%, 0.07 mmol), 180 °C, 15 min, work-up; b) hydrolysis of **2**: **2** (3.2 mmol), KOH (11.2 mmol), MeOH, water, reflux, 4 h, work-up].

Afterwards, the protocol was transferred to commercially available poly(bisphenol A carbonate) **1 a** pellets (dimension: ~3 mm) using 8 equiv. of acetic acid and 5 mol% DMAP based on the monomeric unit of **1 a** (Scheme 3 and Scheme 1, *module A*). In contrast to model compound **3**, no product formation was observed, due to poor solubility of **1 a** in acetic acid. Therefore dimethylformamide (c(**1**) = 2.0 mol/L) was used as solvent revealing a clear orange/brown solution after two hours at 140 °C. The reaction proceeded for a total reaction time of 24 hours. Afterwards, an aliquot of the reaction mixture was dissolved in chloroform-*d*1 and analyzed by NMR. In the aliphatic range of the ^{1}H NMR spectrum two signals with a chemical shift of 1.65 ppm ($C(CH_3)_2$) and 2.27 ppm ($OC(=O)CH_3$) were detected, which are assigned to the depolymerization product bisphenol A diacetate **2**.[24] Moreover, the presence of **2** was verified by ^{13}C{^{1}H} NMR [δ = 21.2 ppm ($C(CH_3)_2$) and 30.9 ppm ($OC(=O)CH_3$)]. After work-up of the reaction mixture and crystallization from petroleum ether **2** was isolated as colorless crystals in 79% yield. The same product was formed applying acetic anhydride as depolymerization reagent in a yield of 77% (Scheme 3). Moreover, the diacetate **2** was converted to bisphenol A by basic ester cleavage in 59% yield for the ester cleavage step or in 48% yield based on the overall process (Scheme 3 and Scheme 1, *module B*).[25] Interestingly, bisphenol A can be used for the synthesis of new polycarbonates as well as for other bisphenol A based polymers. In addition, the microwave assisted depolymerization of **1 a** was studied. In this regard, a mixture of **1 a**, acetic anhydride (8 equiv., 10.8 mmol) and catalytic amounts of DMAP (5.0 mol %) were reacted at 180 °C for 15 minutes (Scheme 3). Interestingly, no additional solvent was necessary as required for conventional heating (vide supra). After distilling off the excess of acetic anhydride (recovered: 53%, 5.7 mmol), which can be reused for depolymerizations, **2** was isolated in an excellent yield of 97%. Decreasing the reaction temperature to 160 °C revealed the formation of **2** in excellent yield (>99%, NMR yield) after 15 minutes. Still good yield (76%, NMR yield) was observed with a lower catalyst loading of DMAP (2.5 mol%) at 180 °C (15 min, 8 equiv. Ac_2O). Furthermore, 1,4-diazabicyclo[2.2.2]octane (DABCO) was applied as precatalyst (5 mol%), but showing a decreased performance (26% yield, NMR yield).

Decreasing the amount of acetic anhydride to 4 equivalents led to the formation of **2** in 96% isolated yield. In case of acetic acid as depolymerization reagent full conversion (>99%) of **1 a** was detected, but a mixture of bisphenol A (**5**), bisphenol A acetate (**7**) and bisphenol A diacetate (**2**) were found in a ratio of 22:43:35 under microwave heating (180 °C, 15 min).

After having demonstrated the operability of the depolymerization process we transferred the protocol to commodities containing poly(bisphenol A carbonate) **1**. In this regard, compact discs (CD) and digital versatile discs (DVD) containing **1** as major ingredient were tested (Scheme 4). Beside **1** the CDs/DVDs containing additives e.g. metal foils, plastic foils and dyes, which can potentially inhibit the depolymerization process. Three different pre-treatment options have been investigated to study the effect of the additives (Scheme 4). In case of *option A* the CDs/DVDs were crushed into small pieces and DMF was added. The mixture was heated to 140 °C and stirred until **1** was dissolved (ca. 30 min). The clear solution contained floating materials (metal and plastic foil). To this mixture catalytic amount of DMAP (5 mol% based on the monomeric unit of **1**) and acetic anhydride (8 equiv. based on the monomeric unit of **1**) was added, while stirring and heating were continued for 24 hours.

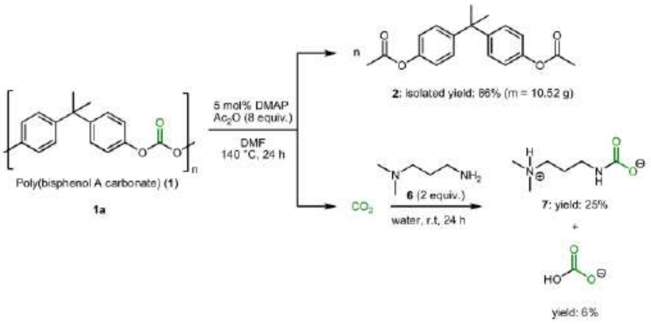


Scheme 4. Depolymerization of poly(bisphenol A carbonate) **1** originated from CDs/DVDs with acetic anhydride [Reaction conditions: *conventional heating*: **1 b/1 c/1 d** (40 mmol, based on the monomeric unit), acetic anhydride (320 mmol), DMAP (5 mol%, 2 mmol), 140 °C, 24 h; *microwave heating*: **1 a** (1.35 mmol, based on the monomeric unit), acetic acid (10.8 mmol) or acetic anhydride (10.8 mmol), DMAP (5 mol%, 0.07 mmol), 180 °C, 15 min, work-up].

Afterwards, the mixture was cooled to room temperature and filtered to remove the floating materials. After work-up, the depolymerization product bisphenol A diacetate **2** was purified by crystallization and was obtained in 57% yield.[26] In contrast to *option A*, in case of *option B* a hot filtration to remove floating materials after dissolving **1** was performed (Scheme 4). The clear solution was subjected to depolymerization as described for *option A*. compared to *option A* product **2** was isolated in a higher yield of 82%, which revealed the need for purification to avoid diminishing effects of the CD/DVD additives. In contrast to *option B*, for *option C* the filtrate was cooled to room temperature after hot filtration, meanwhile the polymer starts to precipitate, which was assisted by addition of acetone (Scheme 4). The polymer was filtered off and washed with acetone. After drying polymer **1** was obtained as colorless powder in a yield of 87 wt% based on the starting weight of the CD/DVD. Noteworthy, this pathway can also be applied for the mechanical recycling of poly(bisphenol A carbonate) **1**. The powder was subjected to depolymerization as described for *option A*. Product **2** was isolated in 86% yield, revealing the necessity for purification of the polycarbonate prior to depolymerization reactions.

As demonstrated for the commercially available polymer **1 a** the depolymerization of polymer **1** derived from option C was performed using microwave heating under neat conditions (180 °C, 5 mol% DMAP, 8 equiv. Ac_2O). Product **2** was obtained in excellent yield (98%) within short reaction time (15 min).

Moreover, attempts were undertaken to capture the carbon dioxide produced during the depolymerization process (Scheme 5 and Scheme 1, *module C*). The formed carbon

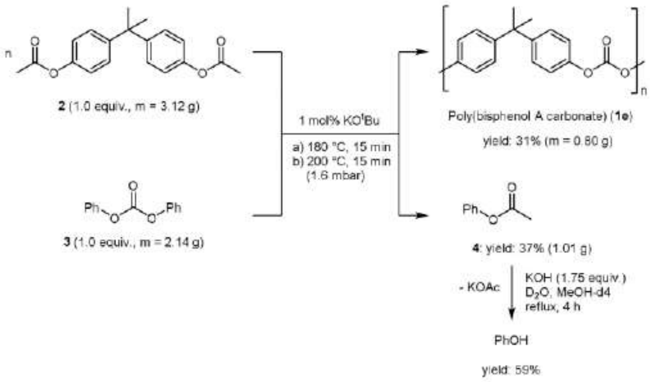


Scheme 5. Depolymerization of poly(bisphenol A carbonate) and carbon dioxide capture [Reaction conditions: a) depolymerization: **1 a** (40 mmol, based on the monomeric unit), acetic anhydride (320 mmol), DMAP (5 mol%, 2 mmol), 140 °C, 24 h; b) Carbon dioxide capture: dimethylaminopropylamine (0.078 mol, 2 M in water, r.t., 24 h].

dioxide was passed in an aqueous solution of 3-dimethylaminopropylamine (2 M) in accordance to the work of Zhang *et al.*[15] The reaction mixture of the carbon dioxide capture experiment was investigated by $^{13}C\{^1H\}$ NMR methods revealing the formation of compound **7** with a carbamate function, which originates from carbon dioxide. Moreover, hydrogen carbonate was detected.

Applying $^{13}C\{^1H\}$IGNMR methods showed an incorporation of 25% of produced carbon dioxide in 3-dimethylaminopropylamine and 6% in hydrogen carbonate, which corresponds to an overall capture of 31%. Interestingly, the carbon dioxide can be easily released by increasing the temperature of the aqueous solution of **7** and hydrogen carbonate and allows the generation of carbon dioxide on demand.[15]

After having demonstrated the operability of the depolymerization process the polymerization of the depolymerization product **2** was studied for closing the recycling system (Scheme 6). In this regard, **2** was reacted with diphenyl carbonate **3** in the presence of catalytic amounts of potassium *tert*-butoxide (5 mol%) under solvent-free conditions in a distillation device.[27] The mixture was stirred and heated in an oil bath to 180 °C and was kept for 15 minutes at 180 °C. Afterwards, the temperature was increased to 200 °C, while setting up a vacuum (1.6 mbar) at 190 °C. During the utilization of the vacuum a colourless liquid is distilled off. After 10 minutes no further liquid was collected and the polymerization process was stopped. The liquid was analysed by ^{1}H NMR revealing the formation of **4** as major component in 37% yield. As figured out in Scheme 1 compound **3** and acetic acid can be regenerated in two steps starting from **4** with an ester cleavage (Scheme 6). Therefore, compound **4** was subjected to a basic ester cleavage reaction.[28] The reaction mixture was afterwards analysed by ^{1}H NMR revealing the formation of phenol and potassium acetate as an acetic acid equivalent. On the other hand, in the polymerization flask a brown viscous residue was formed. The residue was dissolved in dichloromethane and a powder was precipitated by addition of acetone. The powder was washed several times with acetone and petroleum ether, finally yielding an off-white powder, which was analysed by ^{1}H NMR revealing a significant removal of the acetate function, which indicates the formation of polymer **1e**. Moreover, with GPC analysis of synthesized 1e dissolved in tetrahydrofuran a number average molar mass of Mn ~ 3507 g/mol, a mass average molar mass Mw ~ 7586 g/mol and a polydispersity of 2.16 was found. In consequence the proposed cycle for the recycling of poly(bisphenol A carbonate) running via depolymerization and polymerization is closed.



Scheme 6. Polymerization of bisphenol A diacetate (**2**) [Reaction conditions: a) polymerization: bisphenol-A diacetate (**2**) (0.01 mol), diphenylcarbonate (**3**) (0.01 mol) of potassium *tert*-butoxide (1.0 mol%, 0.1 mmol), 180 °C (15 min), 200 °C (15 min, 1.6 mbar); b) hydrolysis of **4**: **4** (3.67 mmol), KOH (6.43 mmol), MeOH-*d4*, water-*d2*, reflux, 4 h, work-up].

In summary, we have set up a straightforward method based on depolymerization and polymerization for the recycling of end-of-life poly(bisphenol A carbonate). On the one hand, depolymerization was carried out with acetic acid or acetic anhydride as a depolymerization reagent to obtain as well-defined product bisphenol A diacetate in up to 97% yield. Moreover, carbon dioxide is formed, which was captured by an amine and can be potentially recycled to produce new poly (bisphenol A carbonate). On the other hand, bisphenol A diacetate in combination with diphenyl carbonate can be applied as starting materials for polymerization chemistry to produce new poly(bisphenol A carbonate) and therefore closing the cycle. Future studies will focus on the improvement of the depolymerization process and the carbon dioxide post-treatment. Moreover, a life cycle assessment will be carried out to evaluate the potential for large-scale applications.

Supporting Information Summary

Experimental details for the depolymerization and polymerization reactions, and characterization data of the compounds are provided in the Supporting Information.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: green chemistry · homogeneous catalysis · polymers · recycling · carbon dioxide capture

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The main issue with this novel recycling concept is the formation of CO_2, that is difficult to fixate and revalorize. Also, acetic anhydride is converted in a stoichiometric fashion resulting in additional costs. The successful application of DMAP as transesterification catalyst led to the next article, in which DMAP was used in combination with MeOH as depolymerization reagent.[246] Advantageously, the carbonate function could be conserved either as DMC (**4**) or diphenyl carbonate which are formed in good yields along with BPA (**1**). Importantly, the DMC (**4**) yield is significantly affected by the reaction temperature, due to thermal decomposition. In addition, new PBAC (**2**) could be regenerated with the recycled building blocks.

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SHORT COMMUNICATION

Depolymerization of End-of-Life Poly(bisphenol A carbonate) via 4-Dimethylaminopyridine-Catalyzed Methanolysis

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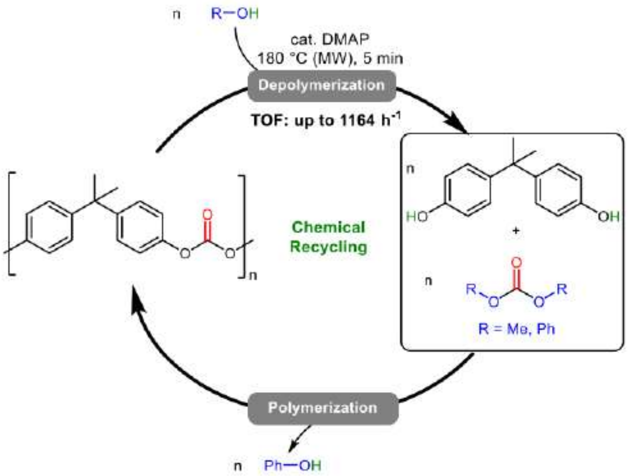
Abstract

The chemical recycling, a sequence of depolymerization and polymerization reactions, of end-of-life plastics/polymers can contribute to a sustainable, resource-conserving and environmental-benign society. In this regard, we have set up a protocol for the depolymerization of end-of-life poly(bisphenol A carbonate). In more detail, applying a combination of methanol and catalytic amounts of 4-dimethylaminopyridine (DMAP) end-of-life poly(bisphenol A carbonate) was depolymerized to bisphenol A and dimethyl carbonate. With the aid of microwave heating an excellent rate of depolymerization (>99%) within short reaction times (5 min) and turnover frequencies up to 1164 h^{-1} were achieved. Moreover, it was demonstrated that phenolysis can be applied under optimized reaction conditions resulting in the formation of the mixture bisphenol A and diphenyl carbonate, which can be used for the synthesis of new poly(bisphenol A carbonate). In consequence a closed cycle for poly(bisphenol A carbonate) is feasible.

Graphic Abstract



Keywords End-of-life poly(bisphenol A carbonate) · Recycling · Depolymerization · Microwave · Waste CDs/DVDs

Statement of Novelty

The chemical recycling (depolymerization-polymerization cyles) of end-of-life plastic is of great importance and offers possibilities to reduce waste streams, avoid the generation of carbon dioxide and save fossil resources. This research work offers an efficient add-on to the depolymerization of end-of-life poly(bisphenol A carbonate) derived from CDs/DVDs

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applying an alcoholysis, because excellent yields were realized within short reaction times (5 min) using microwave heating. Remarkably, in the presence of a simple catalyst excellent turnover frequencies of up to 1164 h^{-1} were achieved, which are among the highest activities obtained so far. This research demonstrates also how to close the cycle to produce new poly(bisphenol A carbonate) from depolymerization products.

Introduction

The amount of end-of-life plastics[1] is steadily increasing every year [1]. The state-of-the-art treatment for collected end-of-life plastic streams is subdivided into energy recovery, recycling and (landfill storage[2]) [2–10]. Disadvantageously, the major treatment method (energy recovery) converts the carbon based chemical functionalities of the polymers derived from fossil resources into not "easily" convertible molecules,[3] e.g. carbon dioxide, therefore for new plastics the steadily decreasing fossil resources will be further decreased [11]. Moreover, the release of the generated carbon dioxide to the atmosphere increases the greenhouse effect and in consequence the negative issues on mankind [12]. On the other hand, treatment of portions of end-of-life plastics is done by recycling processes (back-to-plastics). For instance mechanical recycling (material recycling, material recovery) and downcycling allow the application of the end-of-life plastic stream as raw material for products with same/similar quality or lower quality with respect to the starting material [13–15]. Noteworthy, the change of the basic chemical structure is not envisaged. However, by repeating the processes and external influences the properties of the material change and make further mechanical recycling or downcycling unattractive, hence this portion is finally send to energy recovery or landfills. In consequence, for replacing the plastic material fossil resources are required. An enhanced resource-conserving and environmental-benign procedure represents the chemical recycling of end-of-life plastics [16, 17]. In this regard, the end-of-life polymer as major component of the plastic is primarily transformed to low-molecular weight chemicals (monomers) by depolymerization process. In a following polymerization the monomers are applied as feedstock for new polymers and therefore a recycling of polymers/plastics is feasible. Notably, the quality of the material is not coupled to the quality of the end-of-life polymer as observed in the case of mechanical recycling and downcycling, therefore the quality is adjustable. Conversely, high energy demand, copolymers, additives, selectivity, and the current low price for fossil resources for the production of new polymers/plastics etc. impede the successful implementation of chemical recycling processes [18–20]. Therefore, the search for new methodologies is of importance for realizing the objective of a more resource-conserving and environmental-benign society [21]. In this regards, polycarbonates, e.g. bisphenol A based polymers are a widely used class of polymers e.g. for optical storage (CD, DVD, Blu-ray) or in artificial glass applications [22–25]. For the recycling of poly(bisphenol A carbonate) (**1**) several protocols have been accounted so far including mechanical recycling, blending with other materials, pyrolysis (feedstock recycling), biochemical degradation and chemical recycling (e.g. hydrolysis (hydro)glycolysis, alcoholysis and aminolysis) [26–64].

For instance the alcoholysis/transesterification, especially the methanolysis, has been investigated (Fig. 1). In more detail, the end-of-life poly(bisphenol A carbonate) (**1**, PBPAC) reacts in the presence of a catalyst with an excess of methanol to form bisphenol A (**2**, BPA) and dimethyl carbonate (**3**). In accordance to the industrial protocol, bisphenol A (**2**, BPA) can be reused as monomer in combination with diphenyl carbonate or phosgene for the synthesis of new poly(bisphenol A carbonate) (**1**) [65]. For the mixture of dimethyl carbonate (**3**) and methanol applications in organic chemistry has been proposed [66, 67]. Moreover, the utilization of phenol instead of methanol as depolymerization reagent results in the formation of bisphenol A (**2**, BPA) and diphenyl carbonate (**4**, DPC) the starting chemicals for the synthesis of poly(bisphenol A carbonate) (**1**). We report herein our investigations on the chemical recycling of end-of-life **1** (Fig. 1) [68, 69]. In more detail, the concept bases on a fast depolymerization of **1** via methanolysis or phenolysis applying microwave irradiation (MW) [70], which has been demonstrated to be beneficial for depolymerization reactions to obtain significant amounts of product within short reaction times [62–64]. As catalyst we have chosen the organocatalyst DMAP (4-dimethylaminopyridine), which revealed some catalyst activity applying conventional heating, but high loadings and long reaction times are required [31].

Results and Discussion

Initially, the depolymerization of commercially available poly(bisphenol A carbonate) (**1a**) pellets (dimension: ~ 3 mm) was studied (Table 1). In this regard, **1a**

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[1] Plastics are typically composed of polymers and often other substances e.g. fillers, plasticizers, colorants.

[2] Landfill storage depends strongly on local regulations, e.g. in the European Union landfill storage has been limited to the necessary minimum (see for instance: reference [2]).

[3] A high energy input is required to convert carbon dioxide to plastics again.

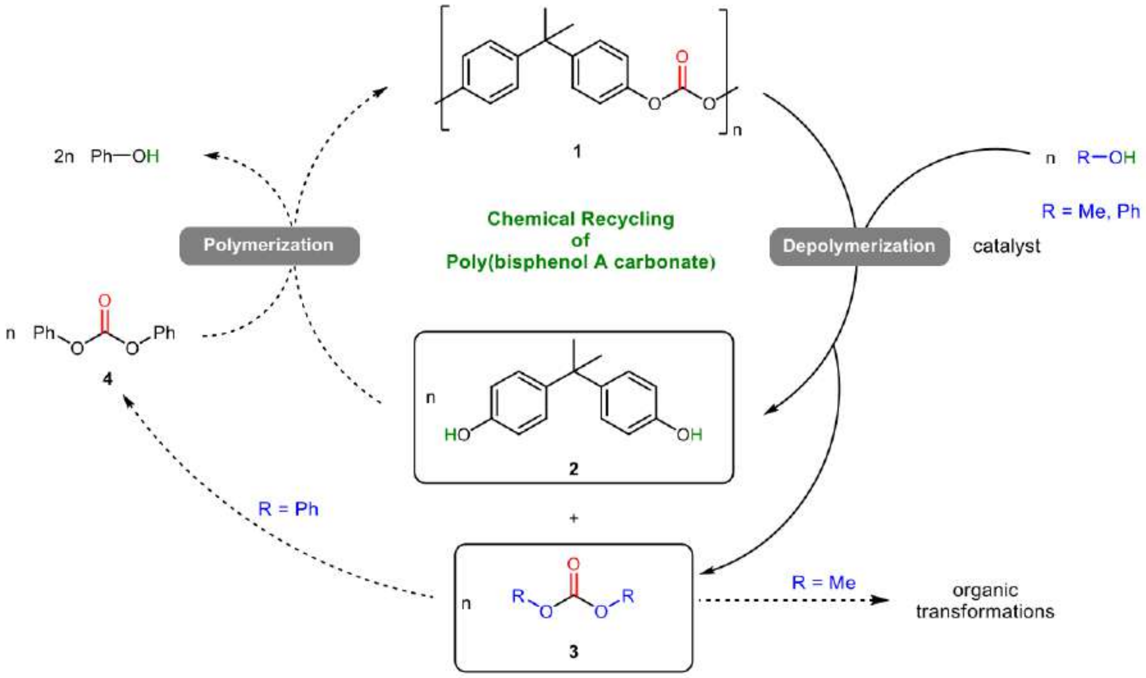

Fig. 1 Concept for the chemical recycling of poly(bisphenol A carbonate) with alcohols

(1.35 mmol) was reacted with an excess of methanol (46.2 equiv.) in the presence of catalytic amounts of 4-dimethylaminopyridine (DMAP, 5.0 mol% based on the monomeric unit of **1**). Noteworthy, no additional solvent was necessary since the methanol acts as reactant as well as solvent [71]. The mixture was stirred in a sealed vial for 10 min at 180 °C in a microwave reactor (Table 1, entry 1). After 2–3 min the suspension became a clear colorless solution. Afterwards, the mixture was cooled to room temperature and an aliquot was dissolved in chloroform-*d* and the mixture was analyzed by ^{1}H NMR. In the aliphatic range of the ^{1}H NMR spectrum one signal with a chemical shift of 1.60 ppm ($C(CH_3)_2$) was observed, which is assigned to the depolymerization product bisphenol A (**2**) [72]. Moreover, in the aromatic region two sets of signals were observed, which can be assigned to the two sets (2×4H) of aromatics C–H in the bisphenol A molecule. Interestingly, no other signals were detected in the aromatic region, which may arise from oligomers/polymers of poly(bisphenol A carbonate), hence full conversion of **1a** to **2** is reached within 10 min. Noteworthy, in comparison to conventional heating (100 °C) **2** was obtained in significantly shorter reaction (10 min vs. 3.25 h) times and lower catalyst loading (5 mol% vs. 10 mol%) [31].[4] Also the second depolymerization product dimethyl carbonate (**3**) was detected by ^{1}H NMR revealing a signal at 3.77 ppm ($2\times CH_3$) [73]. Relating the integral of dimethyl carbonate to the integrals of bisphenol A revealed a lower yield of 57% for **3** (expected: ratio: **3**:**2**[6H, $2\times CH_3$]:**2**[8H, Ar–H] = 6:6:8; found: **3**:**2**[6H, $2\times CH_3$]:**2**[8H, Ar–H] = 3.4:6:8). Since the formation of **2** is coupled with the formation of **3**, a decomposition reaction of **3** may appear, while reducing the reaction time to 5 min showed a higher yield for **3** of 69% accompanied by a yield of > 99% of **2** (Table 1, entry 2). The decomposition of the carbonate function of **1a** or **3** may occur in the presence of small amounts of water [26, 34–40]. Based on that, we studied the stability of dimethyl carbonate under reaction conditions (5 mol% DMAP, MeOH, 160 °C, 10 min). In the absence of water no decomposition was observed, while in the presence of two equivalents of water a conversion of 29% of **3** was detected. Same effect was noticed in case of addition of water to the depolymerization of **1a**. Furthermore, a decarboxylation of **3** at higher temperatures can take place to form carbon dioxide and dimethyl ether [74–76].

Moreover, the stability of bisphenol A under reaction conditions (methanol, 5 mol% DMAP, 180 °C, 60 min) was studied, since some research groups reported on the decomposition at higher temperatures, but no decomposition was noticed in our case [30, 32, 40, 46]. Additionally, the stability of DMAP under reaction conditions (methanol, 180 °C, 60 min) was studied, but no decomposition was noticed. Next, the loading of DMAP was studied, showing still good performance at 0.5 mol% with a yield of 97% for **2** and

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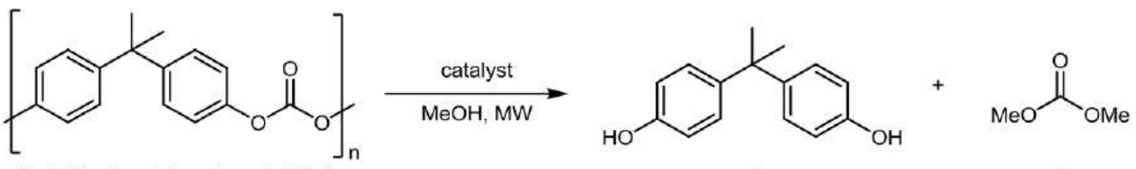
[4] The main focus of the work of Quaranta and coworkers was the application of DBU as the catalyst, therefore the results were not optimized for DMAP.

Table 1 DMAP-catalyzed depolymerization of poly(bisphenol A carbonate) **1a**



Poly(bisphenol A carbonate) (**1a**)

2

3

Entry[a]	Catalyst (mol%)	MeOH (equiv.)	Solvent (g)	T (°C)	t (min)	Yield BPA (%)[b]	Yield DMC (%)[c]
1	DMAP [5.0]	46.2	–	180	10	> 99	57
2	DMAP [5.0]	46.2	–	180	5	> 99	69
3	DMAP [2.5]	46.2	–	180	10	> 99	64
4	DMAP [1.0]	46.2	–	180	10	> 99	63
5	DMAP [0.5]	46.2	–	180	10	97	55
6	None	46.2	–	180	10	< 1	< 1[d]
7	DMAP [5.0]	23.1	–	180	10	> 99	58
8	DMAP [5.0]	11.6	THF [1.5]	180	10	> 99	88
9	DMAP [5.0]	5.8	THF [1.75]	180	10	84	53
10	DMAP [5.0]	2.9	THF [1.88]	180	10	60	35
11	DMAP [5.0]	46.2	–	160	10	> 99	57
12	DMAP [5.0]	46.2	–	140	40	> 99	80
13	DMAP [5.0]	46.2	THF [1.0]	140	40	> 99	77
14	DMAP [5.0]	46.2	THF [1.0]	120	60	85	45
15	DABCO [5.0]	46.2	–	180	10	94	56
16	Pyridine [5.0]	46.2	–	180	10	80	45

[a] Reaction conditions: poly(bisphenol A carbonate) (**1a**) (1.35 mmol), DMAP (0–5 mol%, 0–0.0675 mmol based on the repeating unit of **1a**), methanol (2.9–46.2 equiv. based on the repeating unit of **1a**), THF (0–1.875 g) microwave heating, 120–180 °C, 5–60 min

[b] The yield was determined by ^{1}H NMR

[c] The yield was determined by ^{1}H NMR

[d] 99% of the starting polymer **1a** was recovered

55% for **3**, while in the absence of DMAP no reaction took place (Table 1, entries 3–6). Noteworthy, the NMR yield of 97% corresponds to a turnover frequency (TOF[5]) of ca. 1164 h^{-1}. Comparing the results with established catalysts revealed catalyst activity in the same order of magnitude, e.g. ~ 1164 h^{-1} (DMAP, methanolysis) versus ~ 1844 h^{-1} (KF, methanolysis) [68] versus ~ 78 h^{-1} (DMAP, Ac_2O as depolymerization reagent) [61] and an increased activity compared to conventional heating ~ 1164 h^{-1} (DMAP, 180 °C, MW) versus ~ 3 h^{-1} (DMAP, 100 °C, conventional heating) [31]. Moreover, with respect to the principle of operation of DMAP a similar mechanism as reported by Quaranta et al. is contemplated [31]. Furthermore, the influence of the methanol:**1** ratio was investigated (Table 1, entries 7–10). Reducing the amount of methanol to 11.6 equiv. revealed still excellent yield of **2** (> 99%) and good yield of **3** (88%). Noteworthy, below 23.1 equiv. of methanol THF was added as co-solvent to fulfill the minimum volume requirement for microwave heating (Table 1, entries 8–10). With 11.6 equiv. methanol a higher yield was observed, which may be due to better solubility/faster solution of the polymer in THF. Decreasing the amount of methanol to 2.9 equiv. resulted in the formation of **2** and **3** in decreased yields, which indicates that the underlying process might be an equilibrium, which can be effected by the methanol concentration (Table 1, entries 9, 10). Then the effect of the reaction temperature was studied (Table 1, entries 11–14). Excellent yields of **2** and moderate yields of **3** were detected at a temperature of 140 °C, but a longer reaction time of 40 min was required (Table 1, entries 12, 13). A further decrease to 120 °C gave 85% of **2** and 45% of **3** after 60 min and includes the addition of THF for solubility reasons

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[5] The TOF was calculated: (mole product/mole catalyst)*h^{-1}. The TOF was calculated using the yield of **2** after 10 min, because the determination of the TOF at a yield of 50% was not possible, due to the technical limits and precipitation of the polymer.

(Table 1, entry 14). Moreover, poly(bisphenol A carbonate) (**1a**) was reacted with methanol (46.3 equiv.) in presence of DMAP (1.0 mol%) at 180 °C for 5 min and afterwards the depolymerization products were isolated. In this regard, after the reaction was stopped the reaction mixture was subjected to distillation. Methanol and dimethyl carbonate were quickly removed in vacuum to avoid any back reaction (polymerization) and were collected at low temperature. Due to the formation of an azeotrope of methanol and dimethyl carbonate the mixture was not separated (see for instance and references therein: [77]). The solid residue of the reaction mixture was dissolved in hot toluene and by cooling to room temperature bisphenol A crystallizes from the solution. After filtration and drying bisphenol A was obtained in 92% yield. After having demonstrated the operability of the depolymerization protocol we transferred the procedure to commodities containing poly(bisphenol A carbonate) (**1**). In this regard, an end-of-life digital versatile disc (DVD) based on **1b** as major component was investigated (Fig. 2). Beside polymer **1b** the DVDs containing additives e.g. metal foils, plastic foils and dyes, which can potentially inhibit the depolymerization process. The DVD was crushed into small pieces and THF was added. The polymer **1b** dissolved within 30 min under refluxing conditions, while the label and foils didn't dissolve under these conditions. The mixture was filtered to remove the unsolvable components. Noteworthy, the aluminum foil can potentially also be subjected to aluminum recycling. The THF was removed in vacuum and was recycled for dissolving a fresh portion of end-of-life DVDs. The residue was washed with acetone and dried in vacuum to yield a (colorless) solid.[6] The polymer **1b** was obtained in a yield of 82 wt% based on the starting weight of the DVD. Importantly, this strategy can also be applied for the mechanical recycling of poly(bisphenol A carbonate) (**1b**). Afterwards, the powder was subjected to the depolymerization process. In this regard, a mixture of **1b**, methanol and catalytic amounts of DMAP (1 mol%) were heated in a microwave reactor for 5 min at 180 °C (Fig. 2). An analysis of the sample by ^{1}H NMR revealed a conversion of > 99% and a yield of > 99% for **2** and 93% for **3**. Interestingly, in comparison to the commercially available polymer **1a** a higher yield of **3** was realized. Bisphenol A was isolated in 85% as crystalline solid. In addition, a conventional heating strategy was used for depolymerization of **1b**. A mixture of **1b**, methanol and catalytic amounts of DMAP (1.0 mol%) were heated in an oil bath for 48 h at 80 °C. Noteworthy, for solubility reasons THF was added as solvent. However, the addition of methanol to a hot solution of **1b** and DMAP in THF resulted in the formation of a precipitate, which disappeared after ~ 36 h to obtain a clear solution. An analysis of the sample after 48 h by ^{1}H NMR revealed a conversion of 81% and a yield of 81% for **2** and 63% for **3**. Bisphenol A was isolated in 67% as crystalline solid. In order to maintain a homogeneous reaction mixture the experiment was modified. The methanol was added slowly to a THF solution of **1b** and DMAP via a syringe pump during a period of two hours. Importantly, no precipitation was observed.

After 24 h an improved NMR yield of 77% for **2** and 67% for **3** was found. Moreover, the depolymerization was performed with the THF solution of **1b** after the filtration step, therefore the precipitation-, washing-, and drying steps were excluded (Fig. 2). To an aliquot of the filtered solution methanol and catalytic amounts of DMAP were added and the mixture was subjected to microwave heating (180 °C, 5 min). Based on the initial weight of the DVD bisphenol A was isolated in 54 wt% yield.

Finally, we investigated the use of phenol instead of methanol as depolymerization reagents (Fig. 3). In this regard, the depolymerization experiment of **1b** (*option B*) was performed with an excess of phenol (23.1 equiv.), catalytic amounts of DMAP (5.0 mol%) and THF for solubility reasons. After 10 min at 180 °C the reaction mixture was analyzed by ^{1}H NMR and **2** was detected in 77% yield. **2** and **4** were isolated in 57% and 56% respectively by column chromatography. Moreover, the same experiment was carried out, but distilling of the phenol from the reaction mixture in vacuum. The obtained phenol can be reused for next depolymerization processes. During distillation process a reaction between **2** and **4** occurred forming poly(bisphenol A carbonate) (**1c**), since the conditions are in accordance to polymerization conditions (see for instance and references therein: [78]). Therefore, the mixture of the depolymerization can be used directly for the production of new poly(bisphenol A carbonate) (**1**). **1c** was isolated in 44% yield. Beside NMR techniques a THF solution of polymer **1c** was characterized with GPC analysis, revealing a number average molar mass of Mn ~ 3289 g/mol, a mass average molar mass Mw ~ 7319 g/mol and a polydispersity of 2.23. In consequence the proposed cycle for the recycling of poly(bisphenol A carbonate) proceeding via depolymerization and polymerization is closed (Fig. 1).

Conclusion

In summary, we have installed a straightforward procedure based on depolymerization and polymerization for the recycling of end-of-life poly(bisphenol A carbonate). The depolymerization was carried out applying methanol or phenol as depolymerization reagents producing bisphenol A and dimethyl carbonate/diphenyl carbonate as low molecular weight products. Excellent performance with TOFs up to 1164 h^{-1} was observed in the presence of

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[6] The color of the polymer depends on the starting CDs/DVDs.

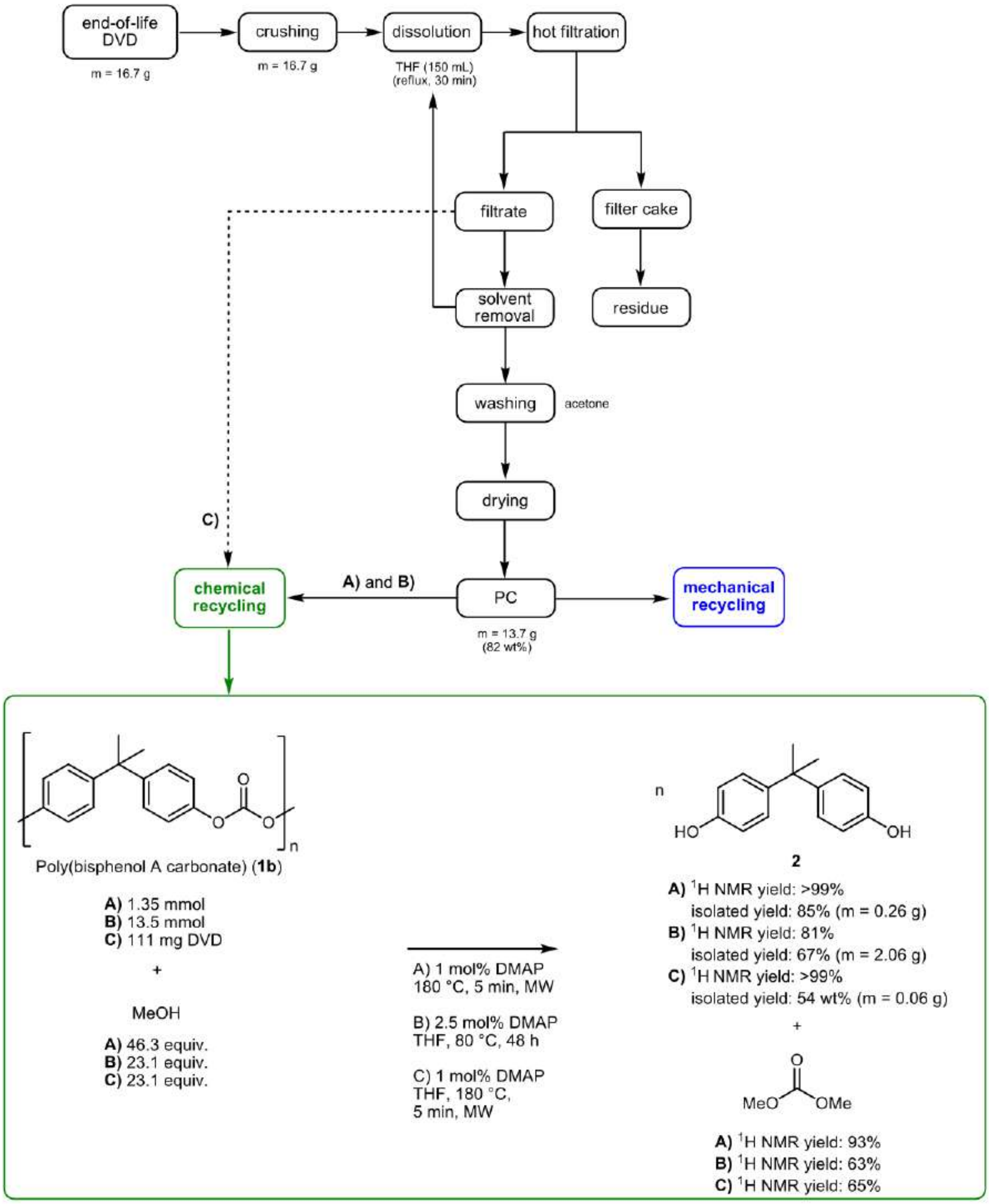

Fig. 2 Depolymerization of poly(bisphenol A carbonate) (**1b**) originated from DVDs with methanol [Reaction conditions: *microwave heating:* **1b** (1.35 mmol, based on the monomeric unit), methanol (23.1–46.3 equiv., 31.2–62.4 mmol), DMAP (1.0 mol%, 0.0135 mmol), 180 °C, 5 min, work-up; *conventional heating:* **1b** (13.5 mmol, based on the monomeric unit), methanol (23.1 equiv., 312 mmol), DMAP (2.5 mol%, 0.34 mmol), 80 °C, 48 h, work-up]

catalytic amounts of DMAP at 180 °C within short reaction times (5 min) using microwave heating. Moreover, the protocol was applicable for poly(bisphenol A carbonate) depolymerization attained from end-of-life DVDs. Bisphenol A in combination with diphenyl carbonate could be reused as monomer for the production of new poly(bisphenol A carbonate) and therefore allowing a partial recycling, while the mixture dimethyl carbonate/methanol can be applied as reagent in organic transformations. Future research will focus on the improvement

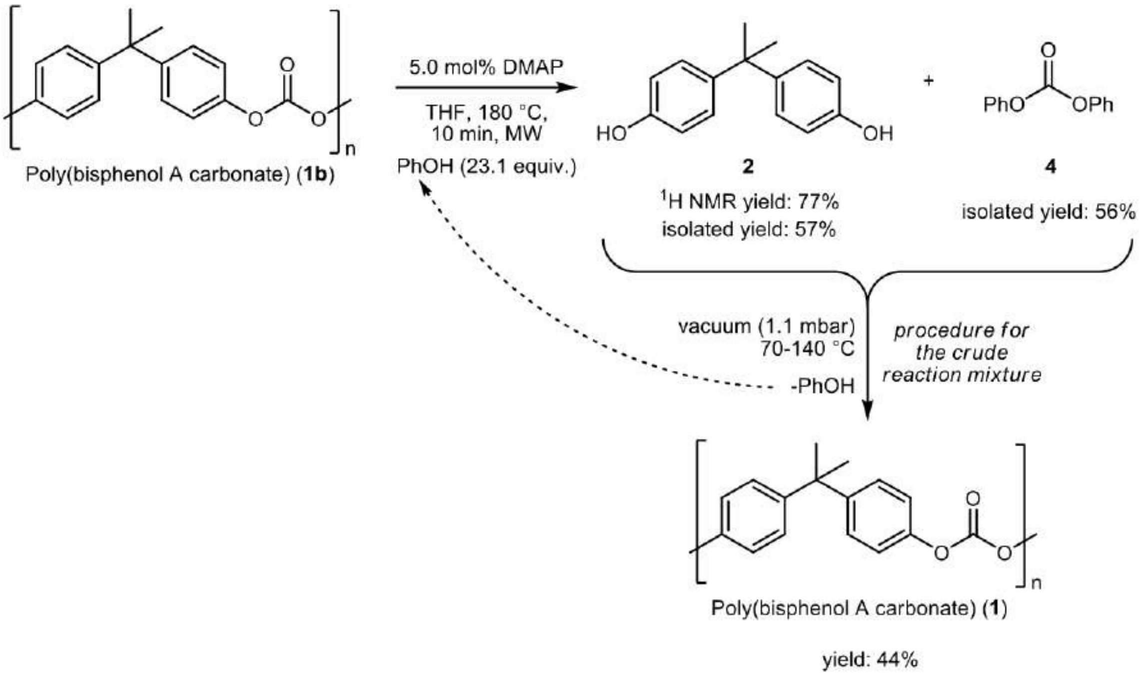

Fig. 3 Depolymerization of poly(bisphenol A carbonate) (**1a**) with phenol and subsequent polymerization [Reaction conditions: *depolymerisation—microwave heating:* **1a** (1.35 mmol, based on the monomeric unit), phenol (23.1–23.1 equiv., 31.2 mmol), DMAP (5.0 mol%, 0.0135 mmol), 180 °C, 10 min, work-up; *polymerization:* 1.1 mbar, 70 °C (1 h), 80 °C (1 h), 90 °C(1 h), 100 °C (1 h), 140 °C (1 h)]

of catalyst activity, scale-up of the process and potential industrial applications.

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Overall, a good maximum TOF of 1164 h^{-1} was observed (0.5 mol% DMAP, 180 °C, 10 min, 46.2 eq. MeOH). However, catalysts with higher activity and lower costs should be found. Therefore, in the next article simple, inexpensive and non-toxic alkali metal halides were investigated.[247] All investigated potassium salts revealed catalytic activity while among the sodium salts only the bromide and iodide were active. This indicates, that the catalytic activity is not generally attributable to either the cation or the anion. It is more likely resulting from a cooperative effect between both. Surprisingly, the observed TOF of 1844 h^{-1} for KF was under comparable reaction conditions (0.5 mol% KF, 180 °C, 5 min, 46.2 eq. MeOH) slightly higher than for DMAP (TOF 1164 h^{-1}). Although microwave heating promoted a rapid depolymerization at elevated temperature (180 °C, 5 min, 87% yield for BPA (**1**)), conventional heating (80 °C, 48 h, 86% yield for BPA (**1**)) in the presence of THF as co-solvent leads to a comparable isolated yield of BPA (**1**).

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Depolymerization of End-of-Life Poly(bisphenol A carbonate) via Alkali-Metal-Halide-Catalyzed Methanolysis

Christoph Alberti and Stephan Enthaler*[a]

Abstract: Chemical recycling, composed of depolymerization and polymerization, of end-of-life polymers (plastics) can contribute to a sustainable and resource-conserving society. In this respect, we have installed a straightforward procedure for the first step (depolymerization) of the chemical recycling of end-of-life poly(bisphenol A carbonate). Operating with a combination of methanol and catalytic amounts of potassium fluoride end-of-life poly (bisphenol A carbonate) was depolymerized to the building blocks bisphenol A and dimethyl carbonate. With the assistance of microwave heating, an excellent rate of depolymerization (>99%) was observed within short reaction times (5 min) and turnover frequencies up to ~1844 h^{-1} were realized. Noteworthy, bisphenol A and dimethyl carbonate could be applied as monomers for new poly(bisphenol A carbonate), therefore a closed cycle for poly(bisphenol A carbonate) is feasible.

The quantity of end-of-life plastics[1] is steadily increasing.[2] The state-of-the-art management for collected end-of-life plastic streams is segmented into energy recovery, recycling and landfill storage.[3,4] The major handling procedure, the energy recovery, transforms the carbon based chemical functions of the polymers into not "easily" convertible molecules,[5] such as carbon dioxide, hence for new plastic materials the steadily decreasing fossil resources will be further shortened.[6] Importantly, the release of the carbon dioxide to the atmosphere increases the greenhouse effect, which has negative effects on current and future society.[7] In case of landfill storage the plastic waste stream is permanently or long-term stored at strictly protected areas to avoid contamination of, e.g., soil or (ground)water. Notably, the deposition of plastic streams in landfills removes resources from the technical cycle. The release of toxic/polluting chemicals (e.g., greenhouse gases) caused by chemical, physical, and biological processes in the landfill occur.[8,9] Another portion of the end-of-life plastics are used as feedstock for new plastic products (back-to-plastics). This treatment is divided into mechanical recycling (material recycling, material recovery), which allows the production of materials with similar/equal quality/abilities with respect to the starting end-of-life plastics, and downcycling, which produces plastics with lower quality with respect to the starting material.[10] Significantly, no transformation of the basic chemical structure is intended. Nevertheless, by repeating the mechanical recycling external effects reduce the quality of the plastics and therefore makes further mechanical recycling/downcycling not useful, hence this portion is directed to energy recovery. In consequence, for new plastic material fossil resources are necessary. An alternative can represent the chemical recycling of end-of-life plastics via the depolymerization of the end-of-life polymer (major component of plastics) to produce low-molecular weight chemicals.[11] In a subsequent polymerization reaction the monomers are utilized as feedstock for new polymers/plastics. Overall a recycling process is achievable. Remarkably, the quality of the new plastic is not coupled to the quality of the end-of-life polymer, hence the quality is adjustable on demand. Unfortunately, high energy demand, copolymers, additives, selectivity, and the current low price for fossil resources hinder the operation of chemical recycling.[12] Therefore, the search for novel procedures is of high significance.[13,14] For instance polycarbonates, e.g. bisphenol A based polymers, are a extensively used polymer class, e.g. for optical storage (CD, DVD, Blu-ray) or as synthetic glass.[15] For the recycling of poly(bisphenol A carbonate) (**1**) several procedures have been stated, including mechanical recycling, blending with other materials, pyrolysis (feedstock recycling), biochemical degradation and chemical recycling (e.g. hydrolysis, (hydro)glycolysis, alcoholysis and aminolysis).[16,17]

In the field of chemical recycling the alcoholysis has been intensively studied (Scheme 1). In more detail, the end-of-life poly(bisphenol A carbonate) (**1**, PBPAC) reacts in the presence of a catalyst with an excess of methanol to form bisphenol A (**2**) and dimethyl carbonate (**3**) as depolymerization products. Bisphenol A (**2**) can be applied as monomer in combination with diphenyl carbonate or phosgene in the industrial synthesis of new poly(bisphenol A carbonate) (**1**). For the mixture of dimethyl carbonate (**2**) and methanol applications in organic chemistry have been suggested as well as the transformation to diphenyl carbonate, which allows an overall recycling of **1**.[18] However, in most cases long reaction times are required to reach full conversion of **1** and/or expensive catalysts are used.

For instance Iannone *et al.* reported on the application of ionic liquids in combination with zinc oxide nanoparticles in the alcoholysis of poly(bisphenol A carbonate) (**1**).[16h] The group proposed an activation of the alcohol by hydrogen bonding interaction of the anion of the ionic liquid, which increase the nucleophilicity of oxygen of the OH-group. Moreover, an

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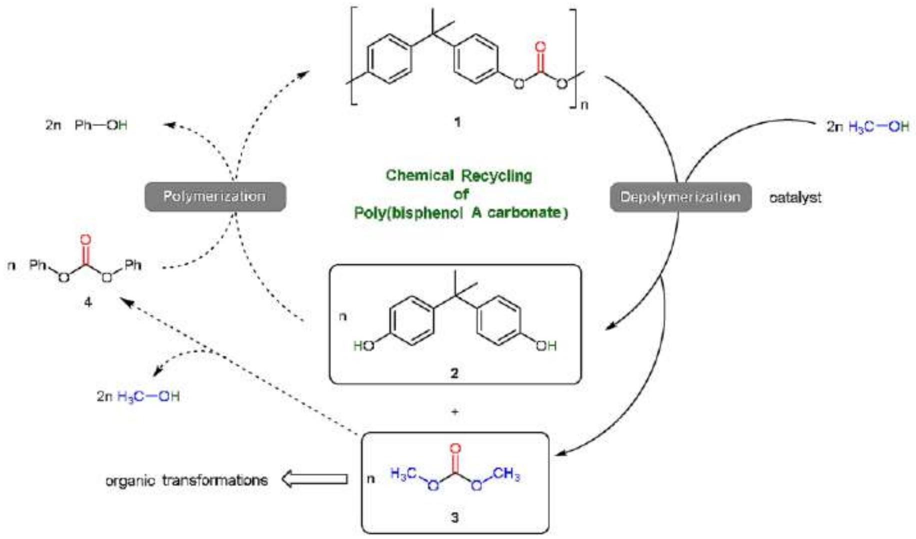
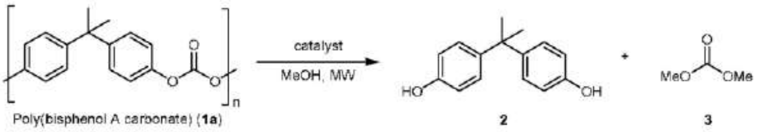


Scheme 1. Concept for the chemical recycling of poly(bisphenol A carbonate) via methanolysis.

Table 1. Alkali metal halide-catalyzed depolymerization of poly(bisphenol A carbonate) 1 a.



Entry[a]	Catalyst	Catalyst loading [mol%]	MeOH [equiv.]	T [°C]	t [min]	Yield BPA (2) [%][b]	Yield DMC (3) [%][c]
1	–	–	46.3	180	10	<1	<1[d]
2	KF	10.0	46.3	180	10	>99	67
3	KF	2.5	46.3	180	10	>99	75
4	KF	2.5	46.3	180	5	>99	69
5	KF	1.0	46.3	180	10	>99	59
6	KF	0.5	46.3	180	5	>99	53
7	KF	1.0	23.1	180	5	>99	>99
8[e]	KF	2.5	23.1	180	10	>99	64
9	KF	5.0	11.6	180	10	65	64
10[e]	KF	2.5	11.6	180	10	93	69
11	KF	2.5	46.3	160	5	97	60
12	KF	2.5	46.3	160	10	>99	65
13	KF	2.5	46.3	140	30	>99	59
14	NaF	2.5	23.1	180	10	<1	<1
15	LiCl	2.5	23.1	180	10	>99	77
16	NaCl	2.5	23.1	180	10	<1	<1
17	LiBr	2.5	23.1	180	5	>99	63
18	NaBr	2.5	23.1	180	5	>99	87
19	KBr	2.5	23.1	180	5	>99	52
20	NaI	2.5	23.1	180	5	>99	83
21	KI	2.5	23.1	180	5	>99	82

[a] Reaction conditions: poly(bisphenol A carbonate) **1 a** (Sigma Aldrich, 1.35 mmol), alkali metal halide (0–10 mol%, 0–0.135 mmol based on the repeating unit of **1 a**), methanol (11.6–46.3 equiv. based on the repeating unit of **1 a**), microwave heating, 120–180 °C, 5–30 min. [b] The yield was determined by ^{1}H NMR. [c] The yield was determined by ^{1}H NMR. [d] 99% of the starting polymer **1 a** was recoverd. [e] THF (1.5 g) was added as solvent.

activation of the carbonyl function of the organic carbonate by the zinc oxide was assumed. In this regard, we wonder if simple metal halides, based on low-cost and earth-abundant alkali metal ions are able to mimic this transformation of carbonate functionalities and act as dual catalyst via activation of the alcohol by hydrogen bonding interactions with the halide anion and activation of the carbonyl function of the organic carbonate by Lewis acid-base interaction with the alkali metal cation.[19] Based on that, we report herein our study on the chemical recycling of end-of-life **1** via alkali metal halides catalysis (Scheme 1).

Initially, the depolymerization of commercially available poly(bisphenol A carbonate) (**1 a**) pellets (dimension: ~3 mm) was investigated (Table 1). In this regard, polymer **1 a** (1.35 mmol based on the monomeric unit) was reacted with an excess of methanol (46.3 equiv.) in the presence of catalytic amounts of potassium fluoride (10.0 mol% based on the monomeric unit of **1**).

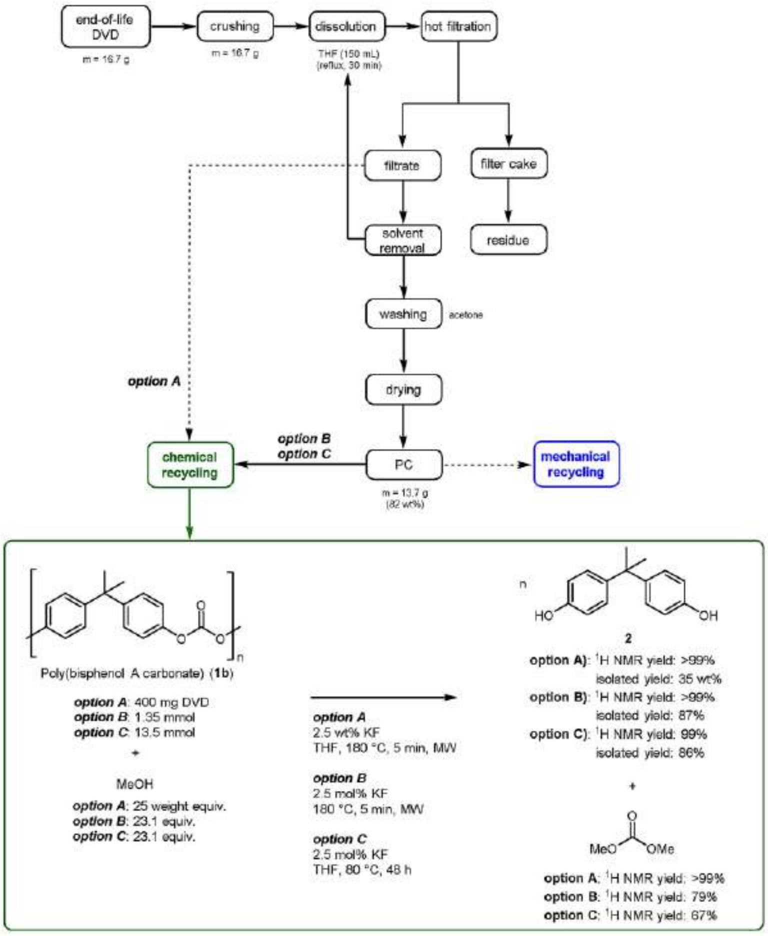
Remarkable, no extra solvent was necessary, because methanol acts as both reactant and solvent. The reaction mixture was stirred in a sealed glass vial, which was placed in a microwave reactor, at 180 °C for 10 minutes (Table 1, entry 2). After approximately 3 minutes the suspension turned to a clear colorless solution. Subsequently, the reaction mixture was cooled to room temperature and an aliquot was dissolved in chloroform-*d* for ^{1}H NMR analysis. In the aliphatic field of the ^{1}H NMR spectrum one signal with a chemical shift of 1.60 ppm ($C(CH_3)_2$, 6H) and in the aromatic field two sets of signals (2×4H) of aromatics C–H were detected, which are assigned to the depolymerization product bisphenol A (**2**).[20] Moreover, the second depolymerization product dimethyl carbonate (**3**) was monitored by ^{1}H NMR revealing a signal at 3.77 ppm ($2xCH_3$, 6H).[21] Importantly, no other aromatic signals and signals in the adjacencies of ($C(CH_3)_2$) were observed, revealing full conversion of **1 a**, >99% NMR yield of **2** and excellent performance of the catalyst. The NMR yield of **3** was obtained by relating the integral of the dimethyl carbonate signal ($2xCH_3$) to the integrals of bisphenol A (expected ratio: **3**:**2**[6H, $2xCH_3$]:**2**[8H, Ar–H] = 6:6:8; found: **3**:2[6H, $2xCH_3$]:2[8H, Ar–H] = 4:6:8). Based on that, a NMR yield of 67% for **3** was achieved. The formation of **2** is coupled with the formation of **3**, therefore the same yield should be obtained. However, a decomposition reaction of **3** via decarboxylation pathways may occur.[22] Importantly, in the absence of KF no depolymerization products were formed and polymer **1 a** was recovered, showing the need for catalytic amounts of KF (Table 1, entry 1). Next the loading of KF was investigated, demonstrating still activity at 0.5 mol% with a yield of >99% for **2** and 53% for **3** within 5 min, which corresponds to a turnover frequency (TOF)[23] of ~1844 h^{-1} (Table 1, entries 1–6). In addition, the influence of the methanol loading was studied (Table 1, entries 7–10). Reducing the amount of methanol to 11.6 equiv. with respect to **1 a** showed a reduced yield of the depolymerization products (Table 1, entry 9). Performing the same experiment with THF as solvent revealed a better yield of **2** and **3** at lower KF loading (Table 1, entry 10). Afterwards the influence of the reaction temperature was investigated (Table 1, entries 11–13). Excellent yield of **2** and moderate yield of **3** were observed at a reaction temperature of 140 °C, nevertheless a longer reaction time of 30 minutes was essential (Table 1, entries 12–13). Finally, different alkali metal halides were tested in the depolymerization of **1 a** (Table 1, entries 14–21).[24] Excellent performance was found with NMR yields of >99% for **2** and good yields of 52–87% for **3**, while in case of sodium chloride no reactivity was observed.

In addition, the reaction was performed on a larger scale. Poly(bisphenol A carbonate) **1 a** (4.05 mmol) was reacted with methanol (23.1 equiv.) in the presence of KF (1.0 mol%) at 180 °C for 5 min and the depolymerization products were detected in 98% (**2**) and 72% (**3**) by ^{1}H NMR. Afterwards the reaction mixture was subjected to distillation. Methanol and dimethyl carbonate **3** were quickly removed in vacuum and were collected at low temperature to avoid any backward reaction (oligomerization/polymerization). A bisphenol A (**2**) free mixture was obtained, which was not separated due to the formation of an azeotrope of methanol and dimethyl carbonate. The leftover in the reaction flask was dissolved in hot toluene and by cooling to room temperature bisphenol A crystallizes from the solution, which was further supported by storing the solution in a freezer. After filtration and drying bisphenol A was obtained in 79% yield and high purity.

After having verified the operability of the alkali metal halide depolymerization procedure we applied the protocol for the depolymerization of commodities containing poly(bisphenol A carbonate) **1**. As commodity a digital versatile disc (DVD) with **1 b** as major component was investigated (Scheme 2). The DVD is a composite material, because together with polymer poly(bisphenol A carbonate) (**1 b**) the DVD contains additives e.g. metal foils, plastic foils and dyes. For separation of the components a DVD (1xDVD = 16.7 g) was crushed into small pieces and THF (100 mL) was added. The mixture was heated to reflux (~80 °C) for 30 min. Within the time frame **1 b** was dissolved in THF, while the label, foil and aluminum foil didn't dissolve under these conditions. Importantly, the metal foil potentially can be also subjected to recycling processes. Noteworthy, some dyes were dissolved in THF giving a colorful solution. The polymer containing solution can be easily separated by filtration. The THF was removed in vacuum and was collected for recycling for dissolving a fresh portion of DVDs. The solid residue was washed with acetone to remove e.g. dyes and dried in vacuum to yield.[25] The polymer **1 b** was obtained in a yield of 82 wt% (13.7 g) based on the starting weight of the DVD. Importantly, at this stage **1 b** can also be applied for the mechanical recycling, if the polymer quality is sufficient. At this point the powder is applicable for depolymerization process.

Initially, a THF solution[26] of **1 b** obtained by *option A* was charged with KF (2.5 wt%) and methanol (25 weight equiv.) and subjected to microwave heating at 180 °C for 5 min. Noteworthy, the addition of methanol caused a precipitation of **1 b** from solution. However, after the reaction was carried out a clear solution was noticed. An analysis of the reaction mixture by ^{1}H NMR revealed a conversion of >99% for **1b** and a yield of >99% for **2** as well as **3**, demonstrating the robustness of the system. From the reaction residue bisphenol A was isolated in 35 wt% as crystalline solid, based on the weight of the starting DVD. Next, the polymer **1 b** obtained via *option B* was tested in the depolymerization reaction.

Under standard microwave conditions (180 °C, 5 min, 2.5 mol% KF, 23.1 equiv. MeOH) a ^{1}H NMR yield of 98% for **2** and 79% for **3** was monitored and **2** was isolated in 87% yield. Similar results (>99% for **2** and 63% for **3**) were obtained with LiCl (5.0 mol%), but at higher loading and longer reaction time (10 min). Moreover, the depolymerization of the polymer **1 b** obtained via *option B* was performed applying a conventional heating approach. A mixture of **1 b**, methanol and catalytic amounts of KF (2.5 mol%) were heated in an oil bath for 48 hours at reflux (oil bath temperature: 80 °C). Importantly, for solubility reasons THF was added to increase the concentration of **1 b** in solution. Nevertheless, the addition of methanol to a hot THF solution of **1 b** and catalytic amounts of KF resulted in



Scheme 2. Depolymerization of poly(bisphenol A carbonate) **1 b** originated from DVD with methanol [Reaction conditions: *microwave heating:* **1 b** (1.35 mmol, based on the monomeric unit), methanol (23.1 equiv., 31.2 mmol), KF (2.5 mol%, 0.034 mmol), 180 °C, 5 min, work-up; *conventional heating:* **1 b** (13.5 mmol, based on the monomeric unit), methanol (23.1 equiv., 312 mmol), KF (2.5 mol%, 0.34 mmol), 80 °C, 48 h, work-up].

the formation of a precipitate, which disappeared after ~12 hours to obtain a clear solution. An analysis of the sample after 24 hours by ^{1}H NMR revealed a yield of 52% for **2** and 27% for **3**. Additional 24 hours increased the yield to 99% for **2** and 67%. Bisphenol A was isolated in 86% as crystalline solid. Based on the precipitation of the polymer **1 b** after addition of methanol in one shot, another experiment was carried out using a syringe pump for slow dosage of methanol (2 hours). Notably, no precipitation of **1 b** was observed. After 24 hours a NMR yield of 75% for **2** and 58% for **3** was monitored.

In summary, we have established an easy to adopt depolymerization protocol for the conversion of end-of-life poly (bisphenol A carbonate). The depolymerization was performed using methanol as depolymerization reagents producing bisphenol A and dimethyl carbonate/diphenyl carbonate as low molecular weight chemicals in the presence of catalytic amounts of cheap and abundant alkali metal halides. Excellent activity with TOFs up to 1844 h^{-1} was observed using potassium fluoride. The depolymerization products were obtained in short reaction times (5 min) at 180 °C using microwave heating. Moreover, the procedure was applicable for poly(bisphenol A carbonate) depolymerization obtained from end-of-life DVDs. Future work will focus on the understanding of the underlying reaction mechanism for improving the activity of the system and a scale up of the depolymerization process.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: depolymerization · alkali metals · catalysis · poly (bisphenol A carbonate) · microwave chemistry

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[23] The TOF was calculated: (mole product/mole catalyst)*h^{-1}. The TOF was calculated using the yield of **2** after 5 min, because the determination of the TOF at a yield of 50% was not possible, due to precipitation of the polymer.

[24] The alkali metal halides were used in high purity. However, the catalytic activity of metal impurities cannot be excluded.

[25] The color of the polymer depends on the starting CDs/DVDs. To some extend the dyes can be removed by washing with acetone.

[26] A THF solution (4 mL) contains 400 mg of DVD and was filtered after 30 min at reflux. The filtrate was subjected to depolymerization.

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Based on the successful application of alkali metal halide catalysts to the methanolysis, we wondered if this system can be transferred to phenolysis.[248] For practical reasons, an additional solvent was required to dissolve the solid depolymerization reagent. Although comparably higher temperatures and longer reaction times were required, to achieve comparable yields to methanolysis, the major advantage of the phenolysis protocol is the increased yield for the carbonate building block, as it is less prone to decomposition. The obtained monomers can be reconverted to PBAC (**2**) without extensive purification.

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Recycling of End-of-Life Poly(bisphenol A carbonate) via Alkali Metal Halide-Catalyzed Phenolysis

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The chemical recycling of end-of-life plastic waste streams can contribute to a resource-conserving and sustainable society. This matter of recycling is composed of a sequence of depolymerization and subsequent polymerization reactions. In this regard, we have studied the chemical recycling of end-of-life poly(bisphenol A carbonate) applying phenol as depolymerization reagent. In the presence of catalytic amounts of alkali metal halides as products bisphenol A and diphenyl carbonate were obtained in excellent turnover frequencies of up to 1392 h^{-1} and short reaction times. These depolymerization products offer the straightforward possibility to close the cycle by producing new poly(bisphenol A carbonate) and as second product phenol, which can be reused for further depolymerizations.

Every year, a steadily increasing amount of end-of-life plastics[1] is generated, which is originated from non-renewable resources.[2] The established management for collected end-of-life plastic streams is composed of energy recovery, mechanical recycling, downcycling and (landfill storage).[3,4,5] Disadvantageously, all these methods finally transform the carbon-based chemical functionalities of the polymers into greenhouse gases (e.g. carbon dioxide), therefore a negative impact on the ecosphere/anthroposphere results and for new plastics fossil resources are needed.[6,7] A potentially more resource-conserving and environmental-benign methodology is the chemical recycling.[8] Initially, the end-of-life polymer is converted via depolymerization processes to low-molecular weight chemicals, which can be used as feedstock in subsequent polymerization processes to produce new polymers/plastics. Notably, linking the depolymerization and the polymerization makes a recycling of polymers/plastics feasible. Moreover, chemical recycling allow a decoupling of the quality/abilities of the new polymer from the quality/abilities of the end-of-life polymer as noticed in the case of mechanical recycling and/or downcycling. Nevertheless, some issues hamper the implementation of chemical recycling, e.g. high energy demand, copolymers, additives, selectivity, and the current low price for fossil resources.[9] Consequently, the development of new chemical recycling methodologies is of significance for reaching the goal of a sustainable society.[10,11]

For instance poly(carbonates), e.g. based on bisphenol A, are widely applied components in plastics, e.g. used in optical storage (CD, DVD, Blu-ray) or as artificial glass.[12] Until now for the recycling of poly(bisphenol A carbonate) (**1**) (PBPAC) a number of methodologies have been described including mechanical recycling, blending with other materials, pyrolysis (feedstock recycling), biochemical degradation and chemical recycling (e.g. hydrolysis, (hydro)glycolysis, alcoholysis and aminolysis).[13–19] Especially, the methanolysis (transesterification with methanol) has been extensively studied. In more detail mixtures of polymer **1** and an excess of methanol are converted to bisphenol A and dimethyl carbonate in presence of catalysts.[15,16] The bisphenol A can be easily isolated and potentially reused for the synthesis of new poly(bisphenol A carbonate) (**1**). Conversely, the second product dimethyl carbonate and methanol forms an azeotrope, which requires some efforts for separation.[20] A potentially more attractive approach is the use of phenol as depolymerization reagents, while forming bisphenol A and diphenyl carbonate as products, which are the components for one of the major industrial synthesis of poly(bisphenol A carbonate) (**1**) (Scheme 1). However, only a few numbers of reactions following this path have been accounted so far, requiring long reaction times and/or "complicated" catalysts.[18] For instance ionic liquids/ ionic compounds have been proven as active catalysts in depolymerization reactions.[14,16,18] It was assumed that the anion activates the alcohol and the cation activates the carbonyl function of the poly(carbonate). In this regard, we wonder if simple and abundant alkali metal halides can mimic the behavior of the ionic liquids.[21] Moreover, straightforward alkali metal salts have some advantages with respect to "Green Chemistry" considerations.[22] Based on that, we report herein our investigations on a concept for the chemical recycling of end-of-life **1** applying simple alkali metal halide as catalyst (Scheme 1).

Initially, the depolymerization of commercially available poly(bisphenol A carbonate) pellets **1a** (dimension: ~3 mm) was investigated (Table 1). In this regard, **1a** (1.35 mmol based

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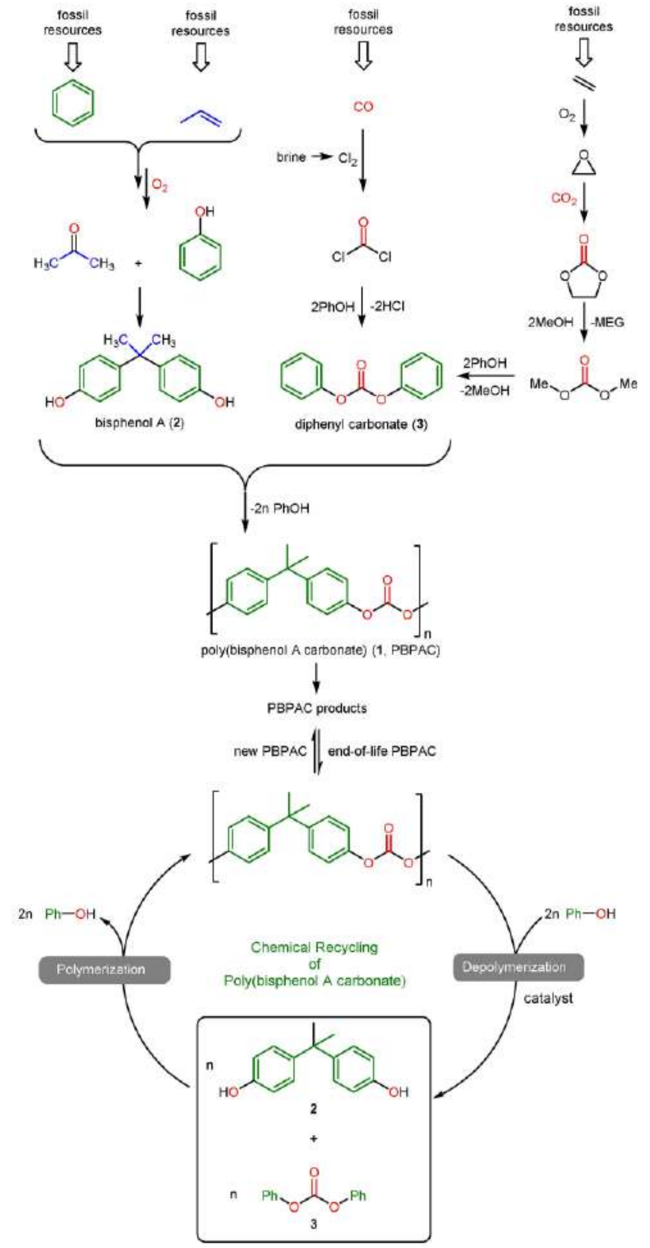


Scheme 1. PBPAC production and concept for the chemical recycling of poly (bisphenol A carbonate).

on the monomeric unit) was reacted with an excess of phenol (technical grade) as depolymerization reagent (47.3 equiv. based on the monomeric unit of **1 a**) in the presence of catalytic amounts of potassium fluoride (5 mol% based on the monomeric unit of **1 a**) and THF as solvent. The reaction mixture was placed in a sealed glass vial in a microwave (MW) and was heated under microwave conditions at 180 °C for 15 minutes, while stirring (Table 1, entry 2). Afterwards, the mixture was cooled to room temperature and an aliquot was dissolved in chloroform-d1 for ^{1}H NMR analysis. Noteworthy, a clear homogenous solution was obtained. In the aliphatic range of the ^{1}H NMR spectrum a signal with a chemical shift of 1.58 ppm ($C(CH_3)_2$) was detected, which are assigned to the depolymerization product bisphenol A **2**.[23,24] Moreover, some minor signals of left-over polymers or oligomers were observed in the aliphatic area, which allow an integral relation to the integrals of bisphenol A and therefore a determination of the rate of depolymerization. A yield of **2** of 85% was calculated. Furthermore, in the aromatic region two sets of signals were observed, which can be assigned to the two sets (2×4H) of aromatics C–H in bisphenol A. Besides, the signals for diphenyl carbonate at 7.36-7.40 ppm (4x *o*-C–H) were found in the aromatic region, which were related to the signals of **2** to calculate the yield of **3**.[25]

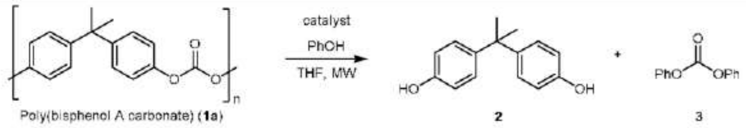
Importantly, for the other signals of **3** an overlap with the signals of the phenol was observed. The occurrence of **2** and **3** was also confirmed by GC-MS analysis. Next, the loading of potassium fluoride was studied, revealing still good performance at 0.5 mol% with a yield of 58% for **2**, while in the absence of KF no reactivity was observed (Table **1**, entries 1, 6–11). Furthermore, in the absence of THF a decrease of the yield was observed, demonstrating the need for THF (Table 1, entry 5). Then the effect of the reaction temperature was investigated (Table 1, entries 11–13). A moderate yield of 31% of **2** was detected at a temperature of 140 °C (Table 1, entry 13). Furthermore, the influence of the phenol:**1 a** ratio was examined (Table 1, entries 15–18). Reducing the amount of phenol to 19.7 equiv. revealed still a good yield of **2** (80%). Decreasing the amount of phenol to 3.9 equiv. resulted in the formation of **2** in a decreased yield of 31% (Table **1**, entries 19). In addition the activity of a selection of alkali metal halides was tested in the depolymerization of **1 a** (Table 1, entries 20–25). Comparable yields to KF were detected for KI and NaI, while other salts resulted in the formation of **2** in moderate yields. However, best performance was realized with potassium fluoride.[26]

Afterwards, the reaction was performed with conventional heating at 180 °C (oil bath temperature, internal temperature 125–130 °C) following the conditions in Table **1**, entry 3 (Table 1, entry 4). Products **2** and **3** were detected in 86% NMR yield and were furthermore separated by column chromatography and isolated in 69% (**2**) and 71% (**3**) yield.[27] Conversely, removal of the excess phenol by vacuum distillation revealed the formation of new poly(bisphenol A carbonate) by the reaction of depolymerization products **2** and **3** observed by ^{1}H NMR.

Moreover, the depolymerization was monitored over the course of reaction using 0.5 mol% KF under conventional heating (Figure 1). Noteworthy, the NMR yield of 58% after 5 min corresponds to a turnover frequency (TOF) of ca. 1392 h^{-1}.

After having verified the operability of the depolymerization we transferred the procedure to commodities containing poly (bisphenol A carbonate) **1**. In this regard, end-of-life digital versatile discs (DVDs) containing **1 b** as major component were studied (Scheme 2). Noteworthy, alongside with poly(bisphenol A carbonate) **1 b** CDs/DVDs containing additives e.g. metal foils, plastic foils and dyes, which can potentially influence/inhibit the rate of depolymerization. Two different pathways of DVD depolymerizations were investigated. Pathway A: The DVDs were crushed into small pieces and THF was added. The polymer **1 b** dissolved within 30 min under refluxing conditions,

Table 1. MX-catalyzed depolymerization of poly(bisphenol A carbonate) **1 a**.



Entry[a]	Catalyst [mol %]	PhOH [equiv.]	T [°C]	t [min]	Yield **2** [%][b]	Yield **3** [%][b]
1[c]	–	47.3	180	15	< 1	< 1
2	KF (5)	47.3	180	15	85	n.d.[d]
3	KF (5)	47.3	180	30	86	88
4	KF (5)	47.3	180	30	86(69)[e]	86(71)[e]
5[f]	KF (5)	47.3	180	15	77	n.d.[d]
6[g]	KF (5)	47.3	180	15	85	85
7[h]	KF (5)	47.3	180	15	85	86
8	KF (10)	47.3	180	15	85	87
9	KF (2)	47.3	180	15	85	86
10	KF (2)	47.3	180	5	85	n.d.[d]
11	KF (0.5)	47.3	180	5	58	n.d.[d]
12	KF (2)	47.3	200	15	84	85
13	KF (2)	47.3	160	15	83	n.d.[d]
14[g]	KF (2)	47.3	140	15	31	n.d.[d]
15[g]	KF (5)	31.5	180	15	80	n.d.[d]
16	KF (5)	19.7	180	15	80	82
17	KF (5)	19.7	180	15	74	74
18	KF (5)	7.9	180	15	52	n.d.[d]
19	KF (5)	3.9	180	15	31	n.d.[d]
20	LiCl (5)	47.3	180	15	13	n.d.[d]
21	NaCl (5)	47.3	180	15	12	n.d.[d]
22	NaF (5)	47.3	180	15	< 1	n.d.
23	KBr (5)	47.3	180	15	< 1	n.d.
24	KI (5)	47.3	180	15	87	88
25	NaI (5)	47.3	180	15	85	n.d.[d]

[a] Reaction conditions: poly(bisphenol A carbonate) **1 a** (1.35 mmol based on the repeating unit of **1 a**), MX (0-5 mol %, 0–0.135 mmol based on the repeating unit of **1 a**), phenol (3.93–47.3 equiv. based on the repeating unit of **1 a**), THF (20.6 equiv.), microwave heating, 140–200 °C, 5–30 min. [b] The yield was determined by ^{1}H NMR. [c] 99 % of the starting polymer **1 a** was recovered. [d] Not determined, due to signal overlap. [e] In parenthesis the isolated yield is stated. [f] Without THF. [g] THF (41.2 equiv.). [h] THF (61.6 equiv.).

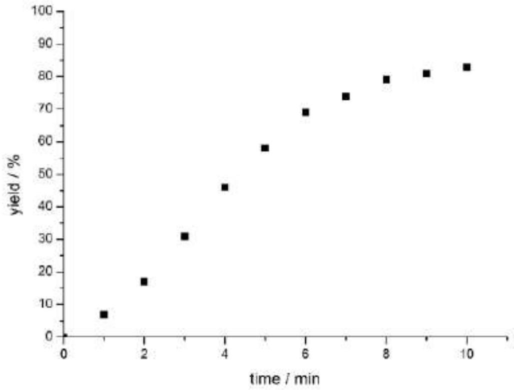
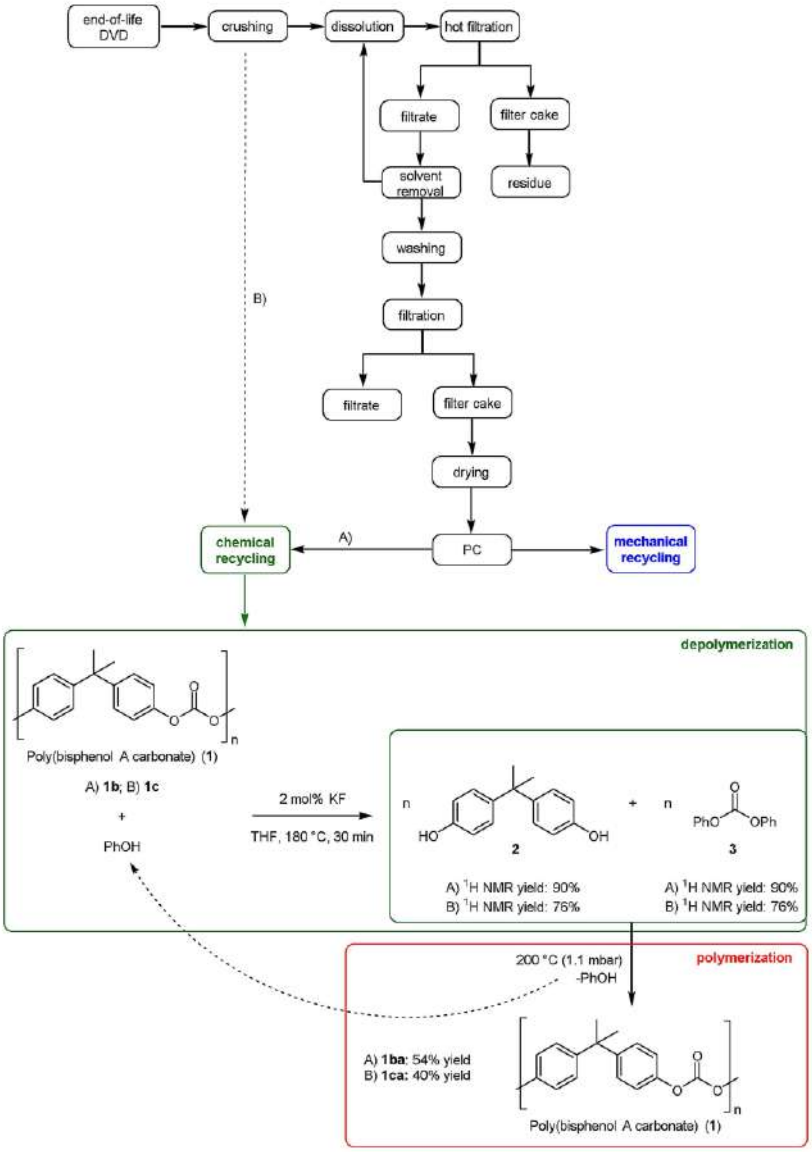


Figure 1. Depolymerization of poly(bisphenol A carbonate) **1 a** originated from DVDs with phenol-time vs. yield of **2** [Reaction conditions: *conventional heating*: **1 a** (1.35 mmol, based on the monomeric unit), phenol (47.3 equiv.), KF (0.5 mol %, based on the monomeric unit), 180 °C, yield determined by ^{1}H NMR].

while the label and foils didn't dissolve under these conditions. The mixture was filtered to remove the insoluble components. Noteworthy, the aluminum foil can potentially also be subjected to aluminum recycling.[28] The THF was removed in vacuum and was recycled for dissolving a fresh portion of end-of-life DVDs.

The residue was washed with acetone and dried in vacuum to yield a (colorless)[29] solid. To the purified polymer **1 b**, phenol and THF was added. The reaction mixture was heated to 180 °C. Afterwards catalytic amounts of potassium fluoride (2 mol%) were added. The mixture was kept for 30 min at 180 °C. Subsequently, the mixture was cooled to room temperature and an aliquot was taken for ^{1}H NMR investigations. A NMR yield of 90 % (**2**) and 90 % (**3**) was detected. The excess of phenol was carefully removed in vacuum (1.1 mbar) at 50–55 °C. Noteworthy, the phenol can be reused for next depolymerizations. At a level of ca. 3 equiv. of phenol with respect to bisphenol A the yield of **2** drops to 85 %, while the polymerization started and new poly(bisphenol A carbonate) **1** is formed. After an increase of the temperature to 200 °C (1.1 mbar) a solid residue was obtained.[30] After washing and drying, compound **1 ba** was obtained in 54 % yield as colorless powder. The powder was characterized by ^{1}H NMR revealing the occurrence of polymer **1 ba**. Moreover, with GPC analysis a number average molar mass of Mn ~ 4162 g/mol, a mass average molar mass Mw ~ 6412 g/mol and a polydispersity of 1.54 was found. In addition, pathway A was performed on a 19.7 mmol scale of **1 b**. A ^{1}H NMR yield of 84 % (**2**) and 84 % (**3**) was measured in the presence of 0.5 mol % KF and the products were separated by successive crystallization after partial removal of phenol by distillation.



Scheme 2. Depolymerization of poly(bisphenol A carbonate) **1** originated from DVDs with phenol [Reaction conditions: **1 b**/**1 c** (1.35 mmol, based on the monomeric unit), phenol (47.3 equiv.), KF (2 mol%), 180 °C, 30 min; yield determined by ^{1}H NMR.

Pathway B: Initially, the DVD was ball-milled to obtain a DVD-powder, which was used without further pretreatments. The DVD-powder was mixed with phenol and THF. After 5 min at 180 °C catalytic amounts of KF (0.5 wt%) were added. After 30 min at 180 °C a sample was taken and investigated by ^{1}H NMR. A NMR yield of 76% (**2**) and 76% (**3**) was obtained. The solution was filtered to remove insoluble components e.g. aluminum foil.[31] The clear solution was subjected to vacuum distillation to remove the excess of phenol (~3 equiv. leftover) a yield of 64% of **2** was obtained. After increasing the temperature to 200 °C (1.1 mbar), washing, filtration and drying **1 ca** was attained in 40% yield. Moreover, with GPC analysis a number average molar mass of Mn~8304 g/mol, a mass average molar mass Mw~24606 g/mol and a polydispersity of 2.96 was found. Also pathway B was performed on a 19.7 mmol scale. A ^{1}H NMR yield of 73% (**2**) and 71% (**3**) was measured in the presence of 0.5 mol% KF and the products were separated by successive crystallization after partial removal of phenol by distillation.

In summary, we have set up a straightforward chemical recycling method for end-of-life poly(bisphenol A carbonate) based on depolymerization and polymerization. On the one hand, depolymerization was carried out with phenol as depolymerization reagent to attain as well-defined products bisphenol A and diphenyl carbonate. In the presence of catalytic amounts of potassium fluoride yields up to 90% and turnover frequencies up to 1392 h^{-1} were achieved. Moreover, the mixture of bisphenol A, diphenyl carbonate and phenol can be used as starting point for polymerization chemistry to produce new poly(bisphenol A carbonate) and therefore closing the cycle. Future studies will focus on the improvement of the depolymerization process.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: green chemistry · catalysis · polymers · recycling · depolymerization

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Due to the importance of zinc(II) catalysis for the preparation of PPC (**6**)[249], we investigated the depolymerization of PPC (**6**) in the presence of either zinc(II) salts or NaOAc/KOAc.[250] The methanolysis of this polymer is more challenging, as it rapidly undergoes RCD at elevated temperature, forming the thermodynamically stable 5-membered ring. It was observed that the methanolysis mainly takes place after complete RCD until an equilibrium state is reached. To shift the equilibrium completely towards the methanolysis product a large excess of MeOH was required. On the other hand, 1,2-propylene carbonate (**8**) was easily accessible by reactive distillation of the polymer in the presence of $Zn(OAc)_2$. The 1,2-propanediol (**7**) derived from PPC (**6**) was used to degrade poly(oxymethylene) (POM) to obtain the valuable 4-methyl-1,3-dioxolane.

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Sustainable Chemistry

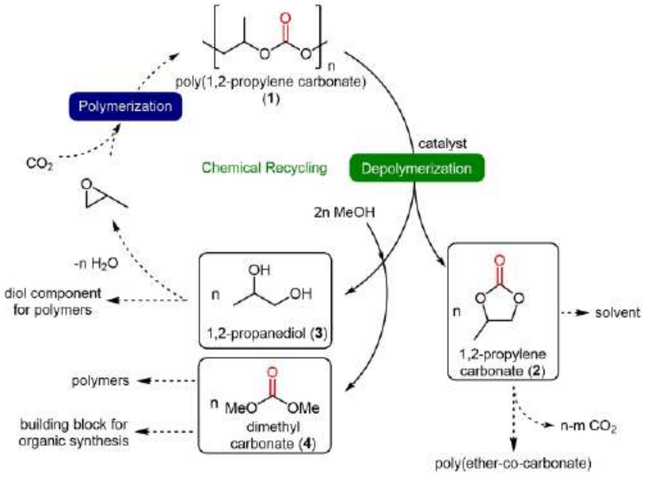
Depolymerization of Poly(1,2-propylene carbonate) via Ring Closing Depolymerization and Methanolysis

Christoph Alberti, Desiree Rijono, Moritz Wehrmeister, Even Cheung, and Stephan Enthaler*[a]

The conversion of end-of-life plastics to useful chemicals can contribute to a resource-conserving and environmental-benign society. In this regard, we studied the depolymerization via methanolysis of poly(1,2-propylene carbonate) using straightforward metal salts as precatalysts. In more detail, in the presence of catalytic amounts of $Zn(OAc)_2$ or NaOAc and methanol 1,2-propylene carbonate (generated by ring closing depolymerization), 1,2-propanediol and dimethyl carbonate (generated by methanolysis) were obtained as beneficial products. Importantly, the selectivity for ring closing depolymerization vs. methanolysis of the polycarbonate depends on various parameters. Moreover, the reaction time is of significance, because in the initial stage of the process the ring closing depolymerization is dominant, while in the further course the amount of the methanolysis products are increasing and the amount of 1,2-propylene carbonate is decreasing, due to conversion by methanolysis. Furthermore, the depolymerization of poly(1,2-propylene carbonate) was connected with a consecutive depolymerization of poly(oxymethylene), that means the depolymerization product 1,2-propanediol acts as depolymerization reagent for poly(oxymethylene) to generate 4-methyl-1,3-dioxolane as suitable compound.

The yearly increasing demand of plastic-based materials[1] and the emerging waste streams cause a great challenge for the waste management.[2] Current plastic waste management depends on techniques like landfill disposal and incineration (energy recovery), which create various issues.[3,4] Moreover, significant amounts of waste are uncontrolled released into the biosphere, which also creates negative issues. As an alternative to overcome these issues recycling techniques have been developed.[4] For instance, mechanical recycling involves melting of the plastic material followed by reprocessing to produce a new products.[5,6] However, during this process degradation and accumulation of contaminants may reduce the properties/quality of the recycled material, which finally may result in the transfer to landfill or incineration.[7,8] On the other hand, downcycling of the plastic waste can be an option to extend the lifetime of the material. However, in consequences also this plastic portion will end in landfill or incineration treatments. In order to revalorize the end-of-life plastic materials, the chemical recycling represents a beneficial option.[9] Hereby, a sequence of depolymerization and polymerization is applied, without loss of quality, allowing for a circular plastic economy.[10]

An attractive example for a thermoplastic material is poly(1,2-propylene carbonate) (**1**), which is easily accessible by copolymerization of CO_2 and propylene oxide in the presence of a catalyst (Scheme 1).[11] With respect to chemical recycling, different depolymerization/degradation pathways have been reported. For instance, the thermally induced ring closing depolymerization (RCD) of solid **1** to generate 1,2-propylene carbonate (**2**) was studied.[12] Interestingly, **2** is an attractive solvent or can be converted to new polycarbonates by ring opening polymerization, but in some cases under partial loss of CO_2.[13] Moreover, in solution the RCD is accelerated by increasing concentration and strength of bases or residues of metal catalysts.[14] Recently, the hydrogenative depolymerization of end-of-life **1** was reported to generate 1,2-propanediol (**3**) and methanol applying different metal catalysts.[15] Impor-



Scheme 1. Chemical recycling of poly(1,2-propylene carbonate) and valorization strategy.

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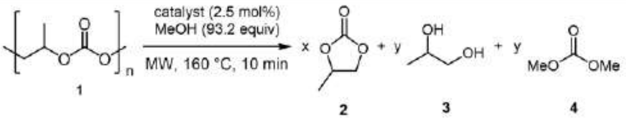
tantly, **3** can serve as feedstock for the regeneration of polymer **1**, requiring a dehydration to propylene oxide or as building block for other polymers.[11,17]

In recent studies, we investigated the depolymerization of polyesters via transesterification reactions, which might be also suitable for end-of-life poly(1,2-propylene carbonate).[16] For instance, depolymerization of **1** via methanolysis will yield **3** and dimethyl carbonate (**4**) as valuable products (Scheme 1). Both compounds can be used for the synthesis of new polymers or as building block in organic synthesis.[11,17–19] Based on that, we report herein the depolymerization of end-of-life poly(1,2-propylene carbonate) (**1**) in the presence of cheap and abundant catalyst.

Initially, we investigated the depolymerization of **1** (pellets, ~3 mm diameter, $M_w = 105{,}000$ g/mol, ca. 5% ether linkages) using methanol as depolymerization reagent and solvent under microwave irradiation (Table 1).

Therefore, pellets of **1** (1.35 mmol based on the monomeric unit) and an excess of methanol (93.2 equiv.) were heated at 160 °C for 10 min under microwave irradiation in a sealed tube (Table 1, entry 1). After cooling to ambient temperature, the methanol was removed carefully and a sample was taken from the residue and dissolved in $CDCl_3$. ^1H NMR analysis revealed only the formation of RCD product **2**, as indicated by a new signal ($\delta = 1.47$ ppm) for the CH_3-function of **2**, while for the polymer **1** a signal for the *C*H-function was observed at $\delta = 4.93–5.07$ ppm.[20] The yield of **2** was determined by correlation of the integrals (*C*H-function of **1** and CH_3-function of **2**) revealing a yield of 20%. Conversely, adding catalytic amounts of $Zn(OAc)_2$ showed full conversion of **1** and formation of **3** along with **2** (Table 1, entry 2). The occurrence of **3** was proven by ^1H NMR (*C*H-function: $\delta = 3.85–3.93$ ppm).[21] A yield of 53% of **3** was detected. In comparison to the uncatalyzed reaction the amount of **2** is increased (47% vs. 20%), indicating that $Zn(OAc)_2$ function as RCD catalyst as well as methanolysis catalyst. In addition, the presence of carbonate **4** was qualitatively confirmed by a singlet at $\delta = 3.77$ ppm.[22] However, its yield could not be determined due to signal overlap. Next, different zinc precursors were tested in the depolymerization reaction (Table 1, entries 3–15). In case of zinc(II) halides the RCD is the dominant process within 10 minutes, but no full conversion of **1** was noticed (Table 1, entries 3 and 4). A better performance was noticed for $Zn(OTf)_2$ (Table 1, entry 5). Based on the formation of significant amounts of **3** by the use of $Zn(OAc)_2$ different zinc(II) carboxylates were studied (Table 1, entries 6–15).[23] In most cases full conversion of **1** was observed, only for $Zn(OOCH)_2$ and $Zn(OOCCCl_3)_2$ small amounts of leftover **1** was monitored (Table 1, entries 7 and 14). Moreover, for all zinc(II) carboxylates both depolymerization products **2** and **3** were detected. Best selectivity for **3** after 10 min was realized with $Zn(OOCtBu)_2$ with a yield of 66% (**3**) vs. 34% (**2**), while best selectivity for **2** was observed for $Zn(OOCPh)_2$ with 67% (**2**) vs. 33% (**3**) (Table 1, entries 8 and 10). Importantly, the carboxylate ligand in zinc(II) carboxylate can influence the catalyst activity by interaction with the substrates, which was reported in earlier works.[24] Based on the performance of zinc(II) carboxylates also sodium and potassium carboxylates were tested (Table 1, entries 16 and 17). Full conversion was observed for both systems, with similar selectivities for **3**. After the precatalyst screening differ-

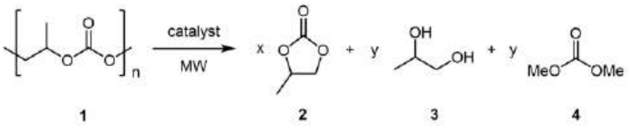
Table 1. Depolymerization of **1**.



Entry[a]	Catalyst [mol%]	**1** [%][b]	Yield **2** [%][c]	Yield **3** [%][c]
1	–	80	20	<1
2	$Zn(OAc)_2$ [2.5]	<1	47	53
3	$ZnCl_2$ [2.5]	14	71	15
4	$ZnBr_2$ [2.5]	71	29	<1
5	$Zn(OTf)_2$ [2.5]	<1	66	34
6	Zinc(II) methacrylate [2.5]	<1	49	51
7	$Zn(OOCH)_2$[d] [2.5]	15	67	18
8	$Zn(COOtBu)_2$[d] [2.5]	<1	34	66
9	$Zn(OOCC_{17}H_{35})_2$[d] [2.5]	<1	52	48
10	$Zn(OOCPh)_2$[d] [2.5]	<1	67	33
11	$Zn(OOC(4\text{-}OMe\text{-}Ph))_2$[d] [2.5]	<1	65	35
12	$Zn(OOC(4\text{-}F\text{-}Ph))_2$[d] [2.5]	<1	61	39
13	$Zn(OOCCH_2Cl)_2$[d] [2.5]	<1	50	50
14	$Zn(OOCCCl_3)_2$[d] [2.5]	18	64	17
15	$Zn(OOCCF_3)_2$[d] [2.5]	<1	40	60
16	NaOAc [2.5]	<1	51	49
17	KOAc [2.5]	<1	41	59

[a] Reaction conditions: **1** (1.35 mmol, based on repeating unit of **1**, $M_w = 105{,}000$ g/mol, 5% ether linkages), catalyst (2.5 mol%, 16.9 µmol based on the repeating unit of **1**), MeOH (93.2 equiv. based on repeating unit of **1**) [b] The leftover of **1** was determined by ^1H NMR. [c] The yield was determined by ^1H NMR assuming that the polymer contains 100% carbonate linkages. [d] The Zn(II) carboxylates were prepared by addition of $ZnEt_2$ (1.0 M in hexane) to 2 equiv. of the corresponding acid with subsequent removal of hexane.

Table 2. Depolymerization of **1** applying zinc catalysis.



Entry[a]	Catalyst [mol%]	MeOH [equiv.]	T [°C]	t [min]	Ratio[b] (**1**:**2**:**3**)
1	$Zn(OAc)_2$ [2.5]	93.2	160	10	<1:47:53
2	$Zn(OAc)_2$ [2.5]	93.2	140	10	<1:68:32
3	$Zn(OAc)_2$ [2.5]	93.2	120	10	24:62:14
4	$Zn(OAc)_2$ [2.5]	93.2	160	60	<1:26:74
5	$Zn(OAc)_2$ [2.5]	93.2	160	120	<1:7:93
6	$Zn(OAc)_2$ [5.0]	93.2	160	10	0:41:59
7	$Zn(OAc)_2$ [1.0]	93.2	160	10	0:61:38
8	$Zn(OAc)_2$ [2.5]	–[c]	160	60	24:76:<1
9	$Zn(OAc)_2$ [2.5]	–[d]	160	60	42:58:<1
10	NaOAc [2.5]	93.2	160	10	<1:51:49
11	NaOAc [2.5]	93.2	140	10	8:79:13
12	NaOAc [2.5]	93.2	120	10	69:31:<1
13	NaOAc [2.5]	186.3	160	10	<1:33:67
14	NaOAc [5.0]	93.2	160	10	<1:12:88
15	NaOAc [1.0]	93.2	160	10	65:35:<1
16	NaOAc [2.5]	–[c]	160	30	>99:<1:<1
17[e]	NaOAc [2.5]	23.7	160	10	<1:19:81
18	NaOAc [2.5]	93.2	160	120	<1:3:97

[a] Reaction conditions: 1 (1.35 mmol, based on repeating unit of 1, $M_w = 105{,}000$ g/mol, 5% ether linkages), catalyst (0–5 mol%, 0–33.8 μmol based on the repeating unit of 1), MeOH (23.7–186 equiv. based on repeating unit of 1). [b] The yield was determined by ^{1}H NMR assuming that the polymer contains 100% carbonate linkages. [c] CH_2Cl_2 (5.2 mL) was used as solvent. [d] THF (5.2 mL) was used as solvent. [e] A polymer sample with $M_n = 50{,}000$ g/mol was used.

ent reaction parameters were investigated for $Zn(OAc)_2$ and NaOAc (Table 2).[25] Initially, the $Zn(OAc)_2$ catalyzed process was studied (Table 2, entries 1–9). Decreasing the reaction temperature to 120 °C revealed the formation of lower amounts of product **3** and a favor for the ring closing depolymerization product **2** (Table 2, entries 1–3). On the other hand, elongation of the reaction time to 120 min at 160 °C showed a significant increase of the yield to 93% of the methanolysis product (Table 2, entries 4 and 5). Increasing the catalyst loading of $Zn(OAc)_2$ to 5.0 mol% improved the outcome of **3** only slightly (Table 2, entries 6 and 7). Importantly, in the absence of methanol as depolymerization reagent and solvent only the ring closing depolymerization product was observed in 58–76% yield depending on the solvent (Table 2, entries 8 and 9).

Next the system based on NaOAc was investigated (Table 2, entries 10–18). Similar to $Zn(OAc)_2$ at lower temperatures the formation of **2** is favored accompanied by a lower conversion of **1** (Table 2, entries 11–12). Moreover, the variation of the catalyst loading has a significant effect on the formation of **3**, at high loadings (5.0 mol%) 88% of **3** are formed, while at low loading (1.0 mol%) no **3** was detected (Table 2, entries 14 and 15). In addition, a polycarbonate with a lower number average molar mass of 50,000 g/mol was successfully converted to **2** and **3** in 19% and 81% (Table 2, entry 17). Furthermore, the reaction time was elongated to 120 min revealing a yield of 97% for **3** (Table 2, entry 18).

Next, the influence of the methanol loading was studied for the $Zn(OAc)_2$ catalyzed depolymerization of polycarbonate **1** within 10 min (Figure 1). Full conversion of **1** was observed by adding 50 equiv. of methanol, while at lower amounts of methanol 10–20% of the polymer/oligomers were detected. In addition, at a loading of 50 equiv. the highest amount of the ring closing product with a yield of 90% was noticed, while increasing the amount of methanol the yield of **2** decreased. Importantly, increasing the amount of methanol revealed an increased yield of **3**Conversely to $Zn(OAc)_2$, for the NaOAc

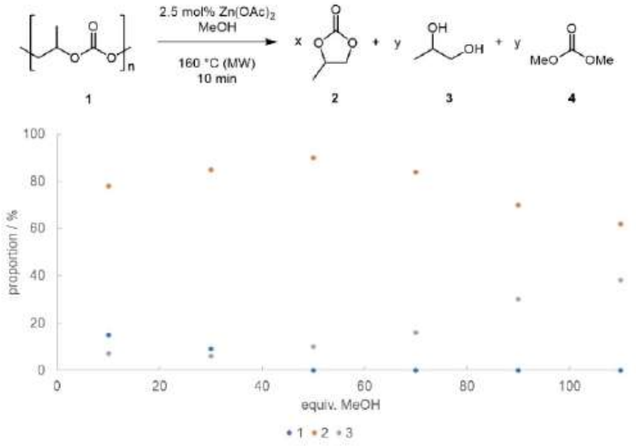


Figure 1. Depolymerization of poly(1,2-propylene carbonate) – yield vs. methanol loading [Reaction conditions: **1** (1.35 mmol, based on repeating unit of **1**, $M_w = 105{,}000$ g/mol, 5% ether linkages), $Zn(OAc)_2$ (2.5 mol%, 33.8 μmol based on the repeating unit of **1**), MeOH (10–110 equiv. based on repeating unit of 1), 160 °C, 10 min, the proportions of **1**, **2** and **3** were determined by ^{1}H NMR].

system decreasing the methanol loading to ca. 20 equivalents increased the yield of **3** to 90%, while at lower loading the yield of **3** decreased to 65 %. Importantly, with all loadings full conversion was observed (Figure 2).

In addition, the progress of the depolymerization appliny $Zn(OAc)_2$ was monitored (Figure 3). The achieved results showed that within 20 min, the depolymerization process is completed. As major product the carbonate **2** is detected with a yield of 71%, indicating that in the first phase the RCD is the dominating process.During progress the amount of **2** decreases, while the yield of **3** increases. For instance, after 180 min the yield of **3** is 86%, while the yield for **2** is decreased to 14%. Based on this, the RCD and the methanolysis process are connected and **2** can be seen as intermediate to produce **3**. In contrast, for NaOAc a longer reaction time (120 min) is required to notice full conversion of the polymer/oligomers (Figure 4).Moreover, after 120 min a ratio of **2**:**3** of 50:50 was observed, while for a reaction time < 120 min compound **2** is the dominant depolymerization product, while for reaction times > 120 min **3** is the dominant depolymerization product. Following, the scale of the reaction was increased to 11.8 g of polymer **1** (M_w = 105,000 g/mol, 5% ether linkages) (Scheme 2). Therefore, the reaction was performed in an autoclave, that

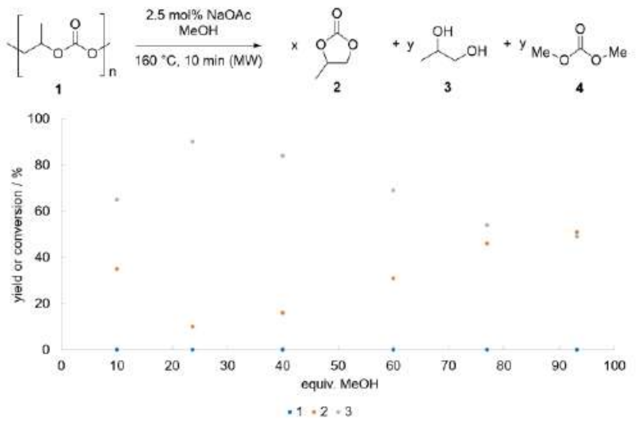


Figure 2. Depolymerization of poly(1,2-propylene carbonate) – yield vs. methanol loading [Reaction conditions: **1** (1.35 mmol, based on repeating unit of **1**, M_w = 105,000 g/mol, 5% ether linkages), NaOAc (2.5 mol%, 33.8 μmol based on the repeating unit of **1**), MeOH (10–93.2 equiv. based on repeating unit of **1**), 160 °C, 10 min, the proportions of **1**, **2** and **3** were determined by ^{1}H NMR].

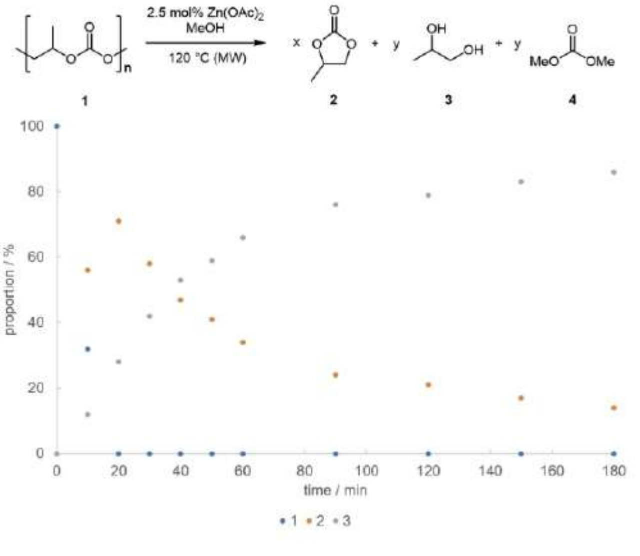


Figure 3. Depolymerization of poly(1,2-propylene carbonate) – yield vs. time [Reaction conditions: **1** (1.35 mmol, based on repeating unit of **1**, M_w = 105,000 g/mol, 5% ether linkages), $Zn(OAc)_2$ (2.5 mol%, 33.8 μmol based on the repeating unit of **1**), MeOH (93.2 equiv. based on repeating unit of 1), 120 °C, 0–180 min, the proportions of **1**, **2** and **3** were determined by ^{1}H NMR].

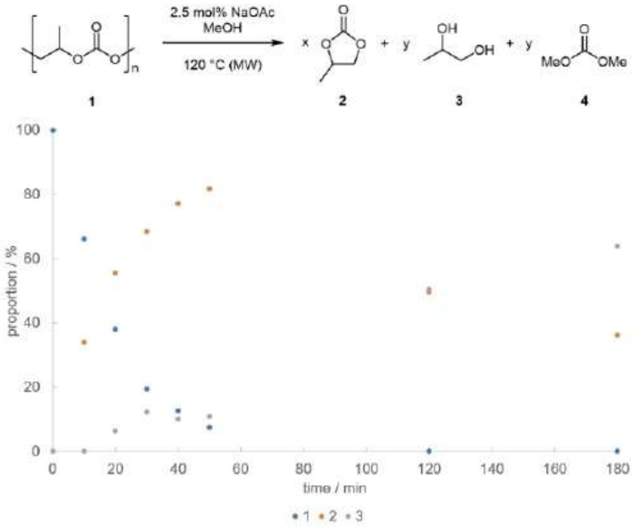
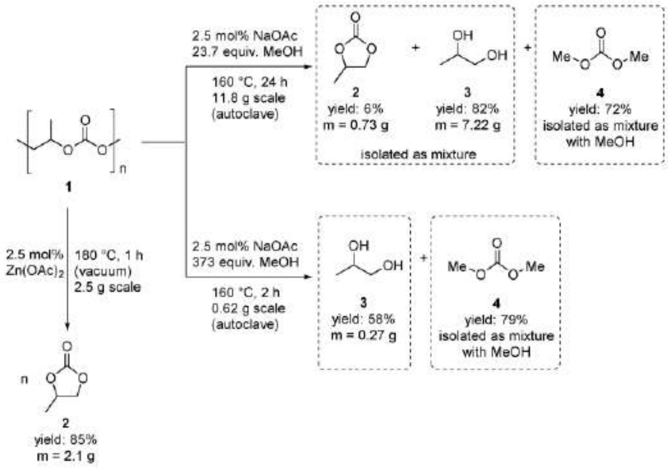


Figure 4. Depolymerization of poly(1,2-propylene carbonate) – yield vs. time [Reaction conditions: **1** (1.35 mmol, based on repeating unit of **1**, M_w = 105,000 g/mol, 5% ether linkages), NaOAc (2.5 mol%, 33.8 μmol based on the repeating unit of **1**), MeOH (93.2 equiv. based on repeating unit of **1**), 120 °C, 0–180 min, the proportions of **1**, **2** and **3** were determined by ^{1}H NMR].

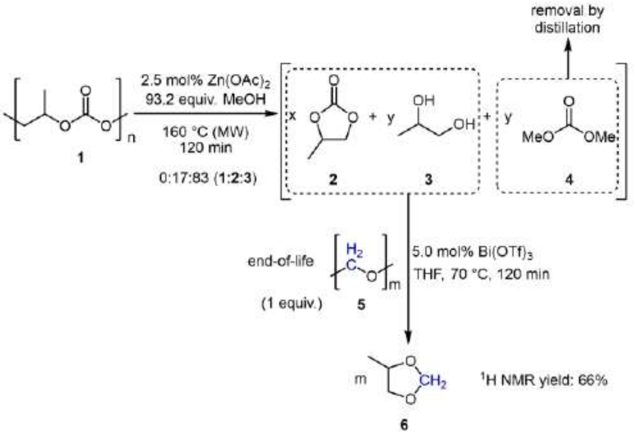


Scheme 2. Depolymerization of poly(1,2-propylene carbonate) – scale-up. The yields are given for the assumption, that the polymer contains 100% carbonate linkages.

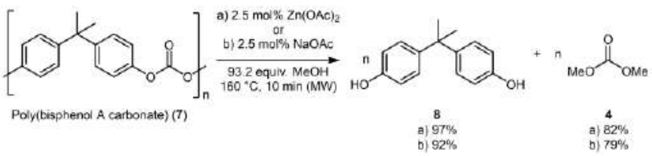
offers a larger reaction volume than the applied microwave vessel. The reaction conditions were in accordance to Table 2, entry 13 and the reaction was carried out for 24 h at 160 °C.[27] After cooling to ambient temperature, methanol and dimethyl carbonate were removed as an azeotrope by distillation. A yield of 72 % for dimethyl carbonate was calculated.[26] The residue of the reaction mixture was submitted to Kugelrohr distillation. The distillate (7.95 g) contained compound **3** as major component (82 %) and small amounts of **2** (6 %).[28] Moreover, the residue of the distillation was analyzed and it contains oligoether fragments, but the presence of carbonates can be excluded. Notably, the ether bonds were not converted under the reaction conditions. Moreover, with an excess of methanol the selectivity towards **3** was increased and **3** was isolated in 58 % yield (Scheme 2). In order to access also compound **2** selectively, polymer **1** was heated at 180 °C under vacuum in the presence of catalytic amounts of $Zn(OAc)_2$ (2.5 mol %) (Scheme 2). Importantly, from the reaction mixture compound **2** was distilled off at 180 mbar and was isolated in 85 % yield.

In addition, consecutive depolymerization processes were studied. In this regard, end-of-life polymer **1** was depolymerized to product **3**, which was applied as depolymerization reagent in the conversion of poly(oxymethylene) (**5**) to produce the valuable acetal **6**.[15c,19] In detail, **1** was depolymerized under optimized conditions to obtain **3** in a ^{1}H NMR yield of 83 % (Scheme 3). After removal of methanol and dimethyl carbonate $Bi(OTf)_3$ (5.0 mol %) and **5** were added to the reaction mixture. After 3 hours at 70 °C compound **6** was obtained in 66 % yield based on **1**.

Moreover, the optimized reaction conditions for the depolymerization of poly(1,2-propylene carbonate) (**1**) were applied for the depolymerization of end-of-life poly(bisphenol A carbonate) (**7**) (Scheme 4).[16] Good yields of 97 % ($Zn(OAc)_2$) and 92 % (NaOAc) were detected for the depolymerization product bisphenol A (**8**), while dimethyl carbonate (**4**) was obtained in lower yields.



Scheme 3. Consecutive depolymerization of end-of-life polycarbonate and end-of-life poly(oxymethylene) [Reaction conditions: depolymerization of polycarbonate: **1** (1.35 mmol, based on repeating unit of **1**, $M_w = 105{,}000$ g/mol, 5 % ether linkages), $Zn(OAc)_2$ (2.5 mol %, 33.8 μmol based on the repeating unit of **1**), MeOH (93.2 equiv. based on repeating unit of **1**), 160 °C, 20 min, the proportions of **1**, **2** and **3** were determined by ^{1}H NMR; depolymerization of poly(oxymethylene): mixture of **2** and **3** after distillation of MeOH and **4**, $Bi(OTf)_3$ (5.0 mol %, 33.7 μmol based on the repeating unit of **1**)), poly(oxymethylene) (1.35 mmol, 1.0 equiv., based on the repeating unit of **1**), THF (4 mL), 70 °C, 120 min, the yield of **6** was determined by ^{1}H NMR].



Scheme 4. Depolymerization of end-of-life poly(bisphenol A carbonate) [Reaction conditions: **7** (1.35 mmol, based on repeating unit of **7**), $Zn(OAc)_2$ (2.5 mol %, 33.8 μmol based on the repeating unit of **7**), MeOH (93.2 equiv. based on repeating unit of **7**), 160 °C, 10 min. The yield of **8** and **4** was determined by ^{1}H NMR.].

In summary, we investigated the methanolysis of poly(1,2-propylene carbonate) applying cheap and abundant $Zn(OAc)_2$ or NaOAc as catalyst to generate 1,2-propanediol as suitable product for new polymers. In the early stage of the depolymerization 1,2-propylene carbonate was observed, which is formed by catalytic ring closing depolymerization. However, during progress the 1,2-propylene carbonate was converted to 1,2-propanediol by reaction with methanol in the presence of catalytic amounts of $Zn(OAc)_2$ or NaOAc.

Supporting Information Summary

The experimental details including the depolymerization reactions and product characterizations can be found in the supporting information.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: catalysis · depolymerization · green chemistry · polymers · recycling

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[26] The formation of **3** and **4** should occur in an 1:1 ratio. However, the lower yield of **4** can be caused different separation processes or by decomposition reaction, which have been reported. See for instance: J. F. Lacroix, A. Soldera, J. M. Lavoie, *J. CO2 Util.* **2014**, *7*, 46–50.

[27] Full conversion of **1** was detected by ^{1}H NMR and a NMR yield of 93% for **3** and a NMR yield of 7% for **2** before distillation.

[28] Further separation by Kugelrohr distillation was not successful, but the purity of **3** should be sufficient for further transformations, see for instance Scheme 3.

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5.2 Depolymerization of poly(lactide)

In this chapter, poly(lactide) was converted by methanolysis to the corresponding methyl lactate (**13**) or L-lactide (**11**). Initially, a variety of organic nitrogen bases was tested.[251] It was found that DBU, DMAP and TBD were more active while other pyridine derivatives and aliphatic amines revealed less activity. As a drawback of these organocatalysts, at least 2.5 mol% were required to achieve quick conversion. Consecutively, DMAP was used for to degrade household goods, indicating a generally good performance. Noteworthy, "clean" goods could be converted with the same efficiency than the corresponding used goods, indicating high robustness towards contamination. In addition, goods with low PLA content, e.g. composite materials that are challenging for other recycling techniques were efficiently converted.

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Depolymerization of End-of-Life Poly(lactide) via 4-Dimethylaminopyridine-Catalyzed Methanolysis

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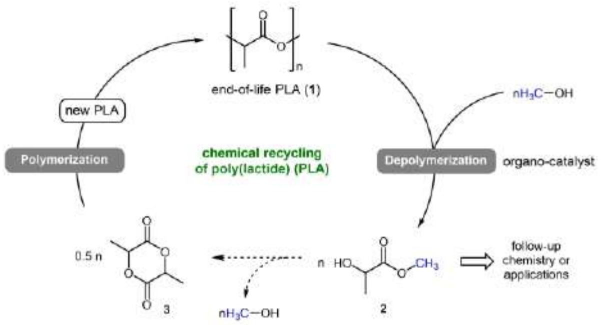
The chemical recycling of end-of-life plastics/polymers can contribute to a more sustainable society. In this regard, the selective degradation (depolymerization process) leading to well-defined low molecular weight chemicals is a key feature of the chemical recycling. Based on that, we have investigated the depolymerization of end-of-life poly(lactide)-based (PLA) goods. In more detail, applying a combination of methanol and catalytic amounts of 4-dimethylaminopyridine (DMAP) end-of-life PLA was depolymerized to methyl lactate, a chemical which can be is used as "green" solvent or as starting material for new poly(lactide) products. With the assistance of microwave heating an excellent rate of depolymerization (>99%) was observed within short reaction times (10-20 min). Interestingly, a set of 16 PLA commodities was efficiently transformed to methyl lactate.

Every year huge amounts of plastics[1] are produced, which are largely converted to waste/end-of-life plastics, once the function of the plastic goods is completed.[2] The state-of-the-art waste management includes landfill storage,[3] energy recovery, mechanical recycling and downcycling.[4,5] On the one hand, the end-of-life plastics can be subjected to incineration producing heat, which can be applied for steam or electricity generation, but the chemical information embedded in the material is (irreversible) lost during its conversion to e.g. carbon dioxide. On the other hand, the end-of-life plastics can be treated by mechanical recycling/downcycling to produce goods with same or lower quality, but after several cycles the plastics are eventually subjected to incineration, due to loss of quality.[6] In consequence, significant amounts of carbon dioxide are generated, which cause negative issues on society.[7] An option to save fossil resources is the application of renewable resources as starting material for plastics.[8] For instance, plastics based on biopolymers as well as bio-based polymers have been established. For example poly(lactide) (PLA, 1) is synthesized in a yearly production volume of ~0.2 million tons and exhibits excellent plastic properties, which allow applications spanning from food packaging to pharmaceuticals.[9] As starting chemicals for poly(lactide) the monomer lactic acid or its derivative lactide (3) are applied in polycondensation or ring-opening polymerization, which arise from biological processes starting from carbon dioxide.[10] After the PLA-plastics have fulfilled their obligations different pathways can be pursued for the end-of-life poly(lactide). In contrast to most fossil resources based plastics, PLA is to a certain amount bio-degradable and can therefore converted to e.g. carbon dioxide by biological processes.[11] However, the decomposition of poly(lactide) is often not possible within the timeframe of established compost works; hence, end-of-life poly(lactide) plastics may subjected to incineration, but importantly the chemical information of the PLA is converted to e.g. carbon dioxide, which can be reused as starting point for new poly(lactide) plastics.[12] Overall a somewhat carbon-neutral process can be envisaged. Nevertheless, the production of biopolymers/bio-based polymers requires cultivable acreage, which in turn cannot be used for the production of edibles or energy production. An interesting alternative can be the chemical recycling via depolymerization-polymerization processes, the first one allows the formation of low-molecular weight valuable monomers by selective degradation of the polymer chain (depolymerization step) (Scheme 1).[13] This can be considered advantageously since the monomers can be applied as feedstock for new high-quality polymers (polymerization step) and therefore a recycling of the polymer is reasonable.[14] Interestingly, the amount of cultivable acreage needed for bioplastic or bio-based plastic production can be reduced. Several studies have been accounted so far including hydrolysis,[15] alcoholysis[16] (catalytic) pyrolysis/thermal degradation.[17] For example the alcoholysis, particularly the methanolysis, has been investigated (Scheme 1). In detail,



Scheme 1. Concept for the chemical recycling of end-of-life poly(lactide).

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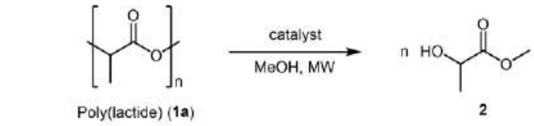
the end-of-life PLA reacts in the presence of a suitable catalyst with an excess of methanol. As major low-molecular weight product methyl lactate (**2**) is formed, which can after isolation be converted to the industrial relevant lactide (**3**), which is the starting point for a ring-opening polymerization to obtain new poly(lactide).[18] Moreover, the released methanol can be reused/recycled for next depolymerization processes. In consequence an atom efficient recycling of **1** is feasible.

Recently, we have reported the use of 4-dimethylaminopyridine (DMAP) as organo-catalyst[19] in the depolymerization of end-of-life poly(bisphenol A carbonate) applying acetic anhydride or methanol as depolymerization reagent.[20] Based on the later methanolysis process, we became attracted in the application of DMAP in the methanolysis of PLA. Interestingly, Nederberg *et al.* reported an investigation on the use of DMAP in the methanolysis of PLA.[21] However, (sub)stoichiometric amounts of DMAP and long reaction times were required to produce significant amounts of low molecular weight chemicals. Based on that, we report herein our investigations on the microwave-assisted chemical depolymerization of end-of-life PLA to produce **2** within short reaction times (Scheme 1).

Initially, the depolymerization of pieces of poly(lactide) (**1 a**) obtained from transparent PLA-plastic cups was studied (Table 1). In this regard, **1 a** (1.35 mmol based on the monomeric unit) was reacted with an excess of methanol (23.1 equiv. based on the monomeric unit of **1 a**) in the presence of catalytic amounts of 4-dimethylaminopyridine (5.0 mol% based on the monomeric unit of **1 a**). No additional solvent was added because methanol as well as the product can act as solvent.[22] The mixture was placed in a sealed glass vial in a microwave and was heated under microwave (MW) conditions at 180 °C for 10 minutes, while stirring (Table 1, entry 1). Afterwards, the mixture was cooled to room temperature and an aliquot was dissolved in chloroform-d_1 for ^{1}H NMR analysis. Noteworthy, a clear and colorless homogeneous solution was obtained. At 1.39 ppm in the ^{1}H NMR spectrum a doublet was detected with a coupling of 6.91 Hz, which corresponds to the CH_3CH-function of the depolymerization product methyl lactate (**2**). At 4.26 ppm a double quartet was monitored with a coupling constant of 6.91 Hz and 5.20 Hz, which corresponds to the CH_3*CH*-function. Moreover, the methyl group of the ester function of methyl lactate was observed at 3.76 ppm and the CHO*H*-function as doublet ($J = 5.20$ Hz) at 2.89 ppm.[23] Integration of the methyl lactate signals and relation to the polymer/oligomer residue signals in the ^{1}H NMR spectrum revealed almost full conversion of **1 a** and 97% NMR yield of **2** and an excellent performance of the catalyst. Furthermore the catalyst loading was investigated (Table 1, entries 1–4). Decreasing the loading of DMAP showed a decreased activity, while in the absence of any catalyst no methyl lactate formation was detected. Next the influence of the amount of methanol was studied (Table 1, entries 5–6). Both increasing (46.3 equiv.) and decreasing (2.9 equiv.) the amount of methanol with respect to the monomeric unit of **1 a** revealed lower yields of **2**. Noteworthy, in case of 2.9 equiv. of methanol THF was added as solvent. A decrease of the reaction temperature to 120 °C resulted in a diminished yield of 22% (Table 1, entries 7–9). A further decrease to 100 °C required longer reaction times to obtain moderate amounts of **2** (Table 1, entry 10). In addition, the reaction time was investigated (Table 1, entries 11–12). Stopping the reaction after 5 min showed the formation of **2** in 78% yield, which corresponds to a turnover frequency of ~187 h^{-1}.[24] Moreover the extension of the reaction time to 60 min resulted in full conversion of **1 a** and a yield of >99% for **2**. Importantly, no decomposition products were detected. Variation of the organo-catalyst showed no significant improvement compared to DMAP (Table 1, entries 13–19). For instance excellent yields were obtained with DBU and TBD, while with DABCO and N^iPr_2Et moderate yields of **2** were detected.

Table 1. DMAP-catalyzed depolymerization of poly(lactide) (**1 a**).

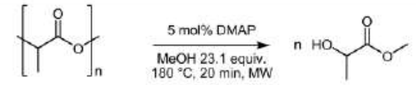


Entry[a]	Catalyst [mol %]	MeOH [equiv.]	T [°C]	t [min]	Yield **2** [%][b]
1	DMAP [5]	23.21	180	10	97
2	DMAP [2.5]	23.1	180	10	74
3	DMAP [1]	23.1	180	10	4
4	None	23.1	180	10	<1[c]
5	DMAP [5]	46.3	180	10	68
6[d]	DMAP [5]	2.9	180	10	11
7	DMAP [5]	23.1	160	10	76
8	DMAP [5]	23.1	140	10	52
9	DMAP [5]	23.1	120	10	22
10	DMAP [5]	23.1	100	20	25
11	DMAP [5]	23.1	180	5	78
12	DMAP [5]	23.1	180	60	>99
13	Pyridine [5]	23.1	180	10	2[e]
14	2,2'Bipy [5]	23.1	180	10	<1[e]
15	4,4'Bipy [5]	23.1	180	10	<1[e]
16	DBU[f] [5]	23.1	180	10	>99
17	DABCO[g] [5]	23.1	180	10	61
18	TBD[h] [5]	23.1	180	10	>99
19	N^iPr_2Et [5]	23.1	180	10	62

[a] Reaction conditions: poly(lactide) (**1 a**) (obtained from transparent plastic cup, 1.35 mmol based on the repeating unit), DMAP (0-5 mol%, 0–0.0675 mmol based on the repeating unit of **1 a**), methanol (2.9-46.3 equiv. based on the repeating unit of **1 a**), microwave heating, 100–180 °C, 5–60 min. [b] The yield was determined by ^{1}H NMR. If not otherwise stated after reaction a clear solution was obtained. Moreover, it is presumed that the PLA-product is composed of 100% of PLA. [c] After the reaction a colorless precipitate was observed. The yield bases on soluble compounds. [d] THF (1 g) was added. [e] After the reaction a colorless precipitate was observed. The yield bases on soluble compounds. [f] 1,8-Diazabicyclo(5.4.0)undec-7-ene. [g] 1,4-Diazabicyclo[2.2.2]octane. [h] 1,5,7-Triazabicyclo[4.4.0]dec-5-ene.

With the optimized conditions (5 mol% DMAP, 23.1 equiv. methanol, 180 °C, 20 min, MW) in hands we performed the reaction on a larger scale (8.1 mmol) (Table 2). The transparent PLA-plastic cup **1 a** was converted in excellent yield to methyl lactate as monitored by ^{1}H NMR. For isolation purpose the reaction mixture, after depolymerization in the microwave, was transferred to a flask, which was connected to distillation equipment. The volatile compounds methanol and methyl lactate were quickly distilled off under vacuum to avoid back reactions and were collected in the collection flask, which was

Table 2. DMAP-catalyzed depolymerization of poly(lactide) products.



Poly(lactide) (**1a-n**)

2

Entry[a]	Product	Yield **2** [wt%][b]	Yield **2** [%][c]
1	transparent plastic cup (**1 a**)	102	70
2	drinking straw with green strips (**1 b**)	83	58
3	lid for espresso mugs with talcum powder (~20-30%) (**1 c**)	55	38
4	transparent disposable food box (**1 d**)	139	96
5	red ice cream spoon (**1 e**)	97	67
6[d]	used yellow ice cream spoon (**1 e**)	122	84
7	black lid for coffee mugs (**1 f**)	90	63
8	used black lid for coffee mugs (**1 f**)	92	64
9	transparent cover of a disposable Sushi box (**1 g**)	98	68
10	black base of a disposable Sushi box (**1 h**)	116	80
11	blue disposable glove (**1 i**)	7	5
12	disposable fork with talcum powder (**1 j**)	77	53
13	transparent disposable serving cup (**1 k**)	133	92
14	transparent plastic sheet (**1 l**)	110	76
15	coffee mug with PLA coating on the inside (**1 m**)	3	2
16	transparent bottle (**1 n**)[f]	103	71

[a] Reaction conditions: poly(lactide) (**1**) (583.2 mg, 8.1 mmol based on the monomeric unit), DMAP (49.2 mg, 5 mol%, 0.405 mmol based on the repeating unit of **1**), methanol (6 g, 187.2 mmol, 23.1 equiv. based on the repeating unit of **1**), microwave heating, 180 °C, 20 min. [b] The mass of isolated **2** was related to the mass of the starting PLA-product. [c] The amount of substance of **2** was related to the amount of substance of the starting PLA-product insinuating that the PLA-product is composed of 100% of PLA. [d]. Used for stirring a mixture of coffee, sugar and milk. The PLA-product was not cleaned before depolymerization. [e] Used with coffee, milk and sugar. The PLA-product was not cleaned before depolymerization. [f] Only the body of the bottle was made of PLA.

cooled with liquid nitrogen. Afterwards, methanol was carefully removed by rotary evaporator in vacuum. Finally, methyl lactate **2** was obtained in 102 wt% (based on the initial weight of **1 a**) or 70% isolated yield (based on the presumption that **1 a** is composed of 100% PLA) as colorless liquid (Table 2, entry 1).

In addition, several PLA-plastic goods were subjected to depolymerization reaction (Table 2, entries 2–16). For instance additional transparent goods like a disposable food box (**1 d**), a Sushi-box cover (**1 g**), a disposable serving cup (**1 k**), a plastic sheet (**1 l**) and a bottle (**1 n**) were tested (Table 2, entries 4, 9, 13, 14, 16). Good to excellent isolated yields of up to 139 wt% (based on the initial weight of the PLA goods) or up to 96% (based on the presumption that **1** is composed of 100% PLA) were realized. Somewhat lower isolated yields[25] of 55–77 wt% or 38–53% are monitored for non-transparent PLA goods, e.g. a lid for espresso mugs (**1 c**), a disposable fork (**1 j**), which contain up to 20–30% talcum powder and dyes (Table 2, entries 3 and 12). Furthermore, PLA goods containing black dyes were investigated, revealing a yield of 90–116 wt% or 63–84% (Table 2, entries 7 and 10). Interestingly, in case of the black lid for coffee mugs (**1 f**) a used sample (contaminated with coffee/sugar/milk leftover) was send to depolymerization showing no disordered effect of the contamination (Table 2, entries 7–8). A similar result was realized in case of colored PLA-ice cream spoons (Table 2, entries 5–6). Furthermore, disposable gloves made of PLA were investigated, but only low yields 7 wt% and 5% were detected (Table 2, entry 11). Finally, a PLA-paper composite was subjected to depolymerization (Table 2, entry 15). A paper coffee mug inside coated with a thin layer of PLA was tested. Only low yields of 3 wt% and 2% were realized due to the large portion of the paper in the good. Nevertheless, the obtained result showed the principle of operation of the PLA depolymerization protocol.

In summary, we have set up a straightforward method to convert end-of-life poly(lactide) to useful low-molecular weight and well-defined products, such as methyl lactate. The depolymerization was performed with methanol as depolymerization reagent and DMAP as organocatalyst. Noteworthy, no additional solvent was required. Excellent yields were realized within short reaction times (10-20 min). Moreover, the protocol was applied to a variety of different PLA goods containing additives, but in all cases methyl lactate was isolated, therefore showing the robustness and the versatility of the method. Future studies will focus on the activity-improvement of the depolymerization process. Moreover, a life cycle assessment will be carried out to evaluate the potential for large-scale applications.

Supporting Information Summary

The experimental details including the depolymerization reactions and product characterization can be found in the supporting information.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Catalysis · Depolymerization · Methanolysis · Poly (lactide) · Recycling

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[24] The TOF was calculated: (mole product/mole catalyst)*h^{-1}. The TOF was calculated using the yield of **2** after 5 min, because the determination of the TOF at a yield of 50% was not possible, due to the technical limits.

[25] The stated yields do not take the talcum powder into account.

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For the same reason as discussed for PBAC (**2**) methanolysis, alkali metal halides were tested for the PLA methanolysis as well.[252] Indeed, a variety of metal halides provides good to excellent yields at temperatures above 140 °C. The trends for observed activity were comparable to the depolymerization of PBAC (**2**). However, for KF a TOF of up to 816 h^{-1} was observed (0.5 mol% KF, 180 °C, 10 min, 23.1 eq. MeOH) which was by far higher than DMAP. However, while KI and KF were active, KCl and KBr were inactive. Again, KF was used to degrade further goods due to its low price. A catalyst recycling experiment revealed constant performance for up to four repetitions until a decay of the yield was noticed. In addition, PLA (**9**) was successfully degraded in the presence of other polymers. PBAC (**2**) also underwent degradation while PET (**14**) and Nylon 6 (**31**) remained unconverted.

Selective Degradation of End-of-Life Poly(lactide) via Alkali-Metal-Halide Catalysis

*Christoph Alberti, Nicole Damps, Roderich R. R. Meißner, Melanie Hofmann, Desiree Rijono, and Stephan Enthaler**

The recycling of poly(lactide) (PLA) is studied. Using methanol and alkali-metal-halides as catalyst, PLA is degraded to produce methyl lactate, which is a suitable chemical for the regeneration of PLA. An excellent degree of degradation (conversions: >99%, yields: >99%) is achieved in less than 20 min utilizing microwave heating. Remarkably, PLA goods are successfully converted into methyl lactate.

Nowadays, petrochemical-based plastics have a significant impact on society, which is underlined by the countless applications, the yearly increasing volume of production, and the deep interweavement with human life.[1,2] However, several issues arise with plastics after the service life ends.[3] In more detail, the current management for end-of-life (EoL) plastic streams is mainly based on energy recovery, (landfill storage), recycling (mechanical and downcycling), and unregulated release to the environment.[4–9] Finally, these treatments convert chemical functions of the polymers into harmful chemicals, for instance, carbon dioxide, consequently affecting on the anthroposphere (e.g., global warming). Importantly, for fresh polymers the declining fossil resources are required.[10,11] Moreover, environmental concerns (e.g., high stability against biodegradation, absorption of chemicals) are caused by end-of-life plastic streams, which are not reaching the collecting system, but discarded directly in the ecosphere.[12] An attractive alternative to petrochemical-based plastics are plastics originated from renewables (biopolymers and bio-based polymers), but so far the rate of production is significantly lower.[13–15] One example from this group is poly(lactide) (**1**), which is accessible from lactic acid (via polycondensation) or the lactic acid derivative lactide (via ring-opening-polymerization, ROP). Lactic acid is available from biochemical processes originated from CO_2, H_2O, and energy (**Scheme 1**).[16–20] Poly(lactide) (PLA) is manufactured in an annual scale of ≈0.2 million tons and has interesting plastic abilities, which enables utilization in a wide range (e.g., food packaging, pharmaceuticals). In contradiction to the majority of fossil-based plastics, poly(lactide) is to some extent biodegradable depending on the conditions and environment and is degraded to, for instance, CO_2; therefore, environmental issues are reduced if PLA is not treated within the current waste management.[21–26] Nonetheless, the breakdown of PLA in composting plants is regularly not fully accomplishable in the scheduled time frame. Conversely, EoL poly(lactide) can be exposed to incineration for energy recovery.[27–33] In contrast to petrochemical-based plastics a nearly carbon-neutral manner can be visualized, since carbon dioxide "embedded" in PLA and the carbon dioxide released from EoL PLA are in a narrow section of the timeline.

Moreover, the EoL plastics can be handled by recycling (mechanical recycling or downcycling) to generate products with identical or lower quality, nonetheless after some sequences the plastics will be send to biological degradation or energy recovery, due to loss of quality.[34–37] Even if several advantages of polymers based on renewables are evident, the production needs cultivable acreage. Noteworthy, by doing so the acreage is blocked and cannot be applied for the cultivation of edibles and cultivation of energy or virgin biotopes have to be transformed to agriculture areas. A possibility to avoid the competitive situation can represent the chemical recycling composed of depolymerization and polymerization reactions.[38–40] Initially, the depolymerization/degradation enables the conversion of the EoL plastic/polymer to monomers or useful compounds. Subsequently, the monomers are utilized as feed in polymerizations to create new polymers. Advantageously, compared to mechanical recycling/downcycling the quality and abilities of the plastics can be adjusted at the polymerization step or the plastic formation stage and is independent of the quality of the EoL plastic. Noteworthy, cultivable acreage required for PLA-plastics can be minimized. A number of investigations have been reported including the hydrolysis,[41–47] alcoholysis,[48–57] and (catalytic) pyrolysis or thermal degradation[58–62] of PLA. For instance, the alcoholysis of PLA, especially the methanolysis, represents an interesting approach toward chemical recycling (Scheme 1). The EoL PLA (**1**) is degraded with the degradation reagent methanol and with the support of a catalyst to form as main chemical methyl lactate (**2**). Subsequently,

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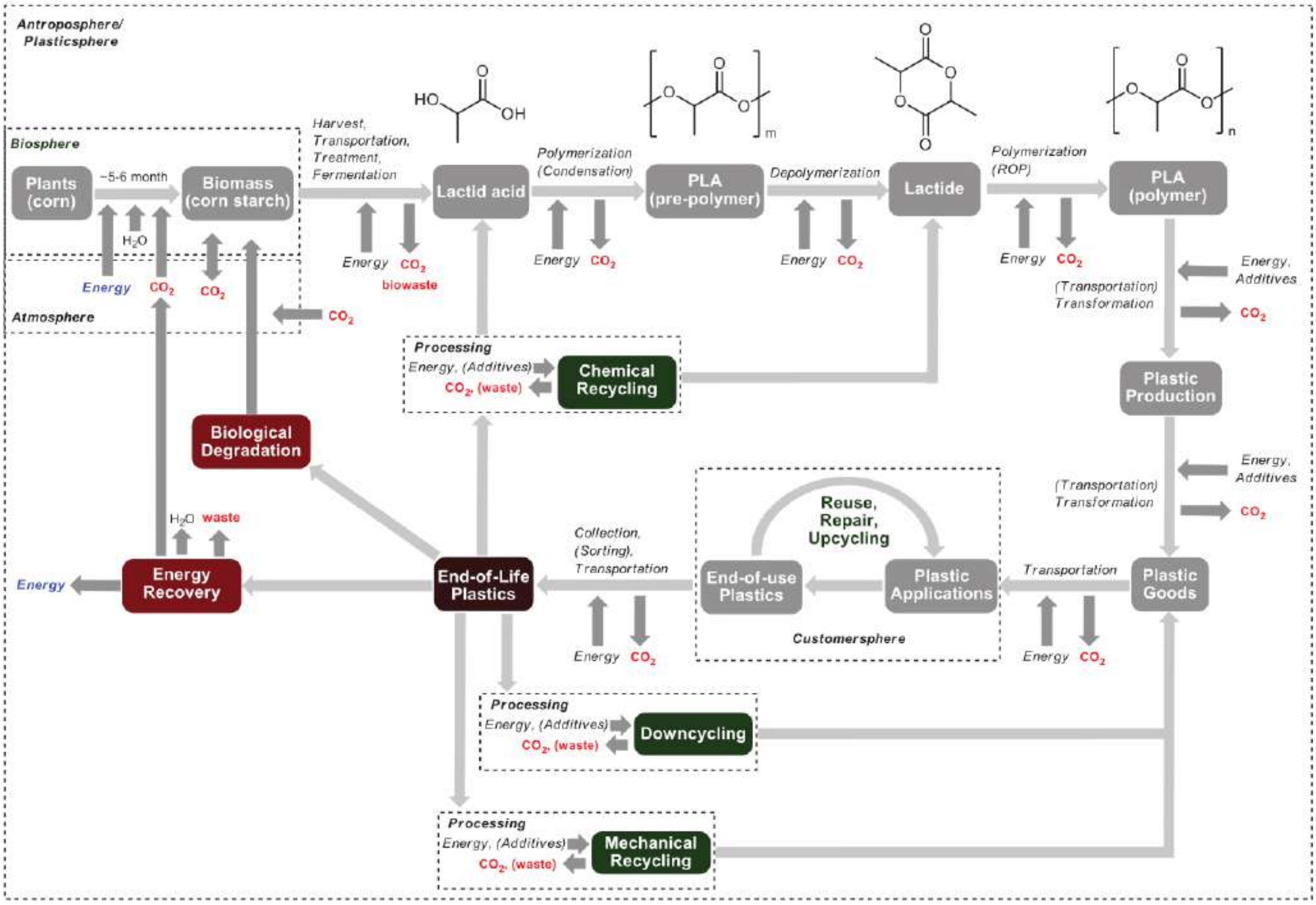
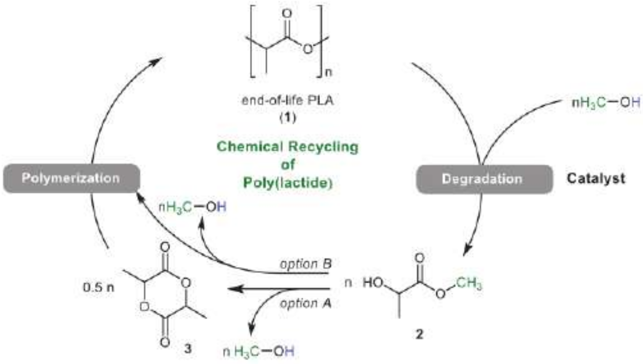


Scheme 1. Potential life cycle of PLA.

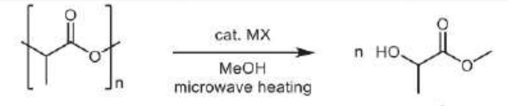
methyl lactate (**2**) can be transformed to compound **3** (lactide), which is a fundamental compound in the industrial production chain of PLA (Scheme 1).[63–70] As second product methanol is produced, which can be recycled for further degradation; therefore, reduced amounts of waste are generated and the whole process is made highly atom efficient. With respect to the degradation process, a number of organocatalysts have been proven to be active, but often long reaction times and "costly" organocatalysts are required; hence, improvements are needed. For example, ionic liquids (ILs) have been established as catalysts.[56,71–75] It was supposed that the alcohol is activated by the anion and the carbonyl function by the cation. In this context, we wondered if straightforward alkali metal halides can mimic the action of ILs.[76–78] Furthermore, alkali metal salts can have benefits regarding "Green Chemistry" and SDGs considerations.[79] For instance, we recently studied the potential of the organocatalyst 4-*N*,*N*-dimethylaminopyridine (DMAP).[57] However, low TOFs (amount of substance of **2**/(amount of substance catalysts) $h^{-1} \approx 178\ h^{-1}$) were observed and moreover to access DMAP several synthetic steps, which create waste, are required starting from fossil resources.[80] In this context, we account our studies on microwave-assisted degradation of EoL PLA catalyzed by alkali metal halides (**Scheme 2**).

Initially, as model for optimization of the degradation reaction conditions a transparent plastic cup containing poly(lactide) (**1a**, $M_n = 57\ 500$ g mol^{-1}, $M_w = 240\ 800$ g mol^{-1}, $Đ = 4.2$, PLLA) as major component was investigated (**Table 1**). Small pieces of the PLA **1a** (1.35 mmol with respect to the monomer unit, implying that **1a** contains 100% of PLA), an excess of methanol (23.1 equivalents with respect to the monomer unit of **1a**) and catalytic amounts of KF (5.0 mol% with respect to the monomer unit of **1a**) were added to a microwave glass vial. After sealing the vial the stirred mixture was reacted for 10 min at 180 °C applying microwave heating (MW) (Table 1, entry 1). During



Scheme 2. Chemical recycling concept for PLA (option A: conversion of **2** to the industrial relevant building block **3**, which can be used as precursor for the synthesis of PLA via ring opening polymerization; option B: direct polymerization of **2** via transesterification).

Table 1. Degradation of **1a** using alkali-metal-halide-catalysis—optimization of reaction conditions.



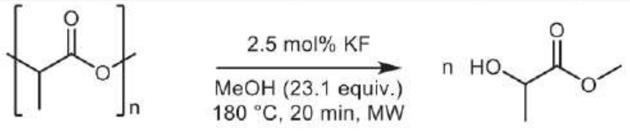
Poly(lactide) (**1a**) → **2**

Entry[a)]	Catalyst	Catalyst loading [mol%]	MeOH [equiv.]	T [°C]	t [min]	Yield **2** [%][b)]
1	KF	5.0	23.1	180	10	98
2	KF	2.5	23.1	180	10	99
3	KF	5.0	23.1	180	5	99
4	KF	5.0	23.1	180	60	>99
5	KF	1.0	23.1	180	10	98
6	KF	0.5	23.1	180	10	68
7	–	–	23.1	180	10	<1
8[c)]	KF	5.0	11.6	180	10	>99
9[d)]	KF	5.0	5.8	180	10	23
10[d)]	KF	5.0	1.0	180	10	<1
11	KF	5.0	23.1	160	10	99
12	KF	5.0	23.1	140	10	98
13	KF	5.0	23.1	120	10	n.d.[e)]
14	LiCl	5.0	23.1	180	10	50
15	NaF	5.0	23.1	180	10	n.d.[e)]
16	NaCl	5.0	23.1	180	10	n.d.[e)]
17	NaI	5.0	23.1	180	10	49
18	KCl	5.0	23.1	180	10	n.d.[e)]ss
19	KBr	5.0	23.1	180	10	n.d.[e)]
20	KI	5.0	23.1	180	10	64
21[f)]	KF	2.5	23.1	180	20	93

[a)] Conditions: **1a** (transparent PLA cup), 1.35 mmol with respect to the monomer unit, it is presumed that **1a** is composed of 100% of PLA), catalyst (0–5 mol%, 0–0.0675 mmol with respect to the monomer unit of **1a**), MeOH (5.8–23.1 equiv. with respect to the monomer unit of **1a**), THF (0–2.0 g), temperature: 120–180 °C (microwave heating), time: 5–60 min; [b)] A homogeneous solution was noticed. The yield of **2** bases on ^{1}H NMR spectroscopy; [c)] Addition of THF (1.0 g); [d)] Addition of THF (2.0 g); [e)] A precipitate was formed; [f)] 8.1 mmol scale of **1a**.

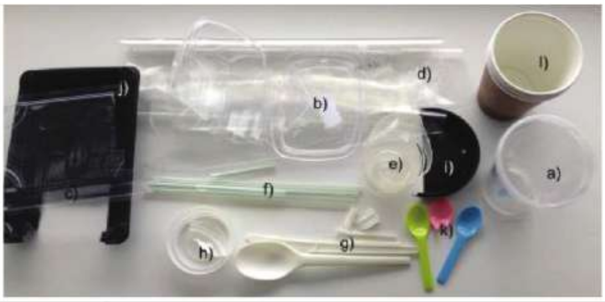
heating/degradation process the PLA was completely dissolved resulting in the formation of a homogeneous solution. After that, to an aliquot of the mixture was added $CDCl_3$ for determination of the yield by ^{1}H NMR spectroscopy. The existence of the desired degradation product **2** was indicated by the appearance of a singlet at 3.76 ppm. The signal corresponds to the methyl ester functionality of **2**. Moreover, the occurrence of **2** was confirmed by a doublet at 2.89 ppm ($^3J_{HH}$ = 5.20 Hz), which is in alignment with the $-CHOH$-functionality. Moreover, a doublet at 1.39 ppm ($^3J_{HH}$ = 6.91 Hz, CH_3CH-function) and quartet of doublets at 4.26 ppm ($^3J_{HH}$ = 6.91 Hz, $^3J_{HH}$ = 5.20 Hz, CH_3CHOH-function) were monitored. Relation of the integral of the CH_3CHOH-function to the integral of the CH_3CHOR-function of the polymer/oligomer leftover (≈5.17 ppm) revealed nearly complete transformation of **1a** to **2**, since a yield of 98% (**2**) was calculated, and showed excellent catalyst abilities of the potassium fluoride (Table 1, entry 1). Importantly, no addition of extra solvents was necessary to perform the degradation, which is beneficial with respect to the Green Chemistry Principles.[78] Interestingly, half of the catalyst loading exhibited the generation of **2** in an excellent yield (Table 1, entry 2). Moreover, the reaction was extended to 60 min at 180 °C to investigate the stability of product **2** under reaction conditions, but no decomposition reactions were noticed (Table 1, entry 4). From this starting point the loading of KF was studied (Table 1, entries 5–7). Decreasing the KF load toward 1.0 mol% the degradation product **2** was still formed in excellent yield (98%). Noteworthy, from the presented catalyst activity a turnover frequency (TOF) of ≈588 h^{-1} was calculated, which is among the highest TOFs reported so far. In case of a further decrease to 0.5 mol% KF a yield of 68% of **2** after cooling to room temperature was noticed (Table 1, entry 6) (TOF ≈ 816 h^{-1}).[81] For instance, with our recently published DMAP system lower TOFs have been obtained (≈178 h^{-1}).[57] Notable, in the absence of KF no formation of **2** was detected by NMR, therefore KF is essential for the degradation process (Table 1, entry 7). Following, the effect of the quantity of methanol on the degradation was studied (Table 1, entries 8–10). Noteworthy, in case of lower methanol loadings (1.0–11.6 equiv.) tetrahydrofuran was used as (co)solvent. Still excellent activity (>99% yield) was observed in the presence of 11.6 equiv. MeOH, while a decrease to 5.8 equiv. resulted in a reduced yield of 23%. In addition, the

Table 2. Potassium fluoride-catalyzed degradation of PLA goods.



Poly(lactide) (**1a-l**)

2



Entry[a)]	Product	M_n [g mol^{-1}][b)]	M_w [g mol^{-1}][b)]	$Ð$[b)]	Yield of **2** [wt%][c)]	Yield of **2** [%][d)]
1	Transparent cup (**1a**)	57 500	240 800	4.2	134	92
2	Transparent disposable food box (**1b**)	43 600	236 000	5.4	104	72
3	Transparent Sushi box cover (**1c**)	54 700	212 700	3.9	87	60
4	Transparent plastic sheet (**1d**)	150 400	262 000	1.7	83	57
5	Transparent bottle (**1e**)	99 100	254 900	2.6	141	97
6	Drinking straw with green strips (**1f**)	112 100	239 900	2.1	70	48
7	Disposable fork with talcum powder (**1g**)	59 000	124 100	2.1	62	43
8	Lid for espresso mugs (contains ≈20–30% talcum powder) (**1h**)	56 100	177 500	3.2	78	54
9	Black lid for coffee mugs (**1i**)	75 400	241 100	3.2	72	50
10[e)]	Black lid for coffee mugs (used) (**1i**)	–	–	–	92	64
11	Sushi box (black base) (**1j**)	80 300	148 400	1.8	84	58
12	Pink ice cream spoon (**1k**)	57 600	133 000	2.3	105	72
13[f)]	Yellow ice cream spoon (used) (**1k**)	–	–	–	122	92
14	Coffee mug (paper with PLA coating) (**1l**)	86 400	221 000	2.6	4	3

[a)] Conditions: **1a–1l** (583.2 mg, 8.1 mmol with respect to the monomer unit), KF (11.8 mg, 2.5 mol%, 0.202 mmol with respect to the monomer unit of **1**), MeOH (6.0 g, 186.3 mmol, 23.1 equiv. with respect to monomer unit of **1**), temperature: 180 °C (microwave heating), time: 20 min; [b)] M_n, M_w, and $Ð$ were obtained from GPC measurements; [c)] The mass of **2** was linked to the mass of the initial PLA good. Yield wt% = $(m(\mathbf{2})/m(\mathbf{1})) \times 100$; [d)] The amount of substance of **2** was linked to the amount of substance of the initial PLA good (presumption: PLA good contains 100% of PLA. Yield % = $(n(\mathbf{2})/n(\mathbf{1})) \times 100$; [e)] Used with coffee, milk, and sugar. The PLA product was not cleaned before degradation; [f)] Contaminations: coffee, sugar, and milk. The PLA good was dried before degradation, but not purified.

impact of the temperature was studied (Table 1, entries 11–13). A yield of 98% for **2** was realized at a decreased temperature of 140 °C, while after 10 min at 120 °C a precipitation of **1** after cooling to room temperature was noted. Finally, a test of a range of different alkali-metal-halides was performed (Table 1, entries 14–20). Moderate-to-good yields (49–64%) were realized with 5 mol% of lithium chloride, sodium iodide, and potassium iodide. Afterward, the degradation of PLA was performed on an 8.1 mmol scale under optimized conditions (2.5 mol% KF, 23.1 equiv. methanol, 180 °C, 20 min, MW). In this regard, product **2** was obtained in an excellent yield of 93% as monitored by ^{1}H NMR (Table 1, entry 21).

Moreover, methyl lactate was isolated after performing the reaction for 20 min at 180 °C. In more detail, the mixture was transferred to distillation apparatus and **2** and methanol were distilled off from the catalyst under reduced pressure, to circumvent side/back processes (polymerization). Subsequently, the mixture of **2** (b.p. ≈ 144 °C) and methanol (b.p. ≈ 65 °C) was separated by distillation. **2** was isolated in 134 wt% (based on the weight of **1a**) or 92% isolated yield (presumption that **1a** contains 100% PLA) (**Table 2**, entry 1).

Noteworthy, the collected methanol (19.7 equiv., 89%) can be reused/recycled for next degradation. In addition, we investigated the reuse of the KF (**Figure 1**). In this regard, the reaction conditions applied were in accordance to the experiment in Table 1, entry 21. After 20 min (180 °C) the reaction was cooled to room temperature and a sample was subjected to ^{1}H NMR. From the reaction mixture methanol and methyl lactate were removed in vacuum. The catalyst containing residue in the flask was transferred with the aid of methanol to a vial

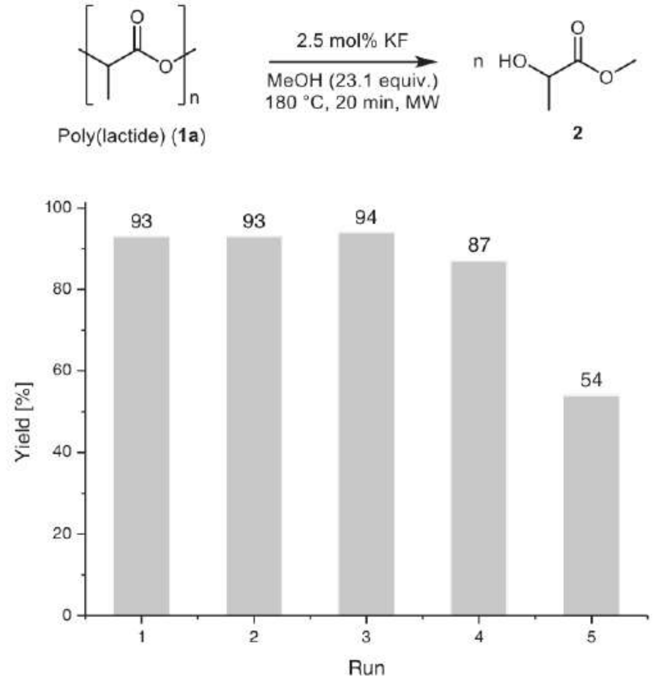


Figure 1. Degradation of PLA: catalyst recycling experiments [Conditions: **1a** (583.2 mg, 8.1 mmol with respect to the monomer unit), KF (first run: 11.8 mg, 2.5 mol%, 0.202 mmol with respect to the monomer unit of **1a**), MeOH (6.00 g, 187.2 mmol, 23.1 equiv. with respect to the monomer unit of **1a**), temperature: 180 °C (microwave heating), time: 20 min. Second run catalyst leftover from first run; third run catalyst leftover from second run; fourth run catalyst leftover from third run; fifth run catalyst leftover from fourth run; the yield was determined by ^{1}H NMR.

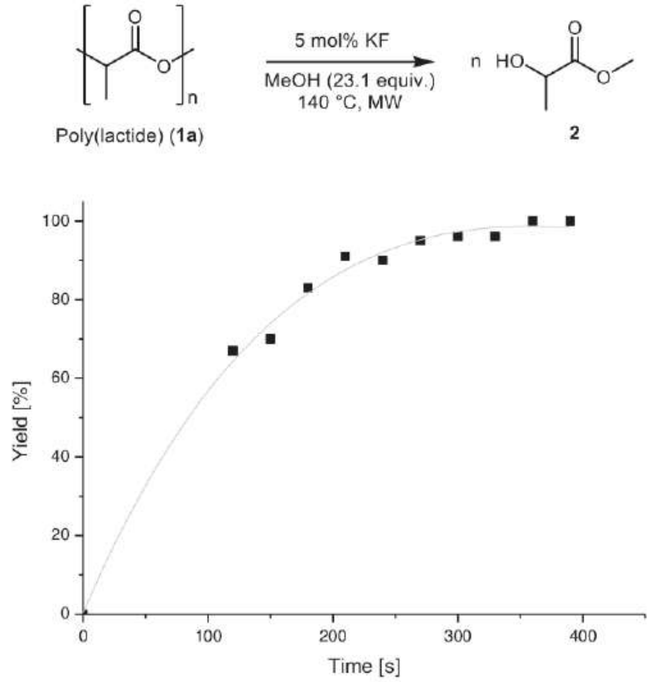
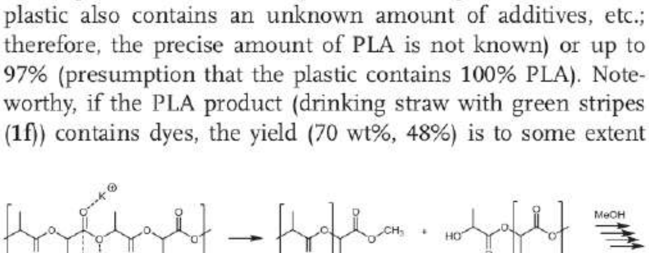


Figure 2. Degradation of PLA: time–yield plot [Conditions: **1a** (583.2 mg, 8.1 mmol with respect to the monomer unit), KF (5 mol%, 0.404 mmol with respect to the monomer unit of **1a**), MeOH (6.00 g, 187.2 mmol, 23.1 equiv. with respect to the monomer unit of **1a**), temperature: 140 °C (microwave heating); the yield was determined by ^{1}H NMR.

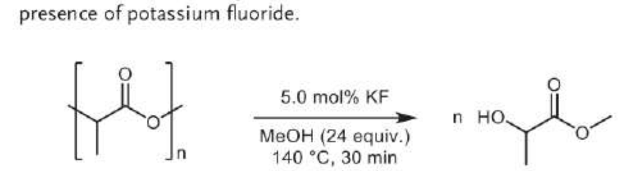
containing a new portion of end-of-life PLA. Afterward, the degradation was carried out at a temperature of 180 °C for 20 min. Until the third run no change in the reaction outcome was monitored, while afterward the yield of **2** drops to 54% in the fifth run. Nevertheless, a reuse/recycling of potassium fluoride is possible, which is in contrast to our earlier reported DMAP system.[58] The distilled-off mixture of methanol and methyl lactate from the catalyst recycling experiments were combined and after removal of methanol methyl lactate was isolated in a total yield of 78% yield. In addition, the time–yield plot relationship was recorded at 140 °C (**Figure 2**). The sample taken after 120 s was investigated by gel permeation chromatography (GPC) analysis revealing the disappearance of long chain polymers.

With respect to the underlying degradation mechanism we assume that the alkali metal halide can act as dual catalyst in accordance to ionic liquid catalysts applied in the methanolysis of polycarbonate (**Scheme 3**).[56,71–75] The potassium cation can function as Lewis acid and coordinates the oxygen of the carbonyl function and by doing so the carbonyl carbon is activated and methanol can attack (oxygen atom of the methanol) the group as nucleophile. The nucleophilicity of the methanol can be increased by the interaction of the fluoride anion with the proton of methanol via hydrogen bonding. Based on that, the PLA chain is dissected and results in the formation of smaller chains and by repeating the process as final product methyl lactate is formed.

Afterward, a selection of PLA products was directed to degradation (Table 2, entries 1–14). Besides the transparent PLA cup further transparent products such as a food box (**1b**), a cover of a Sushi box (**1c**), a PLA sheet (**1d**), and the body of a bottle (**1e**) were studied (Table 2, entries 2–5). Methyl lactate was isolated in yields of up to 141 wt% (the yield base on the weight of the plastic, which not only contains the polymer PLA. The plastic also contains an unknown amount of additives, etc.; therefore, the precise amount of PLA is not known) or up to 97% (presumption that the plastic contains 100% PLA). Noteworthy, if the PLA product (drinking straw with green stripes (**1f**)) contains dyes, the yield (70 wt%, 48%) is to some extent

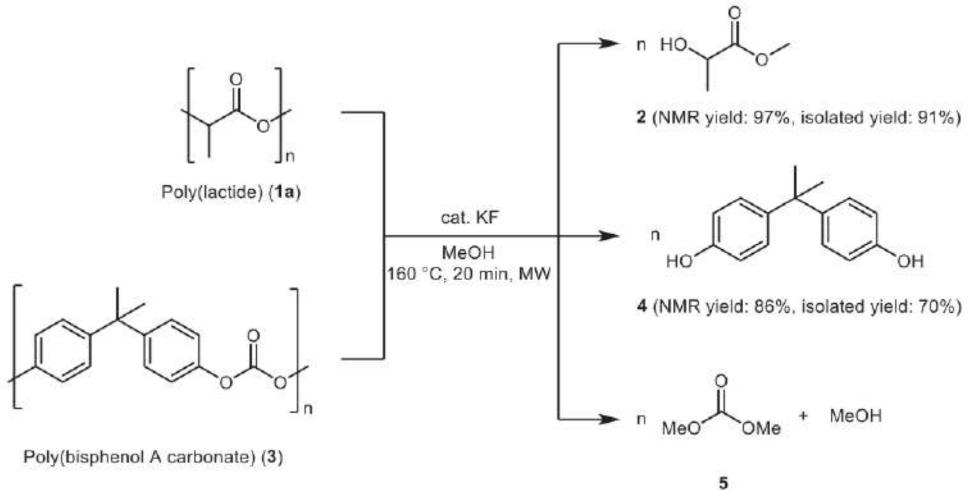


Scheme 3. Tentative degradation mechanism of end-of-life PLA in the presence of potassium fluoride.

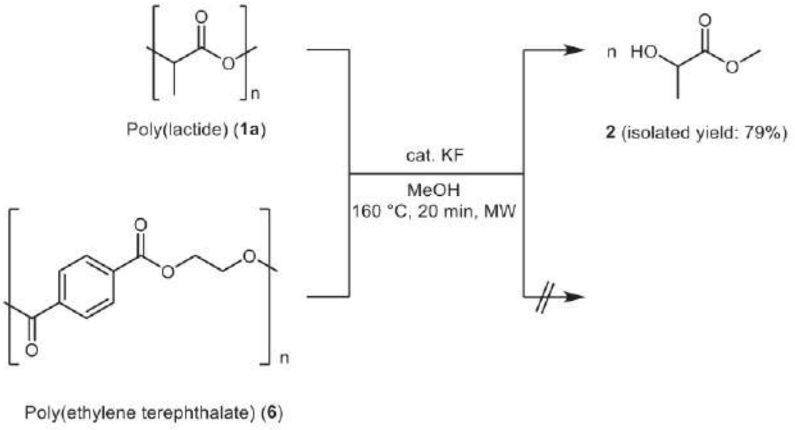


Scheme 4. Scale-up degradation of end-of-life PLA performed with conventional heating in an autoclave [Conditions: **1m** (102.7 mmol), MeOH (2.47 mol; 24.0 equiv. with respect to the monomer unit of **1m**, potassium fluoride (5.13 mmol, 5.0 mol% with respect to the monomer unit of **1a**), temperature: 140 °C (conventional heating), time: 60 min].

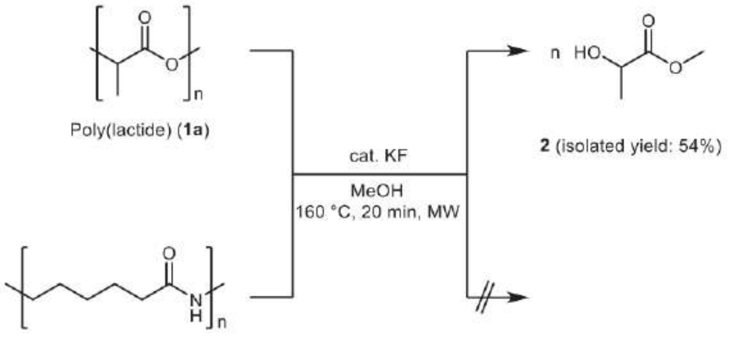
*a) Degradation of **1a** in the presence of poly(bisphenol A carbonate)*



*b) Degradation of **1a** in the presence of PET*



*c) Degradation of **1a** in the presence of Nylon 6*



Scheme 5. Degradation of end-of-life PLA in the presence of different end-of-life plastics [Conditions: **1a** (5.4 mmol), **3**, **6**, or **7** (2.7 mmol), MeOH (124.9 mmol; 23.1 equiv. with respect to the monomer unit of **1a** and 46.3 equiv. with respect to the monomer of **3**, **6**, or **7**), potassium fluoride (0.135 mmol, 2.5 mol% with respect to the monomer unit of **1a**, 5.0 mol% with respect to the repeating unit of **3**, **6**, or **7**), temperature: 160 °C (microwave heating), time: 20 min].

lower (Table 2, entry 6). Moreover, PLA goods containing additive talcum powder (≈20–30%) were tested (Table 2, entries 7–8). Good yields of 62–78 wt% or 43–54% were realized for a disposable fork (**1g**) and a lid for espresso mug (**1h**). Note, taking the amount of talcum powder into account the yields of methyl lactate are comparable to the transparent PLA products.

Next, black PLA products were studied (Table 2, entries 9–11). Yields of **2** in the range of 72–84 wt% or 50–58% were obtained. Remarkably, a used coffee mug lid (**1i**), which was contaminated with coffee/milk/sugar leftovers, even a higher yield of 92 wt% or 64% was noticed (Table 2, entry 10). An analogous observation was made for spoons 105 wt% or 72% versus 122 wt% or 92% (Table 2, entries 12–13). Finally, the degradation of a disposable coffee mug composed of paper and a PLA coating was studied (Table 2, entry 14). However, a low yield of **2** of 4 wt% or 3% was noticed, since the paper component is the main component in the coffee mug.

Besides, for plastic cups (**1a**) a scale-up reaction was carried out (**Scheme 4**). In more detail, the reaction was performed in accordance to the conditions stated in Table 1 entry 12 by charging an autoclave (160 mL) with 7.4 g of **1a**. The reaction was carried out at 140 °C (conventional heating) and the reaction time was extended to 30 min. Following the standard purification/isolation protocol 8.63 g of **2** was attained, which relates to a yield of 81%. Moreover, the optical rotation of the isolated **2** was measured to get information of the optical purity of the product. An enantiomeric excess of ≈93% (of (−)-methyl L-lactate) was obtained, which is in line with the starting polymer and revealed almost no racemization.

In addition, we studied the potassium fluoride catalyzed degradation of PLA (**1a**) accompanied by different end-of-life plastics containing carbonyl functionalities, which can be seen as a fraction of the waste streams. Recently, we have demonstrated the abilities of alkali metal halides as catalyst in the depolymerization of end-of-life poly(bisphenol A carbonate) (**3**).[76] Polycarbonate **3** was converted in the presence of methanol and potassium fluoride as catalyst to the building blocks bisphenol A and dimethyl carbonate, which can be reused as starting materials for fresh polycarbonate.[82,83] Since the reaction conditions are comparable, we investigated the combination of the degradation of a mixture of (solvent-assisted mixing) end-of-life poly(lactide) **1a** and the depolymerization of end-of-life poly(bisphenol A carbonate) **3** (**Scheme 5**). In more detail, to a mixture of **1a** (5.4 mmol) and **3** (2.7 mmol) was added methanol (124.9 mmol; 23.1 equivalents with respect to the monomer unit of **1a** and 46.3 equiv. with respect to the repeating unit of **3**) and catalytic amounts of potassium fluoride (0.135 mmol, 2.5 mol% with respect to the monomer unit of **1a**, 5.0 mol% with respect to the monomer unit of **3**). The mixture was stirred at 160 °C (microwave heating) for 20 min. After that, the mixture was analyzed by ^{1}H NMR revealing the formation of degradation products methyl lactate derived from PLA (NMR yield: 97%) and bisphenol A (NMR yield: 86%) and dimethyl carbonate[84] derived from polycarbonate **3**.[85,86] Besides, the degradation products can be easily separated by distillation. First, methyl lactate, dimethyl carbonate, and methanol were quickly distilled off from the catalyst and **4** under vacuum. The residue was recrystallized from chloroform to isolate **4** as colorless crystals in 70% yield. Subsequently, the mixture of **2**, **5**, and methanol was separated by distillation. Keeping the temperature below 100 °C **5** and methanol were collected, while **2** remains in the distillation flask and was isolated in 91% yield. In consequence, a side-by-side degradation of PLA and poly(bisphenol A carbonate) with the same catalyst is feasible. Moreover, poly(ethylene terephthalate) (PET) (**6**) or polyamide 6 (Nylon 6) (**7**) was added to the mixture of poly(lactide) (**1a**), methanol, and catalytic amounts of potassium fluoride (Scheme 5). In both experiments, the degradation of **1a** was achieved and **2** was isolated in 79% and 54%, respectively. Conversely, the PET and Nylon 6 were not depolymerized and were recovered from the reaction mixture.

In summary, we have installed an easy-to-adopt degradation method as an initial module for the chemical recycling of EoL poly(lactide) (PLA). In more detail, the degradation was performed with methanol as degradation reagent to obtain methyl lactate as product. Noteworthy, as catalyst simple alkali metal halides are required to realize excellent yields of **2** (>99%) within short reaction times (5 min) under microwave heating. Applying potassium fluoride as catalyst turnover frequencies up to ≈588 h^{-1} were obtained. The principle of operation of the concept was proven in the degradation of a variety of PLA goods.

Noteworthy, the produced methyl lactate can be the basis for the synthesis of lactide, the starting material for new PLA as reported in the literature. Finally, the degradation of PLA has the potential to add some value to the UN's Sustainable Development Goals (SDGs), e.g., SDG 13 (responsible use of natural resources), SDGs 2,3 (food security, land use), SDGs 9,11 (clean/green technologies, waste management/urban mining), and SDG 12 (supply chain, more efficient, and less consumptive technologies, recycling, waste streams). Upcoming investigations will focus on the advance of the degradation and the establishment of a continuous method of operation.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

catalysis, degradation, green chemistry, polymers, recycling

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[81] The TOF was calculated by using the H NMR yield: TOF = [mol product/(mol catalyst*h)]. The TOF was calculated using the yield of **2** after 10 min, because the determination of the TOF at a yield of 50% was not possible, due to technical limitations.

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Next, some literature known[253] catalysts with excellent activities in the ROP of L-lactide (**11**) were investigated. Therefore, a variety of bismuth(III) salts were studied for this purpose.[254] Under similar reaction conditions (1 mol%, 160 °C, 10 min, 67.5 eq. MeOH), bismuth(III) halogenides revealed the lowest activities, while bismuth(III) subsalicylate and $Bi(OTf)_3$ were the most active catalysts. Due to its high availability (anti-inflammatory drug) and low cost bismuth(III) subsalicylate was used for further investigations. Under specific reaction conditions (0.1 mol%, 180 °C, 1 min, 67.5 eq. MeOH), TOFs of up to 13800 h^{-1} were achieved. A collection of commercial PLA (**9**) goods was in turn converted to methyl lactate (**13**) in excellent yields. Interestingly, a PLA (**9**) sample obtained with bismuth(III) subsalicylate as polymerization catalyst could be degraded to some extent, when the crude PLA (**9**) (with catalyst residues) was submitted to depolymerization without prior purification. A catalyst recycling experiment showed constant performance for 1 mol% over 5 runs, while a starting catalyst loading of 0.25% resulted in significant decay.

Sustainable Chemistry

Application of Bismuth Catalysts for the Methanolysis of End-of-Life Poly(lactide)

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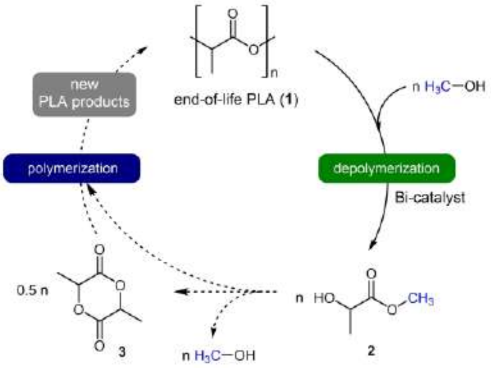
The chemical recycling of poly(lactide) (PLA) was investigated especially the depolymerization for generating useful monomers/polymer precursors. In more detail, applying catalytic amounts of bismuth compounds PLA was converted to methyl lactate using methanol as depolymerization reagent. An excellent performance was observed for bismuth subsalicylate with turnover frequencies of up to 13,800 h^{-1} using microwave heating. Moreover, the usefulness of the bismuth subsalicylate catalyst was demonstrated in the depolymerization of various PLA goods. Interestingly, the bismuth subsalicylate was easily recovered after the reaction and was sent again to depolymerization revealing recyclability of the catalyst.



Scheme 1. Chemical recycling concept for PLA applying bismuth catalysis.

Plastics obtained from renewable resources can be beneficial for a resource-efficient economy.[1,2] As one of this kind of plastics poly(lactide) (PLA, **1**, Scheme 1) containing plastics have been installed based on the valuable properties. PLA is available by a multi-step process with a production rate of 0.2 million tons per year.[3] The key molecule lactic acid is formed by biochemical processes starting from carbon dioxide, water and solar energy.[4] In a polycondensation step lactic acid is converted to PLA. Commonly low molecular weight PLA is generated, which can be degraded to lactide. The lactide is polymerized in a ring-opening polymerization to obtain high molecular weight PLA used for various applications. After finishing the application, the end-of-life PLA (End-of-Life = EoL) is sent to the waste management system. Importantly, the biodegradability of PLA has been discussed, but the dwell time in composting plants hamper a complete degradation.[5] Therefore, EoL-PLA can be incinerated to release the stored energy and generate CO_2 and water, which can be the initialization for new PLA (vide supra) and creates a cycle. Moreover, a certain carbon-neutrality is reasonable on a short time scale.[6,7] Nonetheless, a disadvantage is the requirement for new PLA, which call for land use and cultivation time, consequently a competition with other agricultural processes is obvious. In this regard, the application of recycling techniques for EoL-PLA can be an interesting alternative. In this context, the chemical recycling can create beneficial aspects to sustainability and resource-efficiency.[8] In detail, the chemical recycling is composed of two connected elements, the depolymerization and polymerization process. In the depolymerization the polymer is converted to the monomer or monomer precursors, which are subjected to the polymerization to (re)produce the polymer (Scheme 1). Numerous chemical recycling methods for EoL-PLA were described.[9,10,11] Particularly, methods based on alcoholysis of EoL-PLA has been investigated in detail. For instance, using methanol as depolymerization reagent EoL-PLA is depolymerized to methyl lactate (**2**) containing the former repeating unit of PLA. Subsequently, the methyl lactate can be used as precursor for new PLA. On the one hand, conversion to lactic acid can follow the industrially established route for PLA. Moreover, **2** can directly applied as monomer and polymerized to PLA.[12,13] In both cases methanol is generated, which can be reused in depolymerizations; therefore a recycling of methanol is feasible.

To realize a successful depolymerization via alcoholysis catalysis is necessary. Recently, some of us reported the application of catalytic amounts of tin(II) 2-ethylhexanoate (Sn$(Oct)_2$) in the methanolysis of PLA resulting in excellent catalyst activities of up to 39,600 h^{-1} (turnover frequency).[10] However, due to the toxicity of tin(II) 2-ethylhexanoate we studied herein the potential of bismuth compounds as less toxic substitutes, part of which have been reported as efficient catalysts in the synthesis of PLA.[14,15]

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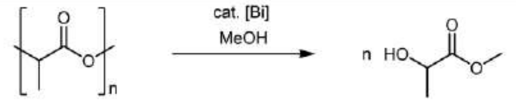
At first, for optimization of the depolymerization process end-of-life transparent PLA-cups (**1a**, $M_n = 57{,}500$ g/mol, $M_w = 240{,}800$ g/mol, $Đ = 4.2$, PLLA) were applied (Table 1). A portion of **1a** (2.78 mmol based on the repeating unit, idealized assumption: **1a** contains only PLA), methanol (67.5 equivalents based on the repeating unit of **1a**) and catalytic amounts of bismuth salts (1.0 mol% based on the repeating unit of **1a**) were placed in a vial suitable for microwave heating (MW). The mixture was reacted at 160 °C under stirring using microwave heating for 10 min, meanwhile the PLA completely dissolved. Afterwards an aliquot was taken from the mixture and was dissolved in $CDCl_3$ to determine the yield/conversion by ^1H NMR analysis. The generation of the depolymerization product **2** was validated by the presence of a singlet at $\delta = 3.78$ ppm, which corresponds to the methyl group of the ester function ($-C(=O)OCH_3$). Furthermore, a doublet at $\delta = 1.40$ ppm ($^3J_{HH} = 6.91$ Hz, CH_3CH-) and a pseudo quartet at $\delta = 4.27$ ppm ($^3J_{HH} = 6.91$ Hz) confirms the existence of **2**.[16] In this regard, for bismuth halides a moderate performance with a yield of 28% was noticed for $BiCl_3$, while using $BiBr_3$ and BiI_3 a decrease of activity was observed (Table 1, entries 2–5). Importantly, for BiF_3 no activity was detected, same was noticed in the absence of any bismuth salt (Table 1, entries 1–2). An excellent yield of >99% was achieved applying catalytic amounts of $Bi(OTf)_3$, while in case of $Bi(OAc)_3$ a moderate yield was obtained (Table 1, entries 6–7). Furthermore, bismuth subsalicylate was tested, revealing an excellent yield (Table 1, entry 8). For further studies bismuth subsalicylate was used, due to lower costs compared to $Bi(OTf)_3$.[17] Following, the influence of the catalyst loading was examined (Table 1, entries 10–12). Decreasing the loading revealed a yield of 86% after 10 min, which agrees to a turnover frequency (TOF) of 5160 h^{-1}. Changing the temperature to 120 °C resulted in a decrease of product yield to 48% (Table 1, entry 14). On the other hand, an increase to 180 °C showed an excellent TOF of 13500 h^{-1} (Table 1, entry 15). Noteworthy, the bismuth subsalicylate catalyst outperforms our earlier reported systems, e.g. DMAP (~178 h^{-1}) and KF (~816 h^{-1}), only the $Sn(Oct)_2$ revealed a higher TOF of 39600 h^{-1}.[10j–l]

Afterwards, the bismuth subsalicylate was studied in the depolymerization of different PLA-products (Table 2, entries 1–14). In all cases excellent performance with yields >99% was detected, demonstrating the robustness of the catalyst. The PLA **1m** was synthesized using bismuth subsalicylate (0.05 mol%) as catalyst (Table 2, entry 13).[14c] Noteworthy, the catalyst embedded in the polymer was not deactivated. Performing the depolymerization without an additional portion of bismuth subsalicylate revealed a yield of 36% after 10 min. After cooling the reaction mixture of the depolymerization applying bismuth subsalicylate to ambient temperature a precipitation of the catalyst was noticed. Therefore, we investigated the reuse/recycling of the bismuth subsalicylate catalyst (Scheme 2). The reactions were performed in accordance with the conditions stated in Table 1, entry 8. After 10 min at 160 °C the catalyst was filtered off at room temperature. A new quantity of EoL-PLA and methanol was added for the next depolymerization. Interestingly, in all cases excellent performance was detected. From the combined mixtures of methanol and **2**, methanol was distilled-off. Product **2** was isolated in an overall yield of 73%. Conversely, using 0.25 mol% catalyst

Table 1. Depolymerization of **1a** applying bismuth catalysis – optimization of depolymerization reaction.



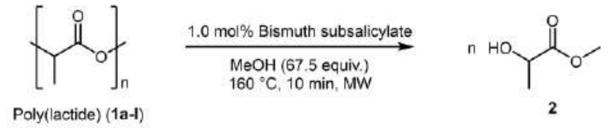
Poly(lactide) (**1a**)

2

Entry	Catalyst	Catalyst loading [mol%]	MeOH [equiv.]	T [°C]	t [min]	Yield 2 [%][b]	TOF [h^{-1}][c]
1	–	–	67.5	160	10	<1	<1
2	BiF_3	1.0	67.5	160	10	<1	<1
3	$BiCl_3$	1.0	67.5	160	10	28	168
4	$BiBr_3$	1.0	67.5	160	10	23	138
5	BiI_3	1.0	67.5	160	10	16	96
6	$Bi(OTf)_3$	1.0	67.5	160	10	>99	600
7	$Bi(OAc)_3$	1.0	67.5	160	10	27	162
8	Bismuth subsalicylate	1.0	67.5	160	10	>99	600
9	Bi_2O_3	1.0	67.5	160	10	<1	<1
10	Bismuth citrate	1.0	67.5	160	10	<1	<1
10	Bismuth subsalicylate	0.5	67.5	160	10	>99	1200
11	Bismuth subsalicylate	0.25	67.5	160	10	>99	2400
12	Bismuth subsalicylate	0.1	67.5	160	10	86	5160
13	Bismuth subsalicylate	1.0	50.0	160	10	>99	600
14	Bismuth subsalicylate	1.0	67.5	120	10	48	288
15	Bismuth subsalicylate	0.1	67.5	180	1	23	13800
15[d]	Bismuth subsalicylate	1.0	67.5	~65	1440	42	2

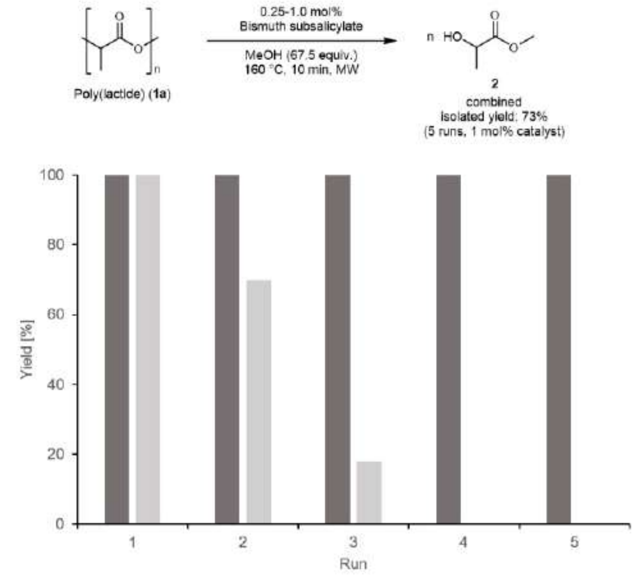
[a] Reaction conditions: **1a** (transparent PLA cup), 2.78 mmol with respect to the repeating unit), catalyst (0–1.0 mol%, 0–0.0278 mmol with respect to the repeating unit of **1a**), MeOH (50.0-67.5 equiv. with respect to the repeating unit of **1a**), temperature: 120–180 °C (microwave heating), time: 1–10 min. [b] The yield of **2** bases on ^1H NMR spectroscopy. [c] The TOF was calculated: (mole product/mole catalyst)*h^{-1}. The TOF was calculated by the yield of **2** after the designated time. [d] The reaction was performed by conventional heating with an oil bath.

Table 2. Bismuth subsalicylate catalyzed depolymerization of EoL-PLA products.



Entry[a]	Product	Yield of 2 [%][b]
1	transparent cup (1 oz) (**1 a**)	>99
2	transparent cup (250 mL) (**1 b**)	>99
3	transparent disposable food box (**1 c**)	>99
4	transparent sushi box cover (**1 d**)	>99
5	transparent bottle (**1 e**)	>99
6	drinking straw with green strips (**1 f**)	>99
7	disposable fork with talcum powder (**1 g**)	>99
8	lid for espresso mugs (contains ~20–30 % talcum powder) (**1 h**)	>99
9	lid for coffee mugs (**1 i**)	>99
10	black lid for coffee mugs (**1 j**)	>99
11	sushi box (black base) (**1 k**)	>99
12	blue ice cream spoon (**1 l**)	>99
13[c]	PLA (**1 m**)	36
14	PLA (**1 m**)	>99

[a] Reaction conditions: **1 a–1 l** (200.0 mg, 2.78 mmol with respect to the repeating unit), bismuth subsalicylate (10.1 mg, 1.0 mol%, 0.0278 mmol with respect to the repeating unit of 1), MeOH (6.0 g, 187.3 mmol, 67.5 equiv. with respect to the repeating unit of 1), temperature: 160 °C (MW), time: 10 min. [b] The yield of **2** bases on ^{1}H NMR spectroscopy. The amount of substance of **2** was related to the amount of substance of PLA. [c] Without additional catalyst. The polymer contains 0.05 mol% bismuth subsalicylate.



Scheme 2. Depolymerization of EoL-PLA – catalyst recycling [Reaction conditions: **1 a** (200.0 mg, 2.78 mmol with respect to the repeating unit), bismuth subsalicylate (1st run: 10.1 mg, 0.25 mol% (light grey) or 1.0 mol% (dark grey), 0.00695 mmol or 0.0278 mmol with respect to the repeating unit of **1 a**), MeOH (6.00 g, 187.2 mmol, 67.5 equiv. with respect to the monomer unit of **1 a**), temperature: 160 °C (MW), time: 10 min. 2nd run catalyst leftover from 1st run; 3rd run catalyst leftover from 2nd run; 4th run catalyst leftover from 3rd run; 5th run catalyst leftover from 4th run; the yield was determined by ^{1}H NMR].

loading in the catalyst recycling experiment a significant decrease was noticed after the third run. Moreover, the ratio of enantiomers of **2** was investigated by reaction of **2** with (*S*)-binol chlorophosphite.[18] A ratio of 84:16 was determined by ^{1}H NMR, revealing some racemization during depolymerization.

In summary, an easy-to-adopt depolymerization protocol for the chemical recycling of EoL-poly(lactide) was established. The depolymerization was carried out with methanol as depolymerization reagent to generate methyl lactate as beneficial chemical, which can be used as starting compound for the synthesis of new PLA. Notable, as best catalyst bismuth subsalicylate was detected attaining excellent yields of **2** (>99 %) under microwave heating. Noteworthy, turnover frequencies of ~13800 h^{-1} were realized with bismuth subsalicylate. This result is of particular interest, because this bismuth compound is a non-toxic inexpensive commercial drug and has quite recently been found to be the most effective polymerization catalyst among the commercial Bi(III) salts.[14c] The principle of operation was verified in the depolymerization of different PLA products.

Supporting Information Summary

The experimental details including the depolymerization reactions and product characterization can be found in the supporting information.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: catalysis · depolymerization · green chemistry · polymers · recycling

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[17] Cost based on Merck/Sigma Aldrich BiF$_3$: ~340 €/mol, BiCl$_3$: ~615 €/mol, BiBr$_3$: ~1508 €/mol, BiI$_3$: ~3986 €/mol, Bi(OTf)$_3$: ~4619 €/mol, Bi(OAc)$_3$: ~1556 €/mol, bismuth subsalicylate: ~98 €/mol, Bi$_2$O$_3$: ~904 €/mol, bismuth citrate: ~112 €/mol. For comparison: Sn(Oct)$_2$: ~76 €/mol.

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Based on the increased activity of Bi(III) compounds we wondered if the industrially relevant catalyst $Sn(Oct)_2$ is active in methanolysis.[255] In fact, excellent activities (TOFs up to 39,600 h^{-1}) were revealed. Due to the excellent activity of the catalyst the reaction could even be carried out with 0.05 mol%. Notably, some conversion was still realized at 100 °C. Additionally, a set of contaminated goods was degraded successfully and no correlation of the yield to the molar mass of the samples could be observed. The reaction was furthermore scaled up to 51 g of PLA (**9**) waste in an autoclave with conventional heating to realize an isolated yield of 58%. In accordance to our prior observations and that of Carné Sánchez *et al*.[132] PET (**14**) could not be degraded with PLA (**9**) in neat MeOH. However, under optimized conditions for PLA (**9**), also PBAC (**2**) was converted in excellent yields.

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Tin(II) 2-ethylhexanoate catalysed methanolysis of end-of-life poly(lactide)†

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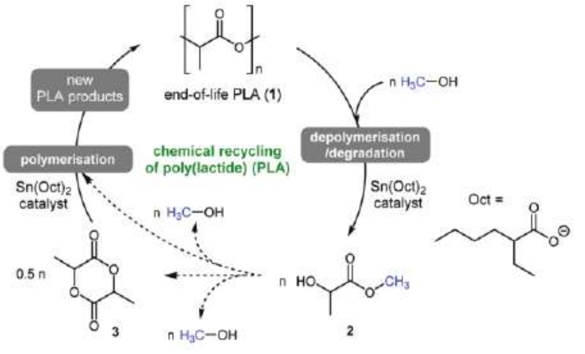
In recent times, plastics derived from renewable resources have received significant consideration as alternatives to plastics based on fossil resources. Nevertheless, some challenging issues, for instance the embedding of these plastics in a future circular economy, are currently under investigation. In this regard, recycling by applying chemical methodologies to reconvert the monomers would be a useful process. The selective depolymerisation/degradation of end-of-life poly(lactide) (EoL-PLA) plastics *via* methanolysis was explored in the presence of the industrially relevant catalyst tin(II) 2-ethylhexanoate ($Sn(Oct)_2$). EoL-PLAs used in daily life were successfully degraded to methyl lactate utilising microwave heating. Outstanding turnover frequencies of up to 39 600 h^{-1} were observed.

In recent times, plastics obtained from renewable resources (*e.g.*, biopolymers, bio-based polymers) have been customized and used as alternatives to solve the diverse negatives of fossil resources-based plastics.[1,2] For instance poly(lactide) plastics (PLA, **1**, Scheme 1) have manifold applications. PLA is factory-made on a ~0.2 mt per year scale.[3] PLA is available through the biological conversion of carbon dioxide, water and energy to its building block, lactic acid.[4] Lactic acid can be utilised as the monomer in a polycondensation reaction to manufacture **1**. As an alternative, lactic acid can be converted to lactide (**3**), which give access to **1** by ring-opening polymerisation (Scheme 1). After completing its operational purpose, PLA is denoted as end-of-life PLA (EoL-PLA). A main benefit of EoL-PLA is its bio-degradability ability.[5] Nonetheless, the degradation of PLA in composting plants cannot commonly be achieved during the dwell time. Consequently, EoL-PLA is reconverted to CO_2, H_2O and energy by incineration. Significantly, the incineration products can be reprocessed by nature to make fresh portions of **2**, for that reason a circular process and carbon-neutrality is attainable.[6,7] On the contrary, accessing new PLA needs cultivation and therefore cultivation time and land use, which uses land that could be used for the creation of foodstuffs or energy. As a result, a circular economy, in which the intrinsic entity of the PLA plastics is cycled, should be favoured and minimises the input acreage. From this perspective the chemical recycling of plastics using depolymerisation and polymerisation reactions can be beneficial.[8] Depolymerisation converts the polymer to the monomer, while the polymerisation produces the polymer from the monomer (Scheme 1). Indeed, several recycling approaches for EoL-PLA have been demonstrated.[9–11] Specifically, the reaction of EoL-PLA with alcohols has drawn attention. For instance, reacting EoL-PLA with methanol produced methyl lactate (**2**) as the carrier of the monomeric unit of PLA. Chemical **2** can then be converted to lactic acid and subsequently transformed to **3** and **1** (an industrially established route) or directly polymerised to **1** maybe *via* **3** (a less investigated route).[12,13] In both reactions methanol is released, which can be applied in new depolymerisations. Notably, to



Scheme 1 Application of $Sn(Oct)_2$ catalyst in the chemical recycling of EoL-PLA.

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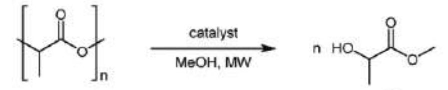
carry out the depolymerisation successfully a catalyst is essential.

Recently, the catalytic potential of 4-dimethylaminopyridine (DMAP) and alkali metal halides (*e.g.* KF) has been examined in the methanolytic depolymerisation of EoL-PLA to attain methyl lactate in turnover frequencies of up to ~816 h^{-1}.[14,15] Regarding the initial studies, attention was drawn to the utilisation of the industrially relevant tin(II) 2-ethylhexanoate [Sn(Oct)$_2$] as a potential catalyst for the depolymerisation. Importantly, Sn(Oct)$_2$ has been proven as a catalyst for the synthesis of PLA.[16] Accordingly, for both sub-processes of PLA-recycling the same catalyst can be employed.

At first, to optimise the depolymerisation reaction conditions, a transparent PLA-cup **1a** (M_n = 57 500 g mol^{-1}, M_w = 240 800 g mol^{-1}, $Đ$ = 4.2, PLLA) was applied as a model (Table 1). Compound **1a** (8.1 mmol with respect to the monomeric unit), an excess of MeOH (23.1 equiv. with respect to the monomeric unit of **1a**) and a catalytic amount of Sn(Oct)$_2$ (0.25 mol% with respect to the monomeric unit of **1a**) were combined in a vial suitable for microwave heating (MW). Due to the excess MeOH no extra solvent was added.[17] The mixture was stirred and heated in a microwave reactor at 160 °C for 20 min (Table 1, entry 1). Then the mixture was cooled to ambient temperature attaining a clear solution, which indicates the absence of PLA. Moreover, a part of the mixture was dissolved in $CDCl_3$ for ^1H NMR analysis. The analysis revealed the existence of a doublet at 1.40 ppm (J = 6.91 Hz, CH_3CH–), a doublet at 2.83 ppm (J = 5.20 Hz, CHO*H*–), a single signal at 3.77 ppm (OCH_3), and a double quartet at 4.27 ppm (J = 6.91 Hz, J = 5.20 Hz, CH_3CH–), which is evidence of the formation of **2**.[18] Importantly, no hint of leftover PLA or PLA-oligomers was observed (5.05–5.20 and 4.27–4.32 ppm), therefore complete conversion of PLA was assumed. Remarkably, Sn(Oct)$_2$ exhibits excellent catalytic performance at a lower catalyst loading and lower temperature compared to established systems DMAP (1.0 mol%, 180 °C, 10 min, yield: 4%), and KF (0.5 mol%, 180 °C, 10 min, yield: 68%).[14,15] Moreover, the obtained activity outperforms the Sn(Oct)$_2$-catalysed ethanolysis of PLA as reported by Petrus *et al.* (1.0 mol%, 200 °C, 60 min, yield ethyl lactate: 87%)[10a] Additionally, the reaction period was shortened, and still showed excellent yields of **2** within 5 min (Table 1, entries 2 and 3). Next, the loading of the catalyst was explored showing a reasonable yield of 31% with a loading of 0.05 mol% Sn(Oct)$_2$ (Table 1, entries 4–8). In the absence of the catalyst, **2** was not detected (Table 1, entry 8). In addition, the influence of the reaction temperature was investigated revealing a decreased yield at 100 °C (Table 1, entries 9 and 10). Moreover, the equivalents of MeOH with respect to the monomeric unit of **1a** were studied (Table 1, entries 13 and 14). Still, excellent yields were detected for 19.3 and 15.4 equiv. of MeOH, but at lower loadings no product formation was observed, perhaps also caused by the addition of THF as the solvent (Table 1, entries 13 and 14). Note, when increasing the temperature to 180 °C and reducing the amount of methanol to 15.4 equiv., excellent turnover frequencies of up to 39 600 h^{-1} were calculated, which are among the highest reported so far. For instance, in the presence of catalytic amounts of DMAP (~178 h^{-1}) or KF (~816 h^{-1}) lower TOFs were observed (Table 1, entry 16). With the optimised conditions in hand (0.25 mol% Sn(Oct)$_2$, 23.1 equiv. methanol, 160 °C, 10 min, MW = microwave heating) attention was directed to obtaining a set of EoL-PLA plastics (Table 2).

Table 1 Sn(Oct)$_2$-catalysed depolymerisation of **1a**



Poly(lactide) (**1a**)

2

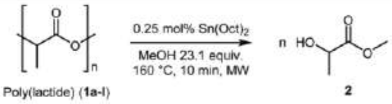
Entry[a]	Catalyst loading [mol%]	MeOH [equiv.]	T [°C]	t [min]	Yield **2**[b] [%]	TOF[c] [h^{-1}]
1	0.25	23.1	160	20	>99	1200
2	0.25	23.1	160	10	>99	2400
3	0.25	23.1	160	5	>99	4800
4	0.10	23.1	160	10	>99	6000
5	0.10	23.1	160	5	48	5760
6	0.10	23.1	160	2	31	9300
7	0.05	23.1	160	10	31	3720
8	—	23.1	160	10	<1	—
9	0.25	23.1	140	10	89	2136
10	0.25	23.1	100	10	10	240
11	0.25	19.3	160	10	>99	1200
12	0.25	15.4	160	10	>99	1200
13[d]	0.25	11.6	160	10	<1	—
14[e]	0.25	5.8	160	10	<1	—
15	0.1	15.4	180	1	64	38 400
16	0.05	15.4	180	1	33	39 600

[a] Reaction conditions: **1a** (obtained from testing a transparent cup, 8.1 mmol with respect to the repeating unit), Sn(Oct)$_2$ (0–0.25 mol%, 0–0.0203 mmol with respect to the repeating unit of **1a**), MeOH (5.8–23.1 equiv. with respect to the repeating unit of **1a**), MW: 100–160 °C, 1–20 min. [b] The yield was determined by ^1H NMR. A clear solution was observed. It is presumed that the PLA-product is composed of 100% PLA. [c] The TOF was calculated: (mole product/mole catalyst) × h^{-1}. The TOF was calculated using the yield of **2** after the designated time, because the determination of the TOF at a yield of 50% was not possible, due to the technical limits. [d] Addition of THF (3.0 g). [e] Addition of THF (4.5 g).

The PLA-cup **1a** was transformed with an excellent yield to **2** as detected by ^1H NMR spectroscopy. Afterwards, **2** was isolated from the crude mixture: the mixture was shifted to a flask; the flask was attached to a distillation set-up; the low-boiling point chemicals, MeOH and **2**, were rapidly distilled-off to circumvent the backward reaction (polymerisation); the collected mixture of MeOH and **2** was carefully separated by evaporation in a vacuum.

Methyl lactate was isolated in 74 wt% (regarding the initial mass of **1a**) or 51% isolated yield (presuming that **1a** contains 100% PLA) (Table 2, entry 1). For example further transparent PLA products such as a food box (**1b**), a cover of a Sushi-box (**1c**), a sheet (**1d**) and a bottle (**1e**) were studied (Table 2, entries 2–5). Good yields of up to 88%, or up to 128 wt%, were realised. Lower yields of 57–67% or 82–97 wt% are obtained for non-transparent EoL-PLAs, *e.g.*, an espresso mug lid (**1g**) and a fork (**1h**), which contain talcum powder (*ca.* 20–30%) (Table 2, entries 6 and 7). In addition, PLA goods containing

Table 2 $Sn(Oct)_2$-catalysed depolymerisation of PLA-products

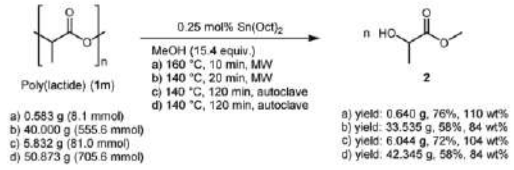


Entry[a]	Product	Yield **2**[b] [wt%]	Yield **2**[c] [%]
1	Transparent cup (**1a**) (M_n = ~57 500 g mol^{-1}, M_w = ~240 800 g mol^{-1}, D = 4.2)	51	74
2	Transparent food box (**1b**) (M_n = ~43 600 g mol^{-1}, M_w = ~236 000 g mol^{-1}, D = 5.4)	78	113
3	Transparent cover of a Sushi box (**1c**) (M_n = ~54 700 g mol^{-1}, M_w = ~212 700 g mol^{-1}, D = 3.9)	88	128
4	Transparent plastic sheet (**1d**) (M_n = ~150 400 g mol^{-1}, M_w = ~262 000 g mol^{-1}, D = 1.7)	69	99
5	Transparent bottle (**1e**) (M_n = ~99 100 g mol^{-1}, M_w = ~254 900 g mol^{-1}, D = 2.6)	56	81
6	Straw (green strips) (**1f**) (M_n = ~112 100 g mol^{-1}, M_w = ~239 900 g mol^{-1}, D = 2.1)	81	117
7	Fork with talcum powder (**1g**) (M_n = ~59 000 g mol^{-1}, M_w = ~124 100 g mol^{-1}, D = 2.1)	57	82
8	Espresso mug lid (~20–30% talcum powder) (**1h**) (M_n = ~56 100 g mol^{-1}, M_w = ~177 500 g mol^{-1}, D = 3.2)	67	97
9	Coffee mug lid (black) (**1i**) (M_n = ~75 400 g mol^{-1}, M_w = ~241 100 g mol^{-1}, D = 3.2)	58	83
10[d]	Used coffee mug lid (black) (**1i**)	54	78
11	Base of a Sushi box (black) (**1j**) (M_n = ~80 300 g mol^{-1}, M_w = ~148 400 g mol^{-1}, D = 1.8)	85	123
12	Spoon (pink) (**1k**) (M_n = ~57 600 g mol^{-1}, M_w = ~133 000 g mol^{-1}, D = 2.3)	75	109
13[d]	Used spoon (yellow) (**1k**)	60	86
14	PLA coated coffee mug (**1l**) (M_n = ~86 400 g mol^{-1}, M_w = ~221 000 g mol^{-1}, D = 2.6)	40	58

[a] Reaction conditions: **1** (583.2 mg, 8.1 mmol with respect to the monomeric unit), $Sn(Oct)_2$ (12.5 mg, 0.25 mol%, 0.031 mmol with respect to the repeating unit of **1**), MeOH (6.0 g, 187.2 mmol, 23.1 equiv. with respect to the repeating unit of **1**), MW: 160 °C, 10 min. [b] The mass of **2** was connected to the mass of the initial PLA. Yield wt% = (m(**2**)/m(**1**)) × 100. [c] The amount of **2** was connected to the amount of initial PLA, insinuating that the product (cup, box *etc.*) contains 100% PLA. Yield % = (n(**2**)/n(**1**)) × 100. [d] Contamination: coffee, sugar, milk. The good was not cleaned.

dyes were tested, displaying a yield of 58–85% or 83–123 wt% (Table 2, entries 9 and 11). Coffee mug lids (**1f**) and colored spoons were also tested after use (contamination: coffee/sugar/milk leftovers). Surprisingly, similar yields were noticed, therefore the direct recycling of EoL-PLA without pretreatment (*e.g.*, cleaning, drying) is feasible (Table 2, entries 10 and 13). Lastly, a composite of paper and PLA was tested (Table 2, entry 14). To a paper coffee mug, coated with a PLA-layer, chloroform was added, and the PLA was soluble and the paper was not. After filtration and removal of the solvent, the PLA was subjected to depolymerisation and methyl lactate was isolated in 67% yield.

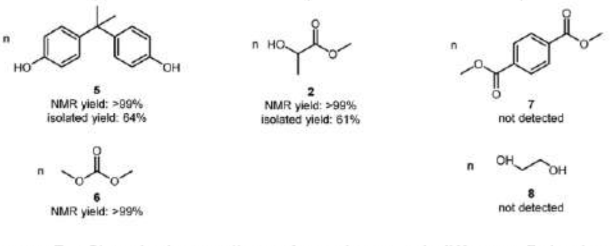
Furthermore, for used plastic cups a scale-up reaction was performed (Scheme 2). The first attempt was carried out in an autoclave (160 mL or 1000 mL), following the conditions stated in Table 1: entry 9, with 5.832 g (approach c: ~5 exemplars) or 50.873 g (approach **d**: ~44 exemplars) of PLA cups. The reaction time was extended to 2 h. Following the standard purification/isolation procedure 6.0 g (approach c) and 42.345 g (approach d) of **2** were obtained, which corresponds to a yield of 72% and 58%, respectively. Comparing this result with the result of the microwave approach (76%), a similar yield was realised. A further increase of the scale was performed in a microwave reactor applying eight microwave tubes (8 × 100 mL) in parallel (Scheme 2). In total 40 g of PLA from cups (~33 exemplars) was depolymerised yielding 33.5 g of **2** (yield: 58%) after 20 min at 140 °C.



Scheme 2 Chemical recycling of PLA cups – scale-up experiments.

Additionally we studied the performance of $Sn(Oct)_2$ when using a mixture of different EoL-plastics (Scheme 3). The one-pot and contemporaneous depolymerisation of different types of polymers may allow for economic recycling processes.[19] In this regard, a mixture of EoL-plastics containing ester functionalities was studied (Scheme 3).

We attempted to depolymerise a mixture of a transparent plastic cup (**1a**) containing poly(lactide), poly(bisphenol A carbonate) (**3**) isolated from a DVD, and a transparent bottle



Scheme 3 Chemical recycling of a mixture of different EoL-plastics and separation.

made of poly(ethylene terephthalate) (**4**). In the presence of 1.5 mol% $Sn(Oct)_2$ after 20 min at 160 °C, **1a** and **3** were successfully converted, while **4** was untouched but was easily separated from the reaction mixture by filtration.

In the case of **1a** the desired methyl lactate was detected with an excellent NMR yield of >99%. Poly(bisphenol A carbonate) (**3**) was converted to its building blocks, bisphenol A (**5**) and dimethyl carbonate (**6**), in excellent yields (>99%), which can be reused for the synthesis of new poly(bisphenol A carbonate) materials.[20] For separation/purification, straightforward distillation (**2**, **6** and methanol) and crystallization (for **5**) were applied. **2** was isolated in 61% yield and **5** in 64% yield.

Conclusions

In conclusion, a straightforward and resource-efficient protocol for the transformation of EoL-PLA to the valuable product methyl lactate was tested. A selection of PLA goods found in daily-life were successfully converted in the presence of the industrially relevant catalyst $Sn(Oct)_2$. Excellent yields of methyl lactate were recognised within a short period of time (5–20 min). Remarkably, turnover frequencies of up to 39 600 h^{-1} were exhibited by the catalyst, which is one of the highest catalyst activities reported so far for the methanolysis of PLA. In addition, the system was tested on a larger scale in an autoclave and in combination with other EoL-plastics revealing comparable performance.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

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In conclusion, four different catalytic systems were successfully applied for the synthesis of methyl lactate (**13**) from waste PLA (**9**). Although being the system of highest activity, Sn(Oct)$_2$ comprises some disadvantages due to its toxicity. Alternatives with lower toxicity with still reasonable activity were the Bi(III) compounds and alkali metal halides. Moreover, microwave irradiation was exploited to achieve excellently short reaction times that are by far lower than the reported in the literature. This is cause by efficient and rapid heating as well as the influence of microwave irradiation on the kinetics of the reaction.[62] All literature known examples, that enable conventional heating where outperformed in terms of reaction times. Furthermore, the literature known trend that the catalytic activity is affected by both, the cation and the anion could be confirmed (for Bi(III) and alkali salts).

In order to simplify the overall chemical recycling, we investigated the straightforward depolymerization of PLA (**9**) to L-lactide (**11**), thus, avoiding the additional condensation step of methyl lactate (**13**).[256] The RCD of molten high M$_w$ PLA (**9**) in the presence of various catalysts proceeds above 180 °C (200 °C ideally). Here, especially Zn(OAc)$_2$ shows good TOFs comparable to the benchmark system Sn(Oct)$_2$. In a simple reactive distillation setup excellent isolated yields of L-lactide (**11**) were realized. The temperature range of this process is very small, because at >230 °C degradation to gaseous products, e.g. CO and CO$_2$, diminishes the selectivity.[120,122] The racemization of the L-lactic acid units was observed by ^{1}H NMR using the separated signals of *meso*-lactide. The racemization was significantly higher for NaOAc and KOAc. Despite the small content of racemization, the setup provides an excellent opportunity for large scale application. Nylon 6 (**31**) and PCL (**28**), that are known to undergo RCD where also attempted to degrade in the presence of PLA (**9**). However, Nylon 6 (**31**) was not converted and PCL (**28**) depolymerized only in a small amount to **30**.

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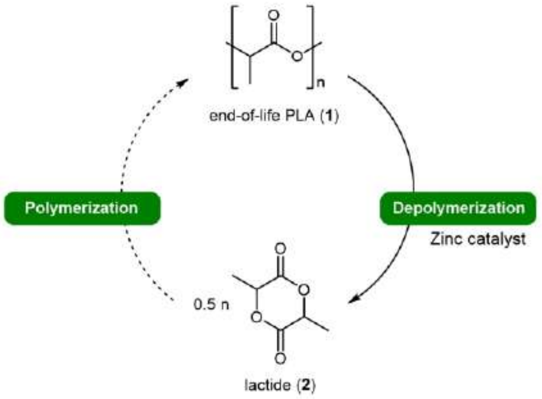
Depolymerization of End-of-Life Poly(lactide) to Lactide via Zinc-Catalysis

Christoph Alberti and Stephan Enthaler*[a]

The chemical recycling of poly(lactide) (PLA), especially the initial depolymerization step was studied. High molecular weight PLA was depolymerized in the presence of zinc catalyst to lactide, the industrial relevant chemical for the synthesis of high molecular weight PLA; therefore, an efficient recycling is feasible without the need for depolymerization reagents. An excellent performance was observed for zinc(II) acetate with turnover frequencies of up to ~260 h^{-1} at 200–210 °C. Noteworthy, the lactide was isolated in high purity by reactive distillation. Furthermore, the zinc(II) acetate catalyst was recycled up to five times.



Scheme 1. Chemical recycling concept for PLA.

Recently, significant attention was directed to plastics derived from renewable resources, which have some advantages compared to fossil resource-based plastics and can add some benefit to a circular economy.[1,2] In this regard, plastics based on poly(lactide) (PLA, **1**, Scheme 1) have been extensively investigated and nowadays PLA is produced on a ~0.2 m t/y scale with wide range of applications have been established.[3] Noteworthy, PLA is accessible by methods based multi-steps processes. Primarily, in plants carbon dioxide, water and solar energy are transformed to biomass by biochemical processes. Afterwards the biomass is converted to lactic acid by industrial fermentation.[4] Lactic acid is transformed by polycondensation to polymer/oligomer **1**. However, to obtain high molecular weight PLA the polymer/oligomers are depolymerized to the dimer lactide **2** (prepolymer route).[3] Finally, lactide is subjected to ring-opening polymerization assisted by catalysis to form high molecular weight **1**. After having fulfilled its obligations the end-of-life PLA will disposed of. For instance composting of PLA is discussed, but the short dwell time in composting plants is an issue.[5] Moreover, incineration of PLA can be carried out, to release energy and generate carbon dioxide and water. Interestingly, the carbon dioxide and water can be reused at the beginning of the PLA process (vide supra), making the whole approach to some extend carbon-neutral.[6,7] However, both treatments of end-of-life PLA require the formation of new PLA right from the beginning, which needs agricultural land and cultivation time, and consequently competes with other agricultural processes. In this regard, the recycling of the PLA can be a beneficial approach to avoid/minimize this "linear" strategy. A circular approach is represented by chemical recycling based on depolymerizations and polymerizations in which the monomeric unit of the polymer circulates in the process (Scheme 1).[8] In case of PLA different types of chemical recycling methodologies have been presented, in which the conversion of the end-of-life polymer to useful low molecular weight compounds is crucial. For instance, hydrolysis and alcoholysis have been studied to yield lactid acid or an ester of lactic acid, but the addition of depolymerization reagents are needed.[9,10,11] However, for resynthesis of the PLA several steps are required (e.g., prepolymer route).[3,12,13] On the other hand, for oligomers and low molecular weight PLA (catalytic) depolymerization to generate lactide was reported.[14,15] Interestingly, Noda *et al.* demonstrated the application of straightforward zinc catalysts for such reactions.[15a] A set of zinc salts were used as catalyst, revealing for the depolymerization of low molecular weight PLA ($M_w = 1170$ g/mol) with $ZnCl_2$ a yield of 89% of **2** containing 96% L-lactide and 2% meso-lactide after 80 min at 190–245 °C and 5–7 mbar. More recently, we demonstrated the potential of $Zn(OAc)_2$ as catalyst in the depolymerization of PLA (M_n ~808 g/mol) obtained from the polymerization of methyl lactate to lactide (yield: 49%, 210 °C, 6 mbar, 240 min).[16] Nevertheless, for high molecular weight PLA, which is mainly used for PLA goods, only a few depolymerizations to lactide have been demonstrated so far.[17]

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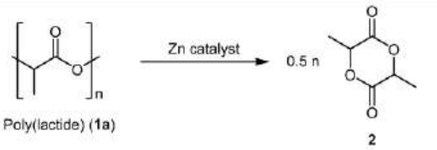
Based on that, we investigated the depolymerization of PLA goods to lactide in the presence of zinc catalysts.

Firstly, for optimization of the depolymerization reaction conditions transparent end-of-life plastic cups containing poly (lactide) (**1 a**, $M_n = 57{,}500$ g/mol, $M_w = 240{,}800$ g/mol, $Đ = 4.2$, PLLA) as major component was studied (Table 1). Pieces of PLA **1 a** (5.0 g, 69.39 mmol with respect to the monomer unit, implying that **1 a** is contains 100% of PLA) and catalytic amounts of $Zn(OAc)_2$ (0.4 mol% with respect to the monomer unit of **1 a**) were added to flask. Distillation equipment was attached and the reaction mixture was heated to 200–210 °C in vacuum (6 mbar), while stirring. During progress the PLA melts and got liquified. At a distillation heat temperature of 140 °C a colorless liquid was collected, which rapidly solidified/crystallized in the collecting flask. After one hour the heating was stopped and the colorless solid was investigated by ^{1}H NMR analysis. The existence of the depolymerization product **2** was confirmed by the presence of a pseudo quartet at $\delta = 5.03$ ppm ($^3J_{HH} = 6.70$ Hz, CH_3CHO-function) and a doublet at 1.67 ppm ($^3J_{HH} = 6.70$ Hz, CH_3CH-function). By comparing the NMR data with an authentic sample, the formation of L-lactide by the depolymerization is approved as major product (proportion of 85% of **2**).

Table 1. Depolymerization of **1 a** using zinc catalysis – optimization of reaction conditions.



Poly(lactide) (**1a**)

2

Entry[a]	Catalyst [mol%]	t [min]	Yield **2** [%][b]	TOF [h^{-1}][c]	Proportion of L-lactide of **2** [%][d]
1	–	60	<1	<1	<1
2	$Zn(OAc)_2$ [0.4]	60	45	113	85
3	$ZnCl_2$ [0.4]	60	33	83	93
4	$ZnBr_2$ [0.4]	60	2	5	–
5	ZnO [0.4]	60	25	63	90
6	$FeCl_3$ [0.4]	60	27	68	88
7	$Fe(OAc)_2$ [0.4]	60	20	50	89
8	$Sn(Oct)_2$ [0.4]	60	52	130	90
9	NaOAc [0.4]	60	11	28	71
10	KOAc [0.4]	60	8	20	64
11	$Zn(OAc)_2$ [0.2]	60	30	150	90
12	$Zn(OAc)_2$ [0.1]	60	26	260	88
13[e]	$Zn(OAc)_2$ [0.4]	60	21	53	88
14[f]	$Zn(OAc)_2$ [0.4]	60	<1	<1	<1
15[g]	$Zn(OAc)_2$ [0.4]	60	2	5	-
16	$Zn(OAc)_2$ [0.4]	360	98	41	88
17[h]	$Zn(OAc)_2$ [0.4]	360	85	36	83

[a] Conditions: **1 a** (transparent PLA cup), 5.0 g, 69.39 mmol with respect to the monomer unit, it is presumed that **1 a** is composed of 100% of PLA), catalyst (0-0.4 mol%, 0–0.278 mmol with respect to the monomer unit of **1 a**), 200–210 °C, 6 mbar, 60–360 min. [b] Isolated yield of **2** (mixture of L-lactide and another lactide isomer). [c] The TOF was calculated: (mole product/mole catalyst)*h^{-1}. The TOF was calculated using the yield of **2** after the designated time. [d] Proportion of L-lactide of the mixture of **2**. Bases on ^{1}H NMR spectroscopy. [e] Poly(ethylene glycol) methyl ether (5 g) as solvent. [f] 160 °C. [g] 180 °C. [h] **1 b** (lid of a coffee cup), 3.6 g, 49.96 mmol.

Along to L-lactide the *meso*-lactide was observed, but in lower amounts, e.g. proportion of 15% of **2**. In consequence a yield of lactide of 45% (sum of isomers) was achieved, which corresponds to a turnover frequency (TOF) of 113 h^{-1} (Table 1, entry 2). Moreover, other zinc salts were tested revealing still good performance for $Zn(OAc)_2$, while zinc halides showed an inferior performance (Table 1, entries 3–4).[18] Importantly, in the absence of any zinc salt no product formation was observed (Table 1, entry 1). Besides, iron salts were tested, revealing a lower yield of lactide, but a somewhat higher yield for L-lactide (Table 1, entries 6–7). Moreover, $Sn(Oct)_2$, which has been used in the prepolymer route for PLA, was used as catalyst, showing a slightly better performance than $Zn(OAc)_2$, e.g., yield (**2**): 52%, L-Lactide: proportion of 90% of **2** (Table 1, entry 8). In addition, potassium and sodium acetate were applied, but lower yields and selectivities were noticed (Table 1, entries 9–10). Reducing the loading of the $Zn(OAc)_2$ catalyst revealed a decrease of product yield with TOFs up to 260 h^{-1} (Table 1, entries 11–12). To allow for a better distribution of the catalyst in the polymer, poly(ethylene glycol) methyl ether was used as solvent, but now positive effect on the reaction outcome was observed (Table 1, entry 13). Moreover, the reaction temperature was studied (Table 1, entries 14 and 15). Lower temperatures revealed the formation of lower amounts of products. Finally, the reaction time was elongated to 6 hours, revealing a yield of lactide of 98% and a L-lactide portion of 88% (Table 1, entry 16). Moreover, a lid of a coffee cup was subjected to depolymerization. A yield of 85% of lactide was obtained after 360 min (Table 1, entry 17).

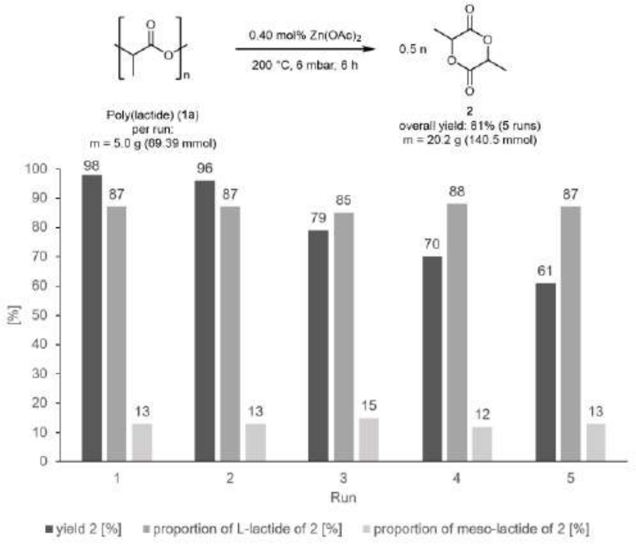
Next, we investigated the reuse/recycling of the $Zn(OAc)_2$ catalyst (Scheme 2). The reaction was performed in accordance to the conditions stated in Table 1, entry 16. After 6 hours at 200 °C and 6 mbar the yield was determined and the product was analyzed by ^{1}H NMR.

Afterwards, a new portion of PLA was added to the reaction flask, which contains the catalyst and polymer leftovers. The outcome of the second run revealed no significant loss of activity, while until run 5 a decrease was noticed to a moderate yield of 61% of lactide (**2**). Interestingly, no change for the portion of L-lactide was detected. Overall a yield of 81% was realized.

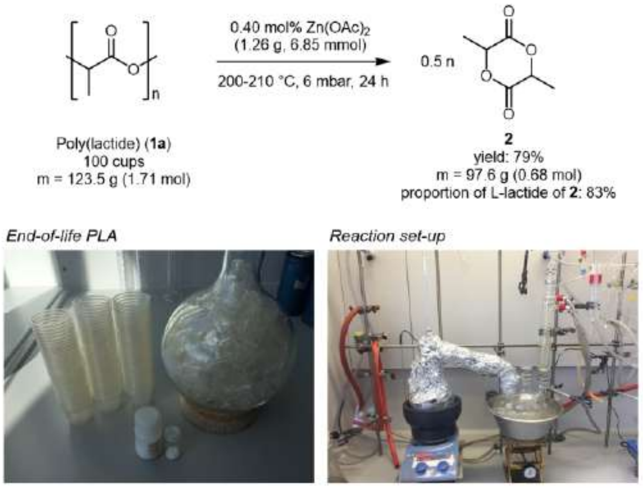
Moreover, for plastic cups (**1 a**) a scale-up reaction was carried out (Scheme 3). In more detail, 100 cups with a total weight of 123.5 g were heated with catalytic amounts of $Zn(OAc)_2$ (0.4 mol%) under reactive distillation conditions. After 24 hours at 200–210 °C 97.6 g of lactide was collected, which corresponds to a yield of 79%. L-lactide was detected with a portion of 83%.

In addition, a mixture of different types of end-of-life PLA goods was subjected to the depolymerization protocol following the conditions described in Table 1 entry 16. After 6 hours product **2** was isolated in 48% yield, which is to some extend lower as observed for **1 a** or **1 b**. Maybe the additives reduce the activity of the catalyst.

In addition, the depolymerization of **1 a** was studied in the presence of two additional polymers (Nylon 6 and poly(ε-caprolactone)), which can also undergo ring-closing depolyme-



Scheme 2. Depolymerization of end-of-life PLA – catalyst recycling [Conditions: **1 a** (5.0 g, 69.39 mmol with respect to the monomer unit, it is presumed that **1 a** is composed of 100% of PLA), $Zn(OAc)_2$ (1st run: 50.9 mg, 0.40 mol%, 0.278 mmol with respect to the monomer unit of **1 a**), temperature: 200 °C, 6 mbar, 360 min. 2nd run catalyst leftover from 1st run; 3rd run catalyst leftover from 2nd run; 4th run catalyst leftover from 3rd run; 5th run catalyst leftover from 4th run. Isolated yield. The portions of lactide isomers base on ^1HNMR spectroscopy].

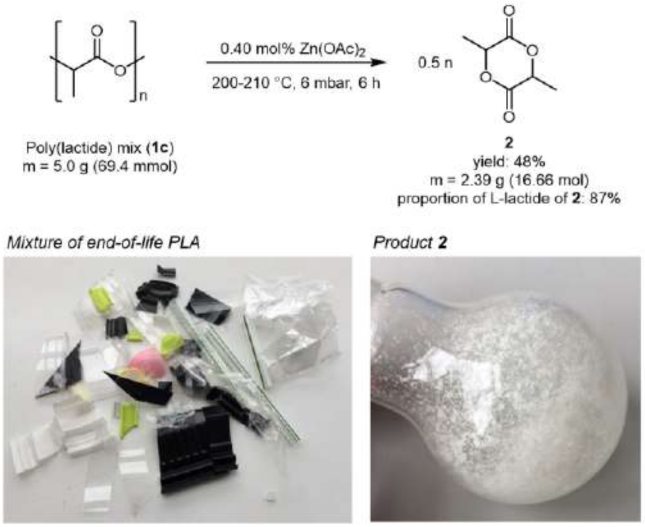


End-of-life PLA

Reaction set-up

Scheme 3. Scale-up of end-of-life PLA depolymerization.

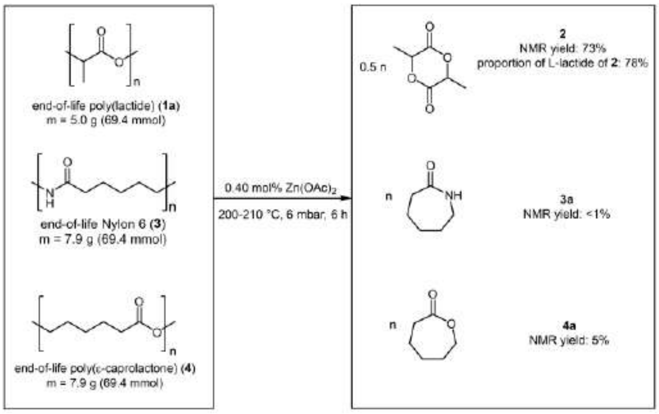
rization (Scheme 5).[19,20] In more detail, a physical mixture of the three polymers were heated at 200–210 °C at 6 mbar in the presence of $Zn(OAc)_2$. After 6 hours **2** was detected in 73% and L-lactide in a proportion of 78%, which is comparable to the scale-up experiment (Scheme 3). Therefore, the additional polymers have no disordered effect on the formation of **2**. The depolymerization product of Nylon 6 ε-caprolactam (**3 a**) was not observed, while the depolymerization product of poly(ε-caprolactone) ε-caprolactone (**4 a**) was detected in only 5%. Noteworthy, the set-up can be applied for the separation of physical plastic/polymer mixtures.



Mixture of end-of-life PLA

Product 2

Scheme 4. Depolymerization of a mixture of end-of-life PLA (transparent cup (1 oz), transparent cup (250 mL), transparent disposable food box, transparent sushi box cover, transparent bottle, drinking straw with green strips, disposable fork with talcum powder, lid for espresso mugs (contains ~20-30% talcum powder), lid for coffee mugs, black lid for coffee mugs, sushi box (black base), ice cream spoons, foil) [Conditions: **1 c**: 5.0 g, 69.4 mmol with respect to the monomer unit, it is presumed that **1 c** is composed of 100% of PLA), $Zn(OAc)_2$ (0.4 mol%, 50.92 mg, 0.278 mmol with respect to the monomer unit of **1 c**), 200–210 °C, 6 mbar, 360 min].



Scheme 5. Depolymerization of a mixture of end-of-life PLA (transparent cup), Nylon 6 (grey dowels) and poly(ε-caprolactone) (M_n ~ 14000 g/mol) [Conditions: **1 a**: 5.0 g, 69.4 mmol, **3**: 7.9 g, 69.4 mmol, **4**: 7.9 g, 69.4 mmol, with respect to the monomer unit, it is presumed that the plastics are composed of 100% polymer), $Zn(OAc)_2$ (0.4 mol%, 50.92 mg, 0.278 mmol with respect to the monomer unit of **1 a**, 0.4 mol%, 50.92 mg, 0.278 mmol with respect to the monomer unit of **3**, 0.4 mol%, 50.92 mg, 0.278 mmol with respect to the monomer unit of **4**), 200–210 °C, 6 mbar, 360 min].

In summary, we have established an easy-to-adopt chemical recycling method for end-of-life poly(lactide) (PLA). In more detail, the method bases on the zinc-catalyzed depolymerization of PLA to obtain lactide as product, which is an industrial relevant precursor for PLA. Notable, as catalyst simple zinc(II) acetate is applied to realize excellent yields of **2** (98%) at 200 °C (6 mbar) within 6 hours.

Supporting Information Summary

The experimental details including the depolymerization reactions and product characterizations can be found in the supporting information.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: catalysis · depolymerization · green chemistry · polymers · recycling

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5.3 Methanolysis of poly(ethylene terephthalate)

Due to its limited solubility in MeOH, we did not observe the methanolysis in neat MeOH in our previous articles. This is reasoned in the poor solubility of PET (**14**) in MeOH even at elevated temperature above 180 °C. For PET, hlorinated solvents show good swelling parameters.[257] Therefore, we wondered, if PET (**14**) can be degraded with CH_2Cl_2 as additional solvent.[258] In fact, complete depolymerization is achieved within 20 min at 160 °C using 1 mol% $Zn(OAc)_2$ as catalyst. Notably, the ratio between MeOH and CH_2Cl_2 affects the overall reaction time. A set of household goods could be degraded with mediocre to excellent yields. The nature of the product affected the crystallization to some extent. In addition, in this case, the mixture of PBAC (**2**), PET (**14**) and PLA (**9**) could be degraded all in one pot in high yields for the corresponding monomers. The obtained DMT (**16**) was in a consecutive experiment converted to related monomers via hydrogenation reaction of either the aromatic system or the carboxylic esters or both. All 3 monomers find application in some commercial polymers, e.g. Tritan®, a polyester with properties comparable to PET (**14**). Following these processes, a so called open-loop-recycling is realized.

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Sustainable Chemistry

Zinc(II) acetate Catalyzed Depolymerization of Poly (ethylene terephthalate)

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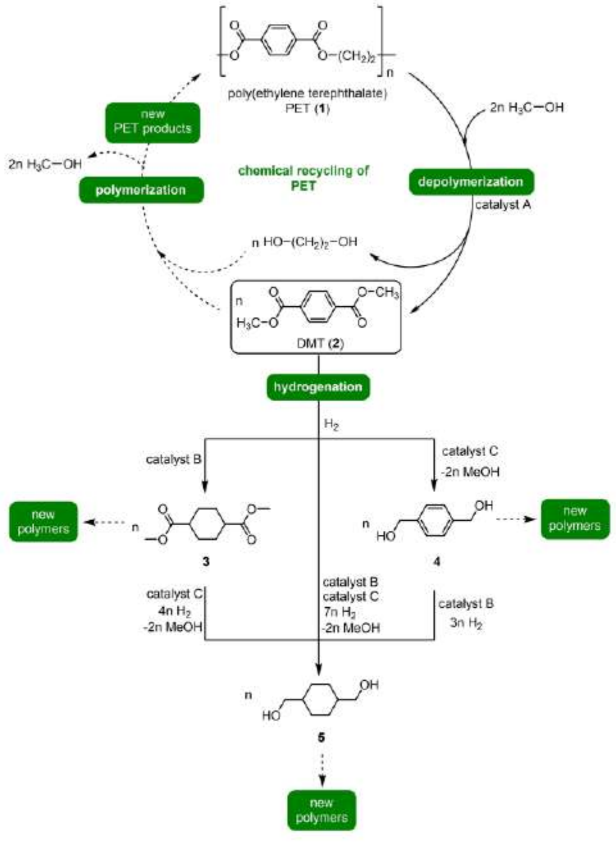
The depolymerization of plastic waste to valuable chemicals (waste-to-chemicals) can be a useful implement for a resource-efficient economy. In this regard, the selective depolymerization of end-of-life poly(ethylene terephthalate) (PET) via zinc(II) acetate-catalyzed methanolysis was investigated. As low molecular weight products dimethyl terephthalate and ethylene glycol were generated. With the support of microwave heating excellent yields and selectivities were realized and a selection of daily-used PET goods were depolymerized. The obtained chemicals can be used for the (re)polymerization to new PET. Additionally, the generated dimethyl terephthalate was used as platform chemical for the synthesis of different molecules relevant for polymerization chemistry.

The thermoplastic polyester poly(ethylene terephthalate) (PET) is one of the well-established multi-ton-scale plastics with numerous applications, due to its outstanding physical and mechanical properties.[1] With the large amount of manufactured and used PET goods issues arise with end-of-life PET products (PET-waste), e.g. high stability, increasing pile of waste, contamination/negative effects in the biosphere, consumption of depleting fossil resource for new PET, therefore solutions are mandatory to reduce the amount of EoL-plastics plastics (end-of-life plastics).[2] Based on these matters, different procedures have been established for solving the problems, e.g. energy recovery, landfill storage, and recycling such as mechanical recycling and downcycling.[3,4,5] Especially the mechanical recycling is a well-established protocol for end-of-life PET to return the plastic to the cycle.[6] However, the energy recovery, and in consequence also the mechanical recycling and the down-cycling, if the plastic quality is too low, transform the polymer structure to "problematic" chemicals (e.g. CO_2) and for replace the EoL-plastics the amount of limited fossil resources is decreased.[7,8] As an interesting and sustainable alternative the chemical recycling of PET can be taken into account.[9] Indeed numerous protocols have been reported, e.g. glycolysis, methanolysis, hydrolysis, ammonolysis.[10] Principally, the EoL-polymer is converted in an initial depolymerization to monomers, which can be converted in a second reaction (polymerization) to make new polymers; therefore, a recycling is feasible. Importantly, the properties of the new polymer are not connected to the EoL-polymer as noticed for other recycling protocols (mechanical recycling and downcycling). Especially the depolymerization via methanolysis of EoL-PET is an attractive process (Scheme 1).[11] In more detail, the ester functionalities of PET (**1**) are reacted with an excess of methanol in the presence of a suitable catalyst to create the monomers dimethyl terephthalate (**2**, DMT) and ethylene glycol (EG), which can be reused in industrial polymerization processes to give access to new PET and allow a recycling.[12] As useful catalyst core zinc was studied, due to e.g. high reactivity,



Scheme 1. Chemical recycling and follow-up chemistry for end-of-life PET.

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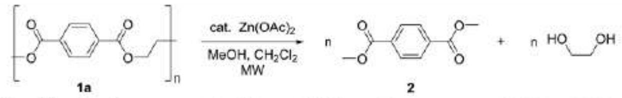
abundancy, low-cost, sustainability issues.[13] However, established protocols often requires high temperatures and long reaction times.[13]

Moreover, the chemical **2** generated from end-of-life PET can be used as platform chemical for accessing different types of monomers and in consequence a series of polymers, e. g. polyesters (Scheme 1). For instance, the aromatic system of **2** can be hydrogenated to obtain dimethyl 1,4-cyclohexanedicarboxylate (**3**), which can be converted with an additional diol in transesterifications to polyesters.[14,15] On the other hand, the ester functionalities of **2** can be hydrogenated to yield alcohol functionalities. Compound **4** can be applied as diol component in transesterification reactions to produce polyesters.[16,17] In addition, **3** and **4** can be reduced to the chemical 1,4-cyclohexanedimethanol (**5**, CHDM), which is used as monomer in the production of polyesters.[18,19,20] Based on that, we report herein our investigations on the microwave-assisted zinc-catalyzed depolymerization of end-of-life PET to produce **2** within short reaction times and an up-grading of **2** to useful chemicals as starting material for other types of polymers (Scheme 1).

For optimization of the reaction conditions transparent end-of-life bottles based on poly(ethylene terephthalate) (**1 a**) were applied as model substrate. Compound **1 a** (1.35 mmol with respect to the monomeric unit), an excess of MeOH as depolymerization reagent (46.2 equiv. with respect to the monomeric unit of **1 a**), dichloromethane as solvent (17.4 equiv. with respect to the monomeric unit of **1 a**) and catalytic amounts of $Zn(OAc)_2$ (1.0 mol% with respect to the monomeric unit of **1 a**) were combined in a vial suitable for microwave heating (MW). The mixture was stirred and heated in a microwave reactor at 160 °C for 20 minutes (Table 1, entry 1). Afterwards the mixture was cooled to ambient temperature to obtain a clear and colorless solution. The analysis of the reaction mixture by ^{1}H NMR spectroscopy revealed signals for the depolymerization products ethylene glycol ($\delta = 1.41$ ppm s, 4H, 2xCH_2; $\delta = 3.71$ ppm, s, 2H, 2xOH)[21] and dimethyl terephthalate (**2**, DMT, $\delta = 3.94$ ppm, s, 2xOCH_3; $\delta = 8.09$ ppm, s, 4xArH).[22] Importantly only small amounts of residual oligomers/polymers were detected. In consequence an NMR yield of 98% of **2** and a NMR yield of 96% of ethylene glycol was noticed. Shortening the reaction time to 10 minutes an adequate yield of 70% of **2** was achieved, which corresponds to a turnover frequency of 450 h^{-1} (Table 1, entries 2 and 3). Comparing the obtained results with established zinc-catalyzed methanolysis of **1 a** revealed an improvement of product formation by addition of dichloromethane as solvent. For instance, Siddiqui *et al.* performed the conversion of **1 a** in neat methanol and achieved a turnover frequency (TOF) of 180 h^{-1} (0.5 g PET, 1 mol% $Zn(OAc)_2$, MeOH (1 mL), 160 °C, 30 min, MW).[23] Next, the influence of the reaction temperature was studied (Table 1, entries 4–6). In case of a decrease to 120–140 °C no product formation was observed. However, by elongation of the reaction time to 60 min at 140 °C an excellent yield was noticed. Moreover, the effect of addition of varying amounts of dichloromethane as solvent was studied (Table 1, entries 7–9). Reducing the amount leads to no product formation, while an increase showed a similar result as revealed for the initial experiment.[24]

Table 1. $Zn(OAc)_2$ catalyzed depolymerization of **1 a**.



Entry[a]	Catalyst loading [mol %]	MeOH [equiv.]	CH_2Cl_2 [equiv.]	T [°C]	t [min]	Yield **2** [%][b]	TOF [h^{-1}][c]
1	1	46.2	17.4	160	20	98	294
2	1	46.2	17.4	160	15	81	324
3	1	46.2	17.4	160	10	75	450
4	1	46.2	17.4	140	20	<1	<1
5	1	46.2	17.4	140	60	92	92
6	1	46.2	17.4	120	20	<1	<1
7	1	69.4	17.4	160	20	<1	<1
8	1	92.5	8.7	160	20	<1	<1
9	1	46.2	26.2	160	20	98	294
10	0.75	46.2	17.4	160	20	76	228
11	0.5	46.2	17.4	160	20	<1	<1
12	-	46.2	17.4	160	20	<1	<1

[a] Reaction conditions: **1 a** (obtained from transparent bottle), 1.35 mmol with respect to the repeating unit), $Zn(OAc)_2$ (0–1 mol%, 0–0.0135 mmol with respect to the repeating unit of **1 a**), MeOH (46.2–69.4 equiv. with respect to the repeating unit of **1 a**), CH_2Cl_2 (8.7-26.2 equiv. with respect to the repeating unit of 1 a), MW: 120–160 °C, 10–60 min. [b] The yield was determined by ^{1}HNMR. A clear solution was observed. It is presumed that the PET product is composed of 100% of PET. [c] The TOF was calculated: (mole product/mole catalyst)*h^{-1}. The TOF was calculated using the yield of **2** after the designated time.

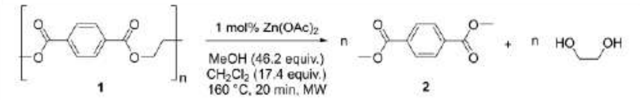
At a lower catalyst loading of 0.75 mol% still a reasonable yield of 76% of **2** is exhibited, while at 0.5 mol% or in the absence no product is formed (Table 1, entries 10–12).

Furthermore, different catalyst precursors based on zinc were tested, e. g., $ZnCl_2$, $ZnBr_2$, $Zn(OTf)_2$, ZnO and ZnS, but no product formation was detected. In addition, tin(II) 2-ethylhexanoate was applied as catalyst following the conditions described in Table 1 entry 1. However, only a moderate yield of 46% was detected.

With the optimized conditions (1.0 mol%, 46.2 equiv. methanol, 17.4 equiv. dichloromethane, 160 °C, 20 min, MW) a variety of PET goods was depolymerized to product **2** and ethylene glycol (Table 2). First the PET bottle was depolymerized to compound **2** in an excellent yield of 98% as detected by ^{1}H NMR spectroscopy. Afterwards compound **2** was isolated from the reaction mixture. In detail, the solvents (excess of methanol and CH_2Cl_2) were removed and the residue was crystallized from a mixture of methanol and dichloromethane. Dimethyl terephthalate (**2**) was isolated in 95% yield (presumption that **1 a** contains 100% PET) (Table 2, entry 1).

Besides, a used transparent bottle was subjected to depolymerization revealing a diminished yield of **2** of 64%, maybe caused by the contaminations (Table 2, entry 2). A similar effect was observed in case of a clean dyed bottle, in which the additives may reduce the catalyst activity (Table 2, entry 3). Moreover, in case of a dish detergent bottle or a soap dispenser the contamination by labels or residues of glue

Table 2. $Zn(OAc)_2$ catalyzed depolymerization of PET products.

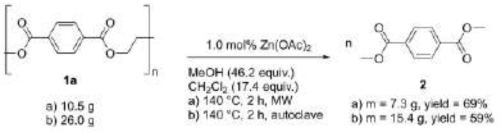


Entry[a]	Product	n (2) [mmol]; m (2) [mg]	Isolated yield 2 [%][b]
1	Transparent bottle (colourless) **1 a**	1.28; 249.1	95
2	Used transparent Cola bottle **1 b**	0.82; 159.4	64
3	Transparent bottle (green) **1 c**	0.49; 94.7	38
4	Dish detergent bottle **1 d**	0.59; 114.6	46
5	Dish detergent bottle with glue contamination **1 e**	0.19; 37.4	15
6	Soap dispenser **1 f**	1.25; 244.1	98
7	Soap dispenser with label contamination **1 g**	0.90; 174.4	70
8	Detergent bottle **1 h**	0.73; 142.0	57
9	Transparent food box **1 i**	1.25; 244.1	98
10	Transparent shampoo bottle **1 j**	0.42; 82.2	33
11	Toothbrush packaging colourless **1 k**	0.87; 169.4	68
12	Filling material colourless **1 l**	0.29; 57.3	23
13	Shampoo bottle (grey) **1 m**	0.26; 49.8	20
14	Softener bottle (purple) **1 n**	0.33; 64.8	26
15	Safety vest (yellow) **1 o**	0.60; 117.1	47

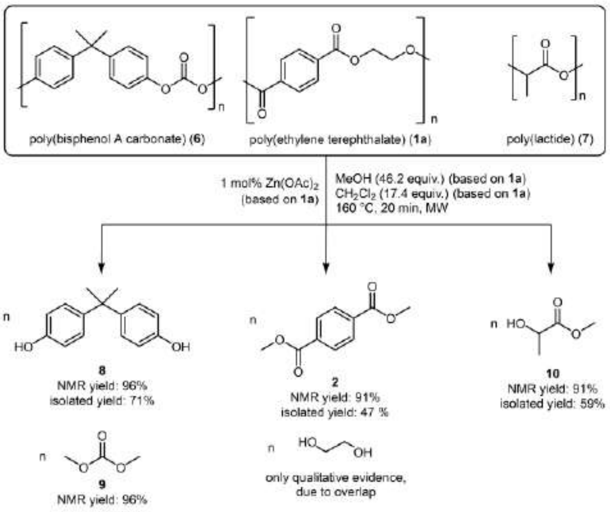
[a] Reaction conditions: **1** (259.4 mg, 1.35 mmol with respect to the monomeric unit), $Zn(OAc)_2$ (2.47 mg, 1 mol%, 0.0135 mmol with respect to the repeating unit of **1**), MeOH (2 g, 62.4 mmol, 46.2 equiv. with respect to the repeating unit of **1**), CH_2Cl_2 (2.0 g, 23.5 mmol, 17.4 equiv. with respect to the repeating unit of **1**), MW: 160 °C, 20 min. [b] Isolated yield of **2** after crystallization. The amount of substance of **2** was connected to the amount of substance of the initial PET, assuming that the good contains 100 % PET. Yield % = (n(**2**)/n(**1**))*100.

reduces the yield of **2** compared with the purified version (Table 2, entries 4–7). Moreover, non-transparent and dyed products were tested, but low to moderate yields of **2** were realized (Table 2, entries 13–15). In addition, a scale-up of the depolymerization reaction was performed in a microwave reactor with eight parallel microwave tubes converting 10.5 g of a transparent PET bottle at 140 °C for 2 hours (Scheme 2). 7.3 g of compound **2** were isolated, which corresponds to a yield of 69 %. Moreover, a scale-up was carried out in an autoclave (1.0 L) with 26.0 g of a transparent PET bottle at 140 °C for 2 hours (Scheme 2). In this case 15.4 g of **2** was isolated (59 %).

Additionally, the potential of zinc(II) acetate was tested in the one-pot depolymerization of a mixture of different polyesters, which can an interesting target to minimize the expenditures of waste stream separation (Scheme 3). A combination of a transparent PET bottle (**1 a**), poly(bisphenol A carbonate) (PC, **6**) isolated from a DVD and a transparent plastic cup containing poly(lactide) (PLA, **7**) was tested.[25] Interestingly, with the optimized conditions (1 mol % $Zn(OAc)_2$, 46.2 equiv. MeOH, 17.4 equiv. CH_2Cl_2, 160 °C, 20 min, MW) all three polymers were successfully converted to the corresponding monomers, which allow the recycling of the polymers.



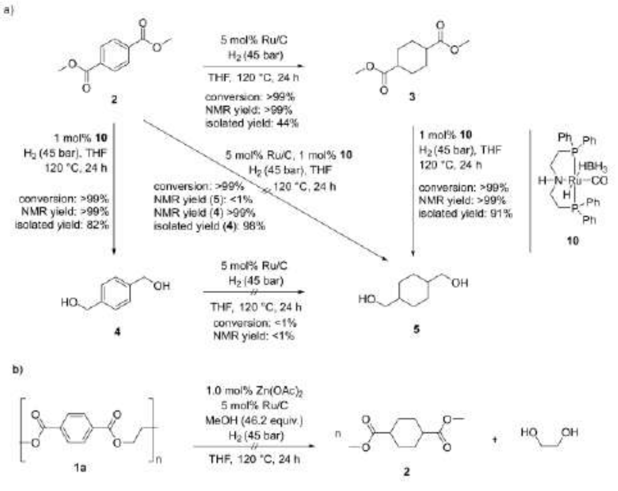
Scheme 2. Chemical recycling of PET - Scale up.



Scheme 3. Simultaneous chemical recycling of PET, PLA and PC.

Dimethyl terephthalate (**2**) was detected in an excellent NMR yield of 91 %. An isolated yield of 47 % was realized by crystallization. The polycarbonate was converted to bisphenol A (**9**) and dimethyl carbonate (**10**) in an excellent NMR yield of 96 %. These two building blocks can also reused in the synthesis of new poly(bisphenol A carbonate) (**6**).[24] Moreover, **9** was isolated by crystallization in 73 % yield. The methyl lactate (**10**) was detected in an NMR yield of 91 % and was isolated by distillation in a reasonable yield of 59 %. Chemical **10** can be converted to lactide acid or polymerized directly to PLA via lactide.[25]

Next the conversion of compound **2** to useful building blocks for polymer synthesis via hydrogenation was investigated (Scheme 4). In the presence of catalytic amounts of Ru (5 wt %)/C chemical **2** is hydrogenated at the aromatic unit to produce dimethyl 1,4-cyclohexanedicarboxylate (**3**) in excellent NMR yield (> 99 %) as a mixture of isomers.[26] In addition, **3** was converted to 1,4-cyclohexanedimethanol (**5**) via hydrogenation of the ester functionality in the presence of catalytic amounts of the Ru-MAHO-BH complex **10**, which has been demonstrated to be useful in organic ester hydrogenations[26] **5** was obtained in > 99 % NMR yield. The same catalyst was also able to convert **2** to **4** in an excellent NMR yield of > 99 %.[27] Moreover, the hydrogenation of **4** in the presence of Ru (5 wt %)/C was tested, but no product formation was observed. Finally, compound **2** was hydrogenated in the presence of the heterogeneous catalyst (Ru (5 wt %)/C) as well as the homogeneous catalyst **10**. However, instead of the expected product **5** compound **4** was produced in an excellent NMR yield of > 99 % and 98 %



Scheme 4. a) Hydrogenation of depolymerization product **2** to chemicals **3**, **4** and **5**. b) One-pot depolymerization and hydrogenation.

isolated yield. Moreover, a one-pot depolymerization and hydrogenation was studied, but no product formation was observed (Scheme 4).

1. Conclusion

In conclusion we have set up a straightforward resource-efficient protocol for the transformation of poly(ethylene terephthalate) (**1**) to the valuable products dimethyl terephthalate (**2**) and ethylene glycol, which can be used as monomers for the resynthesis of PET. A selection of daily used PET goods was depolymerized in the presence of the straightforward catalyst zinc(II) acetate. Excellent yields of **2** were achieved with an excess of methanol and dichloromethane as solvent within short period of time (20 min) under microwave heating. Furthermore, the system was tested in combination with other end-of-life plastics and allows the depolymerization of three polymers at the same time. In addition, the depolymerization product **2** was successfully converted via hydrogenation to different kinds of diesters and diols, which are useful starting materials for polyesters.

Supporting Information Summary

The experimental details including the depolymerization reactions, hydrogenation reactions and product characterizations can be found in the supporting information.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: catalysis · depolymerization · green chemistry · polymers · recycling

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[27] Compared with an authentic sample.

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5.4 Methanolysis of poly(ethylene furanoate)

Based on our investigations on the methanolysis of PET (**14**) under zinc catalysis, we subjected PEF (**24**) to our methanolysis protocol.[258] Zinc(II) carboxylates are in contrast to the corresponding halides more active in this reaction. However, despite its structural similarity to PET (**14**), it undergoes depolymerization under much milder conditions. No additional solvent is required, however DMSO (dimethyl sulfoxide) had an accelerating effect. The reaction proceeds via a pseudo first order kinetics with an activation energy of 105.1 kJ/mol. Other polymers showed no significant influence on the reaction. Converting PEF (**24**) in the presence of PCL (**28**) or PLA (**9**) led to some extent to their depolymerization. In contrast, PET (**14**) was not dissolved and remained unconverted. This provides the opportunity to separate PEF (**24**) from PET (**14**) in mixed waste streams, which are hard to differentiate and separate by other techniques.

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Zinc-Catalyzed Depolymerization of the End-of-Life Poly (ethylene 2,5-furandicarboxylate)

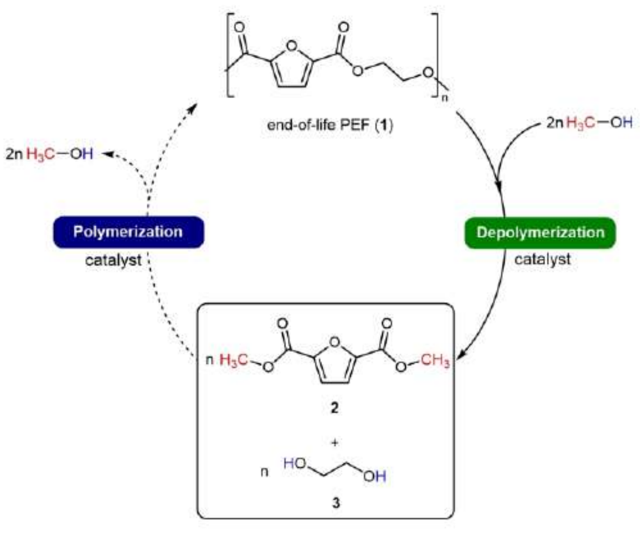
Christoph Alberti, Konstantin Matthiesen, Moritz Wehrmeister, Sergej Bycinskij, and Stephan Enthaler*[a]

The depolymerization of end-of-life polymers to valued chemicals (waste-to-chemicals) can be a suitable tool for the transformation from a linear to a circular economy. Therefore, the depolymerization of end-of-life poly(ethylene 2,5-furandicarboxylate), discussed as sustainable substitute of poly(ethylene terephthalate), was studied. In more detail, in the presence of catalytic amounts of zinc(II) acetate poly(ethylene 2,5-furandicarboxylate) was converted by methanolysis to dimethyl 2,5-furandicarboxylate and ethylene glycol using microwave heating. Turnover frequencies up to 396 h^{1} were realized. Interestingly, the products dimethyl 2,5-furandicarboxylate and ethylene glycol can be used as building blocks for the zinc-catalyzed resynthesis of poly(ethylene 2,5-furandicarboxylate); therefore a recycling is realizable.

Petrochemical-based plastics have a substantial influence on mankind. This fact is underlined by plentiful applications of these plastics and the yearly growing volume of production.[1,2] On the other hand, issues arise from a) depletion of the feedstock and b) generation of plastic waste after the obligations are finished and its follow-up problems.[3–6] For a) biomass has been discussed as alternative feedstock for polymers. Indeed, several biomass-based approaches have been established.[7–9] However, the production of these polymers requires cultivable acreage, which cannot be used for the cultivation of edibles or as biotopes. An option to circumvent the competitive situation can be the application of efficient recycling methods. On the other hand, for b) recycling techniques have been installed as resource-efficient tool for reuse of plastics, e.g. mechanical recycling, downcycling, chemical recycling.[10–18] Especially, chemical recycling of end-of-life polymers has been discussed as a resource-efficient and sustainable methodology.[19,20] Noteworthy, chemical recycling can be beneficial for solving issues a) and b). In detail, the end-of-life polymer is transformed by depolymerization processes to monomers, which can be reconverted in the polymerization step to new polymers. Importantly, the essential units of the polymer are captured in the cycle. Moreover, the properties of the new polymer can be adjusted on demand, because the depolymerization-polymerization approach allows independency from the original polymer.

The thermoplastic polyester poly(ethylene terephthalate) (PET) is one of the well-established multi-ton-scale plastics based on petrochemicals.[21] As a bio-based and sustainable alternative poly(ethylene 2,5-furandicarboxylate) (PEF, **1**) has been recently presented (Scheme 1).[22,23] With respect to chemical recycling until now a few number of methods has been reported, including e.g. hydrolysis, glycolysis and methanolysis of PEF.[24] For instance, Sipos *et al.* performed the methanolysis to generate as depolymerization products dimethyl 2,5-furandicarboxylate (**2**) and ethylene glycol (**3**), which are the industrially relevant monomers for producing PEF (Scheme 1).[24a,22] In more detail, in the presence of catalytic amounts of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (10.7 mol%) dimethyl 2,5-furandicarboxylate (**2**) was obtained in a yield of 63% after 30 min at 90 °C.

Recently, we investigated the depolymerization of different end-of-life polyesters (e.g., poly(lactide), poly(ε-caprolactone), PET) via methanolysis.[25] Based on that, we report herein our



Scheme 1. Chemical recycling concept for PEF.

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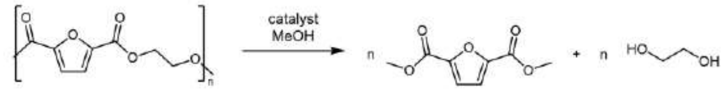
study on the microwave-assisted zinc-catalyzed depolymerization of PEF via methanolysis.

At first, for optimization of the depolymerization conditions poly(ethylene 2,5-furandicarboxylate) was synthesized following the procedure reported by Kucherov *et al.*[26] Polymer **1** was obtained in 96% yield and a number average molar mass of ~3947 g/mol. Next, polymer **1** was subjected to depolymerization (Table 1). In more detail, a mixture of **1** (0.73 mmol with respect to the monomer unit), methanol as depolymerization reagent (67.5 equiv. with respect to the monomer unit of **1**) and $Zn(OAc)_2$ (1.0 mol% with respect to the monomer unit of **1**) was heated at 120 °C for 30 min using microwave heating (Table 1, entry 2). Afterwards, the methanol was carefully removed in vacuum and the residue was dissolved in chloroform and 1-*tert*-butyl-3,5-dimethylbenzene was added as internal standard and an aliquot was taken for ^{1}H NMR analysis. Signals for the depolymerization product dimethyl 2,5-furandicarboxylate were observed for the methyl groups at $\delta=3.94$ ppm (s, $2xOCH_3$) and for the aromatic protons at $\delta=7.23$ ppm (s, $2xCH$).[27,28] Moreover, ethylene glycol (**3**) was detected ($\delta=3.74$ ppm, $2xCH_2$).[28] Based on the integrals a yield for **2** of 39% was calculated. In the absence of $Zn(OAc)_2$ no product formation was observed (Table 1, entry 1). In addition, different zinc precursors were tested as catalyst, but only zinc(II) methacrylate revealed activity (Table 1, entries 3–7). However, best performance was observed for $Zn(OAc)_2$ with a turnover frequency (TOF) of ~162 h^{-1} (Table 1, entry 3). Increasing the loading of $Zn(OAc)_2$ to 2.5 mol% or 5.0 mol% a significant increase of the product yield up to 76% within 10 min was noticed (Table 1, entry 8 and 10). Moreover, the influence of the amount of depolymerization reagent was studied (Table 1, entries 12 and 13). Increasing the amount of methanol revealed no change of reaction outcome, while for a decrease a reduced product yield was achieved. Next, the reaction temperature was increased to 140 °C presenting a yield of 51% of **2** within 10 min, which corresponds to a TOF of ~306 h^{-1} (Table 1, entry 14). Adding dimethyl sulfoxide as solvent a further increase to ~396 h^{-1} was detected, which outperforms the result of Sipos *et al.* (TOF ~11 h^{-1}) (Table 1, entry 17).[24a] An additional increase to 160 °C revealed a further increase of product formation, but an uncatalyzed methanolysis can also take part (Table 1, entries 18 and 19).[29]

In addition, the yield-time dependency was studied (Scheme 2). Full conversion of polymer **1** was observed within 35 min at 120 °C. A turnover frequency of 133 h^{-1} was calculated at 50% yield of product **2**. At higher temperatures higher turnover frequencies were detected (140 °C: 400 h^{-1}, 130 °C: 150 h^{-1}). The reaction rate constant at 120 °C for the methanolysis of **1** was 0.0018 s^{-1} (pseudo first order).[30] Moreover, the activation energy (105.1 kJ mol^{-1}) and the frequency factor (1.53 10^{11} s^{-1}) were calculated.

Moreover, the depolymerization of PEF **1** was investigated in the presence of additional polymers (physical mixture) (Table 3). This approach potentially allows the separation of polymer mixtures after depolymerization and avoids pre-separation processes. In detail, PEF **1** was physically mixed with an equimolar amount of a second polymer. After addition of catalytic amounts of $Zn(OAc)_2$ and methanol as depolymerization reagent, the depolymerization was performed in accordance to Table 1, entry 11. In all cases no significant negative

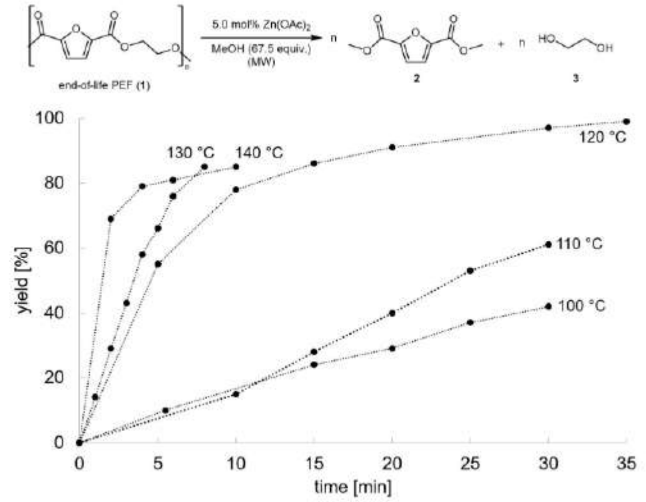
Table 1. Depolymerization of 1 using zinc catalysis – optimization of reaction conditions.



end-of-life PEF (**1**) **2** **3**

Entry[a]	Catalyst	Catalyst loading [mol%]	MeOH [equiv.]	T [°C]	t [min]	Yield **2** [%][b]	TOF [h^{-1}][c]
1	–	–	67.5	120	30	<1	–
2	$Zn(OAc)_2$	1.0	67.5	120	30	39	78
3	$Zn(OAc)_2$	1.0	67.5	120	10	27	162
4	$ZnCl_2$	1.0	67.5	120	10	<1	–
5	$ZnBr_2$	1.0	67.5	120	10	<1	–
6	$Zn(OTf)_2$	1.0	67.5	120	10	<1	–
7	Zinc(II) methacrylate	1.0	67.5	120	10	12	72
8	$Zn(OAc)_2$	2.5	67.5	120	10	60	144
9	$Zn(OAc)_2$	2.5	67.5	120	60	76	35
10	$Zn(OAc)_2$	5.0	67.5	120	10	76	91
11	$Zn(OAc)_2$	5.0	67.5	120	30	86	34
12	$Zn(OAc)_2$	1.0	44.0	120	10	28	168
13	$Zn(OAc)_2$	1.0	90.0	140	10	11	66
14	$Zn(OAc)_2$	1.0	67.5	140	10	51	306
15	–	–	67.5	140	10	3	–
16	$Zn(OAc)_2$	1.0	67.5	140	30	75	150
17[d]	$Zn(OAc)_2$	1.0	67.5	140	10	66	396
18	$Zn(OAc)_2$	1.0	67.5	160	10	91	546
19	–	–	67.5	160	10	64	–

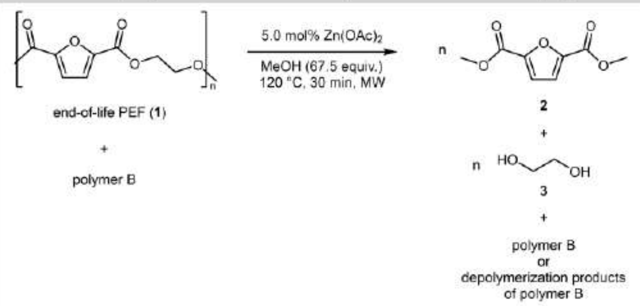
[a] Conditions: poly(ethylene 2,5-furandicarboxylate) 1, 0.73 mmol with respect to the monomer unit), catalyst (0-5.0 mol%, 0–0.036 mmol with respect to the monomer unit of 1), MeOH (44.0-90.0 equiv., 32.1–65.7 mmol with respect to the monomer unit of 1), temperature: 120–160 °C (microwave heating), time: 10–60 min. [b] The yield of 2 bases on ^{1}H NMR spectroscopy using 1-*tert*-butyl-3,5-dimethylbenzene as standard. [d] DMSO as solvent (1.0 g).



Scheme 2. Yield-time dependency of the depolymerization of **1** [Conditions: PEF (**1**, 0.73 mmol) with respect to the monomer unit), $Zn(OAc)_2$ (5.0 mol%, 0.036 mmol with respect to the monomer unit of **1**), MeOH (67.5 equiv., 49.3 with respect to the monomer unit of **1**), temperature: 100–140 °C (MW), the yield of **2** bases on ^{1}H NMR spectroscopy using 1-*tert*-butyl-3,5-dimethylbenzene as standard].

effect on the depolymerization of **1** was observed. The addition of a polyester as second polymer revealed the partial methanolysis of the second polymer (Table 2, entries 7–9).[25] For instance, poly(lactide) was converted in 93% to methyl lactide, while for poly(ε-caprolactone) and poly(ethylene terephthalate) low or no product formation was detected.

Table 2. Depolymerization of **1** in the presence of additional polymers.



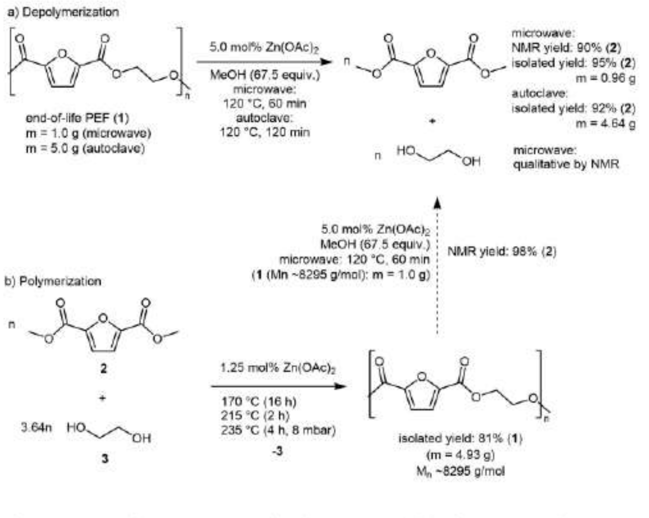
Entry[a]	Additional polymer B	Yield of 2 [%][b]	Yield [%][c]
1	–	86	-
2	Nylon 6	89	<1
3	Poly(phenylene sulfide) (PPS)	87	<1
4	Poly(ethylene) (PE) (Mn ~1,700 g/mol)	96	<1
5	Poly(styrene) (PS) (Mw ~35,000 g/mol)	87	<1
6	Poly(vinyl chloride) (PVC) (Mw ~48,000 g/mol)	87	<1
7	Poly(lactide)	81	83
8	Poly(ε-caprolactone) (M_n ~14,000 g/mol)	81	15
9	Poly(ethylene terephthalate)	86	<1

[a] Conditions: PEF (1, 0.365 mmol with respect to the monomer unit), polymer B (0.365 mmol with respect to the monomer unit), $Zn(OAc)_2$ (5.0 mol%, 0.0175 mmol with respect to the monomer unit of 1 and polymer B), MeOH (67.5 equiv. with respect to the monomer unit of 1 and polymer B), temperature: 120 °C (microwave heating), time: 30 min. [b] The yield of 2 bases on ^{1}H NMR spectroscopy. [c] The yield bases on ^{1}H NMR spectroscopy.

In addition, a scale-up of the depolymerization reaction was performed with polymer **1** (Scheme 3a). Initially, 1.0 g of polymer **1** was reacted with methanol in the presence of catalytic amounts of $Zn(OAc)_2$ (5 mol%) using microwave heating. After 60 min at 120 °C compound **2** was detected in an NMR yield of 90%. Next, the reaction mixture was stored at room temperature, while **2** crystallizes. **2** was filtered off and recrystallized from methanol to obtain **2** in 95% yield (0.96 g). On the other hand, a larger scale-up (5.0 g of **1**) was performed in an autoclave. After 120 min at 120 °C **2** was isolated in 92% yield. After isolation of the depolymerization product **2** the polymerization to regenerate polymer **1** was carried out (Scheme 3b). In detail, **2**, **3** and catalytic amounts of $Zn(OAc)_2$ were heated at 170 °C for 16 hours, 215 °C for 2 hours, and 235 °C for 4 hours in vacuum (8 mbar). After work-up a powder was obtained in 81% yield. The formation of polymer **1** was verified by ^{1}H NMR analysis. For instance, the signals for the C–H of the furan unit was observed at $\delta = 7.34$ ppm (s, 2H), while the CH_2-functions were detected at $\delta = 4.74$ ppm (s, 4H).

Moreover, the number average molar mass was calculated (M_n ~8295 g/mol) based on the end-groups of polymer **1**. Finally, it was also shown that the synthesized PEF can be depolymerized under standard conditions with comparable results (Scheme 3).

In summary, we have installed a depolymerization method for end-of-life poly(ethylene 2,5-furandicarboxylate) based on zinc-catalyzed methanolysis. In detail, in the presence of straightforward $Zn(OAc)_2$ as catalyst dimethyl 2,5-furandicar-



Scheme 3. Depolymerization and polymerization [Conditions: Depolymerization: a) microwave: PEF (**1**, 5.49 mmol) with respect to the monomer unit), $Zn(OAc)_2$ (5.0 mol%, 0.27 mmol with respect to the monomer unit of **1**), MeOH (67.5 equiv., 370.6 mmol with respect to the monomer unit of 1), temperature: 120 °C (MW), time: 60 min; b) autoclave: PEF (**1**, 27.5 mmol) with respect to the monomer unit), $Zn(OAc)_2$ (5.0 mol%, 1.35 mmol with respect to the monomer unit of **1**), MeOH (67.5 equiv., 1853.0 mmol with respect to the monomer unit of **1**), temperature: 120 °C, time: 120 min; Polymerization: **2** (29.8 mmol), **3** (91.2 mmol), $Zn(OAc)_2$ (1.25 mol%, 0.38 mmol), 170 °C (16 h), 215 °C (2 h), 235 °C (4 h, 8 mbar)].

boxylate and ethylene glycol was generated in good to excellent yields within 30–60 min under microwave heating. Noteworthy, the depolymerization products can be applied as starting material for the synthesis of poly(ethylene 2,5-furandicarboxylate).

Supporting Information Summary

The experimental details including the depolymerization and polymerization reactions, and product characterizations can be found in the supporting information.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: catalysis · depolymerization · green chemistry · polymers · recycling

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[28] Compared with an authentic sample.
[29] Also residues of the polymerization catalyst may catalyze the depolymerization.
[30] The solution process of the polymer in the initial stage was not taken into account.

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5.5 Methanolysis of poly(ε-caprolactone)

This chapter bases on the results from the bachelor thesis of Even Cheung.[260] The chemical recycling of PCL (**28**) by methanolysis affords the corresponding methyl ester, which is a suitable monomer for polycondensation to regenerated **28**. Therefore, we tested a variety of different zinc(II) salts.[260,261] Interestingly, with $Zn(OAc)_2$ higher TOFs where observed than for $Sn(Oct)_2$ or KF. However, we found that PCL (**28**) can be degraded at temperatures of 120-180 °C using short reaction times. To achieve full depolymerization within 1 h, 2 mol% of the catalyst were required. The reaction follows a pseudo first order kinetic with an activation energy of 90.9 kJ/mol. Although structurally similar, zinc(II) methacrylate shows a lower activation energy of 74.0 kJ/mol. An effect of the molar mass, e.g. due to diminished solubility, was not found under the stated reaction conditions. Moreover, the reaction was not notably influenced by the presence of other polymers during the depolymerization.

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Zinc-Catalyzed Chemical Recycling of Poly(ε-caprolactone) Applying Transesterification Reactions

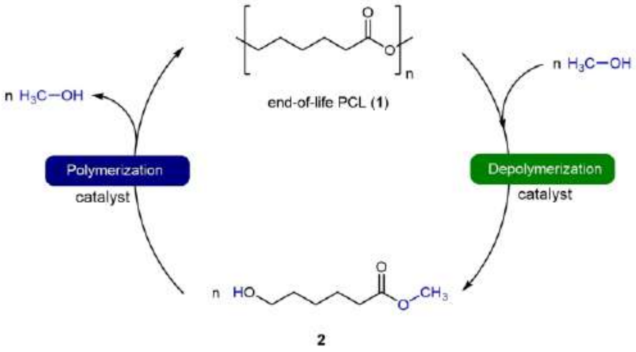
Even Cheung, Christoph Alberti, Sergej Bycinskij, and Stephan Enthaler*[a]

The chemical recycling of poly(ε-caprolactone) (PCL) was explored based on depolymerization and polymerization. The concept bases on the zinc-catalyzed depolymerization via methanolysis to produce methyl 6-hydroxyhexanoate, which is polymerized in a zinc-catalyzed condensation reaction to generate new PCL and close the cycle. In more detail, with zinc (II) acetate as catalyst, PCL was depolymerized with turnover frequencies of up to 468 h^{-1} using microwave heating. On the other hand zinc(II) acetate was also able to catalyze the polymer formation using the monomer methyl 6-hydroxyhexanoate. PCL was obtained in good yield and M_n ~1729 g/mol and M_w ~5823 g/mol were achieved.

The demand for plastic goods is steadily growing year by year, due to excellent material abilities and widespread applications.[1,2] On the other hand, along with the increasing production volume the amount of end-of-life plastics is increasing. After the end of service life the plastics are streamed in the plastic waste management system, which consists of energy recovery, mechanical recycling, downcycling and landfill storage.[3,4,5] However, it turns out on a closer look that all these protocols finally convert chemical functionalities contained in plastics into problematic chemicals (e.g. carbon dioxide). Therefore, new plastics require a new portion of fossil resources and on the other hand add negative effects on the ecosphere/anthroposphere.[6,7] As a resource-conserving alternative the chemical recycling has been discussed.[8] The chemical recycling bases on two interlinked processes, the depolymerization and polymerization. Firstly, the end-of-life polymer is depolymerized to low-molecular weight chemicals (monomers/monomer precursors), which are converted to (re)produce new polymers in the second step. Outstandingly, the chemical recycling decouples the polymer quality/abilities from the initial/end-of-life polymer quality/abilities, which is maybe a problem in case of mechanical recycling and/or downcycling.

A well-established polymer represents poly(ε-caprolactone) (PCL, **1**), a biodegradable and thermoplastic polymer with utilizations in the packaging industry and medicine.[9] Indeed, some chemical recycling approaches have been accounted.[10] For instance, the enzyme-catalyzed ring-closing depolymerizations to generate ε-caprolactone the monomer for the industrial polymerization process. On the other hand, hydrogenative depolymerizations have been presented applying hydrogen as depolymerization reagent. In more detail, the hydrogenation of PCL yields 1,6-hexanediol, which can be used in a subsequent dehydrogenation process to resynthesize PCL.[11–13] Moreover, the depolymerization via methanolysis can be a beneficial process (Scheme 1). The end-of-life PCL is reacted with methanol in the presence of a catalyst to produce methyl 6-hydroxyhexanoate (**2**) in a transesterification reaction. **2** can be converted in a second transesterification (polymerization) to new PCL. Recently, we studied the methanolysis of different end-of-life polyesters to produce suitable monomers applying cheap and abundant catalysts.[14] For example $Zn(OAc)_2$ revealed an excellent performance in the depolymerization of poly(lactide) and poly(ethylene 2,5-furandicarboxylate) with turnover frequencies (TOF) of up to 45,000 h^{-1} or 396 h^{-1} respectively.[14i,j] Based on our initial work we herein describe the zinc-catalyzed methanolysis of end-of-life poly(ε-caprolactone).

Initially, for optimization of the depolymerization reaction conditions commercially available poly(ε-caprolactone) (**1a**, PCL, M_n ~80,000 g/mol) was applied (Table 1). PCL (0.876 mmol with respect to the monomer unit), an excess of methanol (71.3 equivalents with respect to the monomer unit



Scheme 1. Chemical recycling concept for PCL.

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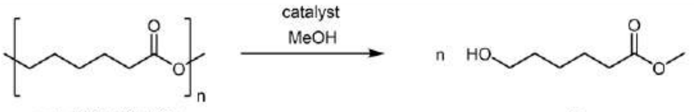
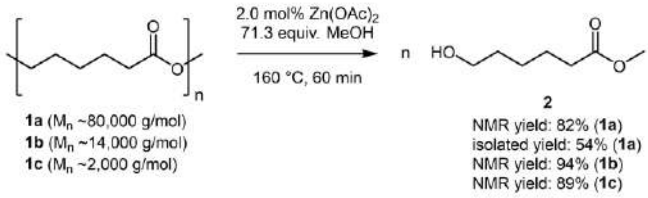
Table 1. Depolymerization of 1 a using zinc catalysis - optimization of reaction conditions.



Entry	Catalyst	Catalyst loading [mol %]	MeOH [equiv.]	T [°C]	t [min]	Yield **2** [%][b]	TOF [h^{-1}][c]
1	-	–	71.3	160	10	<1	<1
2	$Zn(OAc)_2$	1.0	71.3	160	10	48	288
3	$Zn(OAc)_2$	1.0	71.3	160	30	76	152
4	$Zn(OAc)_2$	1.0	71.3	160	60	74	74
5	$ZnCl_2$	1.0	71.3	160	10	<1	<1
6	$ZnBr_2$	1.0	71.3	160	10	<1	<1
7	$Zn(OTf)_2$	1.0	71.3	160	10	13	78
8	Zinc(II) methacrylate [$Zn(MA)_2$	1.0	71.3	160	10	73	438
9[d]	Poly(zinc(II) methacrylate)	1.0	71.3	160	10	12	72
10	KF	1.0	71.3	160	10	11	66
11	$Sn(Oct)_2$	1.0	71.3	160	10	42	252
12	$Sn(Oct)_2$	1.0	71.3	160	30	47	94
13	$Zn(OAc)_2$	1.0	71.3	140	10	40	240
14	$Zn(OAc)_2$	1.0	71.3	120	10	14	84
15	$Zn(OAc)_2$	2.0	71.3	180	5	39	468
16	$Zn(OAc)_2$	2.0	71.3	160	10	58	174
17	$Zn(OAc)_2$	0.5	71.3	160	10	36	432
18	$Zn(OAc)_2$	2.0	71.3	160	30	80	80
19	$Zn(OAc)_2$	1.0	89.1	160	10	43	258
20	$Zn(OAc)_2$	1.0	106.9	160	10	44	264

[a] Conditions: poly(ε-caprolactone) (**1 a**, 0.876 mmol) with respect to the monomer unit), catalyst (0-2.0 mol%, 0–0.0175 mmol with respect to the monomer unit of **1 a**), MeOH (71.3-106.9 equiv. with respect to the monomer unit of **1 a**), temperature: 120–180 °C (microwave heating), time: 5–60 min. [b] The yield of **2** bases on ^{1}HNMR spectroscopy. [c] The TOF was calculated: (mole product/mole catalyst)*h^{-1}. The TOF was calculated using the yield of **2** after the designated time. [d] 1,2,4-Trichlorbenzene (0.5 g) as cosolvent.

of **1 a**) and catalytic amounts of a zinc(II) acetate (1.0 mol%) were filled into a vial. Afterwards the mixture was stirred at 160 °C using microwave heating (MW) for 10 min, meanwhile the polymer completely dissolved in methanol (Table 1, entry 2). After cooling a sample was taken for determination of the yield/conversion utilizing ^{1}HNMR analysis. The formation of the depolymerization product **2** was confirmed by a singlet at $\delta = 3.67$ ppm, which matches to the methyl ester functionality of **2** (3H, $-C(=O)OCH_3$).[15] Moreover, a triplet at $\delta = 3.65$ ppm, which overlaps with signal of the methyl group of the ester function, was observed for the $HOCH_2$-function of **2** (2H). A second triplet was detected at $\delta = 2.33$ ppm for the $-CHCH_2C(=O)$-function of **2** (2H), which was overlapping with the $-CHCH_2C(=O)$-function of **1 a**. Based on the integrals of **1 a** ($-OCH_2$-function at $\delta = 4.05$ ppm) and the combined signal of **1 a** and **2** at $\delta = 2.33$ ppm the yield was calculated. In case of $Zn(OAc)_2$ as catalyst a yield of 48 % after 10 min was observed, which corresponds to a turnover frequency (TOF) of 288 h^{-1} (Table 1, entry 2), while in the absence of any catalyst no product formation was achieved (Table 1, entry 1). Moreover, the potential of other zinc salts was studied revealing in most case no or low product formation (Table 1, entries 5–7). Remarkable, if zinc(II) methacrylate [$Zn(MA)_2$] is applied a yield of 73 % was realized, while for the corresponding polymeric complex lower activity was observed (Table 1, entries 8–9). Moreover, literature known transesterification-depolymerization catalysts were tested, but only in case of $Sn(Oct)_2$ a reasonable yield was observed (Table 1, entry 11 and 12). Based on the results obtained with zinc catalysts, a positive effect of carboxylate ligands/anions on the formation of **2** is observed. Recently, Qu *et al.* observed also a positive effect of carboxylates using ionic liquids with carboxylate anions as catalyst for the methanolysis of poly(ethylene 2,5-furandicarboxylate).[16] It was proposed, that the carboxylate can act as activator for methanol to increase the nucleophilicity and therefore improve the conversion of the polymer. Based on that, the zinc can act as Lewis acid to activate the ester function of the polyester, while the acetate can activate the methanol. A decrease of the temperature revealed the formation of **2** in lower yields, while a temperature increase resulted in an increase of catalyst activities (Table 1, entries 13–15). For instance, at 180 °C a TOF of 468 h^{-1} was realized. Next the influence of the catalyst loading was investigated. Increasing the loading to 2.0 mol% showed an increase of product formation, while lowering the loading to 0.5 mol% revealed a decrease (Table 1, entries 16 and 17). After elongation of the reaction time to 30 min in the presence of 2.0 mol% $Zn(OAc)_2$ a yield of 80 % was observed (Table 1, entry 18). Furthermore, the amount of methanol was varied, but no significant effect was noticed (Table 1, entries 19 and 20). After optimization of the reaction conditions different PCL samples with different number average molar masses were tested (Scheme 2). Yields in the range of 82–94 % were obtained after 60 min at 160 °C, showing in tendency higher yields for PCL with low M_n.



Scheme 2. Depolymerization of PCL samples with different number average molar masses [Conditions: poly(ε-caprolactone) (1, 0.876 mmol) with respect to the monomer unit), $Zn(OAc)_2$ (2.0 mol%, 0.0175 mmol with respect to the monomer unit of 1), MeOH (71.3 equiv. with respect to the monomer unit of 1), temperature: 160 °C (MW), time: 60 min, the yield of **2** bases on ^1H NMR spectroscopy].

As seen in Table 1 entry 18 and Scheme 2 no significant difference in yield is detected after 30 min (80 %) or 60 min (82 %), which may indicate a deactivation of the catalyst during reaction progress. For a better understanding the yield vs. time dependency was investigated (Figure 1).

At the beginning the depolymerization is a very fast process, while with reaction progress the depolymerization slows down. After 90 min a new portion of $Zn(OAc)_2$ (2.0 mol%) was added, which leads to full conversion of **1 a**. Furthermore, for comparison the yield vs. time dependency of the depolymerization of **1 b** was carried out, revealing a higher turnover frequency of ~ 360 h^{-1} vs. ~ 300 h^{-1} at 50 % yield (Figure 1). A comparable activity was observed in the presence of zinc(II) methacrylate at 50 % yield with a TOF of 393 h^{-1}. However, in contrast to $Zn(OAc)_2$ with $Zn(MA)_2$ a higher activity is achieved in case of yields > 60 %. In addition, the yield-time dependency was studied at different temperatures (Figure 2 and 3).

The highest turnover frequency of ~ 754 h^{-1} [$Zn(OAc)_2$] and 943 h^{-1} [$Zn(MA)_2$] was calculated at 50 % yield of product **2** at 170 °C. The reaction rate constant at 170 °C for the methanolysis of **1** was 0.0031 s^{-1} ($Zn(OAc)_2$) and 0.0059 s^{-1} ($Zn(MA)_2$) (pseudo first order). Moreover, the activation energy ($Zn(OAc)_2$:

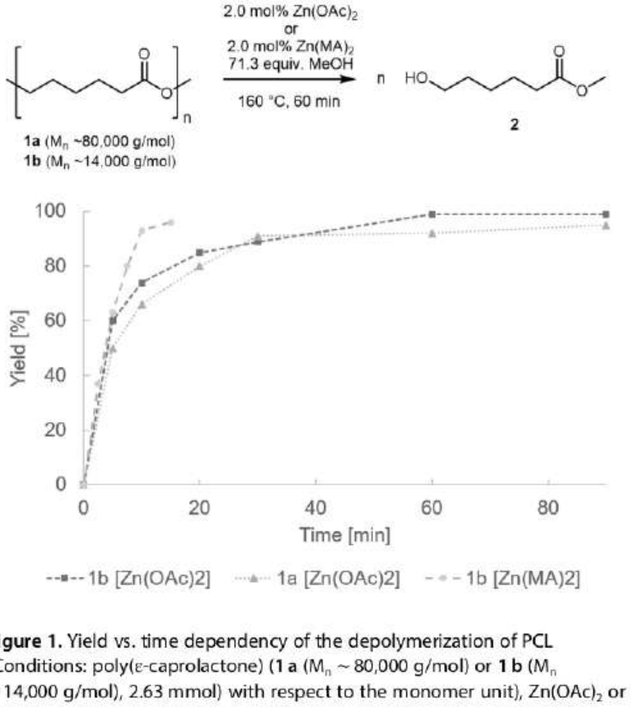


Figure 1. Yield vs. time dependency of the depolymerization of PCL [Conditions: poly(ε-caprolactone) (**1 a** (M_n ~ 80,000 g/mol) or **1 b** (M_n ~ 14,000 g/mol), 2.63 mmol) with respect to the monomer unit), $Zn(OAc)_2$ or $Zn(MA)_2$ (2.0 mol%, 0.0526 mmol with respect to the monomer unit of 1), MeOH (71.2 equiv. with respect to the monomer unit of **1**), temperature: 160 °C (MW), the yield of **2** bases on ^1H NMR spectroscopy].

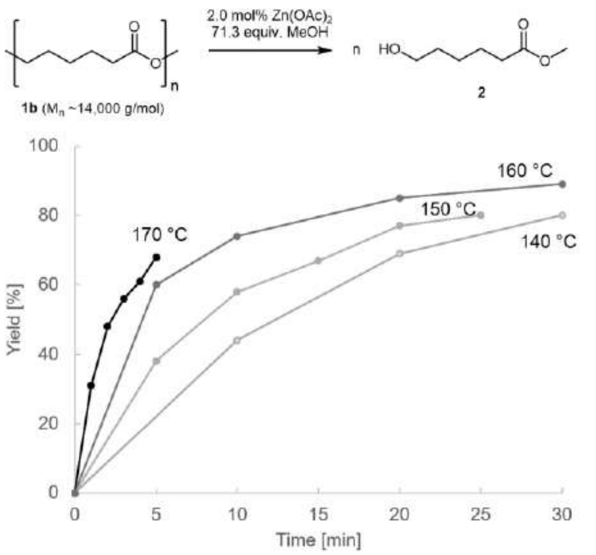


Figure 2. Yield vs. time dependency at different temperatures of the depolymerization of PCL [Conditions: poly(ε-caprolactone) (**1 b** (M_n ~ 14,000 g/mol),, 2.63 mmol) with respect to the monomer unit), $Zn(OAc)_2$ (2.0 mol%, 0.0526 mmol with respect to the monomer unit of **1 b**), MeOH (71.2 equiv. with respect to the monomer unit of **1 b**), temperature: 140–170 °C (MW), the yield of **2** bases on ^1H NMR spectroscopy].

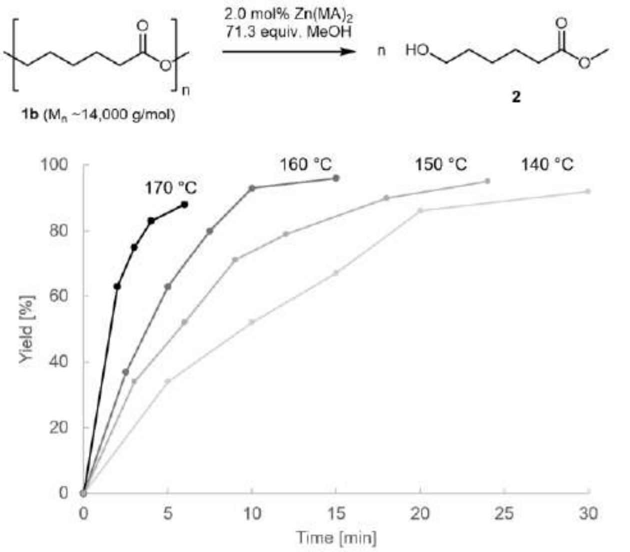
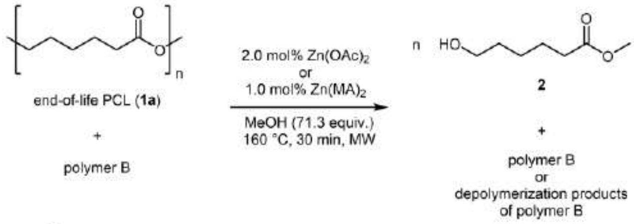


Figure 3. Yield vs. time dependency at different temperatures of the depolymerization of PCL [Conditions: poly(ε-caprolactone) (**1 b** (M_n ~ 14,000 g/mol),, 2.63 mmol) with respect to the monomer unit), $Zn(MA)_2$ (2.0 mol%, 0.0526 mmol with respect to the monomer unit of **1 b**), MeOH (71.2 equiv. with respect to the monomer unit of **1 b**), temperature: 140–170 °C (MW), the yield of **2** bases on ^1H NMR spectroscopy].

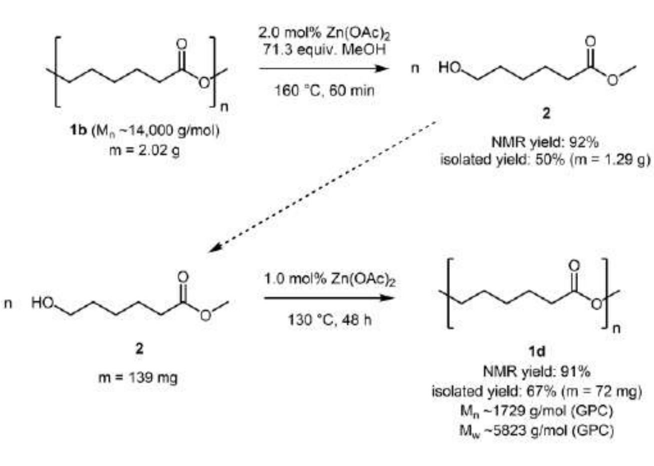
90.9 kJ mol^{-1}; Zn(MA)$_2$: 74.0 kJ mol^{-1}) and the frequency factor (Zn(OAc)$_2$: 1.5 10^8 s^{-1}; Zn(MA)$_2$: 3.3 10^7 s^{-1}) were calculated.[17] In various cases the product formation slows down at a certain point, which can be caused by catalyst deactivation or an equilibrium. (Figure 2 and 3). Therefore, the experiment at 140 °C with Zn(OAc)$_2$ as catalyst was repeated and after 20 min a new portion of the catalyst was added. With the additional catalyst portion a yield of 91 % was achieved after 20 min compared to 80 %. Moreover, addition of a fresh portion of **1b** revealed a yield of 57 % of **2**, which means full conversion the "original" portion.

Table 2. Depolymerization of PCL in the presence of additional polymers.



Entry[a]	Additional polymer B	Yield of **2** [%] [Zn(OAc)$_2$] [b,c]	Yield of **2** [%] [Zn(MA)$_2$] [b,c]
1	–	76	92
2	Nylon 6	80	94
3	Poly(phenylene sulfide) (PPS)	79	95
4	Poly(ethylene) (PE) (M_n ~ 1,700 g/mol)	77	93
5	Poly(styrene) (PS) (Mw ~ 35,000 g/mol)	76	>99
6	Poly(vinyl chloride) (PVC) (Mw ~ 48,000 g/mol)	85	95
7	Poly(ethylene glycol) methyl ether (M_n ~ 5,000 g/mol)	80	95

[a] Conditions: Poly(ε-caprolactone) (**1a**), 0.876 mmol with respect to the monomer unit), Zn(OAc)$_2$ (2.0 mol%, 0.0175 mmol with respect to the monomer unit of **1a**) or Zn(MA)$_2$ (1.0 mol%, 0.00875 mmol with respect to the monomer unit of **1a**), MeOH (71.3 equiv. with respect to the monomer unit of **1a**), temperature: 160 °C (microwave heating), time: 30 min. [b] The yield of **2** bases on ^{1}HNMR spectroscopy. [c] No decomposition of the additional polymer was observed by ^{1}HNMR spectroscopy.



Scheme 3. Scale-up of depolymerization of PCL and subsequent polymerization.

Afterwards, the depolymerization of PCL was studied in the presence of different types of polymers, which can be useful for plastic separation (Table 2). In detail, PCL **1a** was mixed with another polymer. The depolymerization reaction was carried out with 2.0 mol% of Zn(OAc)$_2$ or 1.0 mol% Zn(MA)$_2$ and methanol (71.3 equiv.) at 160 °C for 30 min. In most cases the additional polymer has no significant effect on the depolymerization outcome as noticed for "pure" PCL depolymerization.

Subsequently, a scale-up of the depolymerization was carried out for PCL **1b** (Scheme 3). After performing the reaction at 160 °C for 60 min the excess of methanol and product **2** were removed from the reaction mixture by distillation under vacuum. Next the methanol was removed to obtain **2** as colourless liquid in 50 % yield after distillation. With depolymerization product **2** in hand the polymerization was performed (Scheme 3). In more detail, **2** and catalytic amounts of Zn(OAc)$_2$ were heated at 130 °C for 48 hours. After cooling a sample was sent to ^{1}HNMR analysis for yield/conversion determination. The formation of the polymer **1d** was verified by the presence of a multiplet at $\delta = 4.03\text{-}4.06$ ppm (CH_3CHO-function of **1d**) and an NMR yield of 91 % was monitored. GPC measurements revealed values of M_n ~ 1729 g/mol and M_w ~ 5823 g/mol.

In summary, we have installed a chemical recycling for end-of-life poly(ε-caprolactone). In detail, the protocol is composed of a zinc-catalyzed depolymerization of PCL via transesterification using methanol. As suitable product methyl 6-hydroxyhexanoate is formed in good yields using simple Zn(OAc)$_2$ as catalyst under microwave heating. In a second step the methyl 6-hydroxybutanoate is polymerized in the presence of catalytic amounts of Zn(OAc)$_2$ to obtain new PCL in yields of 67 % and M_n ~ 1729 g/mol and M_w ~ 5823 g/mol.

Supporting Information Summary

The experimental details including the depolymerization and polymerization reactions and product characterizations can be found in the supporting information.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: catalysis · depolymerization · green chemistry · polymers · recycling

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5.6 Depolymerization of Nylon 6

The amide bond in PAs is difficult to cleave by means of RCD. In literature known examples, the amide bond is activated by applying Lewis-basic catalysts to increase the nucleophilicity. In this regard, we wondered if increasing the electrophilicity by chemical modification can govern the backbiting mechanism. Therefore, we attempted the activation by applying Ac_2O as depolymerization reagent that converts the amides functionalities to acyl-imides.[262] Based on the observed intermediates, an underlying reaction pathway was determined. Again, a set of household goods was converted to *N*-acetyl ε-caprolactam and the scale was extended to 70 g of screw anchors. The obtained product was then converted to ε-caprolactam (**33**) selectively by cleavage of the acetyl function. This was accomplished with an amino alcohol to yield the corresponding amide. For this purpose, an amine was chosen that can be used as feedstock for a polymer.

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Sustainable Chemistry

Chemical Recycling of End-of-Life Polyamide 6 via Ring Closing Depolymerization

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The chemical recycling of end-of-life polymers, a sequence of depolymerization and polymerization reactions, enables the conserving of fossil resources and can add some value to the circular economy. In this study, a process for the depolymerization of end-of-life Nylon 6 via ring-closing reactions to produce as building block *N*-acetylcaprolactam have been set up. In detail, a combination of acetic anhydride as depolymerization reagent and catalytic amounts of 4-dimethylaminopyridine allows under microwave irradiation and within short times (15 min) the conversion of end-of-life Nylon 6 to *N*-acetylcaprolactam under solvent-less conditions. Applying optimized conditions a sequence of Nylon 6 goods was transformed in good yields. The product *N*-acetylcaprolactam was converted to ε-caprolactam by transfer of the acetyl functionality to 2-aminoethanol to give *N*-(hydroxyethyl)acetamide a precursor for poly(*N*-vinylacetamide). The generated ε-caprolactam can be used as monomer for the synthesis of new Nylon 6, therefore a chemical recycling of the monomeric unit of Nylon 6 is feasible.

To handle the increasing amounts of end-of-life plastics generated by modern society the current plastic waste management is composed of landfill storage, recycling and combustion (energy recovery).[1–4] Moreover, a significant portion of the waste stream is (unregulatedly) discharged from the anthroposphere to the biosphere/atmosphere.[4] Nowadays most of the plastic waste is "stored" in landfills which causes environmental problems.[5] Another portion of the plastic waste stream is subjected to incineration, which allows the recovery of the energy and yields small molecules e.g. carbon dioxide, which are difficult to (re)convert into valuable molecules. On the other hand, recycling strategies, e.g. mechanical recycling for end-of-life plastics have been established. It is defined as a reprocessing, e.g. by melting and reextrusion to form plastic parts with new shape.[5–7] Due to degradation of the virgin material and additives, fillers and impurities the material loses its quality after each cycle, which leads to a decreased plastic quality after some cycles. As a consequence, the material undergoes a downcycling and can potentially be subjected to incineration or landfill storage.[8–11] The recycling method which circumvents these issues can be the chemical recycling. Hereby, the polymeric material is depolymerized to monomers or precursors for monomers that can be polymerized to generate new polymers with adjustable properties.[8,12,13] Importantly, the basic chemical structure of the repeating units are not changed and can be cycled in the anthroposphere. In consequence, no additional fossil resources are required. In contrast to other recycling methods the properties/quality of the new materials are not coupled to the properties/quality of the virgin feedstock material. So far the application of chemical recycling processes is limited due to high energy demand and sensitivity to contaminations like copolymers, additives and fillers and therefore resulting in higher costs compared to plastics prepared from fossil resources.[7] Nevertheless, new robust methods may enable the end-of-life plastics as a resource-efficient and cost-efficient feedstock for new plastics. For instance, Nylon 6 (**1**) is a versatile polymer with a broad scope of applications, due to its high chemical stability and straightforward access from fossil resources.[14] The industrial synthesis starts with the hydrogenation of benzene and subsequent oxidation to cyclohexanone, which is converted with hydroxylamine to cyclohexanone oxime. A Beckmann rearrangement allows access to the monomer ε-caprolactam (**3**). Via ring opening polymerization of ε-caprolactam (**3**) Nylon 6 at ~250 °C is produced in an annual worldwide multi million ton scale.[15–21] With respect to chemical recycling of Nylon 6 some procedures have been developed. For instance, depolymerization of Nylon 6 involving acidic hydrolysis yielding 6-aminocaproic acid as well as oligomers has been studied.[22–26] Thermal decomposition under pyrolytic conditions[27–34] and sub- und supercritical fluids[35–39] applying high temperature and pressure results in the formation of low molecular weight chemicals. However, high energy input and extensive separation is required. An alternative was reported by Kamimura and coworkers by applying ionic liquids as reaction media and 4-dimethylaminopyridine (DMAP) as organocatalyst for the ring-closing depolymerization of Nylon 6 forming ε-caprolactam in high yields and selectivity at high temperatures (300 °C) and

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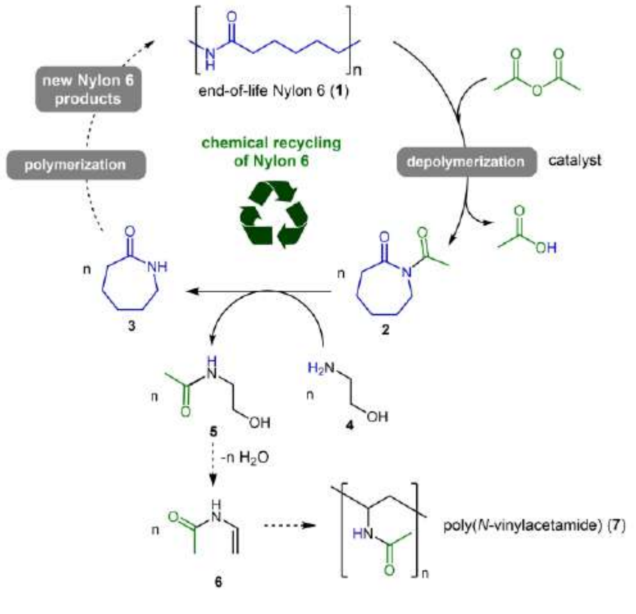
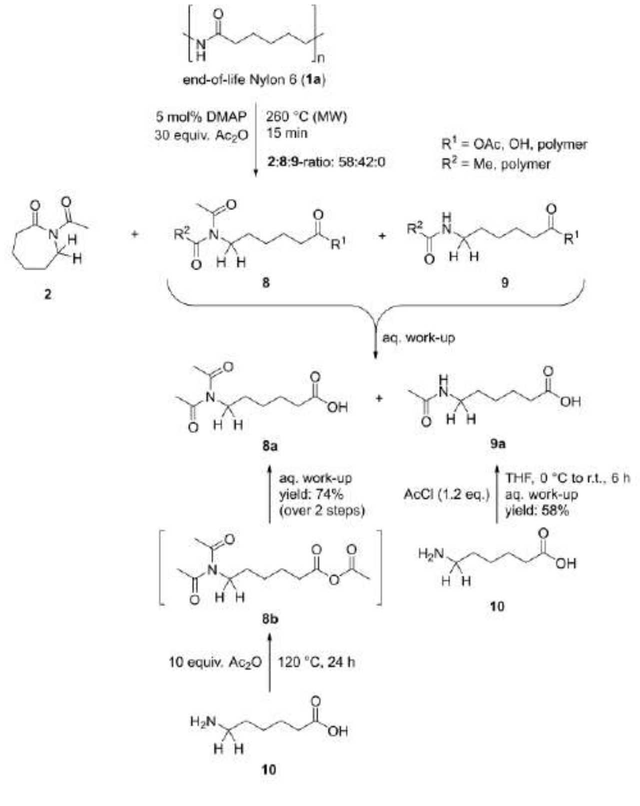
within short reaction times (60 min). Purification of the product was carried out by extraction or distillation to isolate the monomer **3** and to recover the ionic liquid. However, under these conditions the ionic liquid tends to decompose, which hampers the overall atom economy of this procedure.[40–43]



Scheme 1. Valorization strategy for end-of-life Nylon 6 (**1**).



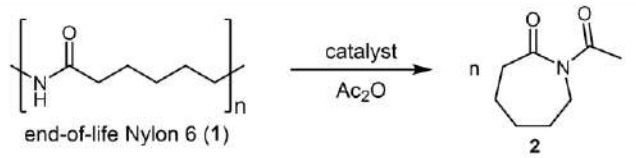
Scheme 2. Depolymerization of Nylon 6 with acetic anhydride.

Recently, we have demonstrated the application of acetic anhydride as depolymerization reagent in the depolymerization of poly(bisphenol A carbonate) in the presence of DMAP as catalyst.[44] As major product diacetylated bisphenol A was obtained. In this regard, we became interested in the transfer of this concept to the depolymerization of Nylon 6 (**1**) (Scheme 1). In more detail, as depolymerization product the *N*-acylated ε-caprolactam (**2**) will be formed. To convert compound **2** to the industrial relevant **3** a deacetylation process is required.

To minimize the amount of waste and to fulfill the requirements of the "Principles of Green Chemistry" a transfer of the acetyl functionality is envisaged.[45] In more detail, a transfer to 2-aminoethanol (**4**) gives *N*-(hydroxyethyl)acetamide (**5**) a precursor for poly(*N*-vinylacetamide).[46–48]

First, we investigated the depolymerization of Nylon 6 (**1 a**) using Ac_2O as depolymerization reagent. Therefore, **1 a** (1.0 mmol with respect to the repeating unit) was mixed with Ac_2O (30 equiv.), DMAP as catalyst (5.0 mol%), and a stir bar in a vial and heated under microwave irradiation at 260 °C for 15 min (Scheme 2). After cooling to ambient temperature, an aliquot of the solution was diluted with chloroform-d_1 for ^{1}H NMR analysis. In more detail, at 3.79-3.85 ppm a multiplet was observed, which can be assigned to the NCH_2-function of the *N*-acylated ε-caprolactam (**2**). Moreover, at 2.41 ppm a singlet for the acetyl functionality ($C(O)CH_3$) of **2** was detected, which indicates the formation of the desired product. Besides, signals for residual polymers or oligomers were observed. Especially, signals for acyclic products containing amide functions, like $R^2C(O)NHCH_2(CH_2)_4C(O)R^1$ (**9**: 3.19-3.27 ppm), and acetylimides, like $((CH_3C(O))(R^2C(O))N)\ CH_2(CH_2)_4C(O)R^1$ (**8**: 3.57-3.65 ppm) (Scheme 2). The occurrence of both functionalities indicates the cleavage of the polyamide chain at the original amide function. Both functions were clarified with model compounds using 6-aminohexanoic acid (**10**) as starting material. For instance acylation of **10** with acetic anhydride (10 equiv.) at 120 °C for 24 h and subsequent aqueous work-up resulted in the formation of **8 a** in 74% yield. Compound **9 a** was obtained by acylation of **10** with 1.2 equiv. AcCl followed by an aqueous work-up in 58% yield (Scheme 2). Both monomeric compounds can also be found after an aqueous work-up of the depolymerization reaction mixture. Moreover, compound **8 a** can be acetylated at the acid functionality to obtain the acetylimides anhydride **8 b**, which can be seen as an intermediate in the depolymerization. A relation of the NMR signals for **2**:**8**:**9** revealed a ratio of 58:42:0, while for the starting polymer no signals have been detected. Interestingly, when no catalyst was applied the polymer was completely consumed and compound **2** was found in a somewhat lower amount, while the amount of **8** was increased (Table 1, entry 2). A catalyst loading of 1.0 mol% led to a decreased yield of **2**, while the yield increased slightly when a higher loading of 10.0 mol% DMAP was applied (Table **1**, entries 3 and 4). Moreover, extension of the reaction time to 30 min improved the yield by 8% for **2** (Table 1, entry 5). Next, we studied the influence of the Ac_2O loading. Applying 5 equiv. of Ac_2O gave an increased yield of 73% of **2** (Table 1, entry 6). When no

Table 1. Optimization of the depolymerization of Nylon 6 (**1a**).



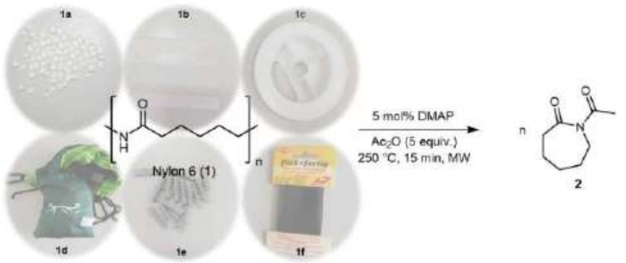
Entry[a]	Catalyst [mol %]	Ac$_2$O [equiv.]	T [°C]	t [min]	ratio **2**:**8**:**9**[b]
1	DMAP (5)	30	260	15	58:42:0
2	-	30	260	15	52:48:0
3	DMAP (1)	30	260	15	56:44:0
4	DMAP (10)	30	260	15	62:38:0
5	DMAP (5)	30	260	30	66:34:0
6	DMAP (5)	5	260	15	73:21:6
7	-	5	260	15	70:25:5
8	DMAP (5)	1.5	260	15	68:15:17[c]
9	DMAP (5)	5	240	15	59:30:11
10	-	5	240	15	45:47:8
11	DMAP (5)	5	220	15	35:51:14
12	-	5	220	15	22:67:11
13	DMAP (5)	30	200	15	0:100:0
14	DMAP (5)	30	180	15	0:83:17
15	DMAP (5)	30	160	15	-[d]
16	DMAP (5)	30	280	15	-[e]
17	$AlCl_3$ (5)	5	260	15	67:24:9
18	$Zn(OAc)_2$ (5)	5	260	15	72:21:7
19	$Sn(Oct)_2$ (5)	5	260	15	70:22:8
20	DBU (5)	5	260	15	70:20:10
21	DABCO (5)	5	260	15	71:24:6

[a] Reaction conditions: Nylon 6 (**1a**) (1 mmol based on the repeating unit of **1**), catalyst (0-10 mol%, 0–100 μmol based on the repeating unit of **1**), Ac$_2$O (1.5-30 equiv. based on the repeating unit of **1a**), microwave heating, 160–280 °C, 15–30 min. [b] The ratio of **2**:**8**:**9** base on ^{1}H NMR data. Full conversion (> 99%) of **1a** was detected. [c] Nylon 6 was not fully dissolved. [d] The Nylon 6 (**1a**) did not dissolve. [e] Decomposition was observed.

catalyst was applied under these conditions, the yield slightly decreases by 3% (Table 1, entry 7). Nevertheless, a further reduced loading of only 1.5 equiv. resulted in incomplete dissolution of the polymer (Table 1, entry 8). As next parameter the temperature was studied (Table 1, entries 9–16). Decreasing the temperature resulted in a decrease of product **2** formation, while the catalyst has a higher influence on product formation at lower temperatures (Table 1, entries 9–12). A further decrease in temperature to 160 °C gave no conversion. An increase to 280 °C revealed the decomposition of the Nylon 6 (**1a**) and an insoluble black solid was formed. Finally, different catalysts were tested (Table 1, entries 17–21). However, the obtained results did not outperform DMAP.

Following, the depolymerization of Nylon 6 (**1**) was performed on a larger scale using the polymer **1a** (Table 2, entry 1). In more detail, optimized conditions were applied (5 mol% DMAP, 5 equiv. Ac$_2$O, 250 °C, 15 min). After cooling to ambient temperature the reaction mixture was transferred to a distillation apparatus containing a Vigreux-column. Residual AcOH and Ac$_2$O were removed from the reaction mixture by vacuum distillation at 50 °C. Subsequently, the dark residue was transferred to a Kugelrohr distillation apparatus and *N*-acetylcaprolactam (**2**) was distilled-off (1.5 mbar, 110 °C oven temperature) and was isolated as colorless oil in 78% yield.

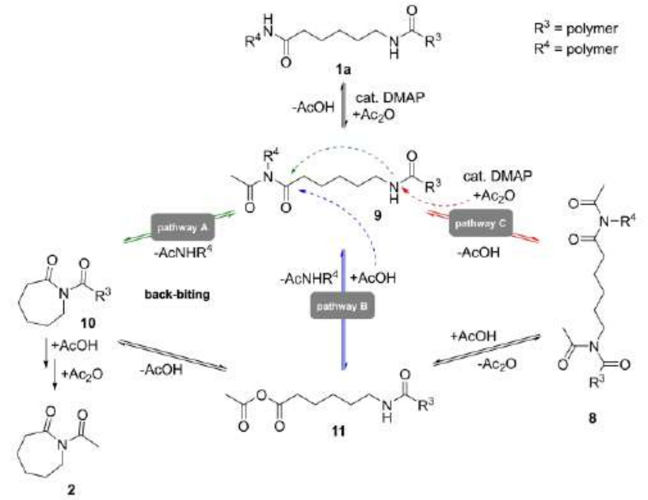
Table 2. DMAP catalyzed depolymerization of different Nylon 6 (**1a-f**) commodities.



Entry[a]	Commodity (mass [g])	Ac$_2$O [equiv.]	Mass of **2** [g]	Yield of 2 [%][b]	Yield of 2 [wt %][c]
1	pellets (1.51 g) (**1a**)	5	1.62	78	107
2	pellets (1.52 g) (**1a**)	5[d]	1.46	70	96
3	test stripe (2.21 g) (**1b**)	5	2.02	67[e]	91
4	thread (1.21 g) (**1c**)	11	1.09	66[e]	90
5	hammock (1.50 g) (**1d**)	5	1.08	52[e]	72
6a	screw anchors (2.27 g) (**1e**)	5	1.62	52[e]	71
6b	screw anchors (70.5 g) (**1e**)	5	45.4	47[e,f]	64
7	patch (1.55 g) (**1f**)	5	0.424	20[e]	27

[a] Reaction conditions: Nylon 6 (**1**) (10.7-20.1 mmol based on the repeating unit, it was assumed that the good contains 100% Nylon 6), DMAP (5 mol%, 557 μmol-1.05 mmol based on the repeating unit of **1**), Ac$_2$O (5-11 equiv. based on the repeating unit of **1a**), microwave heating, 250 °C, 15 min. [b] Isolated yield. **2** was isolated by distillation. The yield is based on the assumption that the good contains 100% Nylon. [c] The yield is based on the weight of the initial Nylon 6 good. [d] A mixture of redistilled AcOH and Ac$_2$O was applied. [e] A heterogeneous solution with insoluble residue was formed. [f] A temperature of 230 °C was reached after 10 min and hold for 5 minutes.

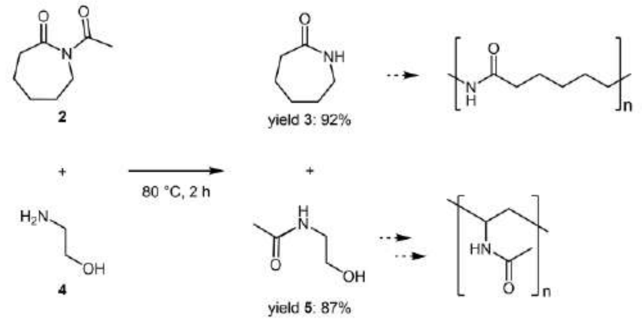
Importantly, the mixture of distilled-off Ac$_2$O and AcOH (~ 60vol% of initial Ac$_2$O) was suitable for further depolymerizations, however revealing a decreased yield of 70% in comparison to pure Ac$_2$O (Table 2, entry 2). Based on experimental findings we assume that the degradation process involves an acetylation of an amide function of the polymer and a subsequent cleavage of the formed imide bond by a backbiting mechanism involving the neighboring amide functionality to produce the cyclic product **10**, which can be transformed to the desired product **2** (Scheme 3, pathway A). Alternatively, the imide function in the polymer backbone can be cleaved by acetic acid (pathway B) yielding the anhydride forming **11** that can undergo cyclization generating **10** and acetic acid. Moreover, **9** can be further acylated by Ac$_2$O to obtain compound **8**, which can be after reaction with acetic acid converted to **11** (pathway C). Afterwards the applicability of this method to convert household commodities containing Nylon 6 (**1**) was investigated (Table 2). In this regard, **2** was isolated in 67% yield from a transparent test stripe (**1b**) (Table 2, entry 3). A similar isolated yield (66%) was realized with a transparent



Scheme 3. Proposed mechanism for the ring closing depolymerization.

Nylon 6 thread (**1 c**), but a higher amount of Ac_2O was required to cover **1 c** with Ac_2O (Table 2, entry 4). In contrast to **1 a**, the reaction mixture after 15 min was an inhomogeneous dark solution, which may results from plastic additives. Nevertheless, the impurities remained in the residue during distillation of **2**. Moderate isolated yields of 52% (**2**) were observed in case of a colored Nylon 6 hammock (**1 d**) and screw anchors (**1 e**) (Table 2, entries 5 and 6). A low yield of 20% (**2**) was found for a black patch (**1 f**) with a glued surface (Table 2, entry 7). Furthermore, the scale was enhanced to 70.5 g of screw anchors (**1 e**) using optimized conditions. ^{1}H NMR analysis of the crude reaction mixture revealed a signal ratio of the main products of 53:35:12 (**2**:**8**:**9**). The time span required for heating in this microwave set-up was significantly increased to 10 minutes and the temperature of 230 °C was hold for only 5 minutes. However, an isolated yield of 45.4 g (47%) was obtained after distillative purification (Table 2, entry 6b).

Finally, we studied the conversion of **2** to ε-caprolactam (**3**), the established monomer for Nylon 6 production by deacetylation (Scheme 3). In consequence the cycle presented in Scheme 1 can be closed.[15–21,49] To increase the atom efficiency we aimed to incorporate the acetyl functionality in a suitable molecule by trans-acetylation. It was reported that **2** reacts as acylation reagent with amines to the corresponding amides in high selectivities.[50] As an amine source we have chosen ethanolamine (**4**) (Scheme 4). The reaction of an equimolar mixture of **2**:**4** was performed by a neat heating at 80 °C for 2 hours. ^{1}H NMR investigations of the reaction mixture showed the formation of **3** and *N*-(2-hydroxyethyl)acetamide (**5**). The formation of **3** was indicated by new ^{1}H NMR signals for the CH_2CONH function at 3.15-3.22 ppm and the NCH_2 function at 2.41-2.47 ppm. The presence of compound **5** was indicated by the presence of new signals for HNCH_2 function at 3.36-3.41 ppm and for CH_2OH function at 3.68-3.72 ppm and a new singlet for the C(O)CH_3 function at 1.99 ppm. The compounds **3** and **5** were separated by column chromatography and **3** was isolated in 92% and **5** in 87% yield, respectively. We also attempted to separate both products by vacuum distillation via a Vigreux column (4.0 mbar, oil bath temperature: 120–180 °C), which resulted in only a partial separation due to similar boiling points.



Scheme 4. Synthesis of ε-caprolactam (**3**) and *N*-(2-hydroxyethyl)acetamide (**5**).

Nevertheless, as reported in the literature chemical **5** can be dehydrated to generate *N*-vinylacetamide,[51] which allows access to polyolefins with interesting properties.[46,47,52–54]

In summary, we developed a method for the depolymerization of Nylon 6 using DMAP as organocatalyst and acetic anhydride as cheap and abundant depolymerization reagent. As low-molecular weight chemical *N*-acetylcaprolactam was isolated in good yields after microwave heating at 250 °C for 15 min which is by far lower than the reaction temperatures and times reported for existing methods and also. Furthermore, we successfully applied the methods on a set of household goods, which proved the practicability and robustness of the methodology. Therefore, the depolymerization product *N*-acetylcaprolactam had to be converted to ε-caprolactam, which is used for the synthesis of new Nylon 6 and therefore closing the cycle. Moreover, the acetyl function can be embedded into a precursor for poly(vinylacetamide).

Supporting Information Summary

The experimental details including the depolymerization reactions and product characterization can be found in the supporting information.

Acknowledgements

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Keywords: Catalysis · Chemical Recycling · Depolymerization · Green Chemistry · Nylon 6

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5.7 Depolymerization of poly(bisphenol A carbonate) via hydrogenation

In the study by Krall *et al.* the Milstein precatalyst (**35**) was successfully applied to a few polycarbonates except PBAC (**2**). In this context, we attempted to transfer this catalytic system to PBAC (**2**) and evaluate the influence of reaction parameters.[263] A minimal reaction temperature of 120 °C was required and the reaction procedes already at 10 bar H_2. However, to achieve full conversion, at least 2.5 mol% of the Milstein catalyst (**35a**) were required. Overall, the addition of KO*t*Bu had a beneficial effect on the yield of BPA (**1**) which might be due to the activation of the carbonyl function by potassium cations. Finally, the reaction was applied to PBAC (**2**) from DVD material that was a) used directly after crushing or b) was extracted from the DVD to remove insoluble residues. Thereby, the obtained yield was only slightly (73% vs. 86% isolated yield) affected by the insoluble components.

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Ruthenium-Catalyzed Hydrogenative Depolymerization of End-of-Life Poly(bisphenol A carbonate)

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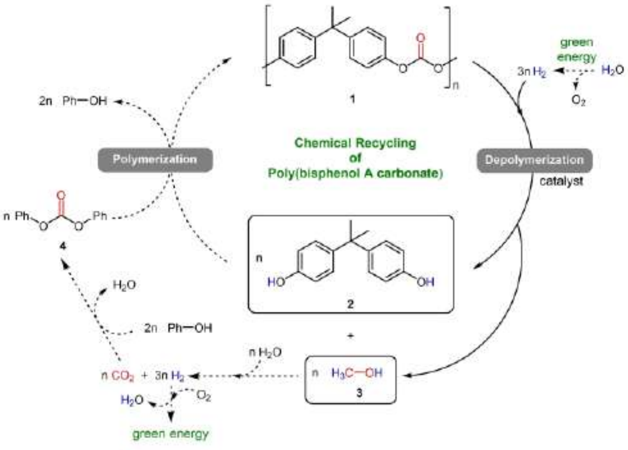
The conversion of end-of-life products to useful chemicals (waste-to-chemicals) can afford a resource-efficient economy. In this context, the depolymerization of end-of-life polymers to yield low molecular weight chemicals can be an interesting target. Based on that, the selective depolymerization of end-of-life poly(bisphenol A carbonate) via hydrogenation was studied. Applying hydrogen and a ruthenium(II) complex as catalyst (Milstein Catalyst) end-of-life poly(bisphenol A carbonate) was hydrogenated to bisphenol A and methanol. The bisphenol A can be reused for the production of fresh polycarbonates; therefore a recycling is possible. On the other hand methanol can be used as hydrogen carrier and can be subjected to the hydrogen economy.

Each year a growing quantity of End-of-Life (EoL) plastics[1] is generated arising from non-renewable resources.[2] The present waste management for plastic waste streams is composed of energy recovery, landfill storage, and recycling such as mechanical recycling and downcycling.[3,4,5] The main treatment method (energy recovery) and in consequence also intermediate steps like the mechanical recycling or down-cycling change the polymer structure to unsuitable chemicals (e.g. CO_2) and release the stored chemical energy. Obviously, for substitution of these plastics the limited fossil resources has to be shortened.[6,7] As a resource-efficient and sustainable option the chemical recycling can be considered.[8] Basically, the EoL-polymer is transformed in a depolymerization reaction to monomers or appropriate chemicals, which can be utilized in a following polymerization to manufacture fresh polymers. Consequently, a polymer recycling is conceivable. Significantly, the abilities of the new polymer are not associated to the value of the EoL-polymer as described for mechanical recycling and downcycling. Nonetheless, currently the chemical recycling is only applied for a minor portion of EoL-polymers, due to several issues e.g. energy demand, additives, costs.[9] To advance the potential of chemical recycling, novel methodologies and improvements of existing protocols are worthwhile.[10,11] A well-established class of polymers are polycarbonates, especially poly(bisphenol A carbonate) (**1**) originated from bisphenol A, which has found a wide range of applications (Scheme 1).[12] In case of EoL-poly(bisphenol A carbonate) treatment all kinds of approaches have been accounted, e.g. energy recovery, mechanical recycling, blends, pyrolysis and biochemical degradation. Moreover, several chemical recycling methodologies have been studied.[13] Recently, Klankermayer and coworkers reported on a recycling concept based on the hydrogenation of **1**.[14,15,16] In detail, in the presence of a ruthenium(II) catalyst ([Ru(tmmm)(triphos)][17]) the carbonate function of **1** was efficiently hydrogenated to yield as low molecular weight chemicals bisphenol A and methanol in good isolated yields (73%) and excellent selectivities (catalyst loading: 0.5 mol%, 0.5 mol% $HNTf_2$, 140 °C, 1,4-dioxane, H_2: 90 bar, 16 h). Interestingly, the bisphenol A can be used directly as monomer together with diphenyl carbonate to produce new **1** following the industrial manufacturing (Scheme 1).[18] On the other hand, the produced methanol can be seen as hydrogen carrier/storage and can be utilized in methanol fuel cells or after decomposition to carbon dioxide and hydrogen in fuel cells for electric energy production.[19] An amount of ~2.4 wt% of hydrogen can be stored in the repeating unit of EoL-**1**. Based on that, a coupling of depolymerization of End-of-Life plastics with energy (hydrogen) storage is feasible. In this regard, we consider if the well-



Scheme 1. Chemical recycling concept for poly(bisphenol A carbonate) via carbonate hydrogenation.

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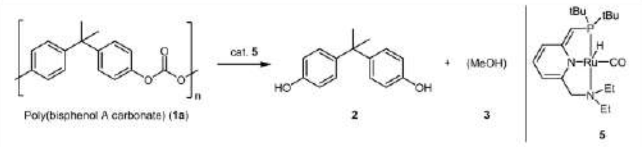
established Milstein catalyst (**5**), which has demonstrated excellent performance in the hydrogenation of organic ester derivatives, is able to hydrogenate the carbonate functionality of poly(bisphenol A carbonate) (**1**).[20,21] Interestingly, the potential of the Milstein catalyst was demonstrated in the hydrogenative depolymerization of poly(propylene carbonate) producing propane-1,2-diol (catalyst loading: 1.0 mol%, 160 °C, THF/anisole, H_2: ~55 bar, 24 h).[15] We state herein our investigations on a conception for the chemical recycling of the bisphenol A unit of EoL-**1** applying the Milstein catalyst (Scheme 1).[22]

Primarily, the depolymerization of **1 a** (pellet dimension: ~3 mm) was studied (Table 1). In this context, **1 a** (1.35 mmol based on the repeating unit) and catalytic amounts of complex **5** (5 mol% based on the repeating unit of **1 a**) were dissolved in THF. The reaction mixture was transferred to an autoclave, which was pressurized with hydrogen (45 bar). Subsequently the stirred mixture was heated at 140 °C for 24 hours (Table 1, entry 3). After cooling the mixture to ambient temperature $CDCl_3$ was added to an aliquot for ^1H NMR spectroscopy. In the spectrum a signal at 1.61 ppm ($C(CH_3)_2$, 6H) and two groups of signals (2x4H) of aromatics C–H were identified (7.06-7.07, 6.70-6.71 ppm). The signals are assigned to **2**.[23] The NMR yield of bisphenol A was gained by linking the integral of the signal of **2** ($2xCH_3$) to the integrals of the leftover of polymer **1**. A yield of 99% for **2** was realized. Noteworthy, methanol was not detected, because of technical limitations (see SI).

Table 1. Ruthenium-catalyzed depolymerization of **1 a**.



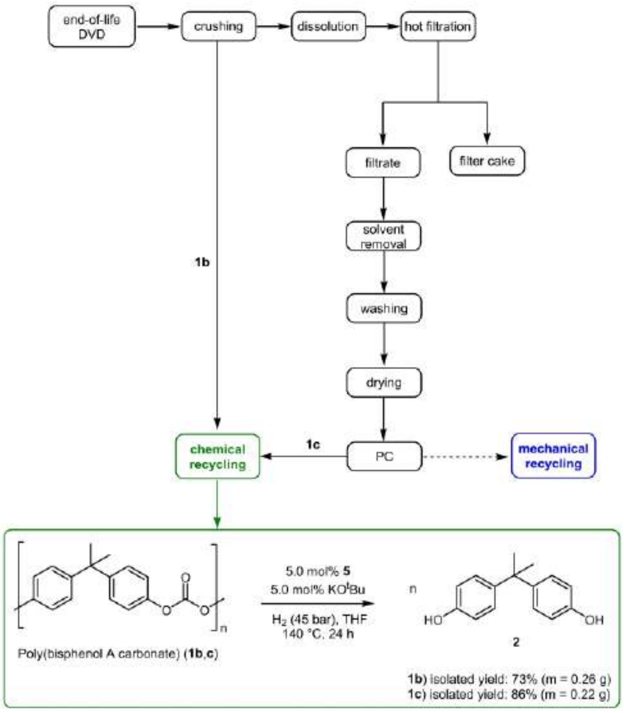
Entry[a]	Catalyst loading **5** [mol%]	KO^{t}Bu [mol%]	T [°C]	t [h]	p [bar]	Yield **2** [%][b]
1	0	0	140	24	45	<1
2	0	5.0	140	24	45	<1
3	5.0	0	140	24	45	95
4	5.0	5.0	140	24	45	99 (91)[c]
5	2.5	5.0	140	24	45	93
6	1.0	5.0	140	24	45	79
7	0.5	5.0	140	24	45	49
8	2.5	5.0	140	6	45	70
9	2.5	2.5	140	6	45	69
10	1.0	5.0	140	6	45	24
11[d]	1.0	5.0	140	6	45	16
12	2.5	25.0	120	24	45	76
13	2.5	0	120	24	45	43
14	5.0	10.0	120	24	45	52
15	5.0	10.0	120	24	20	42
16	5.0	10.0	120	24	10	37
17	2.5	25.0	100	24	45	<1

[a] Reaction conditions: **1 a** (1.35 mmol), **5** (0-5 mol%, 0–0.0675 mmol based on the repeating unit of 1 a), KO^{t}Bu (0-25 mol%, 0–0.27 mmol), THF (2.0 mL), 100–140 °C, 6–24 h, 10–45 bar H_2. [b] The yield was determined by ^1H NMR. [c] In parenthesis the isolated yield of **2** is stated. [d] Solvent: anisole.

Moreover, dimethyl carbonate, which can be formed by the reaction of methanol with the carbonate unit of the polymer/oligomer was not detected.[22] In the next experiment the influence of a base was investigated, which has been shown essential in the hydrogenation of poly(propylene carbonate) (Table 1, entry 4).[15] In this context, potassium *tert*-butoxide (5.0 mol%) was added, but the similar yield was monitored as found in the absence of base. Additionally, bisphenol A was obtained in 91% yield. Noteworthy, in the absence of the catalyst **5** no product formation was observed (Table **1**, entries 1–2). Subsequently, the effect of **5** was studied, revealing still good performance at 2.5 mol% with a yield of 91% for **2**, while at 0.5 mol% a diminished yield was observed (Table 1, entries 5–7). In accordance to the experiment with 2.5 mol% catalyst loading the reaction was stopped after 6 hours, revealing a yield of 70% (Table 1, entry 8). Moreover, the impact of the temperature was studied (Table **1**, entries 12–17). At 120 °C a good yield of **2** of 76% was observed in the presence of 2.5 mol% 4, while at 100 °C no product formation was noticed (Table 1, entries 12 and 17). However, at 120 °C a significant effect of the base was observed.[24] In more detail, better yields at higher base loadings were achieved (Table 1, entries 12–13). Maybe the base can be considered as activator for the carbonate function of the polymer.[22]

In addition, the influence of the hydrogen pressure was investigated at 120 °C revealing best results for high hydrogen pressure (Table 1, entries 14–16).

After having validated the function of the Milstein catalyst the methodology was investigated in the depolymerization of EoL-**1** products. In this context, a digital versatile disc (DVD) containing polymer **1** as main component was studied (Scheme 2). Beside polymer **1** the DVD contains additives for instance metal foil, plastic foil etc., which can theoretically hamper the depolymerization catalyst. Two approaches were performed. On the one hand, the DVD was cut into pieces, which were subsequently ball-milled to obtain a DVD powder **1 b**. The DVD powder (1.35 mmol based on the repeating unit, based on the presumption that the DVD powder is composed of 100% **1**), catalytic amounts of complex **5** (5 mol% based on the repeating unit of **1 b**) and potassium *tert*-butoxide (5 mol% based on the repeating unit of **1 b**) were dissolved in THF. The reaction mixture was transferred to an autoclave, which was pressurized with 45 bar of hydrogen. The mixture was stirred and heated at 140 °C for 24 hours. After cooling to ambient temperature compound **2** was isolated in 73% yield after column chromatography. The content of **1** in the DVD is ~87%; therefore the yield of **2** can be corrected to approximately 84%. Moreover, the formation of methanol as second product was observed by ^1HNMR and was isolated as mixture with THF. Noteworthy, the obtained result demonstrates the robustness of catalyst **5**. In the second approach **1** was isolated from the DVD before depolymerization. In more detail, a mixture of DVD portions and THF was refluxed for 30 minutes. During the 30 min the polymer **1** was dissolved, while the foils were insoluble. After filtration, removal of the solvent, washing with acetone and drying the solid **1 c** was obtained. In accordance to the depolymerization procedure for **1 b** the polymer **1 c** was



Scheme 2. Depolymerization of **1** originated from DVDs [Reaction conditions: **1 b**/**1 c** (1.35 mmol, based on the repeating unit), **5** (5 mol% based on the repeating unit of **1**), KO^{t}Bu (5 mol% based on the repeating unit of **1**), THF (2.0 mL), hydrogen (45 bar) 140 °C, 24 h.

depolymerized (Scheme 2). Bisphenol A was isolated in a higher yield of 86%, which revealed that it is not necessary to purify the End-of-Life DVD before depolymerization. Relating the result with the work of Klankermayer and coworkers a comparable yield of **2** was realized at lower hydrogen pressure, but higher catalyst loading and a longer reaction are required.[14]

In summary, we have arranged an uncomplicated depolymerization procedure for the transformation of EoL poly (bisphenol A carbonate). The degradation was carried-out via hydrogenation generating bisphenol A and methanol as products in the presence of the commercially available Milstein catalyst. Bisphenol A was attained in good to excellent yields after 24 hours at 140 °C under a hydrogen pressure of up to 45 bar. Furthermore, the technique was appropriate for the depolymerization of **1** received from EoL-DVDs.

Supporting Information Summary

The experimental details including the depolymerization reactions and product characterization can be found in the supporting information.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: catalysis · depolymerization · green chemistry · polymers · recycling

[1] Plastics are typically composed of polymers and often other substances e. g. fillers, plasticizers, colorants.

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[24] The KO^{t}Bu may act as activator for the carbonate function or can convert the carbonate function of the polymer to ROC(=O)O^{t}Bu, which can be easier accessible by the catalyst and will lead to the same depolymerization products after hydrogenation.

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In a following study, which is based on the results from the bachelor thesis of Tim-Oliver Kindler, the Milstein catalyst (**35a**) was displaced by the Ru-MACHO-BH precatalyst (**34a**).[264,265] This catalyst provides two major advantages over the Milstein catalyst (**35a**). Even at a reaction temperature of 80 °C notable conversion can be achieved within 6 h. In addition, the reaction still proceeds at 5 bar H_2 pressure, making it more practical than all other reported examples. In addition, the catalytic system is robust towards contamination. In more detail, the PBAC (**2**) from DVD can be used directly or with prior extraction to give PBAC (**2**) in good to excellent yields.

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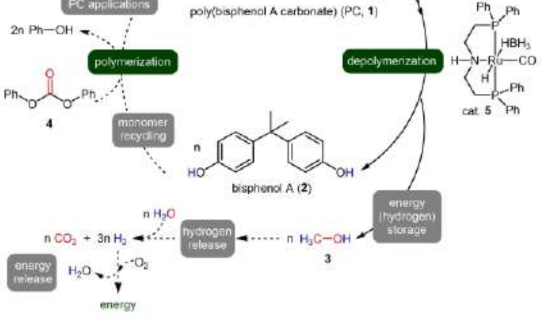
Hydrogenative Depolymerization of End-of-Life Poly(Bisphenol A Carbonate) Catalyzed by a Ruthenium-MACHO-Complex

Tim-Oliver Kindler, Christoph Alberti, Jannis Sundermeier, and Stephan Enthaler*[a]

The valorization of waste to valuable chemicals can contribute to a more resource-efficient and circular chemistry. In this regard, the selective degradation of end-of-life polymers/plastics to produce useful chemical building blocks can be a promising target. We have investigated the hydrogenative depolymerization of end-of-life poly(bisphenol A carbonate). Applying catalytic amounts of the commercial available Ruthenium-MACHO-BH complex the end-of-life polycarbonate was converted to bisphenol A and methanol. Importantly, bisphenol A can be reprocessed for the manufacture of new poly-(bisphenol A carbonate) and methanol can be utilized as energy storage material.

The state-of-the-art waste treatment for collected end-of-life plastic[1] streams is based on energy recovery, mechanical recycling, downcycling and landfill storage and the share of each methods strongly depends on regional conditions.[2,3,4] Disadvantageously, the energy recovery as one of the major treatment protocol, changes the chemical functionalities of the polymers into inappropriate chemicals (e.g. carbon dioxide), therefore for new polymers/plastics the depleting fossil resources are required.[5,6] In contrast, the chemical recycling presents a more resource-conserving and environmental-benign methodology.[7] A key component of the chemical recycling is the selective depolymerization of the polymer chain to generate low-molecular weight substances, which will be converted in the second process (polymerization) to new polymers. The connection of both processes allows the recycling of polymers/plastics. Nevertheless, currently implementation of chemical recycling suffers from high energy demand, copolymers, additives, selectivity, and the current low price for fossil resources for the production of new polymers etc.[8] Consequently, the design and development of new methodologies is of significance for reaching the goal of a more circular economy.[9,10] Polycarbonates, e.g. bisphenol A based polycarbonates are a widely utilized kind of polymers with applications in the area of constructions, automobile industry, electronics, artificial glass, or for optical storage (CD, DVD, Blu-ray).[11] For the recycling of poly(bisphenol A carbonate) (**1**) numerous procedures have been described so far including mechanical recycling, blending with other materials, pyrolysis (feedstock recycling), biochemical degradation and chemical recycling (e.g. hydrolysis, (hydro)glycolysis, alcoholysis and aminolysis).[12] Recently, Westhues *et al.* described the selective hydrogenative depolymerization of **1**.[13,14,15] A ruthenium(II) complex was applied to hydrogenate the carbonate functionality of **1** to obtain bisphenol A (**2**) and methanol (**3**) in excellent yields and selectivities (Scheme 1). Importantly, **2** can be applied in the industrial synthesis as monomer in combination with diphenyl carbonate (**4**) to obtain new **1**.[16] In contrast, the formed methanol can be used as hydrogen (energy) carrier/storage and may be used in fuel cells for electric energy generation.[17,18] Therefore a connection of depolymerization/recycling of end-of-life plastics with energy storage is achievable.

More recently, we have studied the application of the well-established Milstein catalyst in the depolymerization of **1** via hydrogenation to produce **2** (Scheme 1).[19] However, high catalyst loadings (5 mol%), catalytic amounts of a base (5 mol%), high temperatures (140 °C) and long reaction times (24 h) are required to obtain **2** in significant amounts. In this ongoing study we tried to solve the limitations of the Milstein catalyst system by application of another Ruthenium complex **5** containing a tridentate PNP-ligand (Ruthenium-MACHO-BH).



Scheme 1. Concept for the chemical recycling of **1** via hydrogenation.

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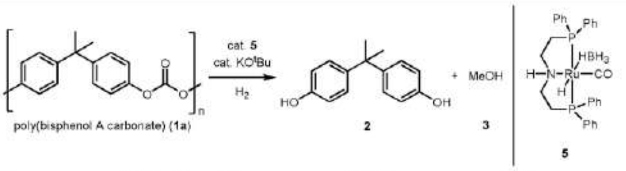
Table 1. Ruthenium-MACHO-BH-catalyzed depolymerization of poly(bisphenol A carbonate) (1 a) – optimization of the reaction conditions.



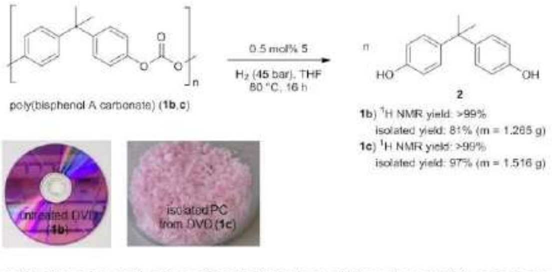
Entry[a]	Catalyst loading [mol %]	KO^{t}Bu [mol %]	T [°C]	t [h]	p [bar]	Yield 2 [%][b]
1	0	0	140	24	45	<1
2	0	5	140	24	45	<1
3	5	5	140	24	45	99
4[c]	5	5	140	24	45	80
5	2.5	5	140	24	45	98
6	1	5	140	24	45	96
7	0.5	5	140	24	45	92
8	5	0	140	24	45	99
9	0.1	0	140	6	45	85
10	0.5	0	120	6	45	82
11	0.5	0	100	6	45	76
12	0.5	0	80	6	45	69
13	0.5	0	140	6	20	87
14	0.5	0	140	6	10	91
15	0.5	0	140	6	5	96
16	0.5	0	140	6	2	23

[a] Reaction conditions: poly(bisphenol A carbonate) (**1 a**) (0.068 mmol), **5** (0-5 mol%, 0–0.0034 mmol based on the repeating unit of **1 a**), KO^{t}Bu (0-5 mol%, 0–0.0034 mmol), THF (1.0 mL), 80–140 °C, 6–24 h, 10–45 bar H_2. [b] The yield was determined by ^{1}H NMR. [c] Solvent: 1,4-dioxane.

Initially, the depolymerization of commercially available pure poly(bisphenol A carbonate) **1 a** (pellet dimension: ~3 mm) was examined (Table 1). First control experiment have been carried out in the absence of any catalysts and/or base (Table 1, entries 1 and 2). Importantly, no depolymerization processes were observed and the polymer was recovered. Next catalytic amounts of complex **5** (5 mol% based on the monomeric unit of **1 a**) and the base potassium *tert*-butoxide (5 mol%) were tested in THF in accordance to the best conditions found for the Milstein system (yield of **2**: 95%). After heating the mixture for 24 hours at 140 °C under a hydrogen pressure of 45 bar, an excellent yield for **2** of 99% was detected by ^{1}H NMR analysis using the methyl functionalities as probe (Table 1, entry 3).[20] Changing the solvent from THF to 1,4-dioxane revealed a decrease of yield to 80% (Table 1, entry 4).

Moreover, the catalyst loading was reduced to 0.5 mol% and still an excellent yield of 92% was detected (Table 1, entries 5–7). Interestingly, the catalyst works also in the absence of base with comparable activity (Table 1, entry 8). Next the reaction time was shortened to 6 hours (Table 1, entry 9). Excellent yields were found with a catalyst loading of 5.0 mol%, while a reduction to 0.1 mol% resulted in 85% yield of **2**. This result corresponds to a turnover frequency (TOF) of ~142 h^{-1}, which is significantly higher as observed for the Milstein catalyst (~4.7 h^{-1}).[19] In addition the influence of the reaction temperature was investigated (Table 1, entries 10–12). Here still product formation was observed at a low temperature of 80 °C with a yield of 69%, while the Milstein catalyst is limited to 120 °C. Moreover, it was possible to reduce the hydrogen pressure to 5 bar and obtaining yields of 96% for **2**, while at lower pressure the yield decreased (Table 1, entries 13–16).

After successful confirmation of the operability of the depolymerization catalyst a digital versatile disc (DVD) mainly composed of **1** was attempted to degradate (Scheme 2). Alongside to **1** the DVD can contain additives like metal as well as plastic foil and dyes. In this regard, the DVD was crushed by ball-milling to get a powder (**1 b**). With respect to the reaction conditions, the conditions stated in Table 1, entry 14 (0.5 mol% **5**, 80 °C, 45 bar, THF), but the reaction time was elongated to 16 hours to allow full conversion. Moreover, the scale was increased to 6.82 mmol (1.74 g) (based on the monomeric unit, presumption that the powder contains 100% of **1**). After heating to 80 °C for 16 hours the mixture was cooled to room temperature and filtered to remove insoluble compounds. An aliquot was dissolved in chloroform-*d* for analysis by ^{1}H NMR revealing a NMR yield of **2** of >99%. Additionally, the generation of methanol during depolymerization process was proven. For purification/isolation of **2** column chromatography and subsequent crystallization was used. In consequence **2** was



Scheme 2. Depolymerization of poly(bisphenol A carbonate) **1** originated from a DVD [Reaction conditions: **1 b**/**1 c** (6.82 mmol, based on the monomeric unit), **5** (0.5 mol%, 0.0341 mmol based on the repeating unit of **1 a**), THF (50.0 mL), 80 °C, 16 h, 45 bar H_2).

obtained in 81% isolated yield or 93% taking into account that the DVD contains 87 wt% of **1**.

In a second attempt polymer **1** was separated from the DVD before hydrogenative depolymerization.[21] In this regard, the DVD was dissolved in THF at refluxing conditions within 30 min. The hot mixture was filtered to remove the insoluble components of the DVD. Subsequently, the solvent was removed and the solid was washed with acetone and dried in vacuum to give **1b**. In agreement to the depolymerization conditions for **1b** the isolated **1c** was degradated (Scheme 2). **2** was detected in >99% NMR yield and was isolated in 97% yield.

In conclusion, an efficient hydrogenation process for the depolymerization of end-of-life **1** to generate **2** and methanol as products was set-up. Both compounds can be beneficial for on the one hand the reproduction of poly(bisphenol A carbonate) (bisphenol A) or on the other hand for the hydrogen economy (methanol). In detail, the commercially available complex Ruthenium-MACHO-BH was able to perform the depolymerization at low reaction temperatures, low pressure and within short time. Noteworthy, compared to established catalysts the Ruthenium-MACHO-BH catalyst showed excellent performance. Lastly, the protocol can add some value to the UN's Sustainable Development Goals (SDGs) e.g. SDGs 9,11 (clean/green technologies, waste management/urban mining) and SDG 12 (supply chain, more efficient and less consumptive technologies, recycling, waste streams).

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Keywords: catalysis · depolymerization · green chemistry · polymers · recycling

[1] Plastics are typically composed of polymers and often other substances e.g. fillers, plasticizers, colorants.

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The previous examples of catalysts for the hydrogenations are all synthesized in a multi-step synthesis. Hence, the simplification of catalyst is of interest. Therefore, we introduced a bidentate ligand together with a metal precursor that is straightforwardly accessible from $RuCl_3$, paraformaldehyde and PPh_3.[266] As ligand a bidentate aminophosphine should mimic the structure of the Ru-MACHO-BH precatalyst (**34a**). Thereby, the bidentate ligand was suggested to substitute two PPh_3 ligands and the third PPh_3 ligand could be replaced with other ligands to modify the electronic and steric properties. In fact, the in situ generated catalyst revealed notable activity even at 80 °C, however a higher catalyst loading was required than for the original Ru-MACHO-BH precatalyst (**34a**). An ^{31}P NMR study suggested the presence of multiple species which is reasoned in the diverse coordination modes of the phosphine to metal center. The catalytic system gave increased yield when in addition 1 mol% of DBU was present. Using PBAC (**2**) goods showed that the yields were diminished compared to pure PBAC (**2**). This indicated a negative effect of additives on the catalyst that was not observed in that extent for the Milstein catalyst (**35a**) and the Ru-MACHO-BH precatalyst (**34a**).

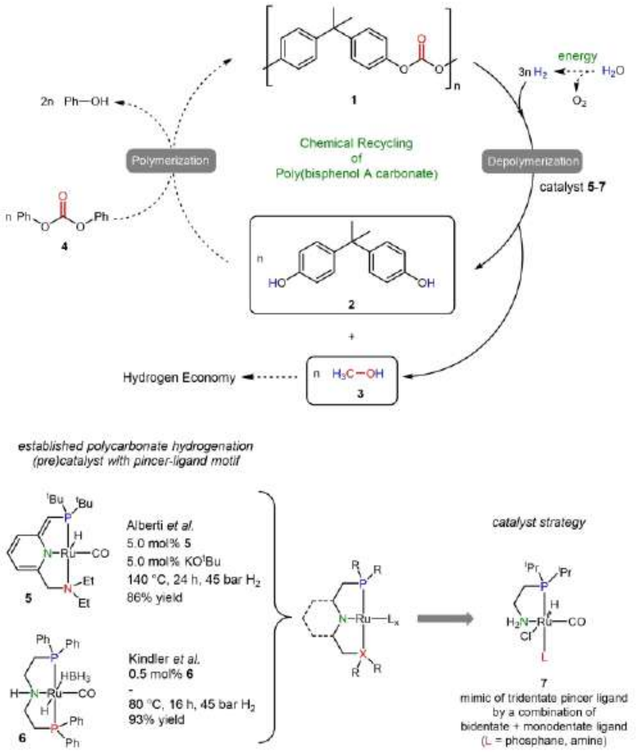
Sustainable Chemistry

Hydrogenative Depolymerization of End-of-Life Poly (bisphenol A carbonate) with *in situ* Generated Ruthenium Catalysts

Christoph Alberti, Jannik Kessler, Sarah Eckelt, Melanie Hofmann, Tim-Oliver Kindler, Nicolo Santangelo, Elena Fedorenko, and Stephan Enthaler*[a]

One essential aspect to create a circular economy can be the valorisation of plastic waste to create valuable chemicals. The depolymerization, the converse reaction of the polymer built-up process, can be promising to reach the targets of a circular economy. Depolymerizations can provide monomers, which are polymerized in a subsequent process. We have explored the hydrogenative depolymerization of end-of-life poly(bisphenol A carbonate) (EoL-PBPAC). Applying an *in situ* generated catalyst derived from the precursors [RuClH(CO)(PPh$_3$)$_3$] and 2-(di-*iso*-propylphosphino)ethylamine EoL-PBPAC, e.g. a DVD, was reduced to methanol and bisphenol A in good to excellent yields. For closing the cycle bisphenol A may be reprocessed as monomer for the reproduction of new PBPAC. The second depolymerization product methanol may be submitted to the hydrogen economy for release of hydrogen and in consequence energy generation.

The chemical recycling of polymers (plastics[1]) is a methodology, which can resolve some negatives of other waste treatment methods (energy recovery, landfill storage, mechanical recycling, downcycling), e.g. carbon dioxide formation, depletion of fossil resources, decrease of plastic quality.[2,3,4,5,6] Consequently, the chemical recycling is creating values like resource-conservation and sustainability and can be a powerful tool for circular chemistry/circular economy.[7,8,9] The basic processes of chemical recycling are the depolymerization, which converts the polymer to monomers, and the polymerization, which reforms the polymer from monomers. The combination of both reactions enables the recycling of polymers. To enhance the potential of the chemical recycling powerful protocols are highly requested.[10] Recently, a number of procedures have been accounted for the chemical recycling of polycarbonates, particularly poly(bisphenol A carbonate) (**1**, PC), which is a well-established plastic.[11,12] For example Klankermayer and coworkers described the hydrogenation of **1** with the support of a well-defined Ruthenium complex.[13,14,15] During hydrogenation of the carbonate function the monomeric unit is converted to the products bisphenol A (**2**) and methanol and consequently the polymer is depolymerized (Scheme 1). Noteworthy, excellent catalyst performance was exhibited and excellent conversions were obtained (0.5 mol% catalyst loading, 140 °C, 16 h, 90 bar H$_2$, conv.: >99%). The bisphenol A can be used as feed for the resynthesis of **1**.[16] On the other hand, methanol can be assumed as hydrogen carrier or hydrogen storage and can be subjected to the hydrogen economy to release the stored energy.[17,18] Remarkably, this concept enables the valorization of plastic waste by chemical



Scheme 1. Chemical recycling of poly(bisphenol A carbonate) via carbonate hydrogenation.

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recycling and energy storage. More recently, we have explored the potential of the well-established and commercialized Milstein catalyst **5** and the Ruthenium-MACHO-BH catalyst **6** (Scheme 1).[19] In case of **5** as catalyst excellent yields for the hydrogenative depolymerization of **1** (derived from a DVD = Digital Versatile Disc) were detected (5 mol% catalyst loading, 5 mol% KO^{t}Bu, 140 °C, 24 h, 45 bar H_2, yield: 86 %). On the other hand, catalyst **6** exhibited a better performance with 93 % yield at a loading of 0.5 mol% within 16 hours at 80 °C. Based on the pincer-type ligand motif (e.g. PNP, PNN) of these polycarbonate hydrogenation catalysts we wondered if a combination of a bidentate PN-ligand and a monodentate P-ligand or N-ligand can mimic the tridentate PNP- or PNN-motif, which in consequence enables more variations (Scheme 1, **7**). Therefore a combination of the commercially available complex [RuClH(CO)(PPh$_3$)$_3$] (**8**) and 2-(di-*iso*-propylphosphino)ethylamine (**9**) as PN-ligand and monodentate phosphanes/amines as P- or N-ligand were selected to generate *in situ* complexes of type **7** for the valorization of end-of-life poly(bisphenol A carbonate) (Scheme 1).[20,21]

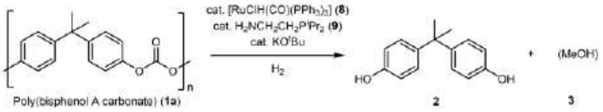
Primarily, for investigation of the reaction conditions the commercially available poly(bisphenol A carbonate) **1a** was chosen as model substrate (Table 1). In more detail, to **1a** was added a mixture of catalytic amounts of complex **8** (2 mol%) and potassium *tert*-butoxide (10 mol%). The mixture was dissolved in THF and transferred to an autoclave, which was pressurized with hydrogen (45 bar) and heated to 140 °C. The temperature was kept for 24 hours at 140 °C (Table 1, entry 3). After cooling to ambient temperature, the mixture was analysed by ^{1}H NMR spectroscopy. In the ^{1}H NMR spectrum a signal for the $C(CH_3)_2$ function (6H) at 1.60 ppm and for the aromatics C–H two sets of signals (2x4H) at 6.67–6.71 ppm and 7.02–7.06 ppm of product **2** were detected.[22] Besides, signals for polymer **1a** were identified, which were used for yield determination of **2**, revealing a yield of 9 % of **2**. Importantly in the absence of complex **8** no product formation was observed (Table 1, entries 1 and 2). Notably, the addition of ligand **9** to complex **8** (ratio 1 : 1) increased the yield of **2** significantly to > 99 % (Table 1, entry 4).[23] Same yield was detected by reducing the amount of base to 5 mol%, while at lower loadings the yield decreases or no product was observed in the absence of the base (Table 1, entries 5–7). Next the loading of the catalyst and the ligand was studied (Table 1, entries 11–13). In case of a loading of 0.1 mol% a good yield of 65 % was detected after 24 hours (Table 1, entry 13). Reducing the reaction time to three hours revealed a moderate yield of **2** (Table 1, entries 14 and 15). In the next experiment the influence of the reaction temperature was investigated (Table 1, entries 17–22). Showing excellent performance at 120 °C, while at 80 °C a moderate yield was obtained. Moreover, the hydrogen pressure was studied. **1a** was fully converted at 120 °C and a hydrogen pressure of 20 bar to **2**, while at lower hydrogen pressure a moderate yield of **2** was realized (Table 1, entries 18 and 19).

In the next experiment the influence of additional ligands added to the *in situ* generated complex of **8** and **9** (ratio: 1 : 1) was investigated (Table 2). In accordance to the reaction conditions stated in Table 1, entry 16 triphenylphosphane (1 mol%) was added to **8** and **9** (ratio 1 : 1 : 1). The detected yield of **2** (23 %) is lower compared to the standard system (yield: 38 %); hence the addition of extra PPh$_3$ is disadvantageous, which was further proven by adding 5 mol% PPh$_3$ (yield: 16 %) (Table 2, entries 1–3). Same effect was observed for other monodentate as well as bidentate phosphane ligands. Only in case of addition of ligand **11** an increase of the yield (58 %) was noticed (Table 2, entry 7). Moreover, nitrogen-based ligands were studied (Table 2, entries 9 and10). In case of DBU an increase of the yield to 51 % was observed.

After having demonstrated the operability of the *in situ* generated catalyst the procedure was applied for the depolymerization of a commodity (digital versatile disc = DVD) containing poly(bisphenol A carbonate) **1**. A (DVD) containing polymer **1** as major ingredient was tested (Scheme 2). Noteworthy, together with polymer **1** the DVD can contain additives for instance metal foil, plastic foil and dyes, which may negatively effect on the catalyst performance. Initially the DVD was ball-milled to become a fine DVD powder **1b**.

The powder (3.4 g, 13.4 mmol based on the monomeric unit, based on the presumption that the DVD powder is composed of 100 % of **1**), catalytic amounts of complex **8** (1 mol% based on the monomeric unit of **1b**), **9** (1 mol% based on the monomeric unit of **1b**) and potassium *tert*-

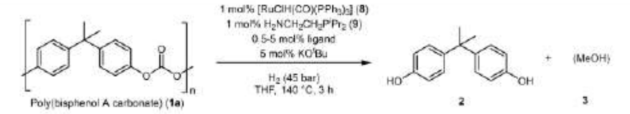
Table 1. Ruthenium-catalyzed depolymerization of **1a** - optimization of the reaction conditions.



Entry[a]	loading **8**:**9** [mol%]	KO^{t}Bu [mol %]	T [°C]	t [h]	p (H_2) [bar]	Yield **2** [%][b]
1	0:0	0	140	24	45	< 1
2	0:0	5	140	24	45	< 1
3	2:0	10	140	24	45	9
4	2:2	10	140	24	45	>99
5	2:2	5	140	24	45	>99
6	2:2	2	140	24	45	55
7	2:2	0	140	24	45	< 1
8	2:4	10	140	24	45	>99
9	1:1	5	140	24	45	>99
10	1:2	5	140	24	45	>99
11	0.5:0.5	5	140	24	45	90
12	0.25:0.25	5	140	24	45	71
13	0.1:0.1	5	140	24	45	65
14	1:1	5	140	3	45	38
15	0.5:0.5	5	140	3	45	21
16	2:2	10	140	72	45	>99
17	1:2	10	120	24	45	>99
18	1:2	10	120	24	20	>99
19	1:2	10	120	24	10	43
20	1:2	10	80	24	20	32
21	1:1	10	80	24	20	30
22	0.5:0.5	10	80	24	20	13

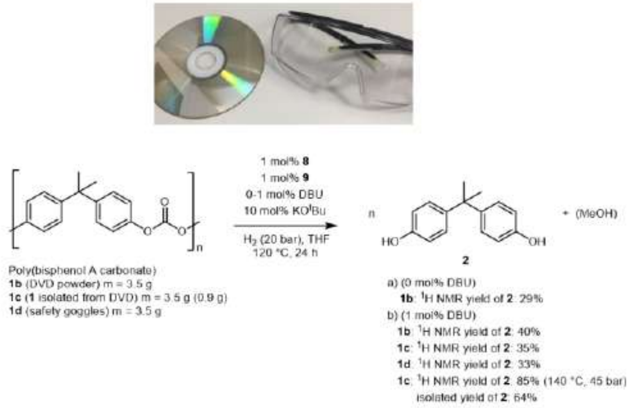
[a] Reaction conditions: **1a** (0.0675 mmol), **8** (0–2 mol%, 0–0.00135 mmol based on the repeating unit of **1a**), **9** (0–4 mol%, 0–0.027 mmol based on the repeating unit of **1a**), KO^{t}Bu (0–10 mol%, 0–0.00675 mmol), THF (2.0 mL), 80–140 °C, 3–72 h, 10–45 bar H_2. [b] The yield was determined by ^{1}H NMR.

Table 2. Ruthenium-catalyzed depolymerization of **1 a** - ligand screening.[a]



Entry	Ligand	Ligand loading [mol %]	Yield 2 [%][b]
1	–	–	38
2	PPh_3	1	23
3	PPh_3	5	16
4	P^tBu_3	1	37
5	P^iPr_3	1	15
6	(2-biphenyl)di-cyclohexylphosphane (**10**)	1	30
7	(2-biphenyl)di-tert-butylphosphane (**11**)	1	58
8	1,2-bis(diphenylphosphino) ethane	0.5	32
9	4-dimethylaminopyridine (DMAP)	1	41
10	1,8-diazabicyclo(5.4.0)undec-7-ene (DBU)	1	51

[a] Reaction conditions: **1 a** (0.0675 mmol), **8** (1 mol %, 0.000675 mmol based on the repeating unit of **1 a**), **9** (1 mol%, 0.000675 mmol based on the repeating unit of **1 a**), ligand (0–5 mol %, 0–0.00338 mmol based on the repeating unit of **1 a**), KO^tBu (5 mol %, 0.00338 mmol), THF (2.0 mL), 140 °C, 3 h, 45 bar H_2. [b] The yield was determined by ^1H NMR.



Scheme 2. Depolymerization of poly(bisphenol A carbonate) **1** originated from a DVD or safety goggles [Reaction conditions: **1 b/c/d** (13.4 mmol, based on the monomeric unit), **8** (1 mol %, 0.134 mmol based on the repeating unit of **1**), **9** (1 mol %, 0.134 mmol based on the repeating unit of **1**), DBU (0–1 mol %, 0–0.134 mmol based on the repeating unit of **1 a**), KO^tBu (10 mol %, 1.34 mmol), THF (20 mL), 120 °C, 24 h, 20 bar H_2. In case of **1 c** an experiment was also carried out at 140 °C with 45 bar H_2 and a 3.58 mmol scale in 15 mL THF.]

butoxide (10 mol % based on the monomeric unit of **1 b**) were dissolved/suspended in THF (Scheme 2).

The reaction mixture was transferred to an autoclave, which was then pressurized with hydrogen (20 bar). The reaction mixture was hold for 24 hours at 120 °C, while stirring. After cooling to room temperature an aliquot was dissolved in chloroform-*d* for ^1H NMR analysis. An NMR yield of 29 % of **2** was observed, which revealed a negative impact of the additives on catalyst performance.[24,25] In addition, the experiment was repeated in the presence of additional 1 mol % DBU. In this regard, bisphenol A was detected in a moderate NMR yield of 40 %. A quite similar result was obtained when using **1 c** isolated from a DVD by dissolution, filtration, precipitation, washing and drying. Finally, the poly(bisphenol A carbonate) containing part of a safety googles was subjected to hydrogenative depolymerization following the conditions described for the DVD (Scheme 2). Here an NMR yield of 33 % was noticed.[24] An improvement of the yield to 85 % (isolated yield: 64 %) was observed for the **1 c** in case of increasing the reaction temperature to 140 °C and the hydrogen pressure to 45 bar.

In summary, we have investigated the hydrogenative depolymerization of EoL poly(bisphenol A carbonate) in the presence of an *in situ* generated Ruthenium catalyst. A mixture of a bidentate ligand (2-(di-*iso*-propylphosphino)ethylamine) and a monodentate ligand (PPh_3 or DBU) was added to the precursor $[RuClH(CO)(PPh_3)_3]$ to mimic tridentate ligands, which have been proven to be active in the hydrogenative depolymerization of poly(bisphenol A carbonate). As product bisphenol A was obtained in good to excellent yields after 24 hours at 120 °C under a hydrogen pressure of 20 bar. Interestingly, the flexibility of the *in situ* generated catalyst system allows an easy optimization of the reaction outcome. Furthermore, the methodology was applied for the depolymerization of poly (bisphenol A carbonate) containing EoL-DVDs.

Supporting Information Summary

The experimental details including the depolymerization reactions and product characterization can be found in the supporting information.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: catalysis · depolymerization · green chemistry · polymers · recycling

[1] Plastics are typically composed of polymers and often other substances e. g. fillers, plasticizers, colorants.

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[24] An insoluble residue was observed, which may contain the aluminum foil and other plastic foils.

[25] The content of **1 b** in the DVD is ~87%; therefore the yield of **2** can be corrected to approximately 33% (without DBU) or 46% (with DBU) respectively.

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A simplification of the ligand sphere allows for a more cost efficient catalyst. However, it requires higher catalyst loading, more forcing conditions and was less efficient for the hydrogenation on non-pure PBAC (**2**). Another possibility to enhance the sustainability of the catalyst was to vary the metal center. In this regard, we introduced the literature known Fe-PNP precatalyst to the hydrogenation of PBAC (**2**) and PPC (**6**).[267] The catalyst can be applied even at 80 °C and gives good results even at low H_2 pressures of 5 bar. Hydrogenation of commercial goods was successfully accomplished with excellent yields. The optimized conditions were furthermore transferred to PPC (**6**). Here, the catalytic hydrogenation to 1,2-propanediol (**7**) and MeOH could be demonstrated. The products could again be isolated in excellent yields. In comparison to our previously reported Ru-MACHO-BH (**34a**) catalyst, to some extend a higher catalyst loading were necessary and the performance under lower pressure and temperature was not as good. In addition, its catalytic activity was hampered by some polymers. Especially, PVC critically reduced the catalyst activity.

In conclusion, the nature of the catalyst was significantly affecting the reaction conditions. As a major drawback, the application of THF did not allow for an isolation of MeOH due to their similar boiling points.

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Hydrogenative Depolymerization of End-of-Life Polycarbonates by an Iron Pincer Complex

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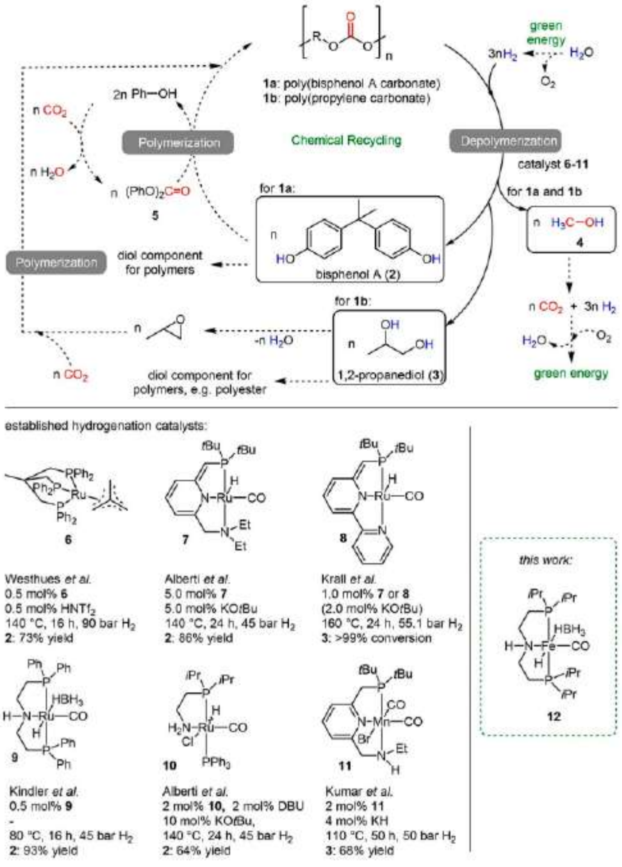
Chemical recycling processes can contribute to a resource-efficient plastic economy. Herein, a procedure for the iron-catalyzed hydrogenation of the carbonate function of end-of-life polycarbonates under simultaneous depolymerization is presented. The use of a straightforward iron pincer complex leads to high rate of depolymerization of poly(bisphenol A carbonate) and poly(propylene carbonate) yielding the monomers bisphenol A and 1,2-propanediol, respectively, as products under mild reaction conditions. Furthermore, the iron complex was able to depolymerize polycarbonates containing goods and mixture of plastics containing polycarbonates.

The high standard of life in modern societies strongly benefits from easily affordable plastic[1] goods, which results at the same time in the generation of plastic waste after completing the operational purpose.[2] In general, waste management depends on landfill storage and incineration that results in long-term environmental problems and pollutions.[3] Moreover, significant amounts of plastic waste are reaching uncontrolled the biosphere generating environmental problems.[4] As an alternative, primary recycling is applied which is defined as reusing the good without mechanical or chemical transformations of the latter, which is in contrast to secondary recycling.[5-6] Hereby, the material is thermally or mechanically converted to another good of similar or lower quality, because chemical degradation, contaminations or additives of the virgin material hamper the properties of the recycled material.[7] Both, primary and secondary recycling are downcycling processes because after several cycles the material has to be submitted to landfill or incineration.[8] This lost material has to be replaced by consumption of fossil resources, whereby several synthetic transformations are required. Alternatively, chemical recycling allows the conservation of the monomeric unit, so that the number of transformations is reduced and significant amounts of energy and resources are saved. As a consequence, it has become a matter of research to enable end-of-life polymers as feedstock for new polymers with adjustable properties.[9-10] Therefore, a sequence of depolymerization followed by purification of the monomers and a (re)polymerization are required, which can, under optimal conditions, substitute fossil resources.[9] Polycarbonates, especially on the basis of bisphenol A (**2**) as diol component, are used as materials for data storage (CD/DVD, hard disk drives, Blu-Ray), suit cases and artificial glass.[11] Moreover, poly(propylene carbonate) (**1b**) based plastics have been established for packaging applications.[12] A variety of chemical depolymerization approaches for polycarbonates are reported, e.g. pyrolysis, biochemical degradation and chemical recycling, e.g. alcoholysis, glycolysis or aminolysis.[13–14] In addition, several procedures were reported for the ruthenium-catalyzed hydrogenative depolymerization (Scheme 1).[15] In case of end-of-life **1a** bisphenol A (**2**) and methanol are formed as suitable chemicals during hydro-



Scheme 1. Chemical recycling concept for poly(bisphenol A carbonate) and poly(propylene carbonate).

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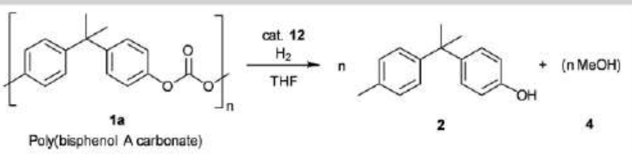
genative depolymerization. The monomer bisphenol A (**2**) can be used to regenerate the polymer **1 a**, while methanol can be used as hydrogen or energy carrier.[16]

After releasing the in methanol stored energy carbon dioxide is formed, which can be converted with phenol to diphenylcarbonate (**5**), which can be applied with **2** for synthesizing **1 a**.[17] On the other hand, poly(propylene carbonate) (**1 b**) is converted to 1,2-propanediol (**3**) and methanol by hydrogenative depolymerization. Chemical **3** can be transformed to propylene oxide, which can react with carbon dioxide to polymer **1 b**.[12,18] In both cases a cycling of monomeric units of the polycarbonates is feasible. A number of ruthenium-based catalyst (**6**-**10**) have been found suitable for the hydrogenative depolymerization of **1 a** (Scheme 1).[15] However, the use of ruthenium as catalyst compartment causes some economic and sustainability problems.[19] In this regard, the use of systems with non-noble, cheap and abundant metals can be an alternative.[20] For instance the group of Milstein reported the application of a manganese complex (**11**) modified with a pincer type ligand in the hydrogenative depolymerization of **1 b**. After 50 h **1 b** was converted to 1,2-propanediol in 68 % yield and propylene carbonate in 30 % yield.[21]

In this regard, we studied the hydrogenative depolymerization of **1 a** and **1 b** in the presence of catalytic amounts of an iron complex modified with a pincer type ligand (**12**), which has been established for the hydrogenation of low-molecular weight organic esters.[22]

At first, the influence of reaction parameters on the hydrogenative depolymerization of commercially available **1 a** (pellets, diameter ~3 mm) was investigated. Therefore, a mixture of **1 a** and catalytic amounts of complex **12** (1.0 mol%) in THF was placed in an autoclave and pressurized with 45 bar of hydrogen and kept at 120 °C for 24 hours (Table **1**, entry 2). After cooling to ambient temperature, quantification of the product was performed by ^{1}H NMR spectroscopy using the ratios of the Ar-*H* of the polymer/oligomers **1 a** (7.06–7.07 ppm) and of the Ar-*H* signal of **2** (6.70–6.71 ppm). Based on that, a NMR yield of 90 % of **2** was calculated. Increasing the amount of catalyst revealed an increase of the yield of **2**, while decreasing the catalyst loading showed a diminished yield (Table 1, entries 3–5). Importantly, in the absence of the catalyst no product formation was observed (Table **1**, entry 1). Lowering the catalyst loading to 0.5 mol% reveals high yields for **2**, while at 0.1 mol% no significant product formation is observed. Next, the influence of the reaction temperature was evaluated. The yield of **2** decreases significantly when the temperature is reduced below 80 °C when the temperature is reduced to 100 °C still excellent yields are observed. At 80 °C, a notable decrease was observed while almost no catalytic activity is observed at 60 °C (Table 1, entries 6–8). When the reaction is stopped after 6 h at 140 °C a yield of 31 % was observed (Table **1**, entry 9). Moreover, the influence of the hydrogen pressure was evaluated, revealing, that at 20 bar or 5 bar pressure, the yield was significantly diminished (Table 1, entries 10 and 11). Replacement of THF by anisole or 1,4-dioxane as solvent had a negative influence on the reaction outcome (Table 1, entries 12 and 13).

Table 1. Iron-catalyzed depolymerization of poly(bisphenol A carbonate) **1 a**.

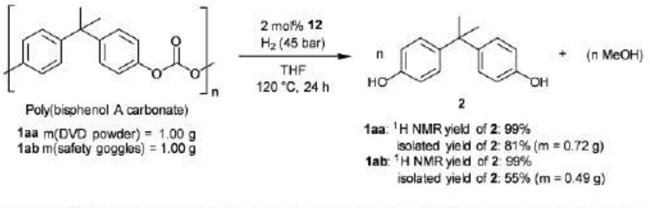


Entry[a]	Catalyst loading [mol%]	T [°C]	t [h]	p (H_2) [bar]	Yield [%][b]
1	0	120	24	45	<1
2	1.0	120	24	45	90
3	2.0	120	24	45	>99
4	0.5	120	24	45	91
5	0.1	120	24	45	4
6	2.0	100	24	45	93
7	2.0	80	24	45	70
8	2.0	60	24	45	2
9	2.0	140	6	45	31
10	2.0	120	24	20	70
11	2.0	120	24	5	26
12[c]	2.0	120	24	45	42
13[d]	2.0	120	24	45	58

[a] Reaction conditions: **1 a** (0.135 mmol, based on repeating unit of **1 a**), **12** (0-2 mol%, 0–2.7 μmol based on the repeating unit of **1 a**), THF (1.0 mL), 60–140 °C, 6–24 h, 5–45 bar H_2. [b] The yield was determined by ^{1}H NMR. [c] 1,4-dioxane (1.0 mL) as solvent. [d] PhOMe (1.0 mL) as solvent.

With the optimized conditions (2.0 mol% **12**, 120 °C, 45 bar H_2, 24 h) two kinds of plastics containing **1 a** were studied in the hydrogenative depolymerization (Scheme 2). For instance, a digital versatile disc (DVD) a composite of **1 a**, aluminum, plastic foils and dyes was tested. The DVD was ball-milled to get a powder (**1 aa**), which was subjected to depolymerization without further pretreatments. Interestingly, after 24 hours a NMR yield of 99 % of **2** was observed, revealing that the depolymerization was successful and the additional compounds had no negative impact on the catalytic activity. A similar result was obtained for a sample of safety goggles (**1 ab**) containing **1 a**.

For purification/isolation of **2** filtration over silica gel and subsequent crystallization was carried out. Chemical **2** was attained in 81 % (**1 aa**) and 55 % (**1 ab**) isolated yield or 93 % (**1 aa**) under the assumption that the DVD contains 87 wt% of **1 a**.[15b–d] The isolated yields obtained for this catalyst systems are comparable to those reported for other catalysts.[15] Importantly, additives for catalyst activation are not required



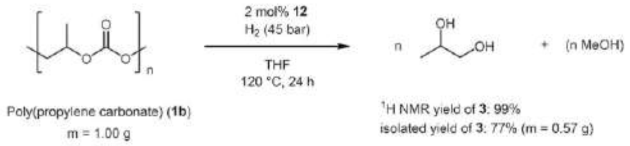
Scheme 2. Hydrogenative depolymerization of poly(bisphenol A carbonate) products (Reaction conditions: **1 aa** or **1 ab** (3.95 mmol, based on repeating unit of **1 a**), **12** (2 mol%, 79.0 μmol based on the repeating unit of **1 a**), THF (20 mL), 120 °C, 24 h, 45 bar H_2).

and reaction temperature and pressure are sufficiently lower than for other system.[15]

Nevertheless, with regards to reaction temperature and time, pressure and catalyst loading, the Fe-catalyst was outperformed by Ru-catalyst **9** (Scheme 1).[15]

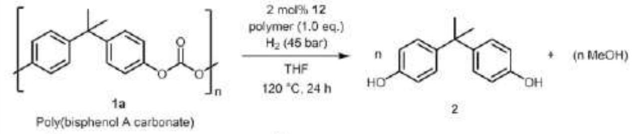
Next, the iron-catalyzed procedure was applied in the hydrogenative depolymerization of poly(propylene carbonate) (**1 b**) (Scheme 3). In accordance to the optimized conditions (2.0 mol% **11**, 120 °C, 45 bar H_2, 24 h) a sample of **1 b** was tested. 1,2-propanediol (**3**) was observed in 99% NMR yield. Purification by distillation gave selectively **3** in 77% yield. In comparison to the Mn-based catalyst established Kumar *et al.*[21] the system does not require the usage of additional base and reveals higher yields for diol formation within shorter reaction times. Moreover, the Fe-based system demonstrated some benefits regarding temperature and pressure compared to the work of Krall *et al.*[15e]

Moreover, the hydrogenative depolymerization of polycarbonate **1 a** was studied in the presence of different types of polymers, which can add some benefits to separation technologies (Table 2). Therefore, best conditions for **1 a** were applied (2.0 mol% **12**, 120 °C, 45 bar H_2, 24 h). In more detail, polymer **1 a** was mixed with an equimolar amount of another polymer (based on its repeating unit) and the mixture was subjected to the hydrogenation. First, a mixture of **1 a** and **1 b** was investigated, revealing the formation of **2** in 91% and **3** in 89% NMR yield, which is comparable to earlier experiments (Table 2, entry 1). Moreover, polymers containing ester functionalities like poly(lactide) (PLA), poly(ethylene terephthalate) (PET) and poly(ε-caprolactone) (PCL) were tested as additives (Table 2, entries 2–4). Excellent NMR yields of **2** of $>99\%$ were detected in the presence of PLA and PET. In case of the experiment with PLA the formation of 1,2-propanediol (**3**) was not observed. However, a reduction of the molecular weight of the initial PLA was observed by DOSY NMR. For PET no formation of 1,4-benzenedimethanol and ethylene glycol was detected maybe due to solubility issues. Conversely, using poly(ε-caprolactone) (PCL) as second polymer the iron catalyst produces 46% (NMR yield) of 1,6-hexanediol and 72% (NMR yield) of **2** as depolymerization products (Table 2, entry 4). Other polymers containing functional groups, which can be potentially hydrogenated by **12**, revealed no hydrogenation of the second polymer (Table 2, entries 5–6). Polymers "inert" to hydrogenation with **12** revealed good to excellent bisphenol A formation (Table 2, entries 6–10). Diminished yields of **2** were observed when poly(vinyl chloride) (PVC), poly(dimethylsiloxane) (PDMS) or poly(ethylene glycol) (PEG) were added (Table 2, entries 11–13).



Scheme 3. Hydrogenative depolymerization of poly(propylene carbonate) (Reaction conditions: **1 b** (9.84 mmol, based on repeating unit of **1 b**), **12** (2 mol%, 197 μmol based on the repeating unit of **1 b**), THF (40 mL), 120 °C, 24 h, 45 bar H_2).

Table 2. Influence of additional polymers on the hydrogenative depolymerization of **1 a**.



Entry[a]	Additional polymer[b]	Yield **2** [%][c]	Yield [%][c]
1	**1 b**	91	89 (**3**)
2	Poly(lactide) (PLA)	>99	<1
3	Poly(ethylene terephthalate) (PET)	>99	<1
4	Poly(ε-caprolactone) (PCL)	72	46[d]
5	Nylon 6	89	<1
6	Poly(formaldehyde) (POM)	>99	–
7	Poly(phenylene sulfide) (PPS)	>99	<1
8	Poly(ethylene) (PE)	87	<1
9	Epoxy resin	99	<1
11	Poly(styrene) (PS)[e]	observed	-
10	Poly(vinyl chloride) (PVC)	11	<1
12	Poly(ethylene glycol) (PEG)	52	<1
13	Silicone (PDMS)	50	<1

[a] Reaction conditions: **1 a** (0.135 mmol, based on repeating unit of **1 a**), **12** (2 mol%, 0–2.7 μmol based on the repeating unit of **1 a**), THF (1.0 mL), 120 °C, 24 h, 45 bar H_2. [b] 0.135 mmol, based on repeating unit. [c] The yield was determined by ^{1}H NMR for **2** and the hydrogenation product of the additional polymer. [d] 1,6-hexanediol. [e] Determination of yield was impossible due to signal overlap. However, the bisphenol A was qualitatively detected.

In summary, we have set up a protocol for the hydrogenation of end-of-life polycarbonates enabled by iron catalysis. High yields of the corresponding diols were obtained under mild conditions. At 120 °C and 45 bar H_2 pressure, bisphenol A was isolated in 93% yield when a DVD was submitted to depolymerization. Moreover, poly(propylene carbonate) was successfully converted to 1,2-propanediol, which was isolated in 77% yield. Furthermore, the catalytic hydrogenation of poly (bisphenol A carbonate) was carried out in the presence of other industrially relevant polymers, demonstrating the robustness of the applied iron catalyst.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: green chemistry · catalysis · polymers · recycling · depolymerization

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5.8 Depolymerization of poly(lactide) via hydrogenation

For the hydrogenation of PBAC (**2**), we found that Ru-MACHO-BH (**34a**) is the most active catalyst. It was therefore also applied to the hydrogenation of PLA (**9**).[265,268] Excellent yields of 1,2-propanediol (**7**) could be realized within only 3 h. However, the hydrogen pressure was crucial to achieve full conversion. At least 30 bar H_2 were necessary to observe conversion of PLA (**9**). Furthermore, at least 0.25 mol% of catalyst and 120 °C were required to achieve significant conversion within 3 h. Comparing the reaction conditions to that of Westhues *et al.*[234], higher catalyst loadings were required. However, the reaction proceeded under lower reaction temperature, hydrogen pressure and with shorter reaction times. Surprisingly, all plastic goods could be converted with good yields except the paper containing composite material. Furthermore, it was shown that PLA (**9**) can be hydrogenated together with either PPC (**6**) or PBAC (**2**), thus, giving excellent yields for both, the 1,2-propanediol (**7**) and BPA (**1**). The diol **7** obtained from the hydrogenation of PLA (**9**) was used as a depolymerization reagent in a consecutive step. Therefore, POM was converted with the diol **7** to a 5-membered acetal in good ^{1}H NMR yields.

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Ruthenium-Catalyzed Hydrogenative Degradation of End-of-Life Poly(lactide) to Produce 1,2-Propanediol as Platform Chemical

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The chemical recycling of end-of-life polymers can add some value to a future circular economy. In this regard, the hydrogenative degradation of end-of-life PLA was investigated to produce 1,2-propanediol as product, which is a useful building block in polymer chemistry. In more detail, the commercially available Ru-MACHO-BH complex was applied as catalyst to degrade end-of-life PLA efficiently to 1,2-propanediol under mild conditions. After investigations of the reaction conditions a set of end-of-life PLA goods were subjected to degradation.

The impact of plastics on mankind or human life is impressively underlined by countless applications and numerous advantages compared to other materials.[1,2] Nevertheless, a significant amount of the plastics is accessed from fossil resources and after the obligations are fulfilled the plastic waste is mainly converted to greenhouse gas carbon dioxide via incineration processes, which creates numerous negative issues.[3] A fossil resources-free and "carbon dioxide-neutral" alternative is created by the use of polymers based on renewable resources.[4] The starting materials are derived from biosynthesis, which converts carbon dioxide, water and energy to useful precursors.[5] For instance one important representative is poly (lactide) (PLA, **1**) which is based on lactic acid derived from biological processes.[6] Lactic acid can either be polymerized to PLA via polycondensation reaction or by initial conversion to lactide, which can be transformed to PLA via ring opening polymerization (ROP).[7] A key benefit of poly(lactide) is the near carbon neutral performance, even if the polymer is incinerated, due to the integration of atmospheric carbon dioxide in biosynthesis.[8] Furthermore, the polymer is to some extend biodegradable, which causes less environmental problems, but it is not applicable in current industrial composting plants, because of the time needed to accomplish complete degradation.[9] However, even if the advantages of plastics from renewable resources are obvious, conflicts can arise from restricted cultivation area and competition with food production and energy production.[10] Therefore the recycling of end-of-life PLA goods can be useful option to solve some of the issues. In this regard the chemical recycling presents an interesting tool for allowing an efficient recycling.[11] In more detail, the polymer is converted to low-molecular weight chemicals in a depolymerization/ degradation step, which can be either applied as monomer or as monomer precursor to regenerate the polymer or produce other polymers in a polymerization step.[12] In consequence a recycling of the chemical functions is feasible. However, currently the implementation of chemical recycling lacks in cost efficiency, high energy demand and toleration of impurities and additives.[13]

Different approaches for the chemical recycling of end-of-life PLA have been accounted so far. For instance alcoholysis, pyrolysis and hydrogenation have been reported.[14,15,16,17,18] Recently Westhues *et al.* and Krall *et al.* reported a hydrogenative degradation reaction based on Ruthenium catalysis to yield 1,2-propanediol (**2**) as low-molecular weight chemical, which can be applied as building block for different types of polymers (Scheme 1).[17,18,19] Both systems require addition of acid or base, high hydrogen pressures and long reaction times. Recently, we have demonstrated the potential of the Ru-MACHO-BH complex **6** in the hydrogenative depolymerization of poly(bisphenol A carbonate), which allowed transformations e.g. acid/base-free conditions, at lower temperatures, low hydrogen pressure and within short times (Scheme 1).[20] Based on that initial study we investigated herein the capability of complex **6** in the hydrogenative degradation of end-of-life PLA.

The optimization of the reaction conditions of EoL-PLA degradation was studied with end-of-life transparent cups of PLA. For this purpose, pieces of the sample (68.2 μmol of **1a** based on the monomeric unit) together with the Ruthenium catalyst **6** (0.5 mol% in respect to **1a**) were dissolved in THF under argon atmosphere and the mixture was transferred to an autoclave. Initially, the autoclave was pressurized with 45 bar of H_2. Subsequently the autoclave was stirred and heated to 140 °C for 6 hours (Table 1, entry 1). Afterward, the reaction mixture was concentrated under vacuum and an aliquot was used for ^1H NMR analysis. The ^1H NMR spectrum revealed a signal at 1.09 ppm (CH_3, 3H, d, $J=6.4$ Hz), 3.33 ppm (CH_2, 1H, dd, $J=11.1$ Hz, $J=7.8$ Hz), 3.56 ppm (CH_2, 1H, dd, $J=11.1$ Hz, $J=3.1$ Hz) and 3.84 ppm (CH, 1H, m). The obtained data are in accordance with an authentic sample of 1,2-propanediol; therefore **2** was produced as major compound.[21]

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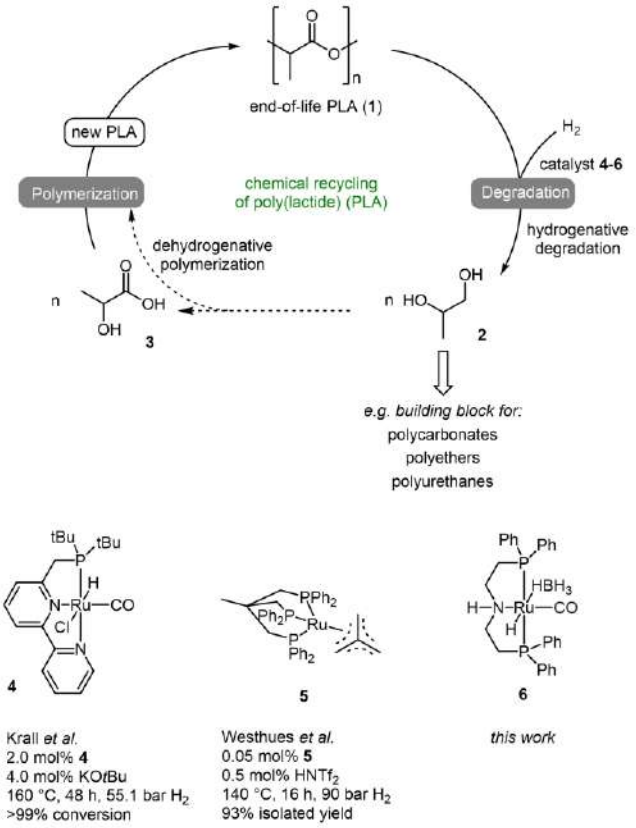
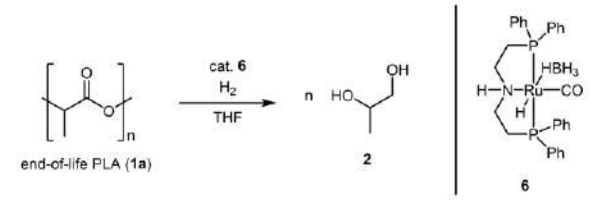


Scheme 1. Synthesis of 1,2-propanediol from end-of-life PLA.

Table 1. Ruthenium-catalyzed hydrogenative degradation of poly(lactide) (**1a**) - optimization of the reaction conditions.

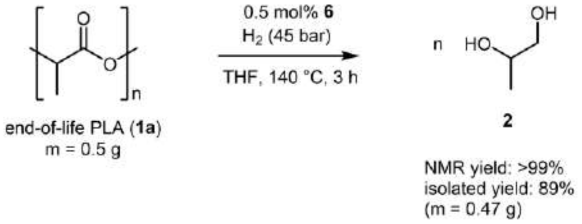


Entry[a]	Catalyst loading [mol %]	T [°C]	t [h]	p [bar]	Yield **2** [%][b]
1	0.5	140	6	45	>99
2	0.5	140	3	45	>99
3	0.5	140	1	45	33
4	0.25	140	3	45	32
5	0.1	140	3	45	<1
6	0	140	3	45	<1
7	0.5	120	3	45	67
8	0.5	100	3	45	4
9	0.5	140	3	30	95
10	0.5	140	3	20	<1
11[c]	0.5	140	1	45	<1
12[d]	0.5	140	1	45	<1

[a] Reaction conditions: poly(lactide) (**1a**) (68.2 μmol based on the repeating unit of **1a**), **6** (0–0.5 mol%, 0–0.341 μmol based on the repeating unit of **1a**), THF (1.0 mL), 100–140 °C, 1–6 h, 20–45 bar H_2. [b] The yield was determined by ^{1}H NMR. [c] Toluene as solvent. [d] Hexane as solvent.

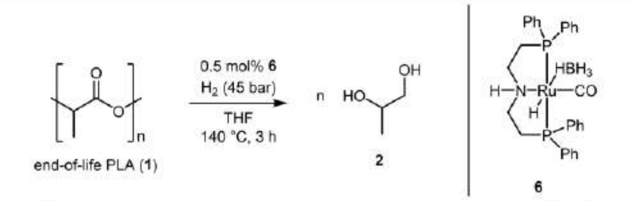
The NMR yield of **2** was determined by relating the integrals of the methyl group at 1.09 ppm from **2** with those of leftover polymer/oligomer at 1.57 ppm. In this regard, an NMR yield of >99% was calculated (Table 1, entry 1). Comparing the obtained result with the performance of Ruthenium-based hydrogenation catalysts (Scheme 1, **4** and **5**) revealed the formation of **2** within shorter reaction times (**4**: 48 h; **5**: 16 h; **6**: 3 h), lower or same temperature (**4**: 160 °C; **5**: 140 °C; **6**: 140 °C), and at lower hydrogen pressure (**4**: 55.1 bar; **5**: 90 bar; **6**: 45 bar).[17,18] However, compared with complex **5** (0.05 mol%) a higher catalyst loading of 0.5 mol% is required. Subsequently, the reaction time was reduced to 3 h revealing the same yield of **2** (Table 1, entry 2). A further reduction to one hour showed a yield of 33% (Table 1, entry 3). In the next experiments the catalyst loading was studied by gradually reducing the loading from 0.5 mol% to 0.1 mol% (Table 1, entries 4–6).

At 0.25 mol% loading a diminished yield of 32% of **2** was noticed, while at lower loading or without any catalyst no product formation was detected. Next the influence of reaction temperature was investigated (Table 1, entries 7–8). A good yield of 67% of **2** was obtained at 120 °C, while at lower temperatures only minor amounts of product **2** were realized. A reduction of the hydrogen pressure to 20 bar revealed an inactivity of the catalyst (Table 1, entries 9 and 10). Moreover, the solvent THF was replaced by toluene or hexane, but no product formation was observed (Table 1, entries 11 and 12). Based on the results of the optimization study, the following reaction conditions were selected for further experiments: 0.5 mol% of catalyst **6**, 140 °C, 45 bar H_2 and 3 h reaction time (Table 1, entry 1). Next a set of PLA containing end-of-life goods were subjected to hydrogenative degradation (Table 2). First different transparent and colourless products were tested (Table 2, entries 1–6). In most cases excellent conversion of PLA was detected, while NMR yields of 65–73% were realized (Table 2, entries 2–6). Noteworthy, for calculation of the yield it was assumed that the goods are composed of 100% PLA, since the number/amount of additives is unknown. Moreover, a transparent cup was tested, which has been used, washed and dried (Table 2, entry 6). Here a good conversion of 78% of **1** and a good yield of 73% of **2** was obtained. Moreover, dyed PLA products were hydrogenated (Table 2, entries 7–14). Excellent conversion of PLA was found for most products, while in case of **1i** a low conversion and for **1m** no conversion was detected (Table 2, entries 9 and 13). However, the obtained yields for **2** are to some extend lower compared with transparent products. After successful degradation of the used cups **1a** under the optimized conditions, a scale up was carried out with 0.5 g of **1a** (Scheme 2). Here product **2** was obtained in >99% NMR yield and in 89% isolated yield after distillation.[22]



Scheme 2. Degradation of PLA cups – scale-up experiment.

Table 2. Ruthenium-catalyzed hydrogenative degradation of PLA goods.



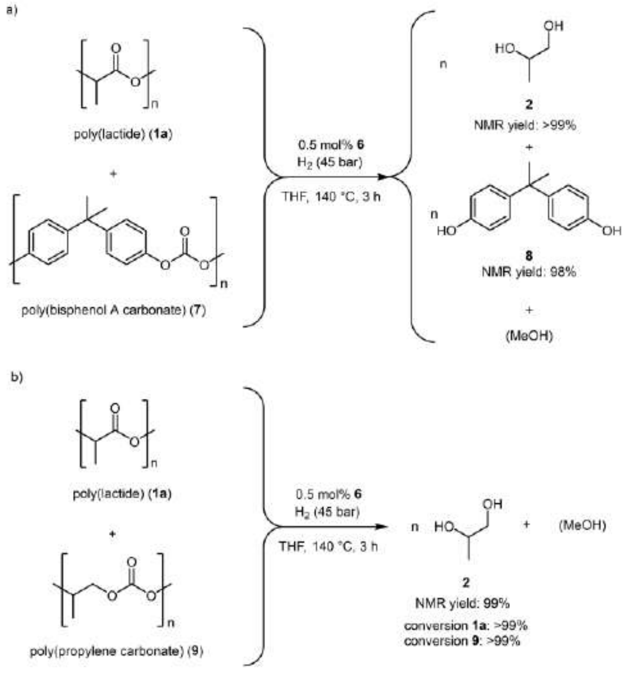
Entry[a]	Product	Conversion of 1[b]	Yield of 2 [%][c]
1	transparent cup (**1 a**)	>99	>99
2	transparent disposable food box (**1 b**)	>99	65
3	transparent Sushi box cover (**1 c**)	>99	67
4	transparent plastic sheet (**1 d**)	>99	68
5	transparent bottle (**1 e**)	>99	66
6	used/washed/dried transparent cups (**1 f**)	78	73
7	drinking straw with green strips (**1 g**)	>99	67
8	disposable knife with talcum powder (**1 h**)	>99	31
9	lid for espresso mugs (contains ~20–30% talcum powder) (**1 i**)	41	<1
10	black lid for coffee mugs (**1 j**)	>99	59
11	Sushi box (black base) (**1 k**)	>99	74
12	pink ice cream spoon (**1 l**)	>99	4
13	coffee paper cup coating (**1 m**)	<1	<1
14	disposable blue gloves (**1 n**)	>99	5

[a] Conditions: **1 a**–**1 n** (4.9 mg, 68.2 µmol based on the repeating unit), **6** (0.2 mg, 0.5 mol%, 0.341 µmol based on the repeating unit of **1**), THF (1.0 mL), 140 °C, 3 h, 45 bar H_2 [b] The conversion of PLA was determined by relating the ^{1}H NMR signals of PLA to the signals of the monomer. [c] The yield was determined by ^{1}H NMR with an internal standard of 5-*tert*-butyl-*m*-xylene. The amount of substance of **2** was linked to the amount of substance in the initial PLA-good (presumption: PLA-good contains 100% of PLA).

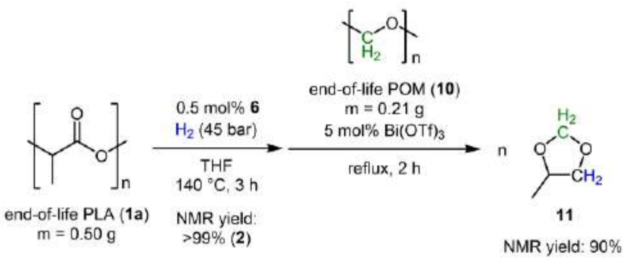
Next the simultaneous hydrogenative depolymerization/degradation was studied (Scheme 3). In this regard, a mixture of end-of-life PLA and end-of-life poly(bisphenol A carbonate) (**7**) was reacted with hydrogen in the presence of complex **6**.[17] Both polymers were converted to the corresponding monomer in good to excellent yields. On the other hand, a mixture of PLA **1 a** and poly(propylene carbonate) (**9**) was subjected to hydrogenative depolymerization/ degradation.[23] Noteworthy, both polymers were converted to product **2** in excellent yield.

In addition, a consecutive degradation approach of PLA and poly(oxymethylene) (**10**) was investigated in accordance to Klankermayer and co-worker (Scheme 4).[24] In this regard, end-of-life PLA is converted to **2**, which is required for the degradation of **10** to produce a cyclic acetal, which can be useful chemical, e.g. as monomer for new polymers.[24]

In more detail, **1 a** was depolymerized with hydrogen in the presence of catalytic amounts of complex **6** to form **2** in >99% yield. After 3 hours the excess of hydrogen was released and into the reaction mixture poly(oxymethylene) **10** (monomeric ratio **1 a**:**10** 1:1) and catalytic amounts of bismuth(III) triflate (5 mol%) was added.[25] After 2 hours at refluxing conditions (oil bath temperature: 90 °C) 4-methyl-1,3-dioxolane (**11**) was obtained in 90% yield.



Scheme 3. Simultaneous hydrogenative depolymerization/degradation of PLA and a) poly(bisphenol A carbonate) or b) poly(propylene carbonate).



Scheme 4. Consecutive degradation of PLA and POM.

In summary, we have studied a homogenous catalyst system for the hydrogenative degradation of EoL-poly(lactide). The commercially available Ruthenium-MACHO-BH complex was used at low catalyst loadings to yield 1,2-propanediol as a beneficial chemical in good to excellent yields. Compared to established hydrogenative degradation methods milder conditions were required for the degradation of PLA goods. This might be one step towards achieving the UN's goals for a sustainable development (SDGs 9,11) and a future waste management system (SGD 12).[26]

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: green chemistry · catalysis · polymers · recycling · degradation

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[21] The NMR data were compared with the NMR data of an authentic sample of **2**.

[22] **2** was obtained in an optical purity of 10%; therefore to some extend racemerization took place. $[a]_D = 2.2°$ (c = 1 g/100 mL, $CHCl_3$, 20 °C). $[a]_{max} = 22.685°$ (c = 1.020 g/100 mL, $CHCl_3$, 20 °C, wavelength: 589.3 nm, 20 °C), L. L. Welbes, R. C. Scarrow, A. S. Borovik, *Chem. Commun.* **2004**, 2544.

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5.9 Depolymerization of poly(ε-caprolactone) via hydrogenation

In our previous study we found that PCL (**28**) can be hydrogenated in the presence of PLA (**9**). Therefore, we wanted to address a detailed study to its hydrogenation 1,6-hexane diol and further repolymerize it using the same catalyst.[269] The Ru-MACHO-BH precatalyst (**34a**) allowed for excellent yields under milder reaction conditions as in other literature reports. However, the repolymerization affords a copolymer of adipic acid, 1,6-hexane diol and 6-hydroxyhexanoic acid with M_n up to 3,200 g/mol.

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Ruthenium-catalyzed Chemical Recycling of Poly(ε-caprolactone) via Hydrogenative Depolymerization and Dehydrogenative Polymerization

Christoph Alberti and Stephan Enthaler*[a]

The chemical recycling of end-of-life polymers can be a beneficial part for a future circular chemistry/economy. In this regard, the chemical recycling of poly(ε-caprolactone) (PCL) was studied. In more detail, end-of-life PCL was depolymerized by hydrogenation with the aid of catalytic amounts of the commercially available Ru-MACHO-BH complex to generate 1,6-hexanediol. The 1,6-hexanediol was used as starting material to synthesize polyesters based on poly(ε-caprolactone) and/or poly(1,6-hexanediol-adipate) in a dehydrogenative polymerization enabled by catalytic amounts of the Ru-MACHO-BH complex. Overall a recycling is feasible.

The establishment of plastics with their diverse properties and applications allows the current way of life and a future without plastics is hardly conceivable.[1,2] Nevertheless, some disadvantages cast a shadow over the success story of plastics. For instance, the use of the depleting fossil resources as source for many plastics and the fate of the plastics after fulfilled obligations causes difficulties. In more detail, the main portion of plastic waste is converted to the greenhouse gas carbon dioxide via incineration processes, which creates numerous negative issues.[3,4] On the other hand, plastic recycling processes allow for the saving of fossil resources and the avoidance of carbon dioxide formation.[5,6] In this regard, mechanical recycling and downcycling have been established, but sooner or later also these plastic portions will end up in the incineration pathway.[7] A possibly more resource-conserving and sustainable method represents the chemical recycling.[8] The chemical recycling bases on two processes. In the first part the end-of-life polymer is transformed via depolymerization reactions to the monomers or low-molecular weight chemicals. Secondly, the monomers/ low-molecular weight chemicals are subjected to polymerization to rebuild a new version of the polymer. Connecting the depolymerization with the polymerization process makes a recycling of polymers/plastics achievable. Importantly, the chemical recycling enables a decoupling of the quality/abilities of the rebuild polymer/plastic from the quality/abilities of the end-of-life polymer/plastic, which can occur for mechanical recycling and/or downcycling.

One interesting type of (mainly) fossil resource-based polymer is poly(ε-caprolactone) (PCL, **1**) a biodegradable and thermoplastic polyester with applications in packaging industry and medicine.[9] With respect to chemical recycling of end-of-life **1** mainly the enzyme-catalyzed ring-closing depolymerizations followed by a potential ring-opening polymerization has been studied.[10] Moreover, organo-catalyzed as well as Zn-$(OAc)_2$-catalyzed methanolysis of PCL has been reported, yielding methyl 6-hydroxyhexanoate after depolymerization, which can be polymerized to new PCL.[11,12]

Another option for the chemical recycling of end-of-life poly(ε-caprolactone) can be the coupling of a hydrogenative depolymerization and a dehydrogenative polymerization (Scheme 1). Importantly, as depolymerization reagent hydrogen is required, which potentially can be recovered from the polymerization process, which allows a high atom economy for the chemical recycling method. In more detail, the hydrogenation of PCL yields 1,6-hexanediol as product, which can be the starting material for the dehydrogenation process to resynthesize a fresh portion of PCL. Interestingly, Krall *et al.* and Westhues *et al.* reported recently the hydrogenative depolymerization of **1** based on ruthenium catalysis (complexes **3** and **4**) to yield 1,6-hexanediol (**2**) as low-molecular weight chemical (Scheme 1).[13,14] Applying precatalyst **3** good yields of **2** were obtained at low catalyst loadings and low hydrogen pressure.[13] Excellent performance was exhibited by complex **4** within short reaction time, but higher hydrogen pressure.[14] On the other hand Hunsicker *et al.* investigated the dehydrogenative polymerization of **2** to form **1** in the presence of the Milstein catalyst **5**.[15] Polymer **1** was obtained in 97 % yield after 5 days with number average molar mass of M_n ~29,4 kg/mol. Moreover, Malineni *et al.* demonstrated the potential of ruthenium carbene complex.[16] Polyesters were isolated after 48 h in 67 % yield and M_n ~4500 g/mol, but high catalyst loadings are required. An analysis of a similar polymer derived from 1,12-dodecanediol revealed the presence of different units in the polymer, e.g., dicarboxylic acids, and hydroxyl-acids, which can be also assumed for C_6-based polymers (Scheme 1, **7**).[16]

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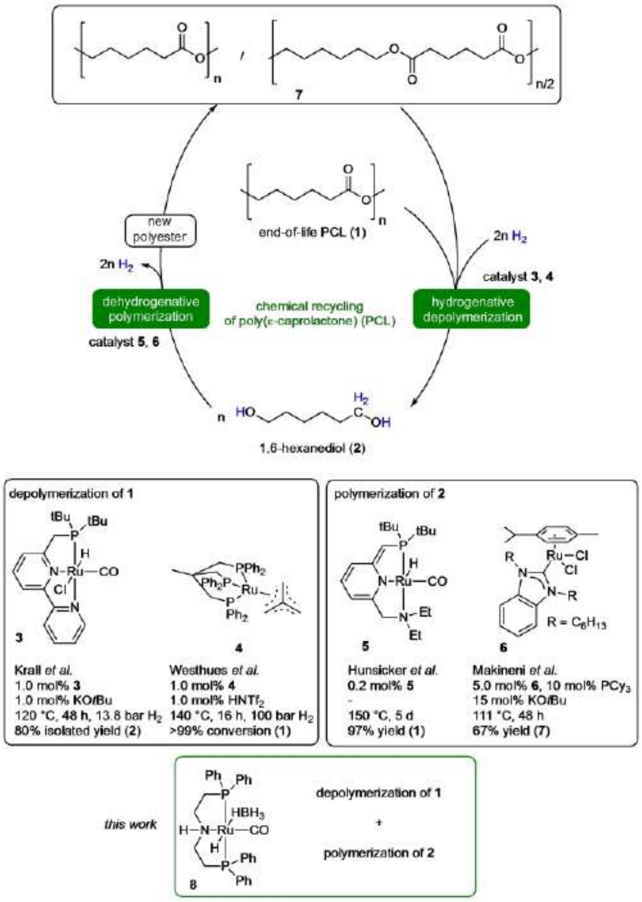
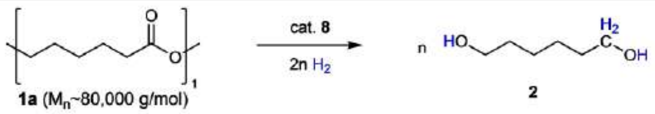


Scheme 1. Chemical recycling of end-of-life polyesters.

Noteworthy, for both parts of the chemical recycling process different catalysts have been established. Nevertheless, based on the general reaction path (hydrogenation/dehydrogenation) we wonder if one catalyst can enable the hydrogenative depolymerization as well as the dehydrogenative polymerization controlled by the presence/absence of hydrogen. Recently, we have demonstrated the benefit of the Ru-MACHO-BH complex **8** in different hydrogenative depolymerization reactions (e.g., poly(bisphenol A carbonate), poly(lactide)).[17] Based on that we studied the capability of complex **8** in the chemical recycling of PCL.

The optimization of the reaction conditions of end-of-life PCL hydrogenation was examined with commercially available PCL (**1 a**, $M_n \sim 80{,}000$ g/mol) (Table 1). In this regard, pellets of **1 a** (0.14 mmol of **1 a** based on the monomeric unit) and the Ruthenium complex **8** (0.5 mol% in respect to the monomeric unit of **1**) were dissolved in THF under argon atmosphere and the mixture was transferred to an autoclave. Primarily, the autoclave was pressurized with 45 bar of H_2. Subsequently the autoclave was heated at 140 °C for 24 hours and the reaction mixture was stirred (Table 1, entry 2). Afterward, an aliquot of the reaction mixture was subjected to ^{1}H NMR analysis. The ^{1}H NMR spectrum revealed the occurrence of a new signal at 3.63 ppm (2xCH_2OH, 4H, t, $J = 6.5$ Hz), which can be assigned to the hydrogenation product **2**. The obtained data are in accordance with an authentic sample of 1,6-hexanediol. A yield of 22% was detected. Increasing the loading of the catalyst resulted in an increase of the yield of **2** (Table 1, entries 3–5). For instance, with 5 mol% of **8** a yield of >99% was observed (Table 1, entry 5). Changing the solvent from THF to toluene showed a better performance at low catalyst loading (Table 1, entries 2 and 6).[18] In more detail, full conversion was reached within 24 hours with a loading of 0.4 mol% of **8**. Same result

Table 1. Ruthenium-catalyzed hydrogenative depolymerization of poly(ε-caprolactone) (**1 a**) - optimization of the reaction conditions.



Entry[a]	Catalyst loading [mol%]	solvent	T [°C]	t [h]	p [bar]	Yield **2** [%][b]
1	0	THF	140	24	45	<1
2	0.5	THF	140	24	45	22
3	1.0	THF	140	24	45	46
4	2.5	THF	140	24	45	57
5	5.0	THF	140	24	45	>99
6	0.4	toluene	140	24	45	>99
7[c]	0.4	toluene	140	24	45	>99
8[d]	2.5	toluene	140	24	45	>99
9	0.4	–	140	24	45	<1
10	2.5	2-PrOH	140	24	45	<1
11	5.0	toluene	140	6	45	>99
12	5.0	toluene	120	24	45	99
13	5.0	toluene	100	24	45	>99
14	5.0	toluene	140	24	30	>99
15	5.0	toluene	140	24	10	91
16[e]	5.0	THF	140	24	45	>99

[a] Reaction conditions: poly(ε-caprolactone) (**1 a**) (0.14 mmol based on the repeating unit of 1), **8** (0–5.0 mol%, 0–0.007 mmol based on the repeating unit of 1), THF or toluene (2.0 mL), 100–140 °C, 6–24 h, 10–45 bar H_2. [b] The yield was determined by ^{1}H NMR. [c] 0.1 mL toluene. [d] KOtBu (2.5 mol%) was added. [e] Poly(ε-caprolactone) (**1 b**) ($M_n \sim 14{,}000$ g/mol).

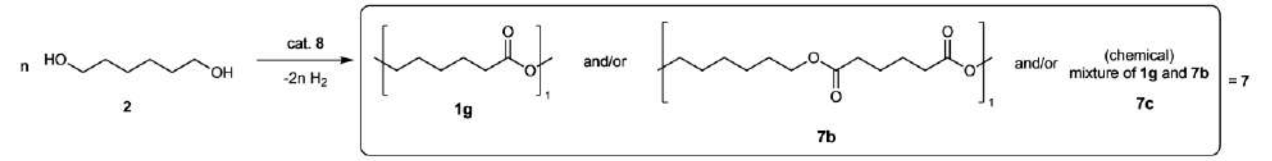
was observed if the amount of solvent was reduced, while under neat conditions no product formation was noticed (Table 1, entries 7 and 9). Moreover, reducing the reaction time to six hours resulted in the formation of $>99\%$ of **2** (Table 1, entry 11). In addition, the influence of the reaction temperature was studied revealing a still excellent performance at 100 °C (Table 1, entries 12 and 13). Furthermore, the hydrogen pressure was decreased showing a lower yield of **2** at 10 bar hydrogen (Table 1, entries 14 and 15). The poly(ε-caprolactone) (**1b**) with a lower number average molar mass ($M_n \sim 14{,}000$ g/mol) was converted in excellent yield to product **2** (Table 1, entry 16). In comparison to the work of Krall *et al.* a higher hydrogen pressure is needed to obtain the product in quantitative yield.[14] Nevertheless, full conversion was reached within shorter reaction time and with lower catalyst loading. Moreover, in contrast to Westhues *et al.* a lower catalyst loading, hydrogen pressure and temperature is required to generate suitable amounts of **2**.[13] Moreover, in contrast to the methanolytic depolymerization product **9** the hydrogenative depolymerization product **2** is established as suitable diol building block in the synthesis of different types of polymers.[11,12,19]

After having demonstrated the potential of complex **8** in the hydrogenative depolymerization of poly(ε-caprolactone) (**1**) to produce 1,6-hexanediol the reverse reaction for closing the cycle was investigated (Table 2). In more detail, 1,6-hexanediol was applied as monomer in the dehydrogenative polymerization to produce polyester **7** under solvent-free conditions. Polyester **7** can be composed of poly(ε-caprolactone) (**1g**), 1,6-1,6-hexanediol-adipate copolymer (**7b**) or a chemical mixture of **1** and **7b**. A mixture of **2** and catalytic amounts of **8** was heated at 130 °C for 24 hours under a constant flow of dinitrogen (Table 2, entry 2).[16] After cooling to room temperature, the conversion of **2** was determined by ^{1}H NMR relating the CH_2-function of **2** to the CH_2-functions of **7**. A conversion of 16 % was observed, which corresponds to a TON of 428. Importantly, in the absence of complex **8** no product formation was noticed (Table 2, entry 1). Changing the ratio of **8**:**2** to 1:250 a conversion of 92 % and a viscous product was noticed, which was solidified after standing at room temperature (Table 2, entry 4). Importantly, without a constant flow of dinitrogen to remove the produced hydrogen a lower conversion of 45 % was obtained (Table 2, entry 6). Increasing and decreasing the temperature revealed lower conversion compared to 130 °C (Table 2, entries 7 and 8). In case of high catalyst loading a number average molar mass of $M_n \sim 3200$ g/mol, a mass average molar mass $M_w \sim 10706$ g/mol was detected by GPC analysis (Table 2, entry 4).[20] Noteworthy, the M_n is in the range of the values reported by Malineni *et al.*[16]

In contrast, for reactions with low catalyst loadings only oligomers were observed by ESI-MS. In some cases, small amounts of ε-caprolactone were detected in the reaction mixture of the dehydrogenative polymerization by ^{1}H NMR. The formation of ε-caprolactone may occur by ring-closing reaction of 6-hydroxyhexanal, which have been proposed as intermediate after catalytic dehydrogenation of one hydroxy function, to form the cyclic hemiacetal, which is dehydrogenated by the catalyst to generate ε-caprolactone.[15] The ε-caprolactone can be subjected to catalytic ring opening polymerization (ROP) to form the desired poly(ε-caprolactone). On the other hand, the formation of ε-caprolactone can be caused by side reaction, e.g. back-biting processes.[21]

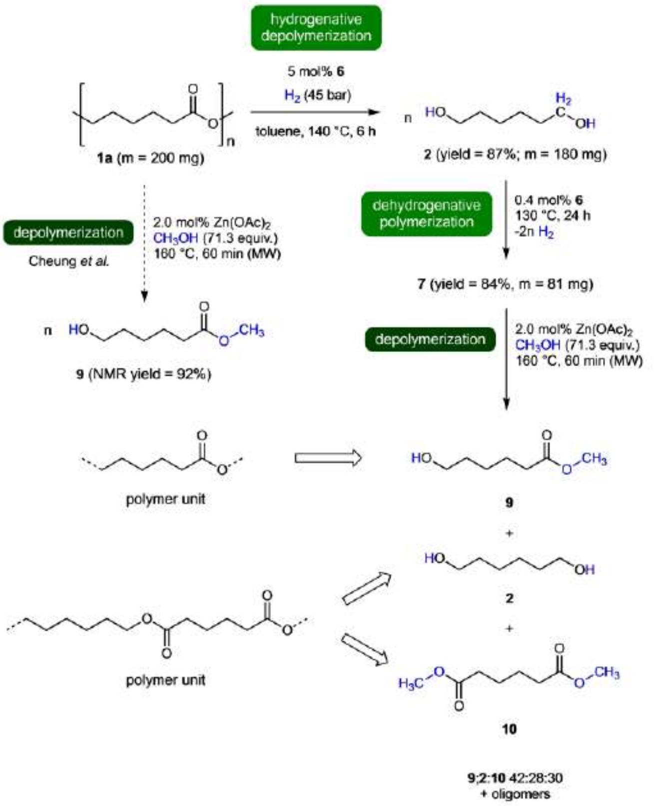
In addition, a scale-up of the hydrogenative depolymerization of **1** was performed (Scheme 2). In this regard, end-of-life **1** was converted to 1,6-hexanediol under optimized conditions (Table 1, entry 7). **2** was isolated from the reaction in 87 % yield. The isolated chemical **2** was subjected to dehydrogenative polymerization process under optimized conditions (Table 2, entry 4). Polymer **7** was isolated in 84 % yield (m = 81 mg). For a better understanding of the composition of polymer **7** a depolymerization via methanolysis was carried out.[22] Recently, we have studied the chemical recycling of different polyesters applying as key step a methanolysis to obtain methyl esters as beneficial depolymerization product.[12,23] In case of polymer **1**

Table 2. Ruthenium-catalyzed dehydrogenative polymerization.[a]

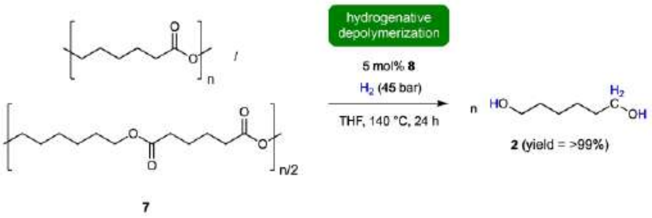


Entry	Catalyst loading [mol%]	**8**:**2** ratio	T [°C]	Conv. **2** [%][b]	TON	M_w (**7**) [g/mol][c]	M_n (**7**) [g/mol][c]
1	–	–	130	<1	–	–	–
2	0.037	1:2674	130	16	428	n.d.[d]	n.d.[d]
3	0.019	1:5348	130	2	107	–	–
4	0.400	1:250	130	92	230	10706	3200
5	0.200	1:500	130	31	155	n.d.[d]	n.d.[d]
6[e]	0.400	1:250	130	45	113	n.d.[d]	n.d.[d]
7	0.400	1:250	150	12	30	5250	1838
8	0.037	1:2674	100	3	80	–	–

[a] Reaction conditions: 1,6-hexanediol (**2**) (2.27–24.33 mmol), THF solution of **8** (0–0.4 mol %, 0–0.0045 mmol, 0.5 mL), 100-150 °C, 24 h, dinitrogen was passed through. [b] The conversion was determined by ^{1}H NMR. [c] GPC measurements in THF. [d] not detectable. Oligomers were observed by ESI-MS. [e] Reaction was performed in a closed vial without dinitrogen flow.



Scheme 2. Hydrogenative depolymerization and dehydrogenative polymerization.



Scheme 3. Hydrogenative depolymerization of **7**.

zinc catalysis was used to generate compound **9**, which can be used to resynthesize polymer **1** (Scheme 2).[12] Transferring this approach to polymer **7**, revealed in the presence of $Zn(OAc)_2$ (2.0 mol%) after 60 min at 160 °C under microwave heating the formation of low molecular weight chemicals (monomers, oligomers). On the one hand methyl 6-hydroxyhexanoate (**9**) was detected by GC-MS, which is formed by methanolysis of ε-caprolactone units of polymer **7**. Moreover, 1,6-hexanediol (**2**) and dimethyl adipate (**10**) were detected, which are the products of methanolysis of hexanediol-adipate-units of polymer **7**. Based on that, the dehydrogenative polymerization process produces a combination of poly(ε-caprolactone) (**1 f**) 1,6-hexanediol-adipate (**7b**) and/or copolymers of these two polymers (**7b**). The low molecular weight chemicals were observed in a ratio of 42:28:30 (**9**:**2**:**10**). Noteworthy, along with **2**, **9** and **10** oligomers were detected.

Finally, the polymer obtained by dehydrogenative polymerization was subjected to hydrogenative depolymerization to close the cycle (Scheme 3). 1,6-Hexanediol was obtained in >99% after 24 hours at 140 °C.

In summary, we have studied a catalyst system, which allows the chemical recycling of poly(ε-caprolactone) via hydrogenative depolymerization and dehydrogenative polymerization. The commercially available Ruthenium-MACHO-BH complex was used for the hydrogenative depolymerization of poly (ε-caprolactone) to yield 1,6-hexanediol as a valuable chemical in good to excellent yields. In a subsequent polymerization step the Ruthenium-MACHO-BH complex transforms the monomer 1,6-hexanediol to polyesters, which contains poly(ε-caprolactone), poly(1,6-hexanediol-adipate) or their copolymers. These polymers can be converted back to 1,6-hexanediol to close the cycle.

Supporting Information Summary

The experimental details including the depolymerization and polymerization reactions and product characterizations can be found in the supporting information.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: green chemistry · catalysis · polymers · recycling · sustainability

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[18] The catalyst loading is in accordance to the catalyst loading for the dehydrogenative polymerization (Table 2).

[19] Comparison of i) methanolytic depolymerization of PCL and ii) hydrogenative depolymerization of PCL (even if different products with different follow-up chemistry are formed: catalyst loading to reach highest conversion/yield: i):ii) 1.0 mol%:0.4 mol%; catalyst costs: i) Zn(OAc)$_2$: 314 €/mol, ii) **9**: 66265 €/mol; reaction temperature: i) 160 °C, ii) 140 °C; reaction time: i) 60 min, ii) 360 min; pressure: i) ca. 20 bar, ii) 45 bar.

[20] Comparison of i) polymerization to PCL and ii) dehydrogenative polymerization of **2** (even if different products with different follow-up chemistry are formed: catalyst loading to reach highest conversion/yield: i):ii) 1.0 mol%:0.4 mol%; catalyst costs: i) Zn(OAc)$_2$: 314 €/mol, ii) **9**:66265 €/mol; reaction temperature: i) 130 °C, ii) 130 °C; reaction time: i) 48 h, ii) 24 h; M$_w$: i) 5823 g/mol, ii) 10706 g/mol; M$_n$: i) 1729 g/mol, ii) 3200 g/mol.

[21] See for instance: M. Labeta, W. Thielemans, *Chem. Soc. Rev.* **2009**, *38*, 3484–3504.

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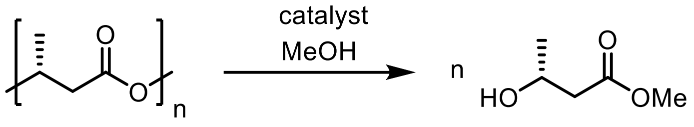
6. Non-cumulative part

6.1 Discussion

6.1.1 Methanolysis of poly(3-hydroxybutyrate)

This chapter bases on the results from a submitted article, which was part of the bachelor thesis of Even Cheung.[260,270] Initially, different catalysts were tested for the methanolysis of P3HB (**26**). Therefore, the polymer, the catalyst and methanol were heated under microwave irradiation. The yield of **27** was calculated on the basis of the ^{1}H NMR signals of the methine protons of **26** and **27**. It was found that only Zn(II) carboxylates and $Sn(Oct)_2$ were active. The inactivity of $ZnCl_2$ is in accordance to the observations of Song *et al*.[196] Surprisingly, Xie *et al*. described $(Me_4N)F$ as a highly active catalyst and accounted this to the F^--ions.[198] However, KF did not promote formation **27** under the chosen reaction conditions. As $Zn(OAc)_2$ revealed the highest TOF, it was used to explore the influence of the reaction parameters. For the reaction, at least 140 °C were required and at 180 °C, the highest activity (TOF 1740 h^{-1}) was observed. Moreover, reducing the catalyst loading, the MeOH loading or the reaction time, had a diminishing effect on the yield of **27**. At 160 °C, the reaction was run to completeness after 30 min.

Table 1: Depolymerization of **26** – optimization of reaction conditions. Conditions: P3HB (**26**), 1.16 mmol with respect to the monomer unit), catalyst (0-1.0 mol%, 0-0.0116 mmol with respect to the monomer unit of **26**), MeOH (37.5-67.5 equiv. with respect to the monomer unit of **26**), temperature: 120-180 °C (microwave heating), time: 1-30 min.



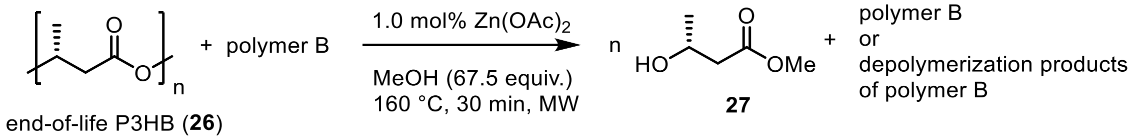
end-of-life P3HB (**26**)

27

Entry	Catalyst	Catalyst loading [mol%]	MeOH [equiv.]	T [°C]	t [min]	Yield **27** [%]	TOF [h^{-1}]
1	-	-	67.5	160	10	<1	<1
2	$Zn(OAc)_2$	1.0	67.5	160	10	59	354
3	$ZnCl_2$	1.0	67.5	160	10	<1	<1
4	$ZnBr_2$	1.0	67.5	160	10	<1	<1
5	$Zn(OTf)_2$	1.0	67.5	160	10	<1	<1
6	Zinc(II) methacrylate	1.0	67.5	160	10	50	300
7	KF	1.0	67.5	160	10	<1	<1
8	$Sn(Oct)_2$	1.0	67.5	160	10	29	174
9	Bismuth subsalicylate	1.0	67.5	160	10	<1	<1
10	$Zn(OAc)_2$	1.0	67.5	140	10	26	156
11	$Zn(OAc)_2$	1.0	67.5	120	10	<1	<1
12	$Zn(OAc)_2$	1.0	67.5	180	1	29	1740
13	$Zn(OAc)_2$	0.5	67.5	160	10	29	348
14	$Zn(OAc)_2$	1.0	56.3	160	10	51	306
15	$Zn(OAc)_2$	1.0	37.5	160	10	38	228
16	$Zn(OAc)_2$	1.0	67.5	160	5	31	186
17	$Zn(OAc)_2$	1.0	67.5	160	30	>99	200

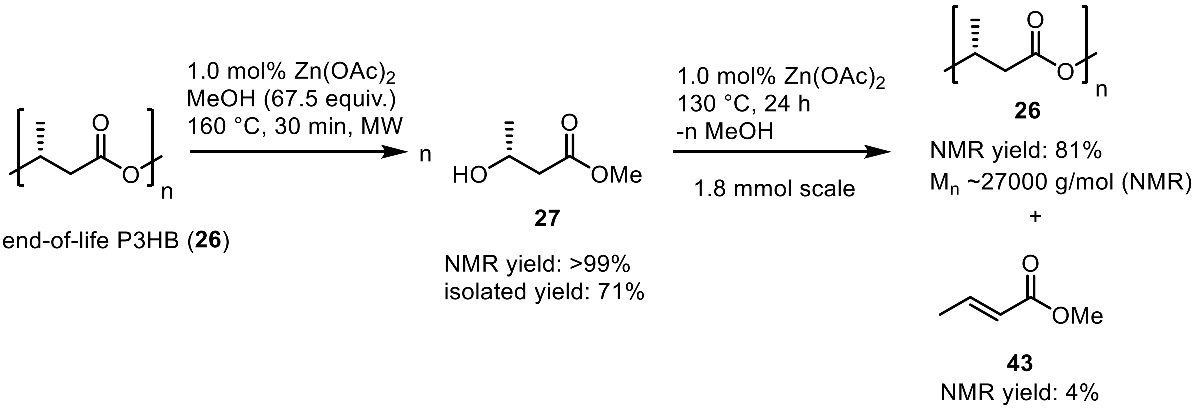
Next, the reaction was carried out under optimized conditions in the presence of one additional polymer. All polyesters and PBAC (**2**) underwent methanolytic depolymerization but in case of PLA (**9**) and PBAC (**2**) the yield of **27** was slightly diminished. Surprisingly, PET (**14**) did undergo depolymerization in the presence of P3HB (**26**). As PET (**14**) alone does not react in neat MeOH at 160 °C due to insolubility,[270] the depolymerization product of **26** might be a suitable solvent that is generated in situ. This effect could potentially by exploited to accomplish the depolymerization of PET (**14**). The co-depolymerization of PLA (**9**) and P3HB (**26**) (table 2, entry 3) reveals that PLA (**9**) is more rapidly converted compared to P3HB (**26**). In addition, polymers that are not conveniently degraded by methanolysis were not found to affect the methanolysis, except for Nylon 6 (**31**), PVC and poly(vinyl alcohol) (table 2, entries 5, 9-10).

Table 2: Influence of additional polymers on the methanolysis of **26**: [a] Conditions: P3HB (**26**), 1.39 mmol with respect to the monomer unit), $Zn(OAc)_2$ (1.0 mol%, 0.0139 mmol with respect to the monomer unit of (**26**)), MeOH (67.5 equiv. with respect to the monomer unit of **26**), temperature: 160 °C (microwave heating), time: 30 min. [a] DMT (**16**) and EG (**17**). [b] Methyl 6-hydroxycapronate. [c] Methyl lactate (**13**). [d] BPA (**1**) and DMC (**4**).



Entry[a]	Additional polymer B	Yield of **27** [%]	Yield [%]
1	PET (**14**)	>99	93[a]
2	PCL (**28**) (M_n ~80,000 g/mol)	>99	95[b]
3	PLA (**9**)	48	99[c]
4	PBAC (**2**)	91	96[d]
5	Nylon 6 (**31**)	67	<1
6	Poly(phenylene sulfide)	>99	<1
7	PE (M_n ~1,700 g/mol)	98	<1
8	PS (Mw ~35,000 g/mol)	>99	<1
9	PVC (Mw ~48,000 g/mol)	74	<1
10	Poly(vinyl alcohol) (M_w ~67,000 g/mol)	42	<1
11	Poly(ethylene glycol) methyl ether (M_n ~5,000 g/mol)	>99	<1
12	Epoxy resin (M_n ~1,750 g/mol)	>99	<1
13	Poly(dimethylsiloxane)	>99	<1

Next, the methyl ester **27** was obtained by filtration and removal of the solvent. Consecutively, its polymerization to new **26** was carried out in the presence of 1 mol% $Zn(OAc)_2$. Notably, methyl crotonate (**43**) was formed as side product. On the other hand, the polymer was obtained after 24 h at 130 °C by precipitation into water and revealed an M_n of 27000 g/mol, as determined by end-group analysis using the ^1H NMR signals of the end-groups and repeating units.



Scheme 15: $Zn(OAc)_2$ catalyzed depolymerization with subsequent polycondensation to P3HB (**26**).

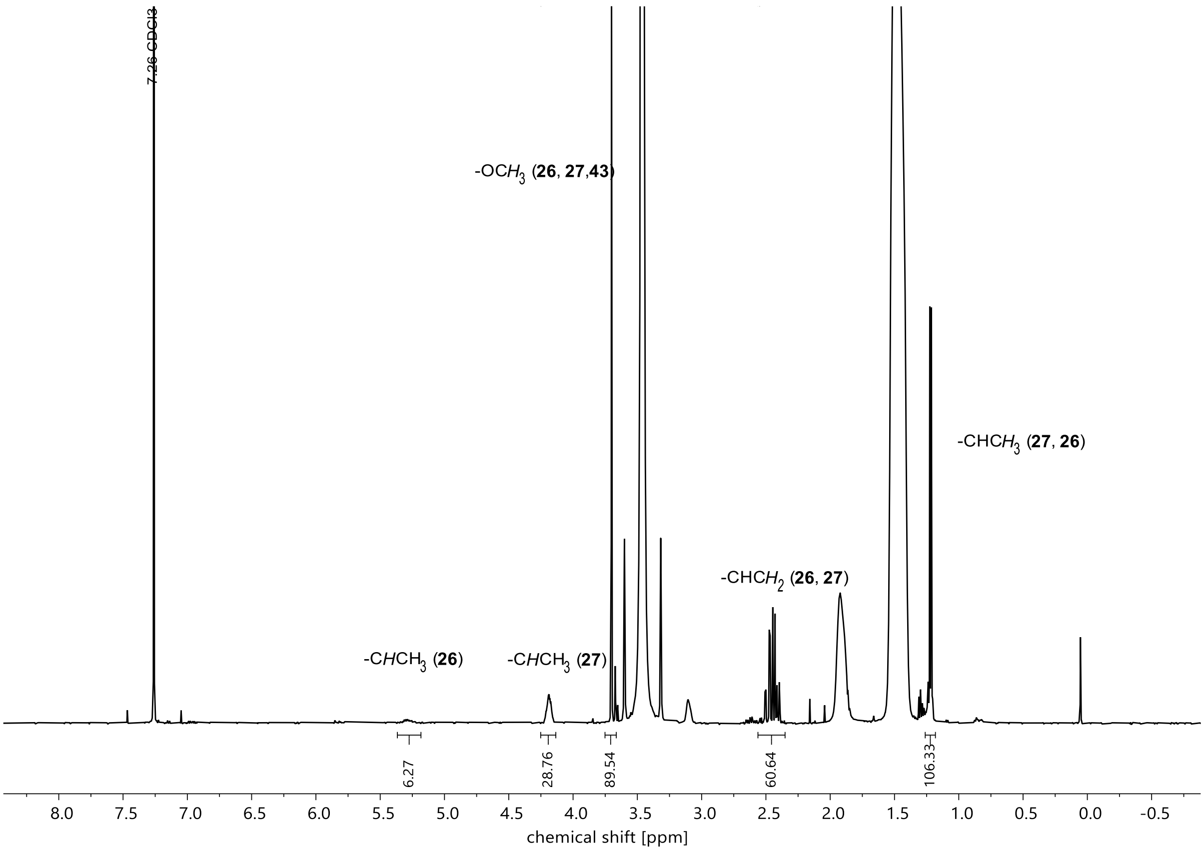
Summarizing the results of this study, it was shown that a robust chemical recycling process for P3HB using methanol as reagent is feasible. The depolymerization affords **27** that does not require extensive purification. The depolymerization can be carried out in the presence of other polymers while the yield for **27** was reduced in the presence of PLA (**9**), PVC, Nylon 6 (**31**) and poly(vinylalcohol). A beneficial effect on the depolymerization of PET (**14**) was observed. Furthermore, without extensive purification, the monomer can be repolymerized to **26** in the presence of $Zn(OAc)_2$.

6.2 Experimental part

6.2.1 Methanolysis of poly(3-hydroxybutyrate)

General: All chemicals were used as received without further manipulations. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a *Fourier 300 MHz* (^{1}H: 300 MHz, ^{13}C: 75 MHz), *Avance I-400* (^{1}H: 400 MHz, ^{13}C: 101 MHz) or *Avance I 500* (^{1}H: 500 MHz, ^{13}C: 126 MHz) by Bruker, using the signals of the deuterated solvents as reference or external standards. For microwave heating experiments a Microwave Synthesis Reactor Monowave 400 (Anton Paar GmbH) was used.

General procedure for the depolymerization of P3HB (26): (optimization of the reaction conditions): A mixture of P3HB (**26**, Sigma Aldrich/Merck 363502) (100 mg, 1.16 mmol based on the repeating unit of **26**), methanol (1.7-3.0 g, 52.0-93.65 mmol, 37.5-67.5 equiv. equiv. based on the repeating unit of **26**) and a catalyst (0-1.0 mol%, 0-0.0116 mmol based on the repeating unit of **26**) was placed with a stir bar in a vial. The vial was sealed and heated by microwave irradiation. The reaction was performed for 1-30 minutes (hold time) at 120-180 °C and with a stirring of 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature. An aliquot of the clear solution was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^{1}H NMR to determine the yield of methyl 3-hydroxybutyrate (**27**) [The yield of (**27**) was calculated on the basis of the C*H* function of **27** and the leftover signals of the C*H* function of the polymer/oligomers].



Procedure for the depolymerization of P3HB (26): A mixture of P3HB (**26**, Sigma Aldrich/Merck 363502) (100 mg, 1.16 mmol based on the repeating unit), methanol (3.0 g, 93.65 mmol, 67.5 equiv. equiv. based on the repeating unit of **26**) and $Zn(OAc)_2$ (1.0 mol%, 2.1 mg, 0.0116 mmol based on the repeating unit of **26**) was placed with a stir bar in a vial. The vial was sealed and heated by microwave irradiation. The reaction was performed for 30 minutes (hold time) at 160 °C and with a stirring of 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature. An aliquot of the clear solution was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^1H NMR to determine the yield of methyl 3-hydroxybutanoate (**27**) [The yield of **27** was calculated on the basis of the C*H* function of **27** and the leftover signals of the C*H* function of the polymer/oligomers]. The reaction mixture was filtered and the solvent was quickly removed in vacuum. As product a colorless oil was obtained (Yield = 71%, m = 194.4 mg). The analytical data is in accordance to the literature.[196]

Methyl 3-hydroxybutanoate (**27**): ^1H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 4.15\text{-}4.25$ (m, 1H, $\mathrm{CH_3C}\mathit{H}$), 3.71 (s, 3H, $\mathrm{C}\mathit{H}_3\mathrm{O}$-), 2.47 (dd, $J = 16.45$ Hz, $J = 2.48$ Hz, 1H, $\mathrm{CHC}\mathit{H}_2$-), 2.46 (dd, $J = 16.52$ Hz, $J = 11.42$ Hz, 1H, $\mathrm{CHC}\mathit{H}_2$-), 2.37-2.53 (m, 2H, $\mathrm{CHC}\mathit{H}_2$), 1.23 (d, $J = 6.33$ Hz, 3H, $\mathrm{C}\mathit{H}_3\mathrm{CH}$-) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25 °C): $\delta = 173.5, 64.4, 51.9, 42.7, 22.6$ ppm.

Figure 7: Spectrum of **27** (^{1}H NMR (300 MHz, CDCl$_3$, 25 °C)).

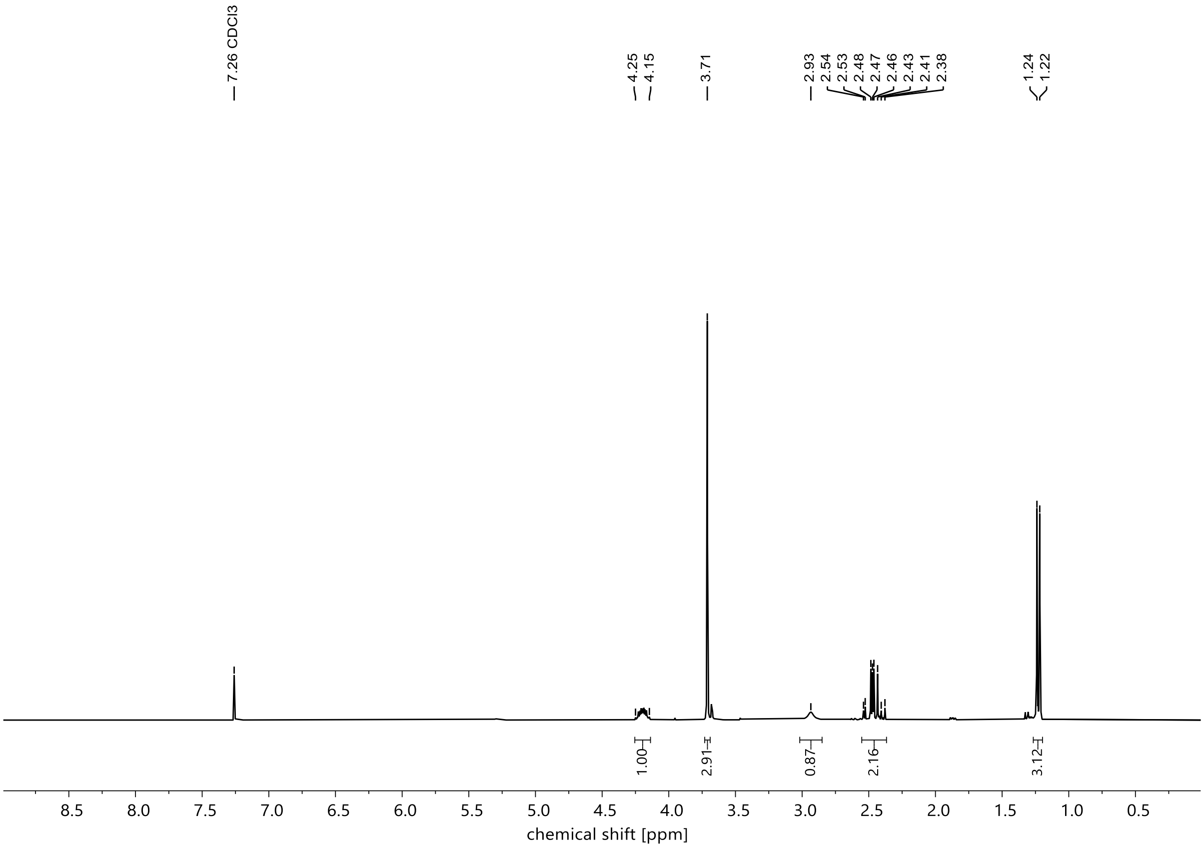
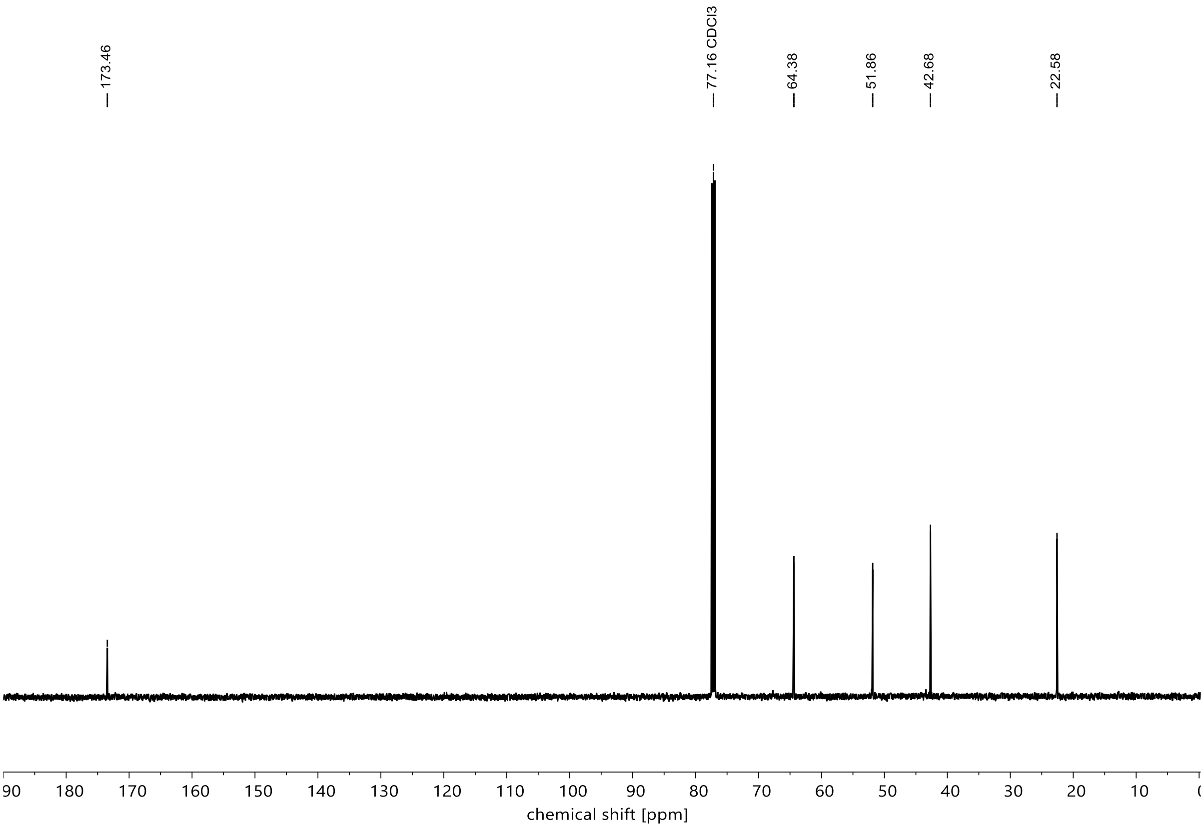


Figure 8: Spectrum of **27** (^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, 25 °C)).



General procedure for the depolymerization of P3HB (26) in the presence of other polymers: A mixture of P3HB (**26**, Sigma Aldrich/Merck 363502) (100 mg, 1.16 mmol based on the repeating unit), polymer B (1.16 mmol based on the repeating unit), methanol (3.0 g, 93.65 mmol, 67.5 equiv. equiv. based on the repeating unit of **26**) and $Zn(OAc)_2$ (1.0 mol%, 2.1 mg, 0.0116 mmol based on the repeating unit of **26**) was placed with a stir bar in a vial. The vial was sealed and heated by microwave irradiation. The reaction was performed for 30 minutes (hold time) at 160 °C and with a stirring of 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature. An aliquot of the clear solution was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^1H NMR to determine the yield of methyl 3-hydroxybutyrate (**27**) [The yield of **27** was calculated on the basis of the C*H* function of **27** and the leftover signals of the C*H* function of the P3HB-polymer/oligomers]. Moreover, the conversion of the polymer B was also investigated by NMR.

Procedure for the polymerization of 3-hydroxybutanoate (27): A mixture of 3-hydroxybutanoate (**27**, 213 mg, 1.8 mmol, 1.0 equiv.) and catalytic amounts of zinc(II) acetate (1.0 mol%, 3.3 mg, 0.018 mmol) were placed with a stir bar in a flask. The reaction was performed for 48 hours at 130 °C. Afterwards the mixture was cooled to room temperature. An aliquot was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^1H NMR to determine the yield of **26**. The yield of **26** was calculated on the basis of the C*H* function of **27**, the C*H* function of the polymer **26** and the C*H* function of methyl crotonate (**43**). Afterwards the residue was dissolved in dichloromethane/methanol and water was added. The organic solvents were removed with a rotary evaporator. The water was removed by filtration and the residue was dried in vacuum (40 °C, 1 mbar, 6 hours). The obtained polymer contains traces of **27** and methyl crotonate (**43**).

Figure 9: Spectrum of the precipitated **26** (^{1}H NMR (500 MHz, $CDCl_3$, 25 °C)).

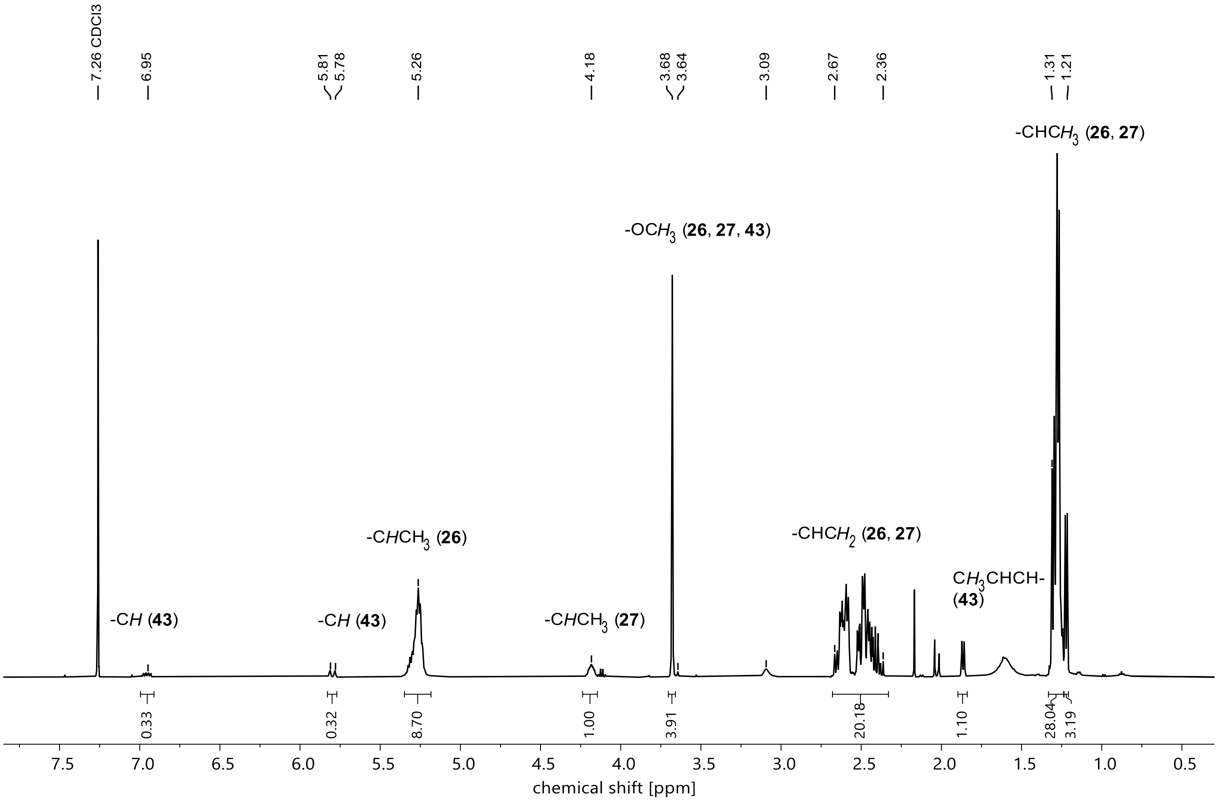
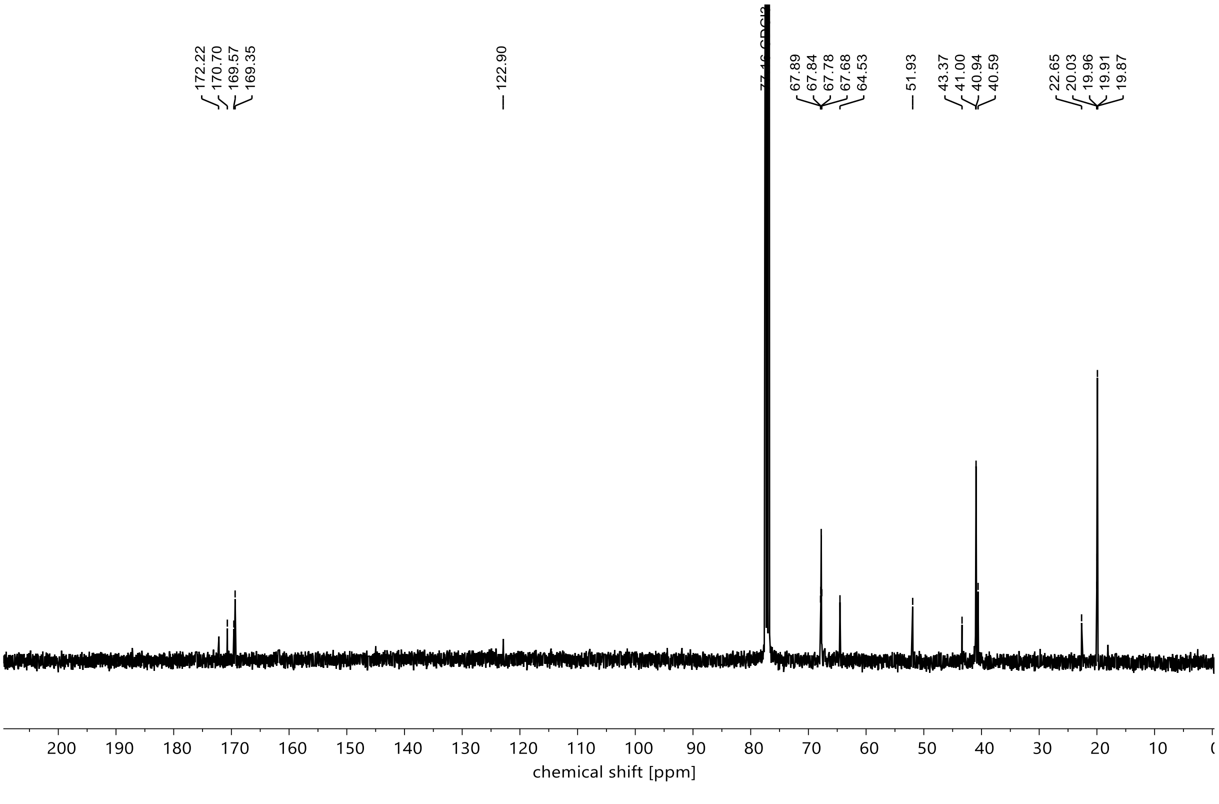


Figure 10. Spectrum of the precipitated **26** ($^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25 °C)).



Calculation of M_n of 26 by ^{1}H NMR: The signal of the C*H*-function of the substrate was integrated and set to 1H. The signals for the CH-function of the polymer and methyl crotonate (**43**) were integrated. The methyl groups of the ester end-groups of **26** was integrated and the integral was divided by three and the value was corrected by deducting the part of methyl 3-hydroxybutanoate (**27**) and methyl crotonate (**43**) to give A. Furthermore, the signals for the CH_3CH-function and $CHCH_2$-function were integrated and the values were corrected by deducting the part of methyl 3-hydroxybutanoate (**27**) and methyl crotonate (**43**). The integrals of the repeating unit were summed up and divided by the number of protons of the repeating unit and divided by A giving the number of repeating units n. M_n was calculated by M_n = 32.04 g/mol (molecular mass of end groups) + 86.04 g/mol (molecular mass of the repeating unit)(n). M_n ~26,866 g/mol, n ~311.7. The analytical data is in accordance to the literature.[196]

P3HB (**26**): ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 5.26 (m, 1H, CH_3CH), 3.64-3.68 (m, 3H, CH_3O-end group), 2.36-2.67 (m, 2H, $CHCH_2$), 1.21-1.31 (m, 3H, CH_3CH-) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ = 170.7, 169.6, 169.4, 69.9, 67.84, 67.80, 67.7, 41.0, 40.9, 40.6, 20.03,19.96, 19.91, 19.87 ppm.

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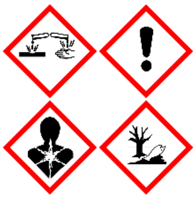
9. Appendix

9.1 Precautonary and hazard statements

Table 3: Precautonary and hazard statements.

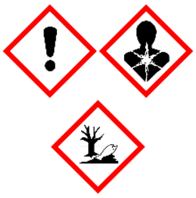
Substance	GHS pictogram and signal word	Hazard statements	Precautionary statements
Acetic acid		226, 314	280, 301+330+331, 307+310, 305+351+338
Acetic anhydride		226, 302, 314, 331, 335	210, 260, 280, 303+361+353, 305+351+338, 312
Acetone		225, 319, 336	210, 233, 240, 241, 242, 305+351+338
Acetone-d_6		225, 319, 336	210, 233, 240, 241, 242, 305+351+338
Acetonitrile		225, 302+312+332, 319	210, 261, 280, 305+351+338, 370+378, 403+235
Acetyl chloride		225, 314	210, 233, 240, 280, 303+361+353, 305+351+338
N-Acetyl-caprolactam		302, 319	264, 270, 280, 301+312+330, 337+313, 501
Aluminium chloride		314, 318,	260, 280, 303+361+353, 304+340+310, 305+351+338

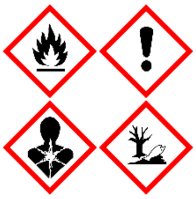
Substance	GHS pictogram and signal word	Hazard statements	Precautionary statements
2-Amino ethanol		302, 332, 312, 314, 318, 335, 412	273, 280, 301+312+330, 303+361+353, 304+340+312, 305+351+338+310
Anisol		226, 336	210, 233, 240, 241, 242, 243
Benzene-d_6		225, 304, 315, 319, 340, 350, 372, 412	201, 210, 280, 308+313, 370+378, 403+235
Bis(2-chloroethyl)-ammonium chlorid		290, 302, 314	234, 260, 280, 301+312, 303+361+353, 305+351+338
1,2-Bis(diphenyl-phosphino)ethane		335	261, 271, 304+340+312, 403+233, 405, 501
Bismuth(III) acetate	The substance is not classified by GHS according to regulation (EC) No 1272/2008.		
Bismuth(III) bromide	The substance is not classified by GHS according to regulation (EC) No 1272/2008.		
Bismuth(III) chloride		315, 319	305+351 338
Bismuth(III) fluoride		314	260, 280, 303+361+353, 304+340+310, 305+351+338

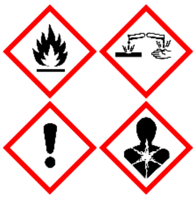
Substance	GHS pictogram and signal word	Hazard statements	Precautionary statements
Bismuth(III) iodide		314	-
Bismuth(III) subsalicylate	The substance is not classified by GHS according to regulation (EC) No 1272/2008.		
Bismuth(III) triflate	The substance is not classified by GHS according to regulation (EC) No 1272/2008.		
BPA		317, 318, 335, 360F, 411	201, 273, 280, 302+352, 305+351+338, 308+313
2,2-Bis-(4-acetoxyphenyl)-propane		315, 319, 335	261, 305+351+338
ε-Caprolactam		302+332, 315, 319, 335	301+312+330, 302+352, 304+340+312, 305+351+338
Carbon monoxide		220, 280, 331, 360D, 372	201,202,260, 304+340+311, 308+313, 410+403
Carbonylchlorido-hydrido(triphenyl-phosphan)-ruthenium(II)	The substance is not classified by GHS according to regulation (EC) No 1272/2008.		
Chlorodiisopropyl-phosphin		225, 314	210, 233, 240, 280, 303+361+353, 305+351+338

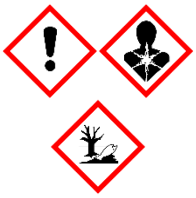
Substance	GHS pictogram and signal word	Hazard statements	Precautionary statements
Chloroform		302, 315, 319, 331, 336, 351, 361d, 372, 412	260, 280, 301+312+330, 304+340+312, 305+351+338, 403+233
Chloroform-*d*		302, 315, 319, 331, 336, 351, 361d, 372	260, 280, 301+312+330, 302+352, 304+340+311, 305+351+338, 308+313
2-Chloropropane		225, 302+312, 332	210, 233, 280, 301+312, 303+361+353, 304+340+312
1,8-Diazabicyclo-[5.4.0]undec-7-en		290, 301, 341, 412,	234, 273, 280, 303+361+353, 304+340+310, 305+351+338
2-(Di-cyclohexyl-phosphin)biphenyl	The substance is not classified by GHS according to regulation (EC) No 1272/2008.		
2-(Di-*tert*-butyl-phosphin)biphenyl	The substance is not classified by GHS according to regulation (EC) No 1272/2008.		
Dichloro-methane[22]		315, 319, 336, 351	201, 261, 264, 280, 304+340+312, 308+313
Diethyl ether		224, 302, 336	210, 240, 403+235
Diethylzinc (1 M in *n*-hexane)		290, 301, 314, 412	234, 273, 280, 303+361+353, 304+340+310, 305+351+338

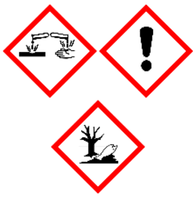
Substance	GHS pictogram and signal word	Hazard statements	Precautionary statements
2-(Di-*iso*-propylphosphino)ethyl-amine (10 wt% in THF)		225, 302, 315, 319, 335, 336, 351	201, 210, 301+312, 303+361+353, 305+351+338, 308+313
Dihydrogen		220, 280	210, 277, 381, 410+403
3-(Dimethylamino)-1-propylamine		226, 302+ 314, 317, 335	210, 303+361+353, 304+340+310, 305+351+338, 333+313, 403+235
4-(Dimethyl-amino)pyridin		301, 310, 315, 319, 335	280, 301+310+330, 302+352+310, 304+340,312, 305+351+338, 3337+313
Dimethyl carbonate		225	210, 403+235
1,4-Dioxane		225, 319, 335, 351	202, 210, 233, 240, 305+351+338, 308+313
Ethylene glycol		302, 373	260, 301+312+330
Diphenyl carbonate		302, 410	264, 270, 273, 301+312, 391, 501

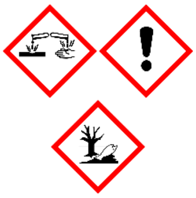
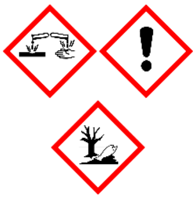
Substance	GHS pictogram and signal word	Hazard statements	Precautionary statements
Ethyl acetate		225, 319, 336	210, 233, 240, 305+351+338, 403+235
Hydrochloric acid (37 %)		290, 314, 335	260, 280, 303+361+353, 304+340+310, 305+351+338
N-(2-Hydroxyethyl)-acetamide		315, 335, 319	261, 302+352, 280, 305+351+338
Iodine		302+312+332, 315, 319, 335, 372, 400	273, 280, 301+312, 302+352+312, 304+340+312, 314
Iron(II) bromide		315, 319, 332, 335	261, 305+351+338
Iron(III) chloride		290, 302, 315, 318	234, 264, 280, 301+312, 302+312, 305+351+338
L-Lactide		315, 319, 335	302+352, 337+313, 304+340+311, 332+313
Lithium		260, 314	223, 231+232, 380, 305+351+338, 370+378, 422
Lithium bromide		302, 315, 317, 319	261, 264, 280, 301+312, 302+352, 305+351+338
Magnesium (powder)		228, 251, 261	210, 223, 231+232, 235, 240, 403+235

Substance	GHS pictogram and signal word	Hazard statements	Precautionary statements
Methanol		225, 301+311+ 331, 370	210, 233, 280, 301+310, 303+361+353, 304+340+311
Methanol-d_4		225, 301+311+331, 370	210, 233, 280, 301+310, 303+361+353, 304+340+311
Methyl L-lactate		226, 319, 335	210, 305+351+338
Milstein precatalyst		319, 351	281, 305+351+338
n-Hexane		225, 304, 315, 336, 361f, 373, 411	201, 210, 273, 301+310, 303+361+353, 331
n-Pentane		225, 304, 336, 411	210, 233, 240, 273, 301+310, 331
Petroleum ether		224, 304, 315, 336, 340, 350	210, 233, 301+310, 303+361+353, 331, 403+233

Substance	GHS pictogram and signal word	Hazard statements	Precautionary statements
Potassium bromide		319	264, 280, 305+351+338, 337+313
Potassium fluoride		301+311+331, 318	261, 280, 302+352+312, 304+340+311, 305+351+338
Potassium iodide		272	260, 264, 270, 314, 501
Potassium-*tert*-butanolat		228, 260, 314	210, 231+232, 260, 280, 303+361+353, 308, 303+361+353, 305+351+338
Phenol		301+311+331, 314, 341, 373, 411	260, 273, 280, 303+361+353, 304+340+310, 305+351+338
Phenyl acetate		302	-
Poly(formaldehyde)		228, 302+332, 315, 317, 318, 350	201, 210, 280, 302+352, 305+351+338
2-Propanol		225, 319, 336	210, 223, 240, 241, 242, 243, 264, 280, 303+361+353, 305+351+338, 337+313
1,2-Propylene carbonate		319	264, 280, 305+351+338, 337+313

Substance	GHS pictogram and signal word	Hazard statements	Precautionary statements
Pyridine		225, 302+312+332, 315, 319	210, 280, 305+351+338
Sodium methoxide		228, 251, 290, 302, 314	210, 235, 260, 280, 303+361+353, 305+351+338
Sodium borohydride		260, 301, 314, 360f	201, 231+232, 280, 308+313, 370+378, 402+404
Sodium fluoride		301, 315,319	264, 270, 280, 301+310, 302+352, 305+351+338
Sodium iodide		315, 319, 372, 400	260, 264, 273, 302+352, 305+351+338
Tetrahydrofurane		225, 302, 319, 335, 351	210, 280, 301+312+330, 305+351+338, 370+378, 403+235
Tin(II) octanoate		317, 318, 361, 412	201, 273, 280, 302+352, 305+351+338, 308+313

Substance	GHS pictogram and signal word	Hazard statements	Precautionary statements
Triethylamine		225, 302, 311+331, 314, 335	210, 280, 303+361+353, 304+340+310, 305+351+338, 403+233
Trifluoroacetic acid		314, 332, 412	261, 273, 280, 303+361+353, 304+340+310, 305+351+338
Tri-*iso*-propyl-phosphine		250, 314	222, 231, 280, 305+351+338, 310, 422
Trimethylsilyl chloride		225, 301+331, 312, 314	210, 233, 280, 303+361+353, 304+340+310, 305+351+338
Triphenylphos-phine		302, 317, 373	280
Tri-*tert*-butyl-phosphine		250, 314	222, 231, 280, 305+351+338, 310, 422
Toluene		225, 304, 315, 336, 316d, 373	210, 240, 301+310+330, 302+352, 403+233
Zinc acetate		302, 318, 410	280, 301+312+330, 305+351+338

Substance	GHS pictogram and signal word	Hazard statements	Precautionary statements
Zinc bromide		302, 314, 317, 411	273, 280, 305+351+338, 310
Zinc chloride		302, 314, 411	260, 273, 280, 301+312+330, 303+361+253, 305+351+338
Zinc methacrylate		315, 319, 334, 335	302+352, 305+351+338
Zinc oxide		410	273, 391, 501

9.2 Supporting information

In the following part, the supporting informations are listed. The material is depicted as published without further manipulation. The article “Ruthenium-Catalyzed Hydrogenative Degradation of End-of-Life Poly(lactide) to Produce 1,2-Propanediol as Platform Chemical”[267] was published without supporting information

ChemistrySELECT

Supporting Information

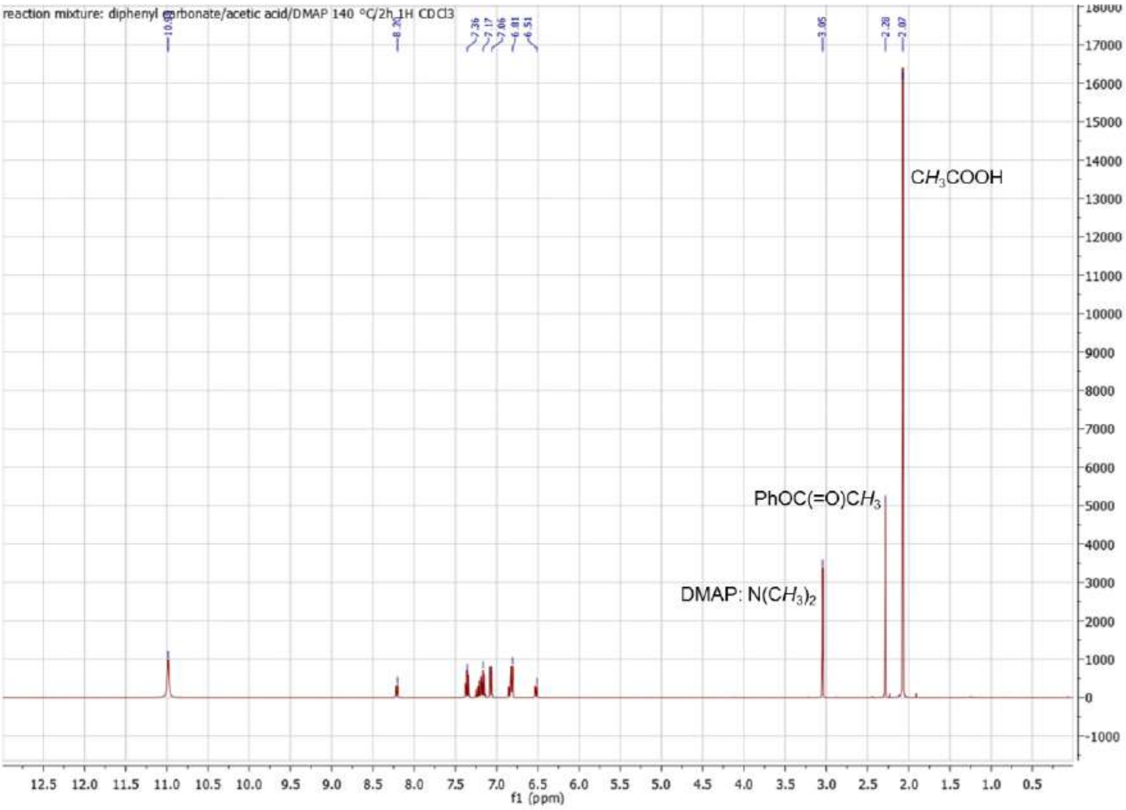
Depolymerization of End-of-Life Poly(bisphenol A carbonate) via Transesterification with Acetic Anhydride as Depolymerization Reagent

Christoph Alberti, Felix Scheliga, and Stephan Enthaler*

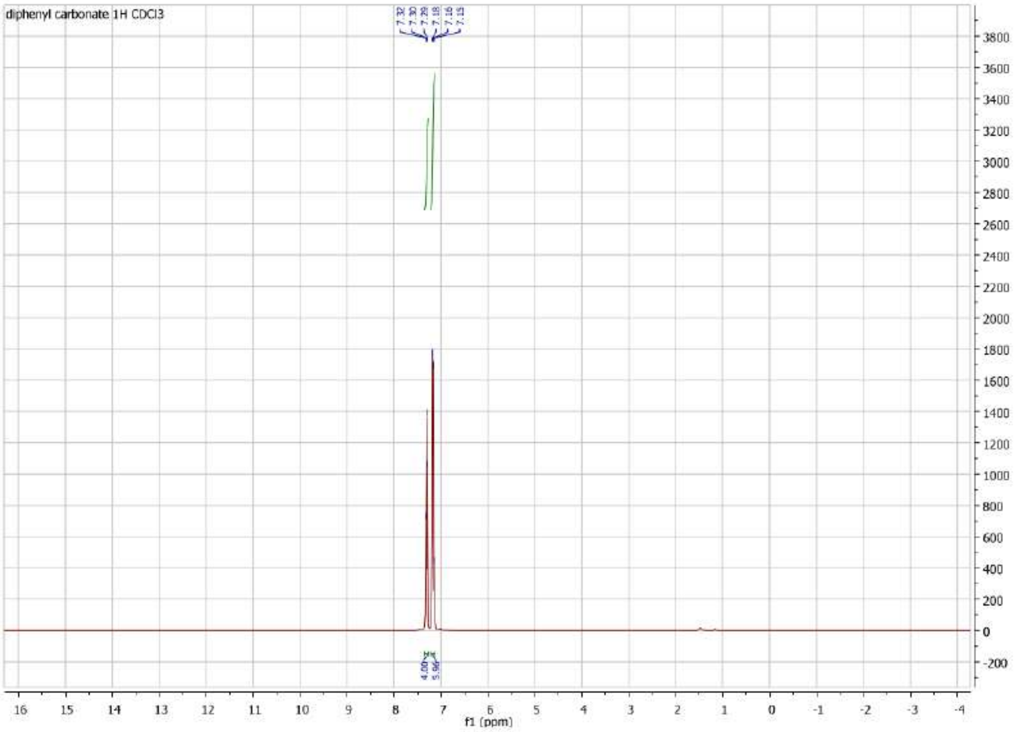
General: All chemicals were used as received without further manipulations. ^{1}H and ^{13}C{^{1}H}NMR spectra were recorded on a *Fourier 300 MHz* (^{1}H: 300 MHz, ^{13}C: 75 MHz) or *Avance I-400* (^{1}H: 400 MHz, ^{13}C: 101 MHz) by Bruker, using the proton signals of the deuterated solvents as reference or external standards. Mass spectrometry was performed using a *Thermo ISQ LT EI* by Thermo Fisher Scientific. TLC was performed on *ALUGRAM XTRA SIL G/UV$_{254}$* cards from *Macherey-Nagel* GmbH & Co. KG with a thickness of 0.20 mm. Detection succeeded with UV-light (254 nm). For preparative column chromatography silica gel 60 (particle size 40 – 63 µm) from *Fluka* was used. For microwave heating experiments a Microwave Synthesis Reactor Monowave 400 (Anton Parr GmbH) was used. GC-MS was measured with Agilent Technologies 5977B GC/MSD.

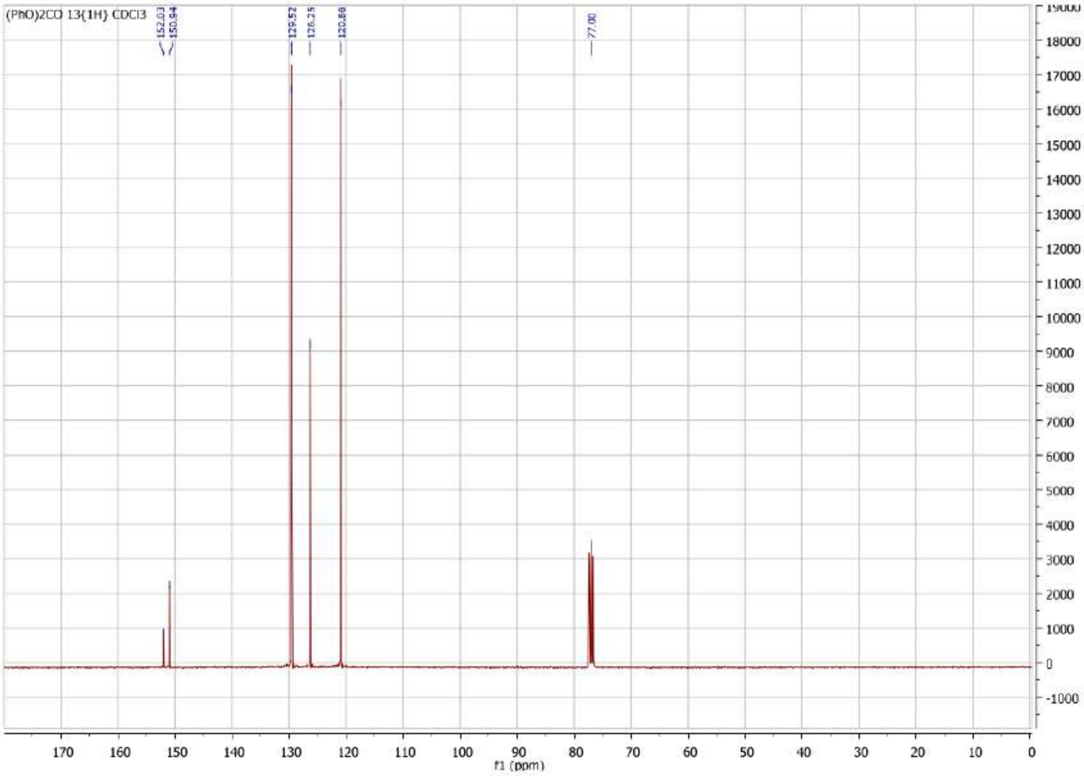
General procedure using diphenyl carbonate as model compound: A mixture of diphenyl carbonate (**3**) (30 mg, 0.14 mmol), acetic acid (4 equiv.: 0.56 mmol, 34 mg; or 8 equiv.: 1.12 mmol, 67 mg) or acetic anhydride (4 equiv.: 0.56 mmol, 57 mg; or 8 equiv.: 1.12 mmol, 114 mg) and catalytic amounts of 4-dimethylaminopyridine (5 mol%, 0.007 mol, 1 mg) was stirred at 140 °C for 2 or 24 hours in a flask (10 mL) connecting to a reflux condenser. The reaction mixture was cooled to room temperature, chloroform-*d*1 (0.7 mL) was added and the mixture was transferred to a NMR-tube and subjected to NMR measurements. The yield of phenyl acetate (**4**) was calculated using the CH_3 functionality of DMAP as standard.

Representative ^1H NMR of the reaction mixture using acetic acid:

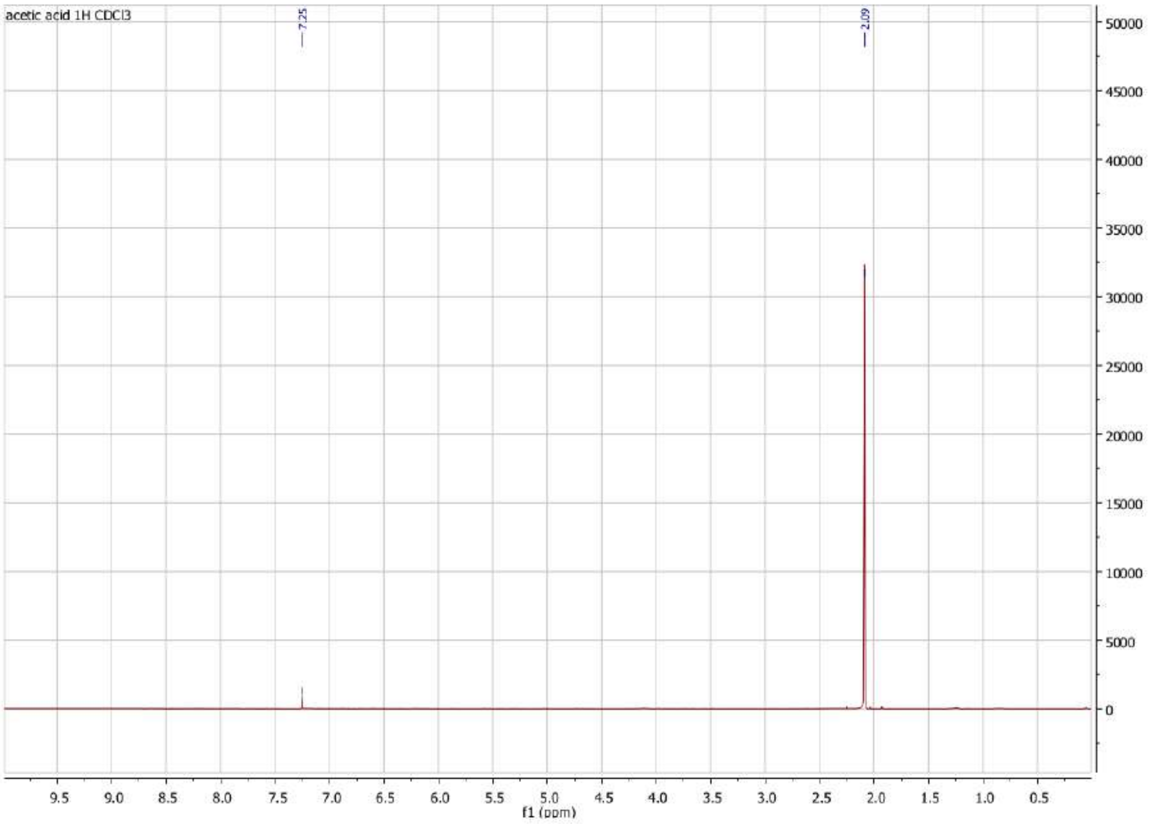


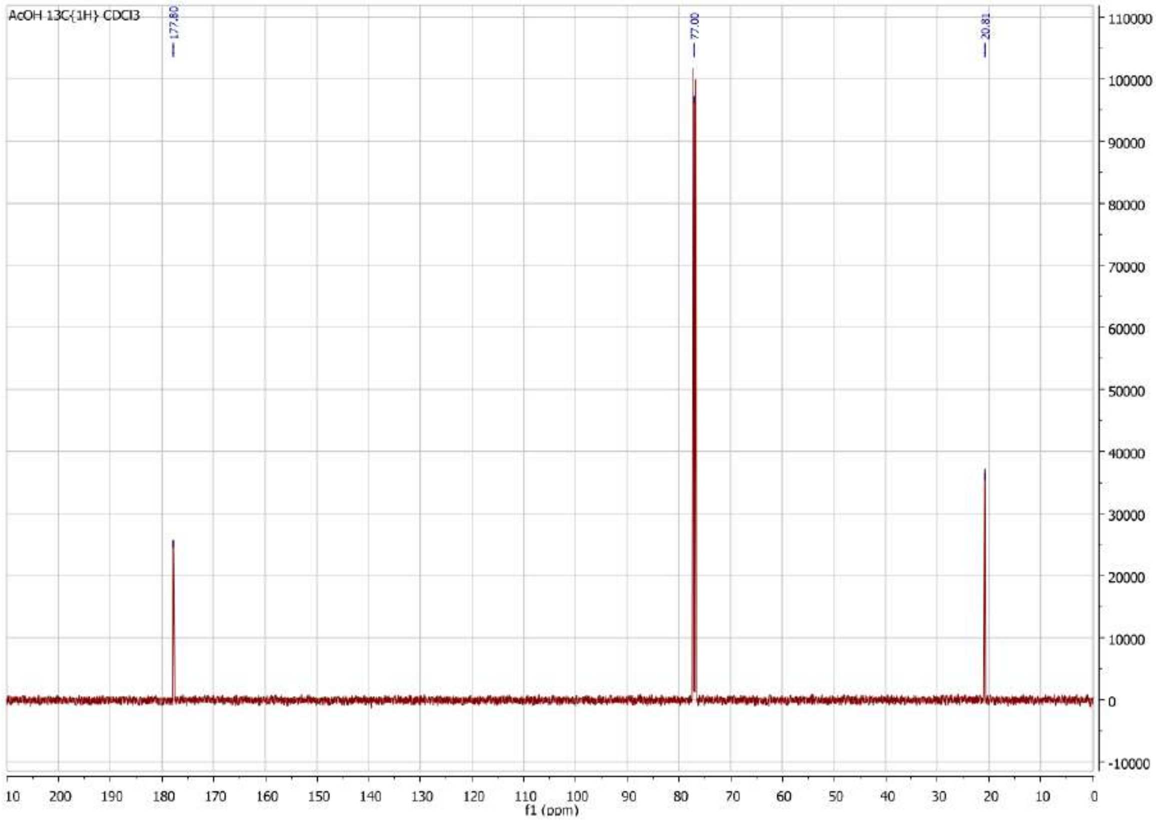
Diphenyl carbonate (**3**): ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.35-7.40 (m, 4H), 7.20-7.28 (m, 6H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C): δ = 152.0, 150.9, 129.5, 126.3, 120.9 ppm.



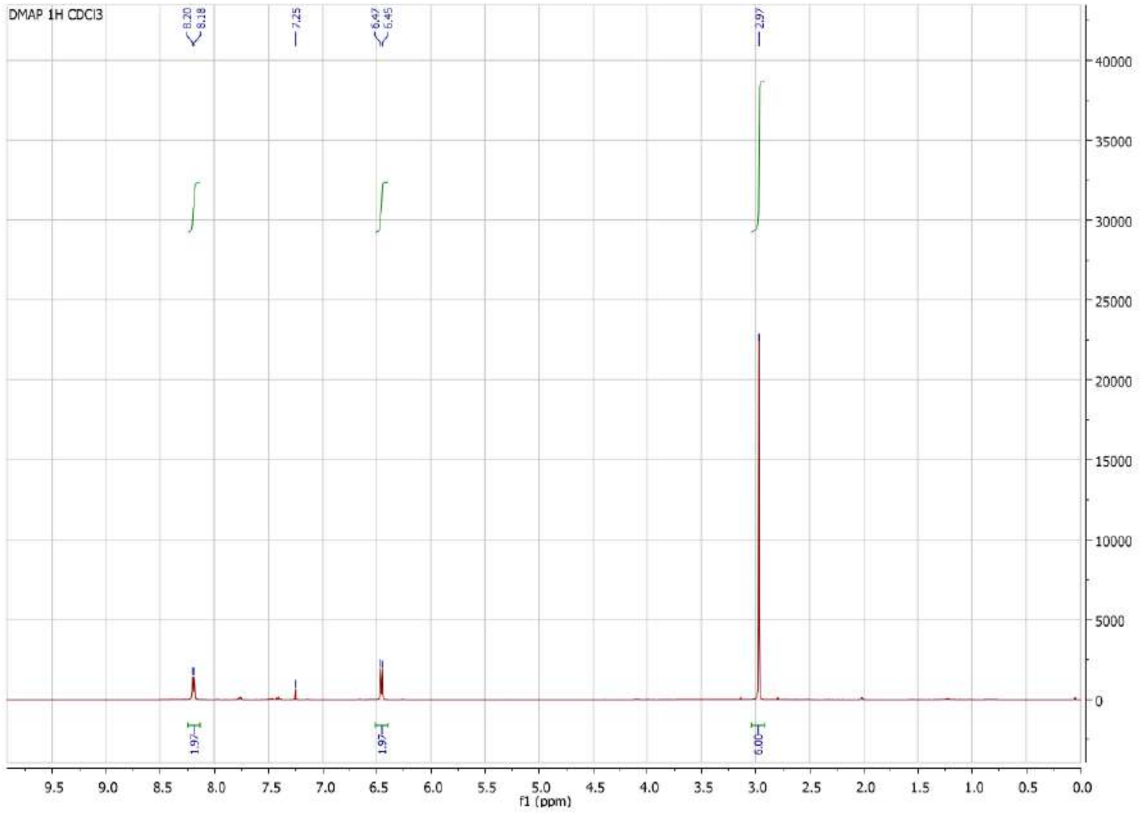


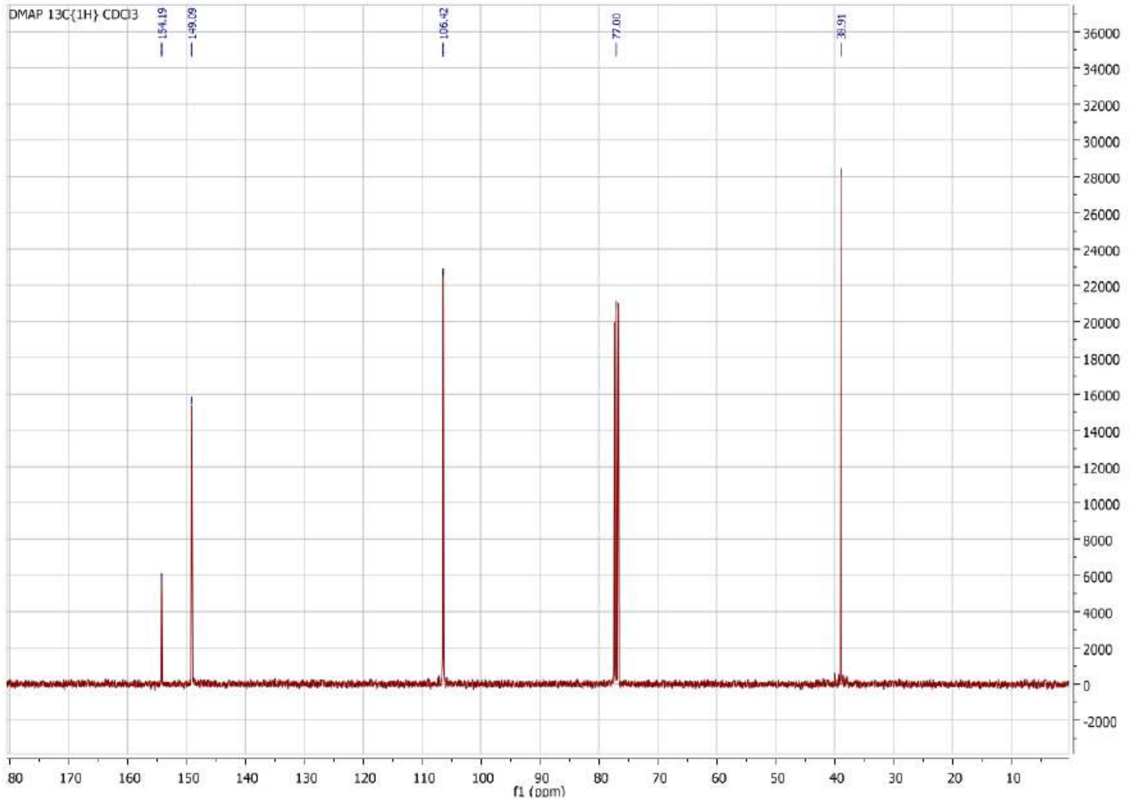
Acetic acid: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 2.09 (s, 6H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C): δ = 177.8 (C), 20.8 (CH_3) ppm.



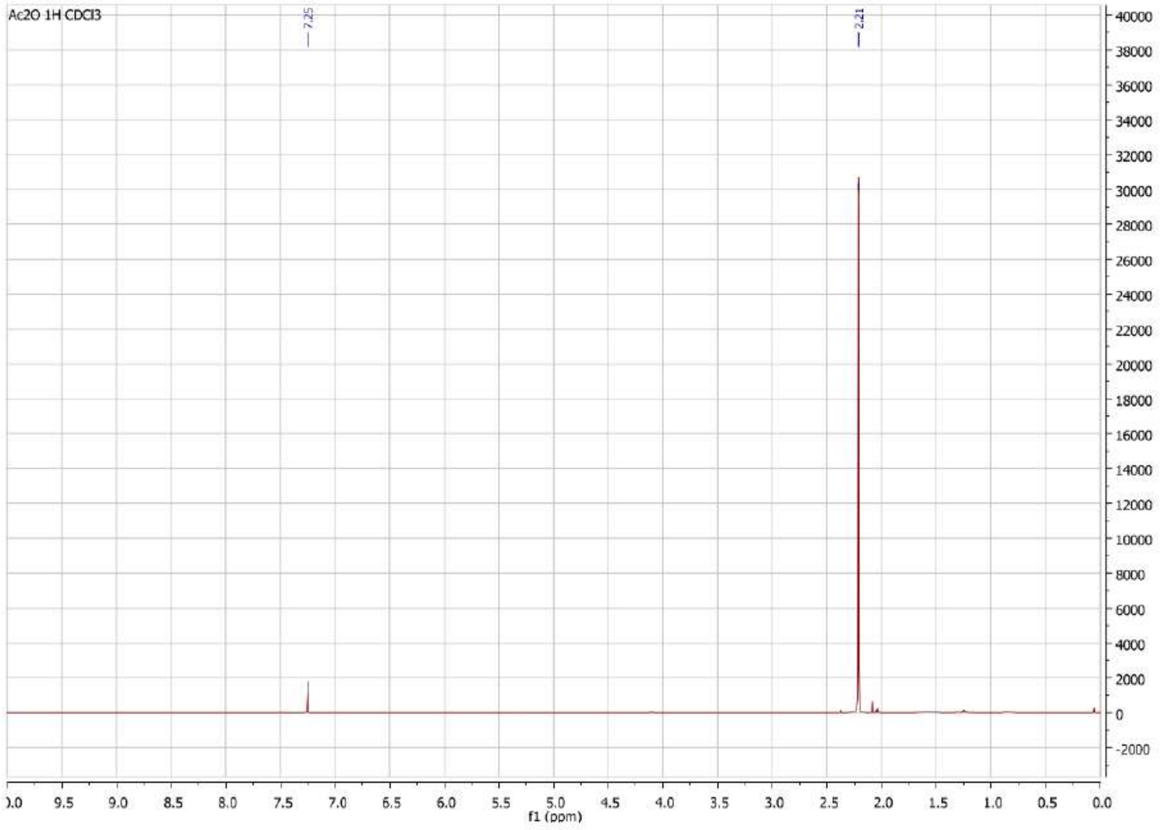


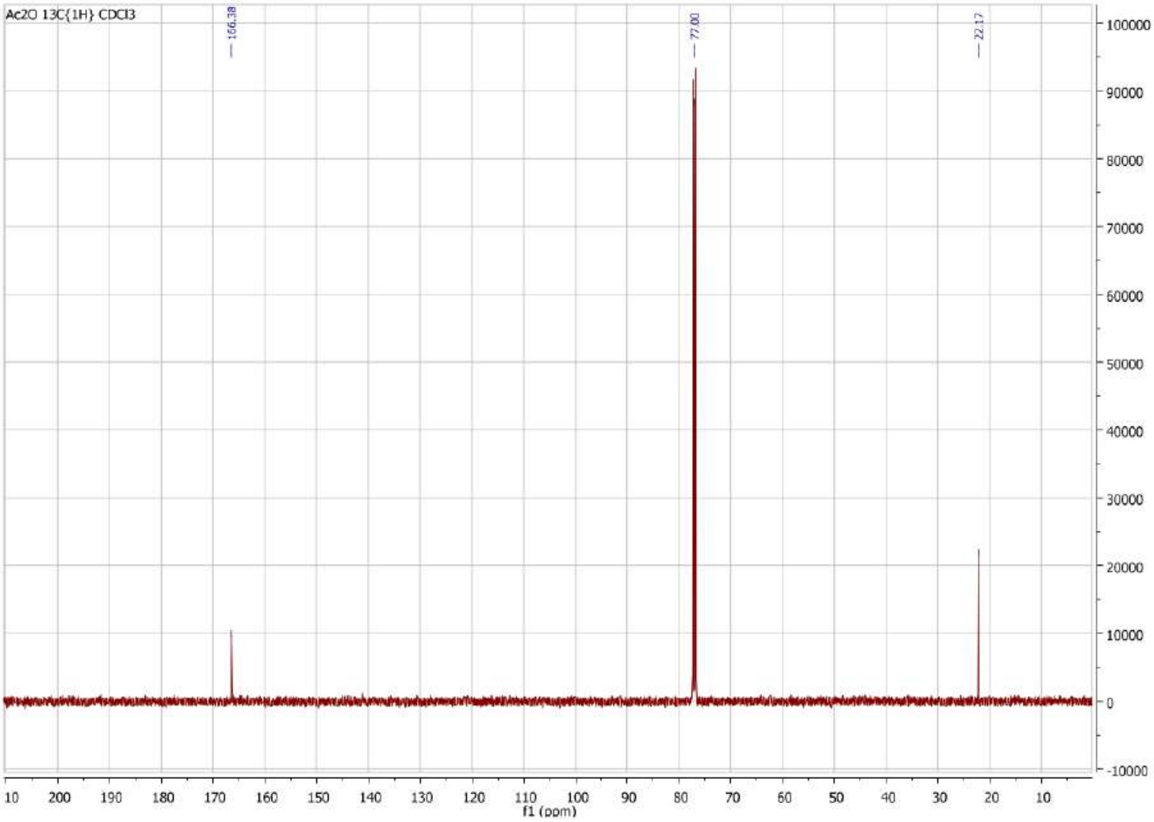
4-Dimethylaminopyridine: ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): δ = 8.18-8.20 (m, 2H, C-H), 6.45-6.47 (m, 2H, C-H), 2.97 (s, 6H, CH_3) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, 25 °C): δ = 154.2, 149.1, 106.4, 38.9 ppm.





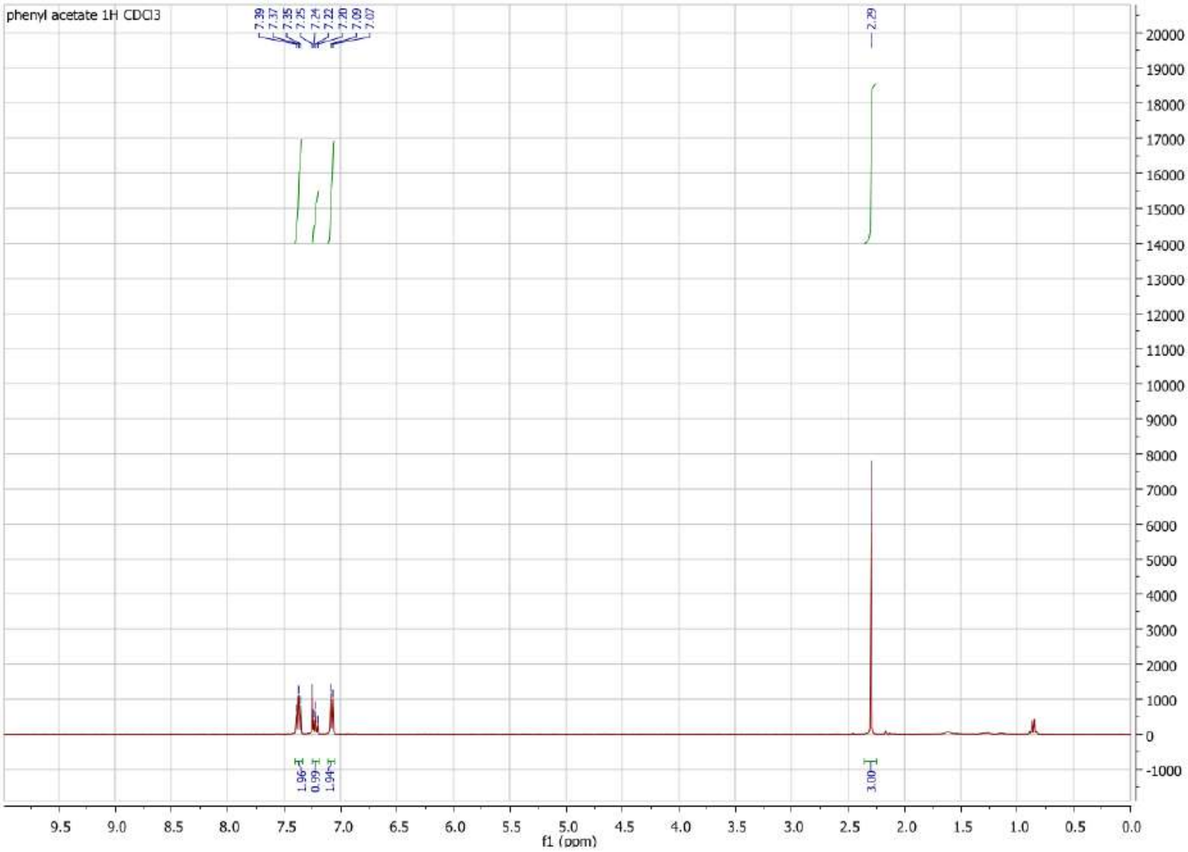
Acetic anhydride: ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): δ = 2.21 (s, 6H, C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, 25 °C): δ = 166.4 (C), 22.2 (CH$_3$) ppm.

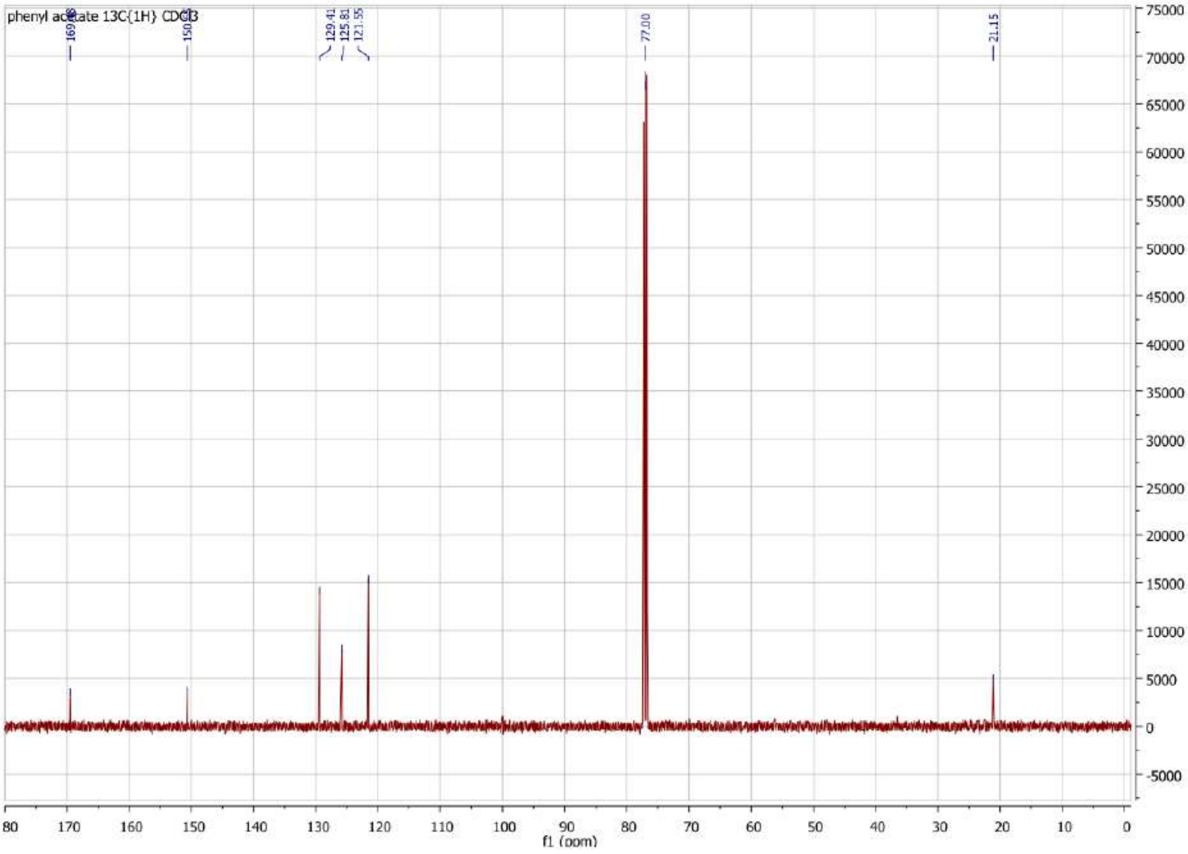




Procedure for isolation of phenyl acetate (4): A mixture of diphenyl carbonate (**3**) (0.5 g, 2.0 mmol), acetic acid (0.96 g, 16.0 mmol) and catalytic amounts of 4-dimethylaminopyridine (12.2 mg, 0.1 mmol) was stirred at 140 °C for 24 hours in a flask (10 mL) connected to a reflux condenser. Afterwards, the reaction mixture was cooled to room temperature and subjected to column chromatography (silica gel 60) using a mixture of petroleum ether/acetone (90:10) as eluent. Phenyl acetate (**4**) [R_f = 0.31 (petroleum ether/acetone 90:10)] was isolated in 83% yield.

Phenyl acetate[1] (**4**): ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.35-7.39 (m, 2H), 7.20-7.24 (m, 1H), 7.07-7.09 (m, 2H), 2.29 (s, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 °C): δ = 169.5, 150.7, 129.4, 125.8, 121.6, 21.2 (CH_3) ppm. MS (EI) m/z = 136.02 ($C_8H_8O_2$: 136.05 g/mol).


phenyl acetate 1H CDCl3
7.39
7.37
7.35
7.25
7.24
7.22
7.20
7.09
7.07
2.29
1.96
0.99
1.94
3.00
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

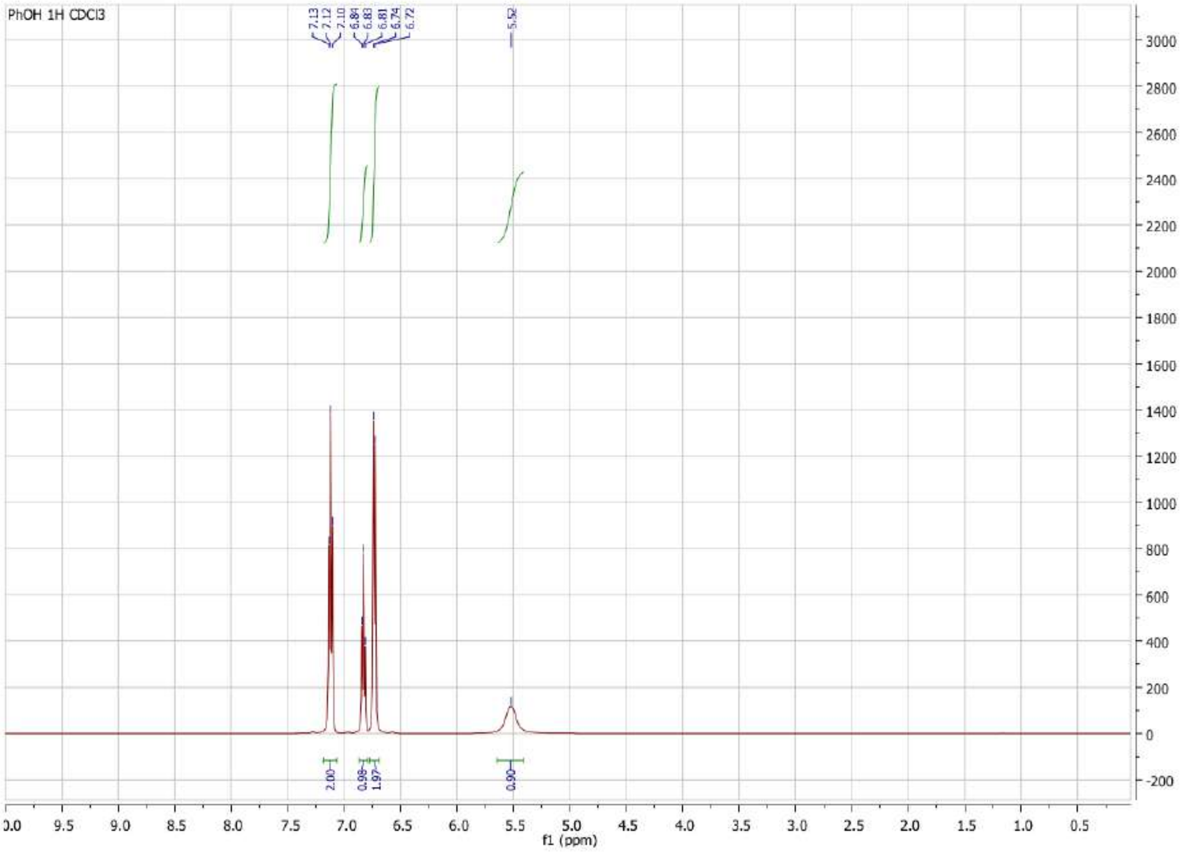

phenyl acetate 13C{1H} CDCl3
169
150
129.41
125.81
121.55
77.00
21.15
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

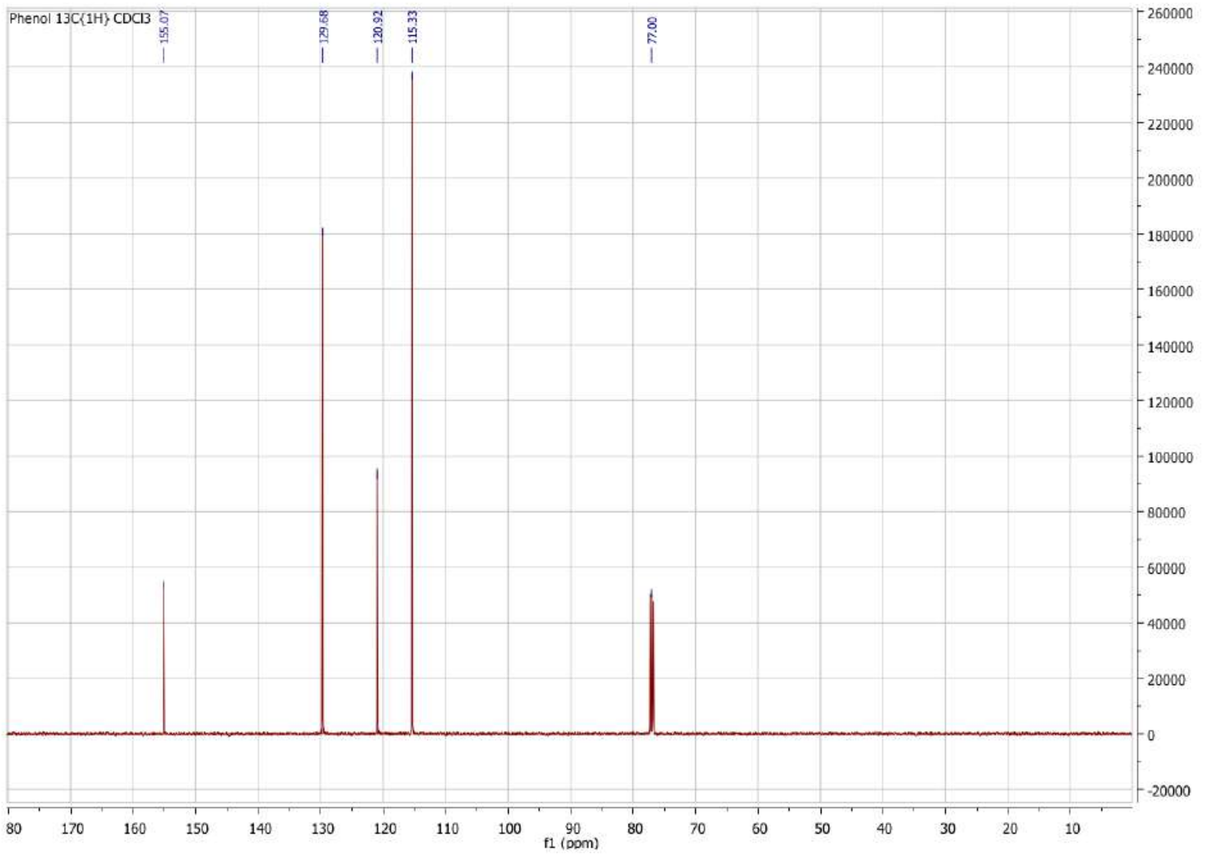
Procedure for the detection of carbon dioxide during the transesterification of diphenyl carbonate: A mixture of diphenyl carbonate (**3**) (30 mg, 0.14 mmol), acetic acid (8 equiv.: 1.12 mmol, 67 mg) or acetic anhydride (8 equiv.: 1.12 mmol, 114 mg) and catalytic amounts of 4-dimethylaminopyridine (5 mol%, 0.007 mol, 1 mg) was stirred at 140 °C for 24 hours in a flask (10 mL) connected to a reflux condenser. The condenser was sealed with a fermentation lock containing an aqueous solution of $Ba(OH)_2$. After a while a white precipitate was formed in the $Ba(OH)_2$ solution at the meniscus of the reaction side. Afterwards, the reaction mixture was cooled to room temperature and chloroform-*d*1 (0.7 mL) was added and the mixture was transferred to a NMR-tube and subjected to NMR measurements, revealing the formation of phenyl acetate (**4**). The obtained spectra are in accordance to the spectra as aforementioned.

Figure S1. Detection of carbon dioxide formed during the transesterification of diphenyl carbonate with acetic acid.

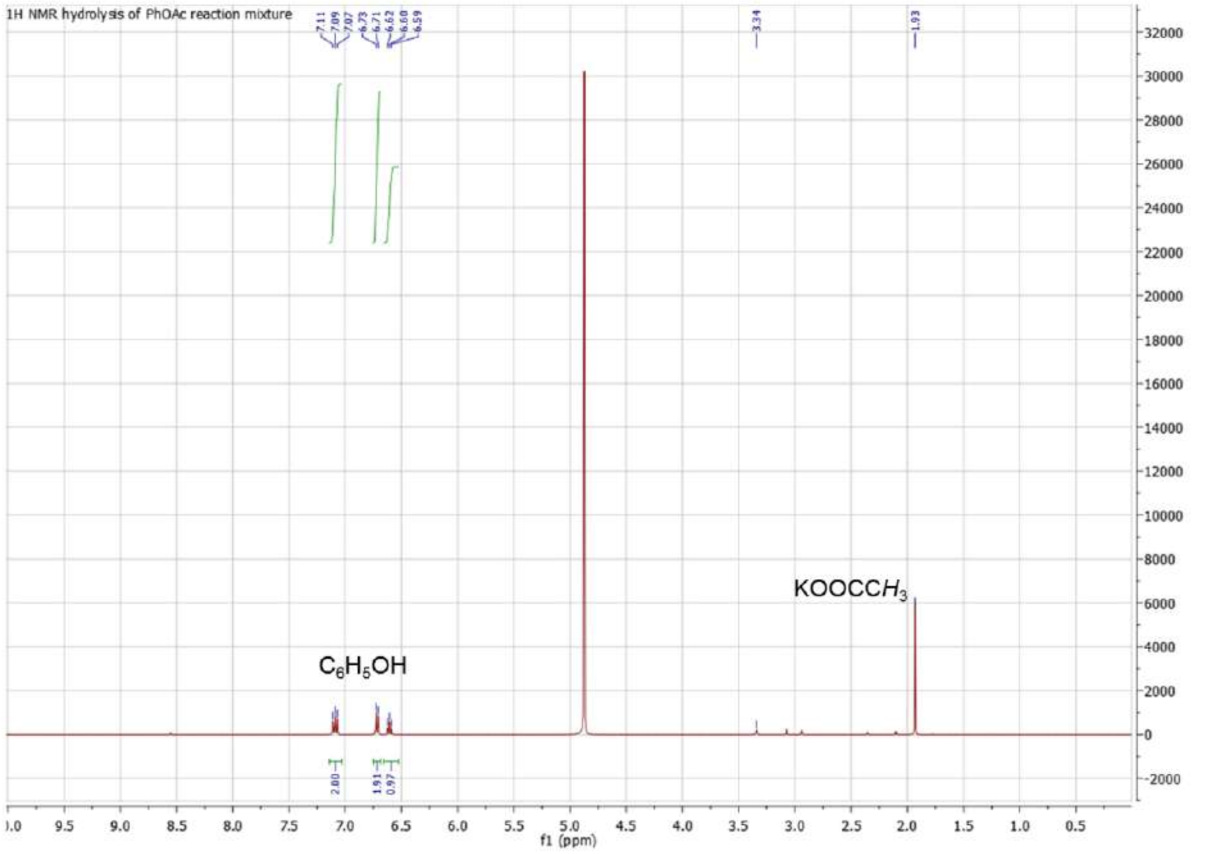
Procedure for the hydrolysis of phenyl acetate (4): To a 50 mL flask equipped with a reflux condenser was added phenyl acetate (**4**) (0.50 g, 3.67 mmol), methanol-*d*4 (1.0 mL) and water-*d*2 (1.0 mL). The mixture was stirred and solid potassium hydroxide (1.75 equiv., 0.36 g, 6.43 mmol) was added. The mixture was stirred and heated for 4 hours at 90 °C. Afterwards, the mixture was cooled to room temperature and an aliquot was taken for NMR analysis for detection of potassium acetate. The mixture was transferred to a separation funnel and water (20 mL) and toluene (20 mL) were added. The mixture was neutralized with hydrochloric acid. The aqueous layer was removed and extracted with toluene (2x10 mL). The combined organic layers were washed with brine and subsequently dried over magnesium sulfate. The solvent was removed in vacuum yielding colorless crystals (m = 205 mg, 59%).

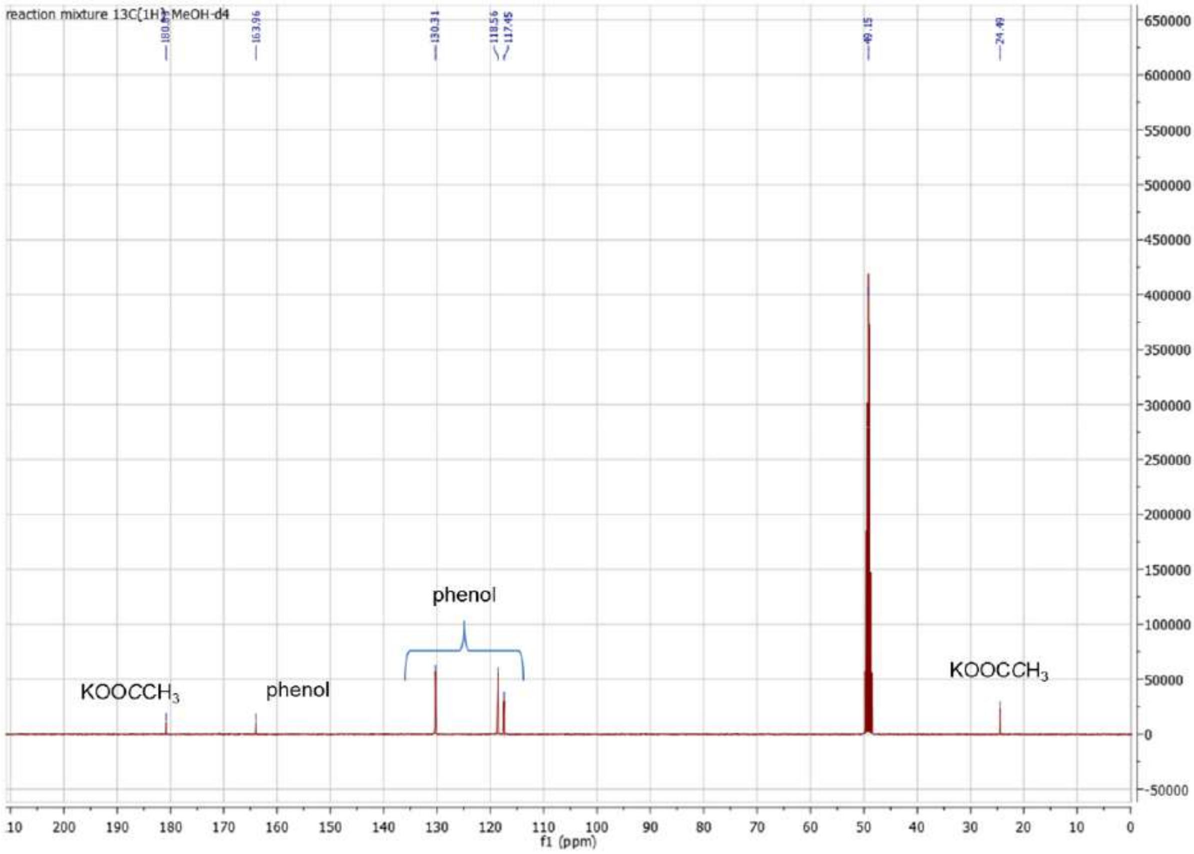
Phenol[2]: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.12 (t, 2H, *J* = 7.9 Hz, *m*-H), 6.83 (t, 1H, *J* = 7.4 Hz, *p*-H), 6.73 (d, 2H, *J* = 8.0 Hz, *o*-H), 5.52 (s, 1H, O*H*) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C): δ = 155.1, 129.7, 120.9, 115.3 ppm.





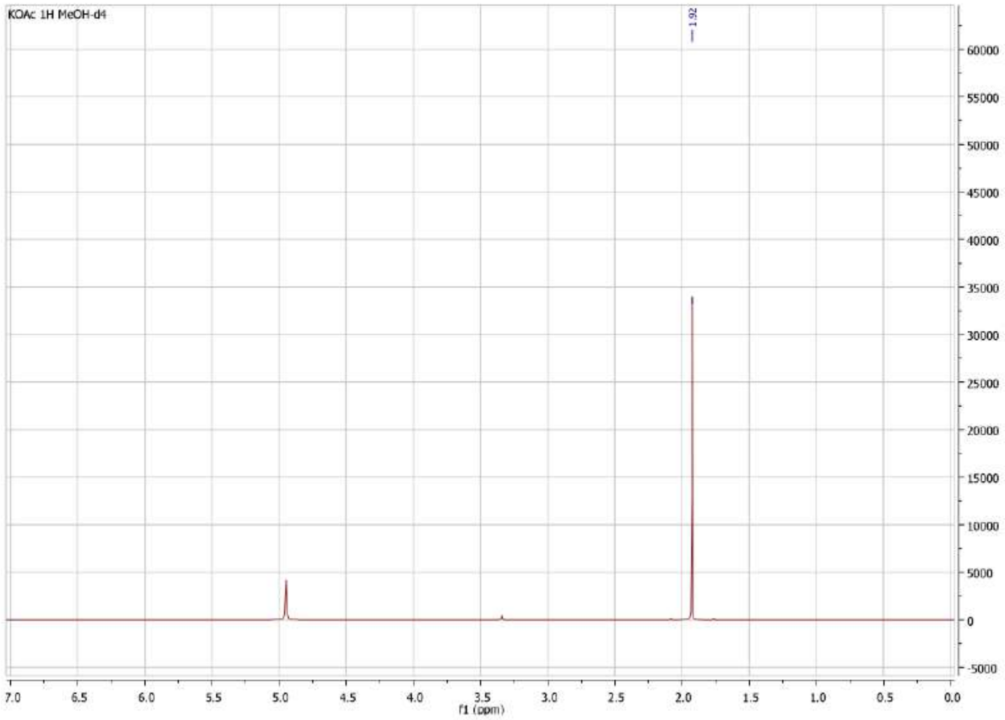
^{1}H NMR of the reaction mixture (MeOH-*d*4, D_2O)

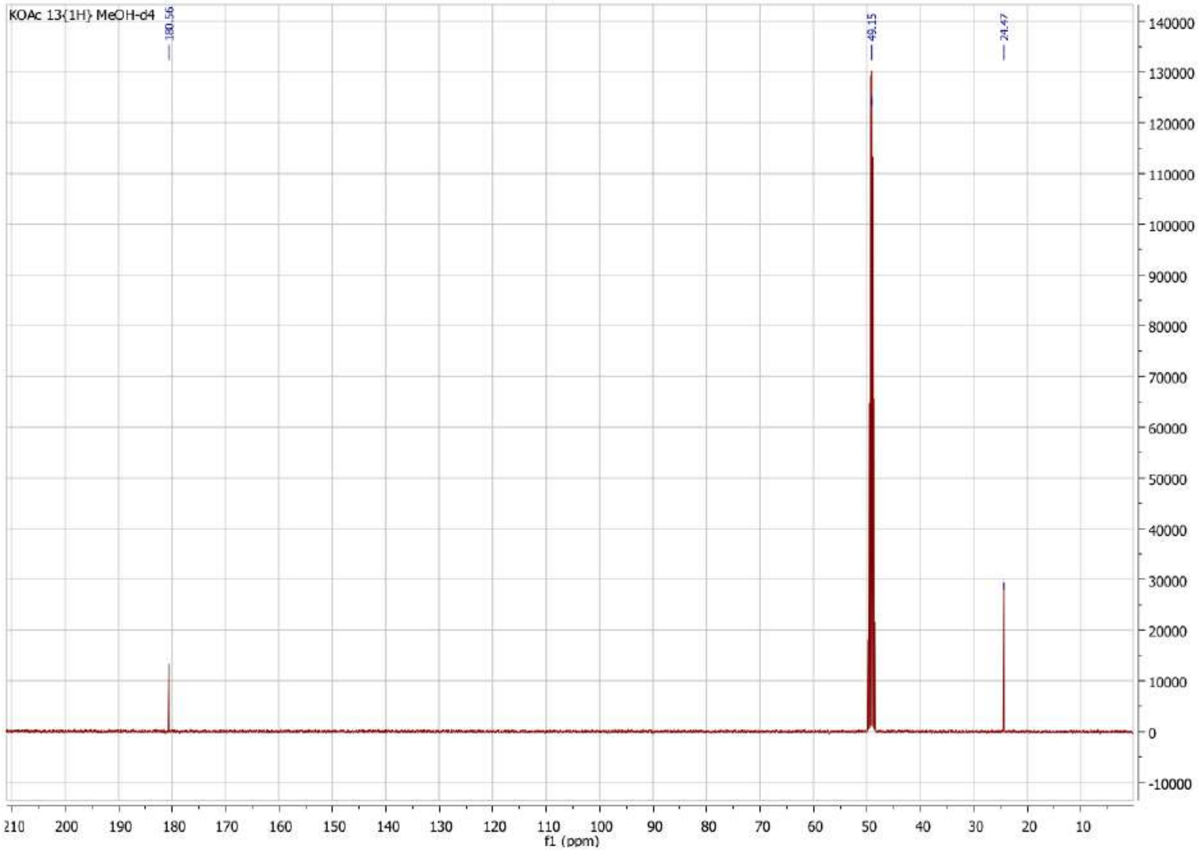




Potassium acetate: ^{1}H NMR (500 MHz, MeOH-*d*4, 25 °C): δ = 1.92 (s, 3H) ppm. ^{13}C{^{1}H} NMR (125 MHz, MeOH-*d*4, 25 °C): δ = 180.6, 24.5 ppm.

^{1}H NMR of an authentic sample of potassium acetate

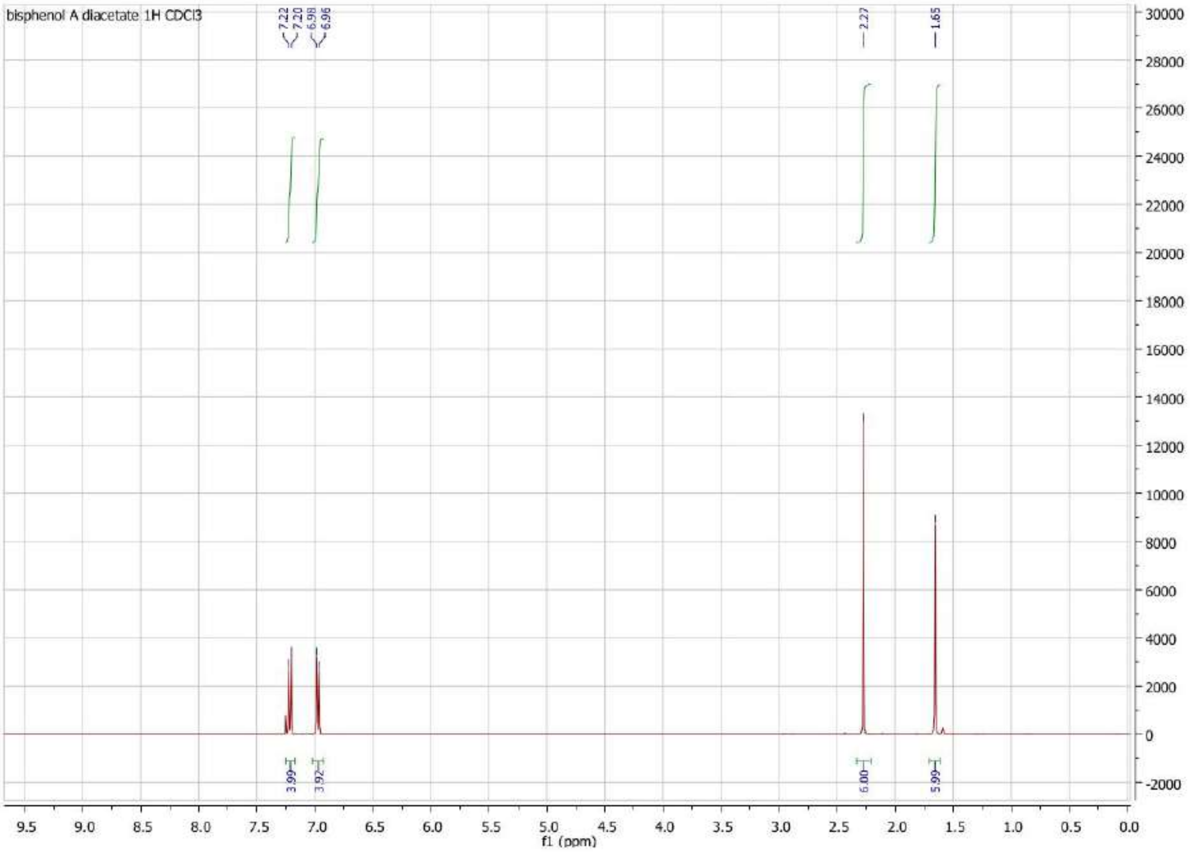


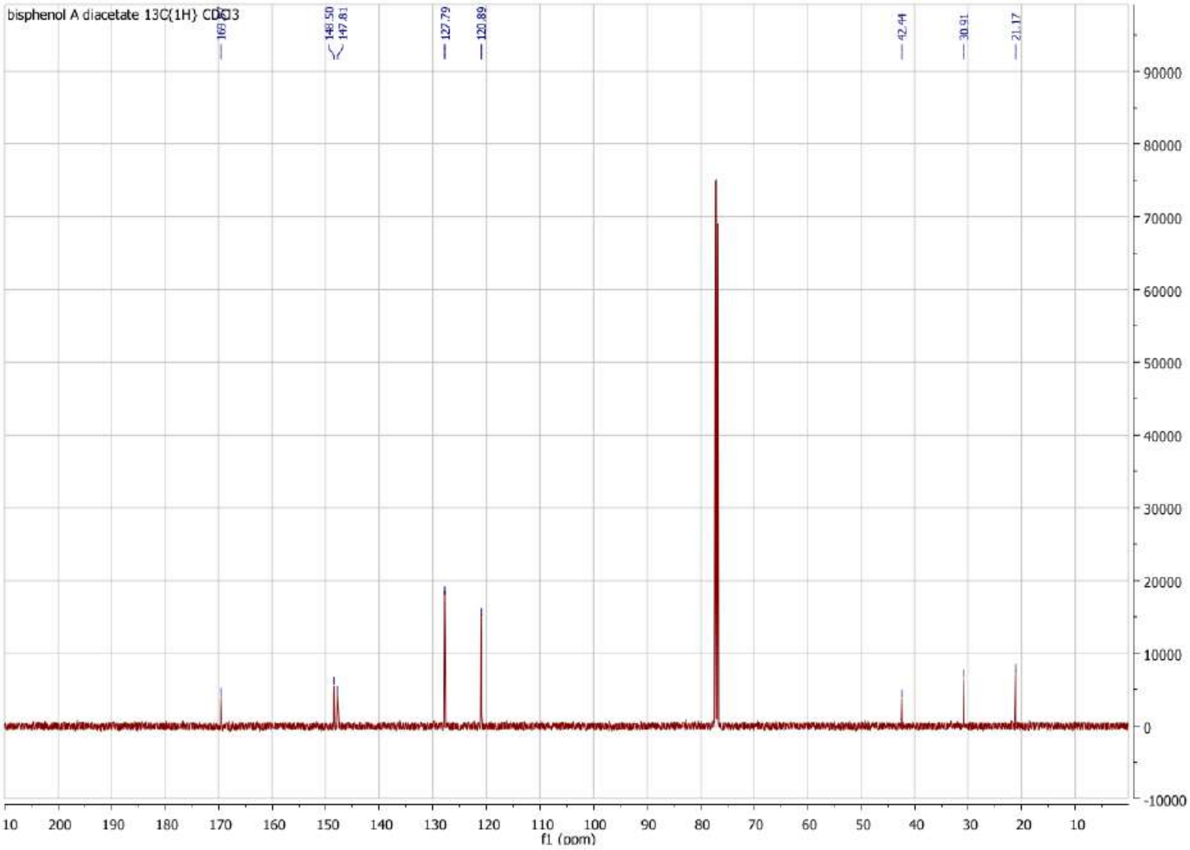


Procedure for the synthesis of bisphenol A diacetate (2): A mixture of commercially available poly(bisphenol A carbonate) (**1a**) (10.0 g, 40.0 mmol based on the repeating unit, obtained from Sigma Aldrich), acetic acid (19.2 g, 320 mmol) or acetic anhydride (32.6 g, 320 mmol), dimethylformamide (20 mL) and catalytic amounts of 4-dimethylaminopyridine (280 mg, 2.0 mmol) was stirred in a 250-mL flask equipped with a condenser at 140 °C for 24 hours. The mixture was cooled to room temperature. Water (200 mL) was added and the mixture was neutralized with a saturated aqueous $NaHCO_3$ solution. Afterwards toluene (200 mL) was added and the mixture was transferred to a separation funnel. The aqueous layer was extracted with toluene (50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and filtered. All volatiles were removed in vacuum. The oily residue was recrystallized from hot petroleum ether and afterwards stored in a freezer. The colorless crystals were filtered off and dried in vacuum. Bisphenol A diacetate (**2**) was isolated in 79% (m = 9.91 g) for the acetic acid approach and in 77% (m = 9.57 g) for the acetic anhydride approach.

Figure S2. Commercially available poly(bisphenol A carbonate) (**1a**).

Bisphenol A diacetate[3] (**2**): ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): δ = 7.35-7.39 (m, 2H), 7.20-7.22 (m, 4H), 6.96-6.98 (m, 4H), 2.27 (s, 6H, C(=O)CH_3), 1.65 (s, 6H, C(CH_3)$_2$) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, 25 °C): δ = 169.6, 148.5, 127.8, 120.9, 42.4, 30.9, 21.2 ppm. MS (EI) m/z = 312.09 ($C_{19}H_{20}O_4$: 312.14 g/mol).

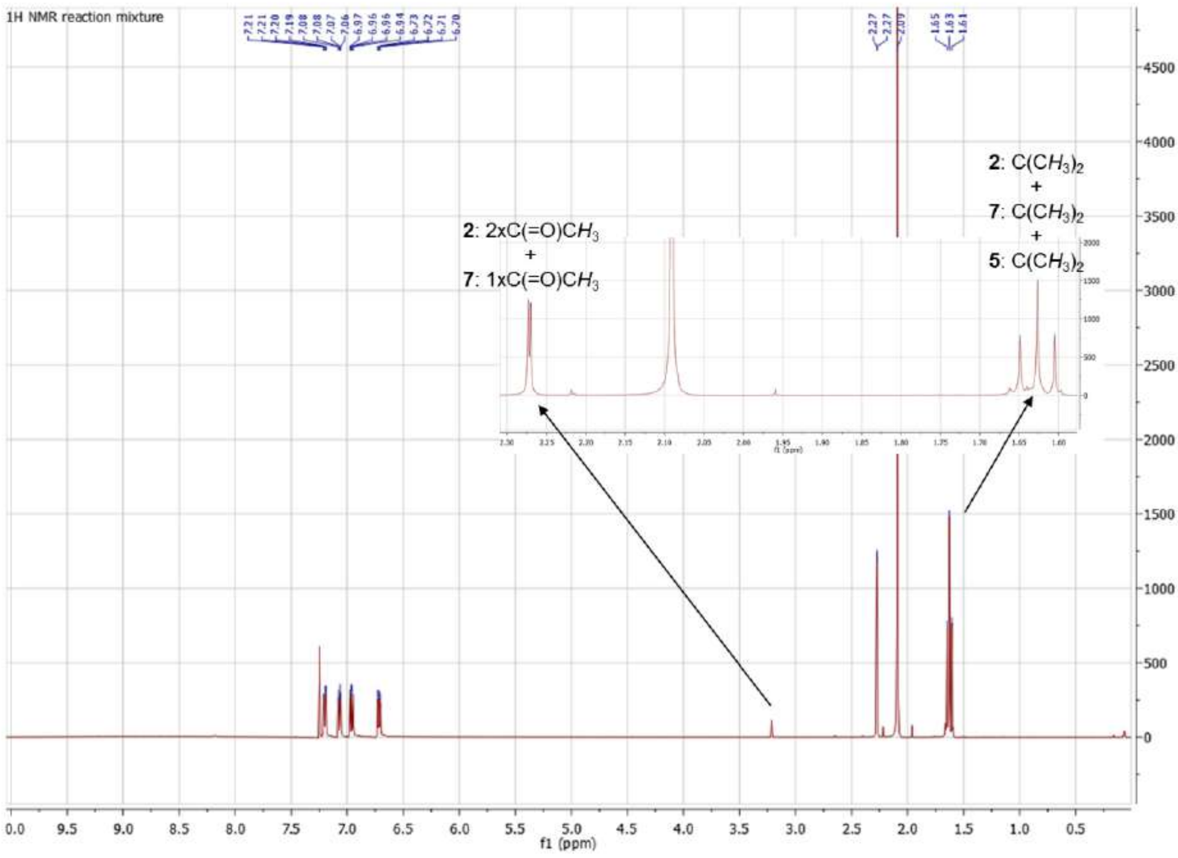




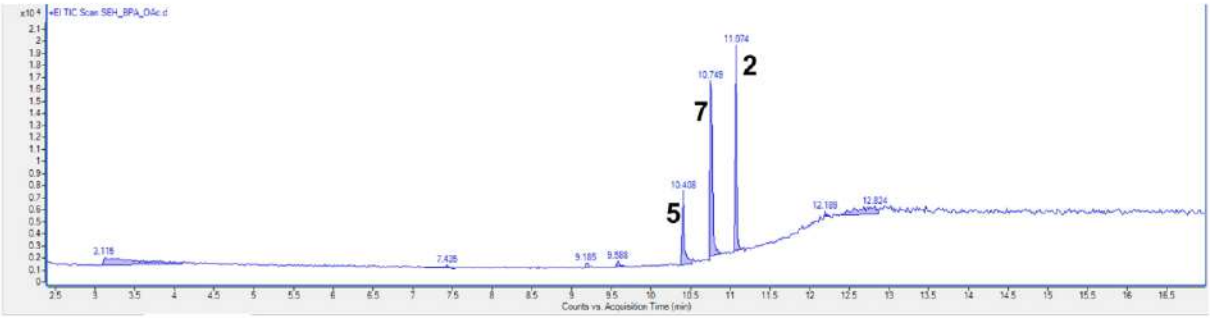
Procedure for the detection of carbon dioxide during the synthesis of bisphenol A diacetate (2): A mixture of commercially available poly(bisphenol A carbonate) (**1a**) (10.0 g, 40.0 mmol based on the repeating unit, obtained from Sigma Aldrich), acetic acid (19.2 g, 320 mmol) or acetic anhydride (32.6 g, 320 mmol), dimethylformamide (20 mL) and catalytic amounts of 4-dimethylaminopyridine (280 mg, 2.0 mmol) was stirred in a 250-mL flask equipped with a condenser at 140 °C for 24 hours. The condenser was sealed with a fermentation lock containing an aqueous solution of $Ba(OH)_2$. After a while a white precipitate is formed in the $Ba(OH)_2$ solution at the meniscus of the reaction side. The reaction mixture was cooled to room temperature. Water (200 mL) was added and the mixture was neutralized with a saturated aqueous $NaHCO_3$ solution. Afterwards, toluene (200 mL) was added and the mixture was transferred to a separation funnel. The aqueous layer was extracted with toluene (50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and filtered. All volatiles were removed in vacuum. The oily residue was recrystallized from hot petroleum ether and afterwards stored in a freezer. The NMR spectra are in accordance to the spectra presented for commercially available poly(bisphenol A carbonate) (vide supra).

Procedure for the synthesis of bisphenol A diacetate (2) applying microwave heating: A mixture of commercially available poly(bisphenol A carbonate) (**1a**) (344 mg, 1.35 mmol based on the repeating unit, obtained from Sigma Aldrich), acetic acid (648 mg, 10.8 mmol) or acetic anhydride (1102 mg, 10.8 mmol or 551 mg, 5.4 mmol), catalytic amounts of 4-dimethylaminopyridine (5.0 mol%, 8.2 mg, 0.068 mmol or 2.5 mol%, 4.1 mg, 0.034 mmol) and a stir bar was placed in a vial. The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 15 minutes (hold time) at 180 °C or 160 °C and stirring with 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible) and a pressure of up to 6 bar were created. Afterwards the vial was cooled to room temperature. The reaction mixture was transferred to a flask (50 mL) and the acetic anhydride or acetic acid was removed in vacuum. [In case of isolation of the acetic anhydride the reaction mixture was transferred to a Schlenk-flask containing a stir bar. A second Schlenk-flask was attached via a U-shaped tube. The second Schlenk-flask was cooled with liquid nitrogen and vacuum was subjected. The reaction mixture containing Schlenk-flask was heated to 50 °C. After a solid residue was formed in the reaction mixture containing Schlenk-flask the procedure was stopped. Acetic anhydride was recovered with an amount of 0.584 g (5.7 mmol, 53% based on the initial used amount). The NMR spectrum is in accordance to the spectrum of an authentic sample (vide supra).] The residue was dissolved in ethyl acetate and the mixture was filtered through a short plug of silica, which was washed with ethyl acetate. The solvent was removed in vacuum yielding an off-white crystalline residue. The NMR spectra are in accordance to the spectra presented for commercially available poly(bisphenol A carbonate) (vide supra).

In case of acetic acid as depolymerization reagent a mixture of bisphenol A (**5**), bisphenol A acetate (**7**) and bisphenol A diacetate (**2**) were observed in a ratio of 22:43:35. The ratio was obtained by GC-MS measurements (50-300 °C in 10 min; 300 °C hold 7 min). Retention time (**5**): 10.408 min (MS (EI) m/z = 228.1, 213.1); Retention time (**7**): 10.749 min (MS (EI) m/z = 270.2, 255.1, 228.2, 213.1); Retention time (**2**): 11.074 min (MS (EI) m/z = 312.3, 270.1, 255.1, 228.2, 213.1).

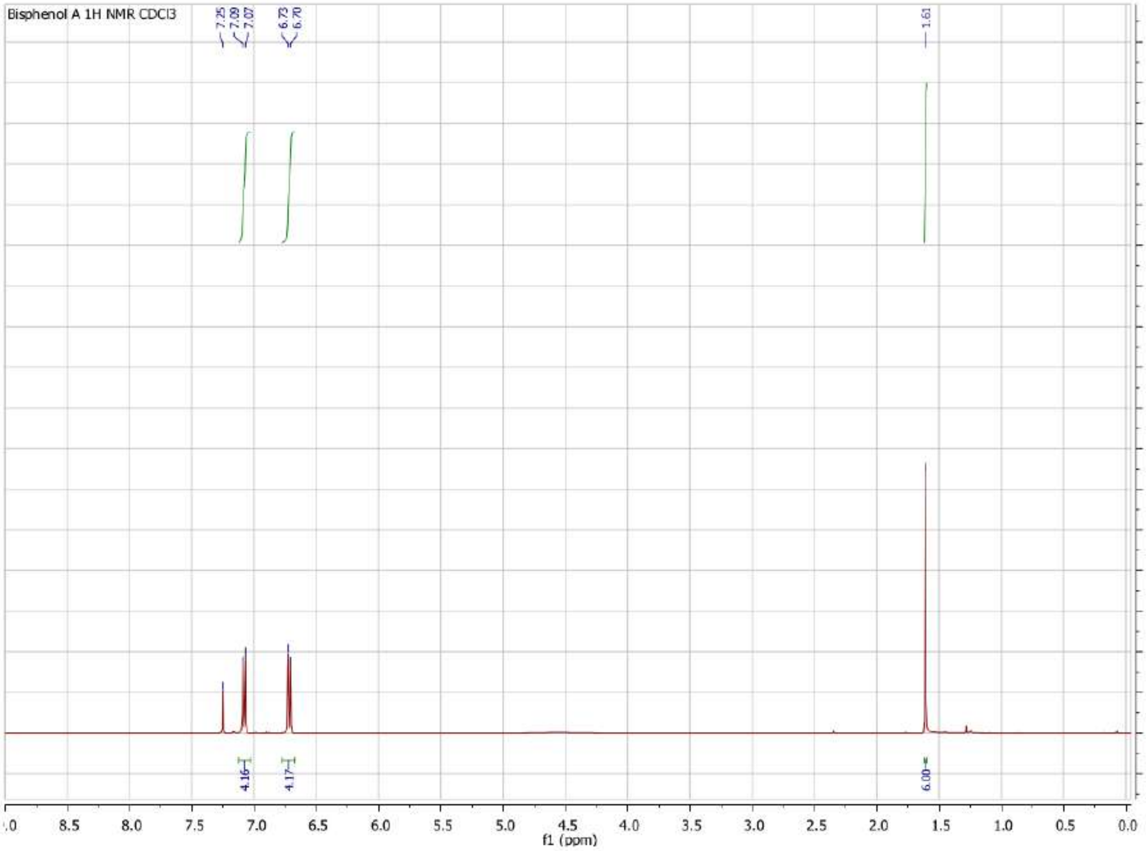


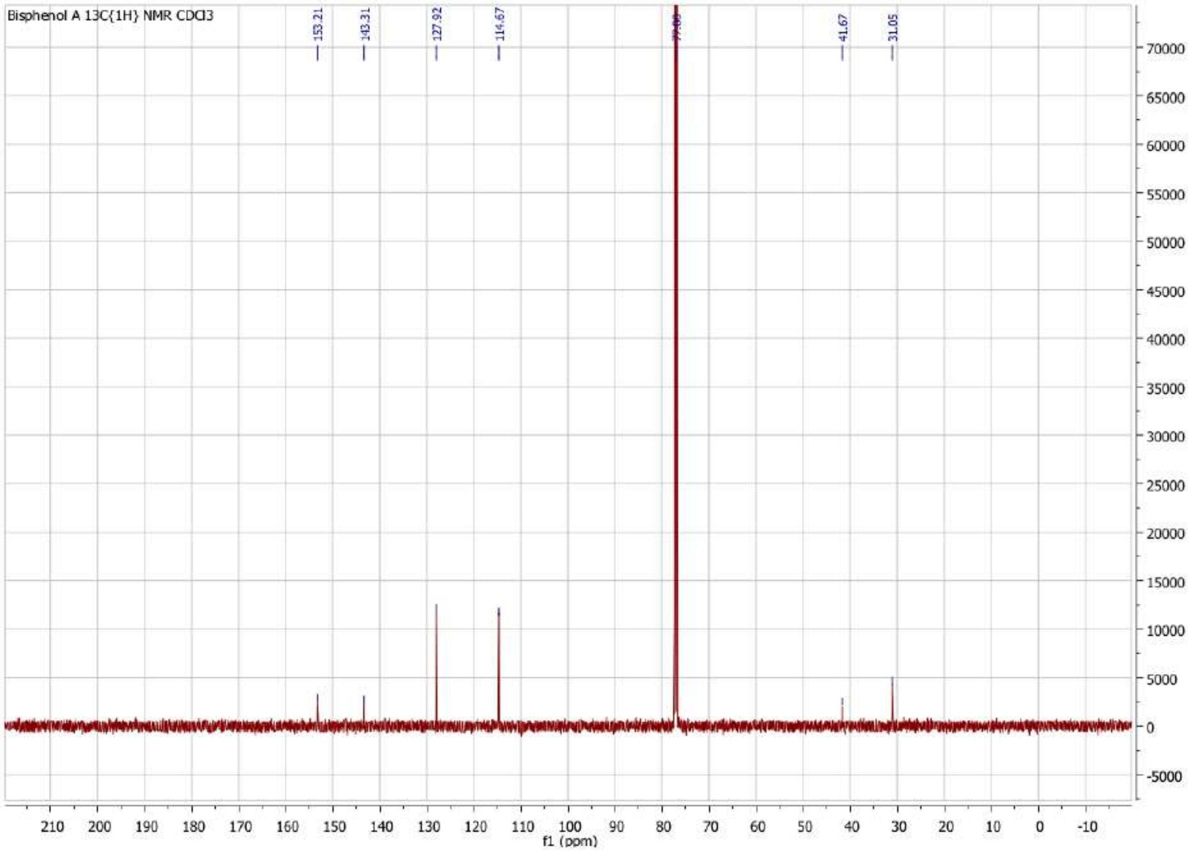
GC-chromatogram



Procedure for the hydrolysis of bisphenol A diacetate (2): Bisphenol A diacetate (**2**) (1.0 g, 3.2 mmol) was dissolved in methanol (20 mL) in a 100 mL flask equipped with a condenser. Afterwards, water (20 mL) and KOH (0.63 g, 11.2 mmol, 3.5 equiv.) were added. The mixture was stirred and heated to reflux for 4 hours. The mixture was cooled to room temperature. Water was added and the mixture was neutralized with concentrated HCl. Afterwards, toluene (100 mL) was added and the mixture was transferred to a separation funnel. The aqueous layer was extracted with toluene (2x50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and filtered. All volatiles were removed in vacuum yielding a colorless powder in 59% yield (m = 431 mg).

Bisphenol A[4] (**5**): ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.35-7.39 (m, 2H), 7.06-7.10 (m, 4H), 6.69-6.74 (m, 4H), 1.61 (s, 6H, $C(CH_3)_2$) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C): δ = 153.2, 143.3, 127.9, 114.7, 41.7, 31.1 ppm. MS (EI) m/z = 228.08 ($C_{15}H_{26}O_2$: 228.12 g/mol).





Procedure for the synthesis of bisphenol A diacetate (2) starting from CDs: A mixture of pieces of CDs (10 g, cut in small pieces) and dimethylformamide (20 mL) were stirred at 60 °C for ca. 30 min in a 250 mL flask equipped with a condenser. Afterwards, acetic anhydride (32.6 g, 320 mmol) and catalytic amounts of 4-dimethylaminopyridine (280 mg, 2.0 mmol) were added and the mixture was stirred at 140 °C for 24 hours. The mixture was cooled to room temperature and filtered. Water (200 mL) was added and the mixture was neutralized with a saturated aqueous $NaHCO_3$ solution. Afterwards, toluene (200 mL) was added and the mixture was transferred to a separation funnel. The aqueous layer was extracted with toluene (50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and filtered. All volatiles were removed in vacuum. The oily residue was recrystallized from hot petroleum ether and afterwards stored in a freezer. The colorless crystals were filtered off and dried in vacuum. Bisphenol A diacetate (**2**) was isolated in 57% (m = 7.10 g). The NMR spectra are in accordance to the spectra presented for commercially available poly(bisphenol A carbonate) (vide supra).

Figure S3. Starting material (CD pieces) for the depolymerization.

Procedure for the synthesis of bisphenol A diacetate (2) starting from CDs with initial filtration of poly(bisphenol A carbonate) solution: A mixture of pieces of CDs (10 g, cut in small pieces) and dimethylformamide (20 mL) were stirred at 60 °C for ca. 30 min in a 250 mL flask equipped with a condenser. Afterwards, the mixture was filtered through a filter paper into a 250 mL flask. The residue on the filter paper was washed with DMF (2 mL) and afterwards dried to yield 0.93 g of the residue (9.3 wt%, based on the starting CDs). A stirring bar was placed in the flask and a condenser was attached. Afterwards, acetic anhydride (32.6 g, 320 mmol) and catalytic amounts of 4-dimethylaminopyridine (280 mg, 2.0 mmol) were added and the mixture was stirred at 140 °C for 24 hours. The mixture was cooled to room temperature and filtered. Water (200 mL) was added and the mixture was neutralized with a saturated aqueous $NaHCO_3$ solution. Then, toluene (200 mL) was added and the mixture was transferred to a separation funnel. The aqueous layer was extracted with toluene (50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and filtered. All volatiles were removed in vacuum. The oily residue was recrystallized from hot petroleum ether and afterwards stored in a freezer. The colorless crystals were filtered off and dried in vacuum. Bisphenol A diacetate (**2**) was isolated in 82% (m = 10.24 g). The NMR spectra are in accordance to the spectra presented for commercially available poly(bisphenol A carbonate) (vide supra).

Figure S4. CDs in DMF.

Figure S5. Leftover after filtration of the poly(bisphenol A carbonate) solution.

Procedure for the synthesis of bisphenol A diacetate starting from CDs with initial purification of poly(bisphenol A carbonate): A mixture of pieces of CDs (10 g, cut in small pieces) and dimethylformamide (20 mL) were stirred at 60 °C for ca. 30 min in a 250 mL flask equipped with a condenser. Afterwards, the mixture was filtered through a filter paper into a 500 mL beaker. The residue on the filter paper was washed with DMF (2 mL). Acetone (200 mL) was added to the poly(bisphenol A carbonate) solution to precipitate the poly(bisphenol A carbonate). The colorless solid was filtered off, washed with acetone and dried in an oven at 90 °C for 8 hours. The powder was isolated in 87 wt% (8.7 g) based on the starting CDs. The colorless powder was placed together with a stirring bar in a 250 mL flask equipped with a condenser. Afterwards, acetic anhydride (32.6 g, 320 mmol) and catalytic amounts of 4-dimethylaminopyridine (280 mg, 2.0 mmol) were added and the mixture was stirred at 140 °C for 24 hours. The mixture was cooled to room temperature and filtered. Water (200 mL) was added and the mixture was neutralized with a saturated aqueous $NaHCO_3$ solution. Then, toluene (200 mL) was added and the mixture was transferred to a separation funnel. The aqueous layer was extracted with toluene (50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and filtered. All volatiles were removed in vacuum. The oily residue was recrystallized from hot petroleum ether and afterwards stored in a freezer. The colorless crystals were filtered off and dried in vacuum. Bisphenol A diacetate (**2**) was isolated in 86% (m = 10.86 g). The NMR spectra are in accordance to the spectra presented for commercially available poly(bisphenol A carbonate) (vide supra).

Figure S6. Purified poly(bisphenol A carbonate).

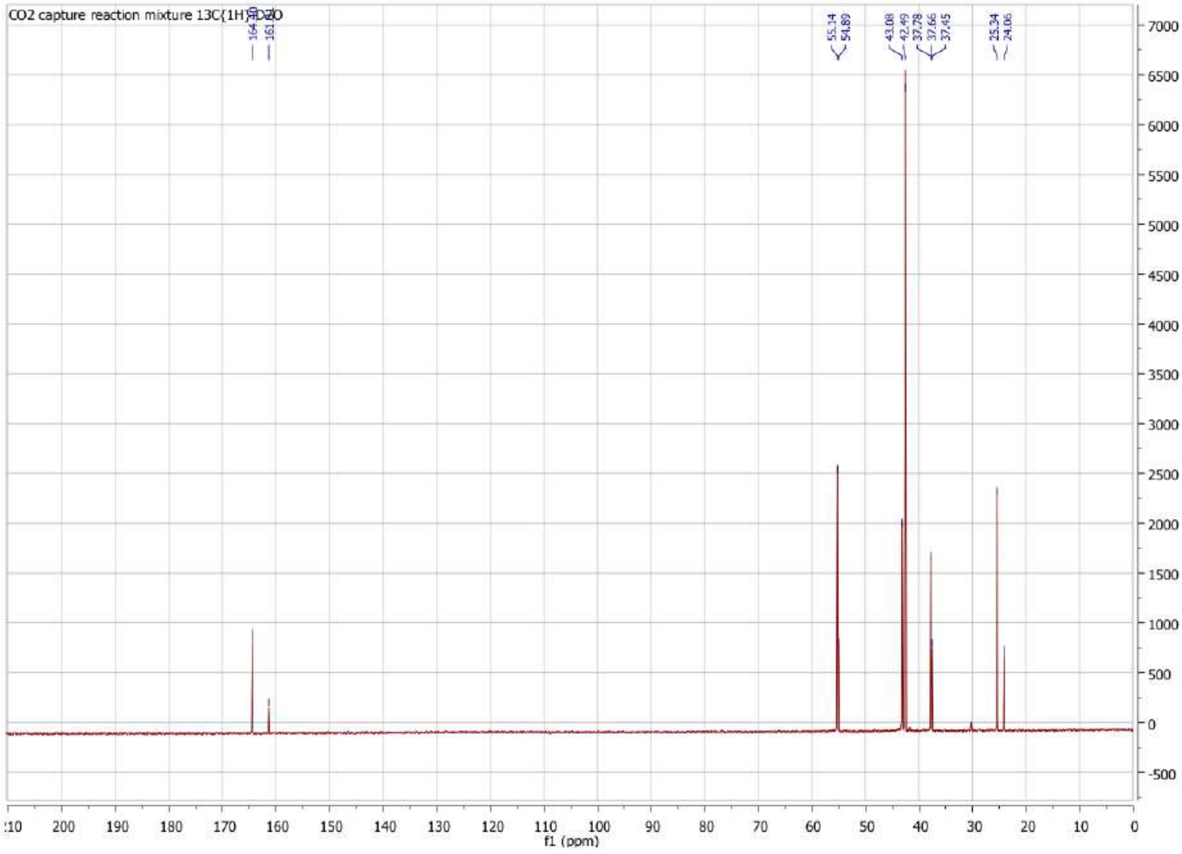
Procedure for the synthesis of bisphenol A diacetate starting from CDs with initial purification of poly(bisphenol A carbonate) applying microwave heating: A mixture of poly(bisphenol A carbonate) (**1d**) (344 mg, 1.35 mmol based on the repeating unit), acetic anhydride (1102 mg, 10.8 mmol), catalytic amounts of 4-dimethylaminopyridine (5.0 mol%, 8.2 mg, 0.068 mmol) and a stir bar was placed in a vial. The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 15 minutes (hold time) at 180 °C and stirring with 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible) and a pressure of up to 6 bar were created. Afterwards the vial was cooled to room temperature. The reaction mixture was transferred to a flask (50 mL) and the acetic anhydride or acetic acid was removed in vacuum. The residue was dissolved in ethyl acetate and the mixture was filtered through a short plug of silica, which was washed with ethyl acetate. The solvent was removed in vacuum yielding an off-white crystalline residue. The NMR spectra are in accordance to the spectra presented for commercially available poly(bisphenol A carbonate) (vide supra).

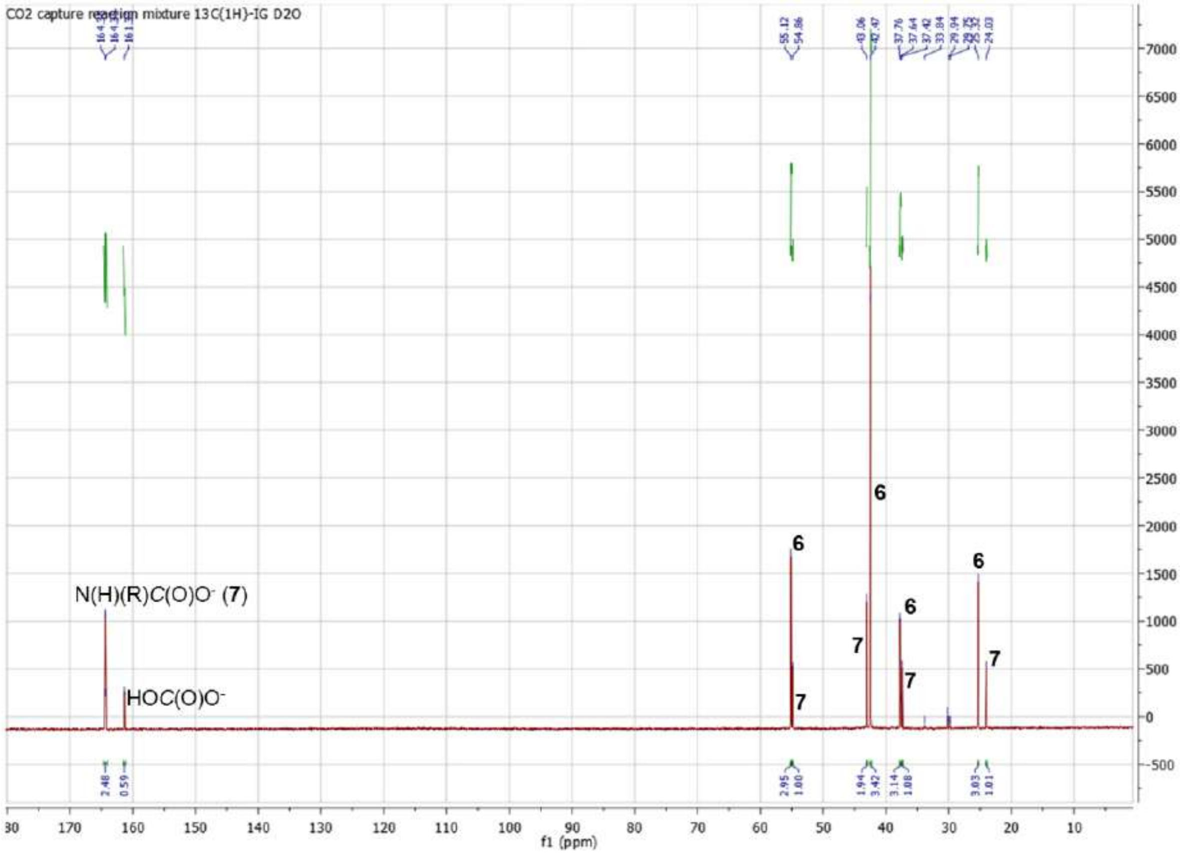
Procedure for the carbon dioxide capture produced by the depolymerization of poly(bisphenol A carbonate): A mixture of commercially available poly(bisphenol A carbonate) (10.0 g, 40.0 mmol based on the repeating unit, obtained from Sigma Aldrich), acetic anhydride (32.6 g, 320 mmol), dimethylformamide (20 mL) and catalytic amounts of 4-dimethylaminopyridine (280 mg, 2.0 mmol) was stirred in a 250 mL flask equipped with a condenser at 140 °C for 24 hours. On the top of the condenser a stop-cock was attached, which was connected by a flexible tube to a carbon dioxide leading-in tube, which was attached to a second flask (1 L). In the flask an aqueous solution of 3-dimethylaminopropylamine (7.96 g, 0.078 mol, 2 M in water (39 mL water)) was stirred at room temperature (the temperature was controlled by a water bath). The outlet of the leading-in tube was connected to a balloon.

a) The depolymerization reaction mixture was cooled to room temperature after 24 h at 140 °C. Water (200 mL) was added and the mixture was neutralized with a saturated aqueous $NaHCO_3$ solution. Afterwards, toluene (200 mL) was added and the mixture was transferred to a separation funnel. The aqueous layer was extracted with toluene (50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and filtered. All volatiles were removed in vacuum. The oily residue was recrystallized from hot petroleum ether and afterwards stored in a freezer. The NMR spectra are in accordance to the spectra presented for commercially available poly(bisphenol A carbonate) (vide supra).

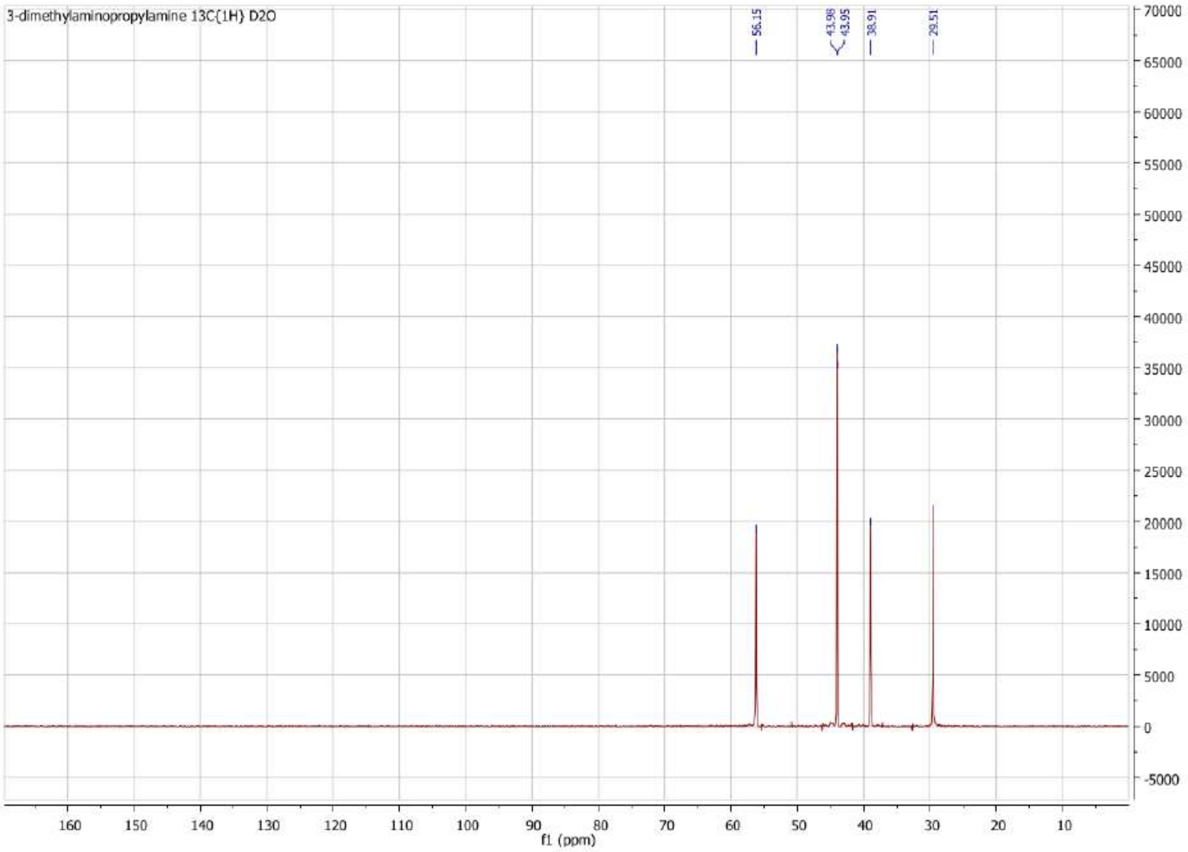
b) An aliquot (0.6 mL) of the reaction mixture of the aqueous solution of 3-dimethylaminopropylamine (**6**) was added to a NMR tube containing 0.1 mL D_2O and subjected to NMR measurements. The yield and the incorporation of carbon dioxide was determined by $^{13}C\{^1H\}$-IG NMR.

Figure S7. Reaction set up for depolymerization coupled with carbon dioxide capture.


CO2 capture reaction mixture 13C{1H}-D2O
164.30
161.20
55.14
54.89
43.08
42.49
37.78
37.66
37.45
25.34
24.06
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


CO2 capture reaction mixture 13C(1H)-IG D2O
164.3
164.3
161.1
55.12
54.86
43.06
42.47
37.76
37.64
37.42
33.84
29.94
25.35
25.32
24.03
N(H)(R)C(O)O⁻ (7)
HOC(O)O⁻
6
7
6
7
6
7
6
7
2.48
0.59
2.95
1.00
1.94
3.42
3.14
1.08
3.03
1.01
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

3-Dimethylaminopropylamine: $^{13}C\{^1H\}$ NMR (125 MHz, D_2O, 25 °C): δ = 56.2, 43.98, 43.95, 38.9, 29.5 ppm.

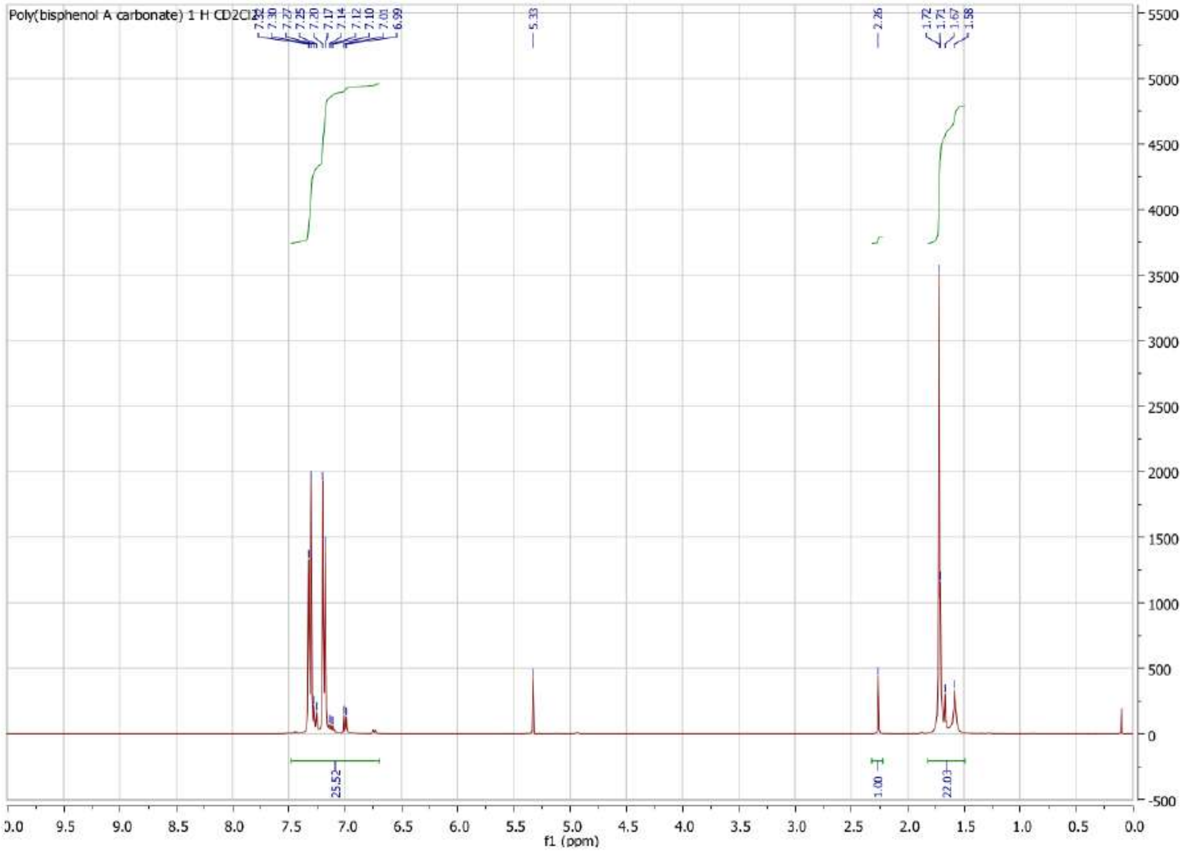


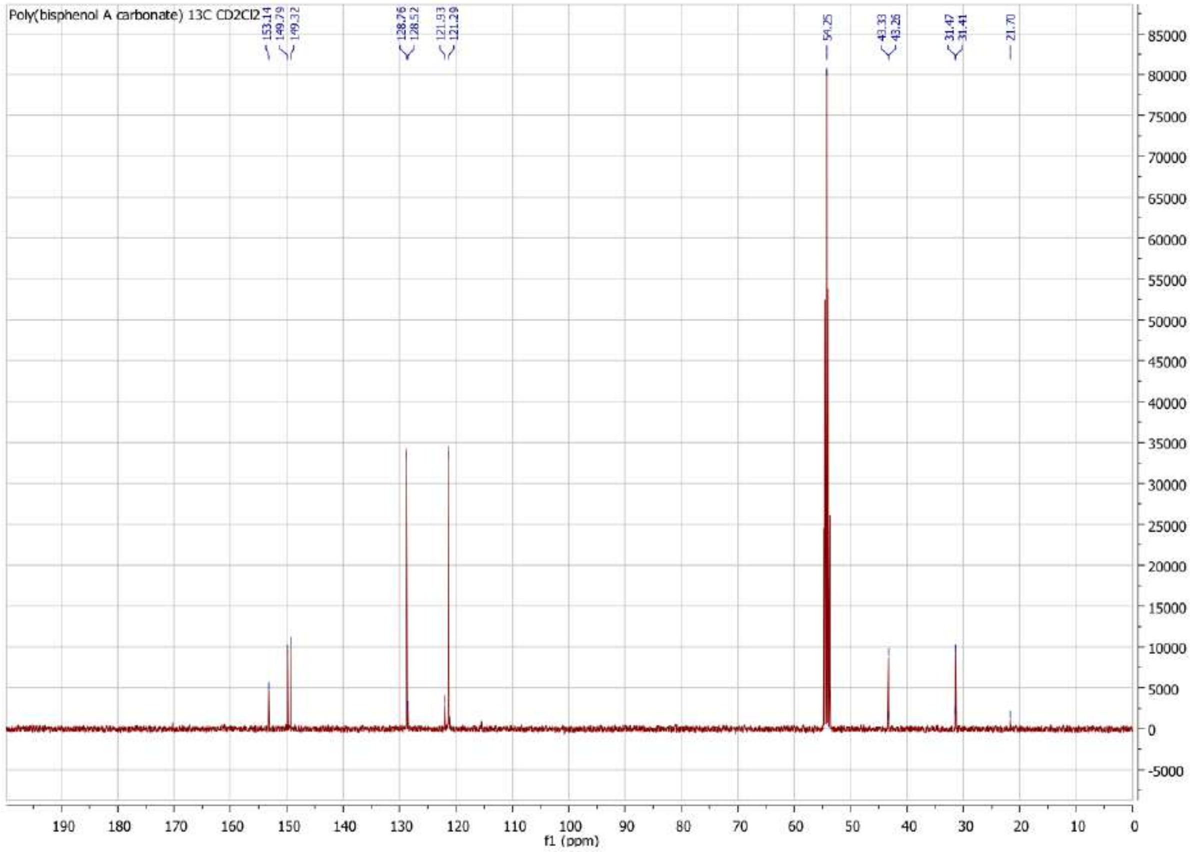
Synthesis of poly(bisphenol A carbonate) via polymerization of bisphenol-A diacetate (2) and diphenyl carbonate (3)[5]: Bisphenol-A diacetate (**2**) (3.12 g, 0.01 mol), diphenylcarbonate (**3**) (2.14 g, 0.01 mol) and catalytic amounts of potassium *tert*-butoxide (11.2 mg, 0.1 mmol) were added to a 10 mL flask. A stirring bar was added and a Vigreux column, a distillation bridge, a collecting flask and connection to a vacuum system were attached. The mixture was stirred and heated to 180 °C in an oil bath. The mixture was kept at 180 °C for 15 minutes. Afterwards, the temperature was increased to 200 °C. At 190 °C a vacuum (1.6 mbar) was set up. During the utilization of the vacuum a colorless liquid was distilled off and collected in the collecting flask. After 10 minutes no further liquid was collected and the polymerization process was stopped. The liquid was analyzed by ^1H NMR revealing the formation of **4** as major component in 37% yield. In the polymerization flask a brown, viscous residue was formed. The residue was dissolved in dichloromethane and a powder was precipitated by addition of acetone. The powder was washed several times with acetone and petroleum ether finally yielding 0.8 g (31%) of an off-white powder.

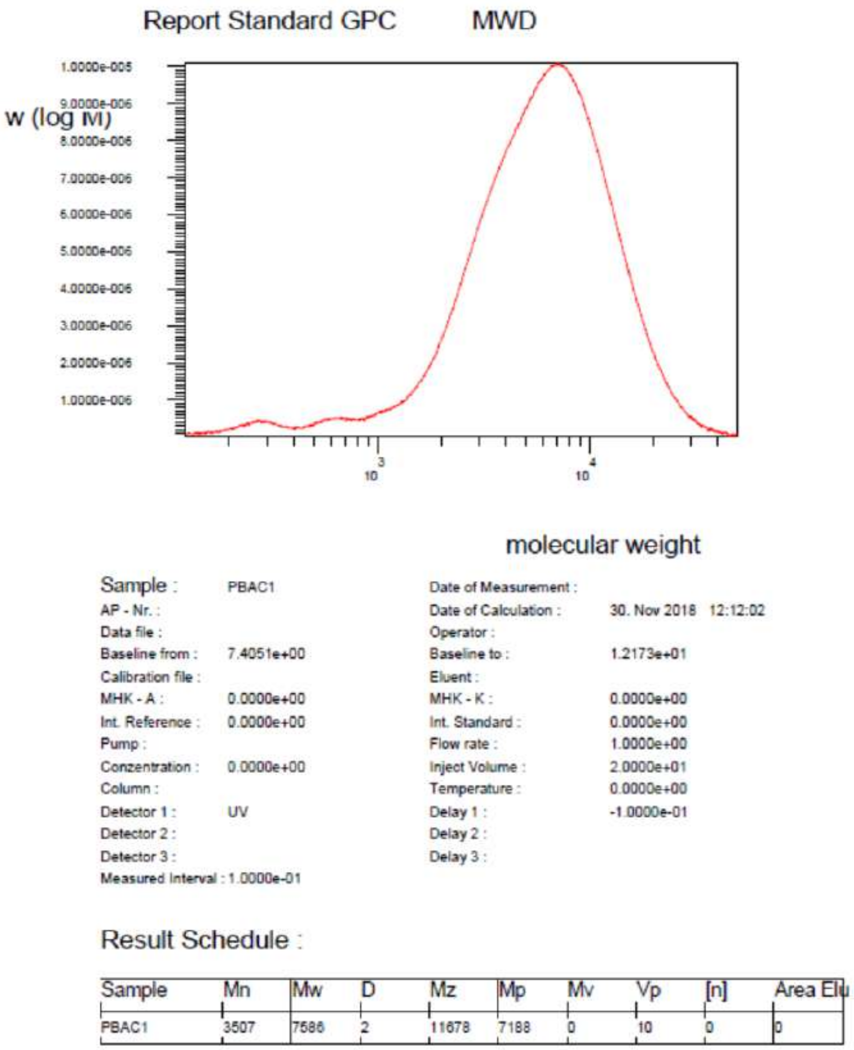
Figure S8. Reaction set up for polymerization.

Figure S9. Poly(bisphenol A carbonate) synthesized by polymerization of bisphenol-A diacetate and diphenyl carbonate.

Poly(bisphenol A carbonate) (**1e**)[6]: ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 6.75-7.32 (m, 8H, Ar-H), 2.26 (br, C(=O)CH_3, end group) 1.58-1.72 (m, 6H, C(CH_3)$_2$) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2, 25 °C): δ = 153.1, 149.8, 149.3, 128.8, 128.5, 121.9, 121.3, 43.33, 43.26, 31.5, 31.4, 21.7 ppm.


Poly(bisphenol A carbonate) 1 H CD2Cl2
7.32
7.30
7.27
7.25
7.20
7.17
7.14
7.12
7.10
7.01
6.99
5.33
2.26
1.72
1.71
1.67
1.58
25.52
1.00
22.03
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Poly(bisphenol A carbonate) 13C CD2Cl2
153.14
149.79
149.32
128.76
128.52
121.93
121.29
54.25
43.33
43.26
31.47
31.41
21.70
85000
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



Report Standard GPC MWD

Sample : PBAC1
AP - Nr. :
Data file :
Baseline from : 7.4051e+00
Calibration file :
MHK - A : 0.0000e+00
Int. Reference : 0.0000e+00
Pump :
Conzentration : 0.0000e+00
Column :
Detector 1 : UV
Detector 2 :
Detector 3 :
Measured Interval : 1.0000e-01

Date of Measurement :
Date of Calculation : 30. Nov 2018 12:12:02
Operator :
Baseline to : 1.2173e+01
Eluent :
MHK - K : 0.0000e+00
Int. Standard : 0.0000e+00
Flow rate : 1.0000e+00
Inject Volume : 2.0000e+01
Temperature : 0.0000e+00
Delay 1 : -1.0000e-01
Delay 2 :
Delay 3 :

Result Schedule :

Sample	Mn	Mw	D	Mz	Mp	Mv	Vp	[n]	Area Elu
PBAC1	3507	7586	2	11678	7188	0	10	0	0

Figure S9. GPC analysis of poly(bisphenol A carbonate) synthesized by polymerization of bisphenol-A diacetate and diphenyl carbonate (calibration curve based on narrow polydispersity polystyrene standards).

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Depolymerization of End-of-Life Poly(bisphenol A carbonate) via 4-Dimethylaminopyridine-catalyzed Methanolysis

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General: All chemicals were used as received without further manipulations. ^{1}H and ^{13}C{^{1}H}NMR spectra were recorded on a *Fourier 300 MHz* (^{1}H: 300 MHz, ^{13}C: 75 MHz) or *Avance I-400* (^{1}H: 400 MHz, ^{13}C: 101 MHz) by Bruker, using the proton signals of the deuterated solvents as reference or external standards. Mass spectrometry was performed using a *Thermo ISQ LT EI* by Thermo Fisher Scientific. TLC was performed on *ALUGRAM XTRA SIL G/UV$_{254}$* cards from *Macherey-Nagel* GmbH & Co. KG with a thickness of 0.20 mm. Detection succeeded with UV-light (254 nm). For preparative column chromatography silica gel 60 (particle size 40 – 63 µm) from *Fluka* was used. For microwave heating experiments a Microwave Synthesis Reactor Monowave 400 (Anton Paar GmbH) was used. GC-MS was measured with Agilent Technologies 5977B GC/MSD. SEC analysis was performed using a "mixed bed" linear SEC-column (5 µm porous styrene-divinylbenzene particles, separation range 200-1000k g/mol) at a flow rate of 1 mL/min in tetrahydrofuran as eluent. Molecular weights refer to a so-called relative calibration based on narrow polystyrene samples supplied by Agilent Technologies. The SEC system was equipped with a Shimadzu LC-10ATvP pump, an AS1000 autosampler from Thermo Separation Products and a RI2012 refractive index detector from Schambeck SFD GmbH.

General procedure for the depolymerization of poly(bisphenol A carbonate) 1a (optimization of reaction conditions): A mixture of commercially available poly(bisphenol A carbonate) (**1a**) (344 mg, 1.35 mmol based on the repeating unit, obtained from Sigma Aldrich), methanol (0.125−2.00 g, 3.90−62.4 mmol, 2.88−46.22 equiv. based on the repeating unit of **1a**) and catalytic amounts of 4-dimethylaminopyridine (0.00−8.25 mg, 0−67.5 µmol, 0−5 mol% based on the repeating unit of **1a**) were placed with a stir bar in a vial. In case of <23.1 equiv. of methanol THF was added as solvent (1.00-1.88 g). The vial was sealed and subjected to microwave irradiation. The reaction was performed for 5−60 minutes (hold time) at 120−180 °C and with a stirring rate of 600 rpm. The reaction temperature was reached within 1−2 minutes (heat as fast as possible) and a pressure of up to 25 bar was created. Afterwards the vial was cooled to room temperature. An aliquot of the clear solution was transferred to a NMR tube and dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^{1}H NMR to determine the yield and the ratio of bisphenol A (**2**) and dimethyl carbonate (**3**). [The yield of **2** was calculated on the basis of the Ar-H or $C(CH_3)_2$ and the Ar-H or $C(CH_3)_2$ leftover signals of the polymer/oligomer. The yield of **3** was calculated on the ratio of the Ar-H of **2** to $(CH_3O)_2C{=}O$.]

Bisphenol A (**2**):[1] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.03−7.07 (m, 4H, Ar-*H*), 6.68−6.71 (m, 4H, Ar-*H*), 1.60 (s, 6H, $(CH_3)_2C$-) ppm. (The signal for 2xOH was not observed).

Dimethyl carbonate (**3**):[2] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.77 (s, 6H, $(CH_3O)_2C{=}O$) ppm.

Figure S1. a) Microwave Synthesis Reactor Monowave 400 (Anton Paar GmbH); b) reaction mixture before microwave heating; c) reaction mixture after microwave heating.

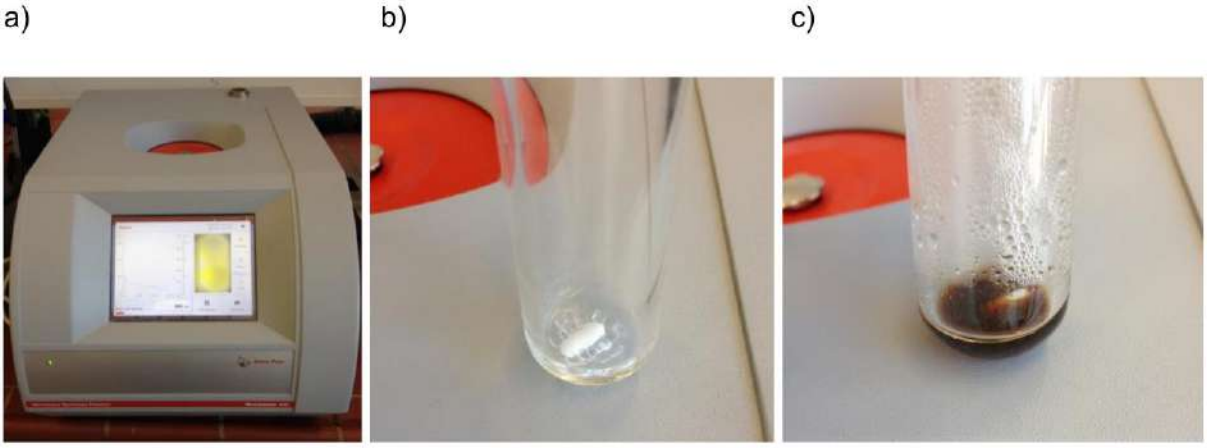
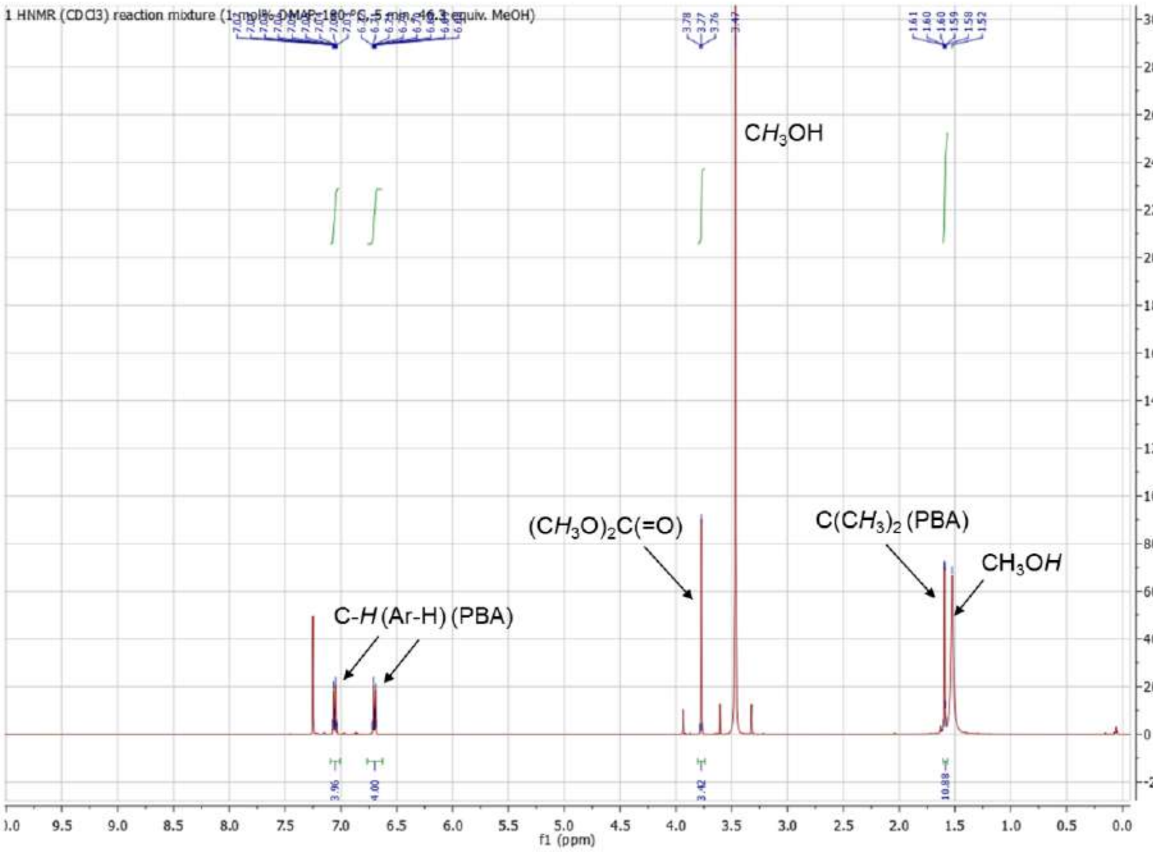


Figure S2. Spectrum of a reaction mixture (1 mol% DMAP, 46.2 equiv. MeOH, 180 °C, 5 min) (^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)).



Procedure for the depolymerization of poly(bisphenol A carbonate) 1a: A mixture of commercially available poly(bisphenol A carbonate) (**1a**) (344 mg, 1.35 mmol based on the repeating unit, obtained from Sigma Aldrich), methanol (1.95 g, 62.4 mmol, 46.2 equiv.) and catalytic amounts of 4-dimethylaminopyridine (1.70 mg, 139 µmol, 1.03 mol%) were placed with a stir bar in a vial. The vial was sealed and subjected to microwave irradiation. The reaction was performed for 5 minutes (hold time) at 180 °C with a stirring rate of 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible) and a pressure of up to 25 bar was created. Afterwards the vial was cooled to room temperature. An aliquot was added to a NMR tube and dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^1H NMR revealing a NMR yield of >99% (**2**) and 57% (**3**). The reaction mixture was transferred to a flask (50 mL) and all volatiles were removed in vacuum. The residue was dissolved in hot toluene (15 mL) and stored in a fridge overnight. The colorless crystals were collected by filtration and washed with small amounts of cold toluene. After drying bisphenol A was obtained in 97% yield (299 mg, 1.31 mmol).

Bisphenol A **2**: ^1H NMR (400 MHz, acetone-d_6, 25 °C): δ = 8.09 (s, 2H, -O*H*), 7.03−7.08 (m, 4H, Ar-*H*), 6.72−6.75 (m, 4H, Ar-*H*), 1.59 (s, 6H, $(CH_3)_2C$-) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, acetone-d_6, 25 °C): δ = 155.8, 142.8, 128.4, 115.4, 42.0, 31.5 ppm.

Figure S3. Spectrum of **2** (^1H NMR (400 MHz, acetone-d_6, 25 °C)).

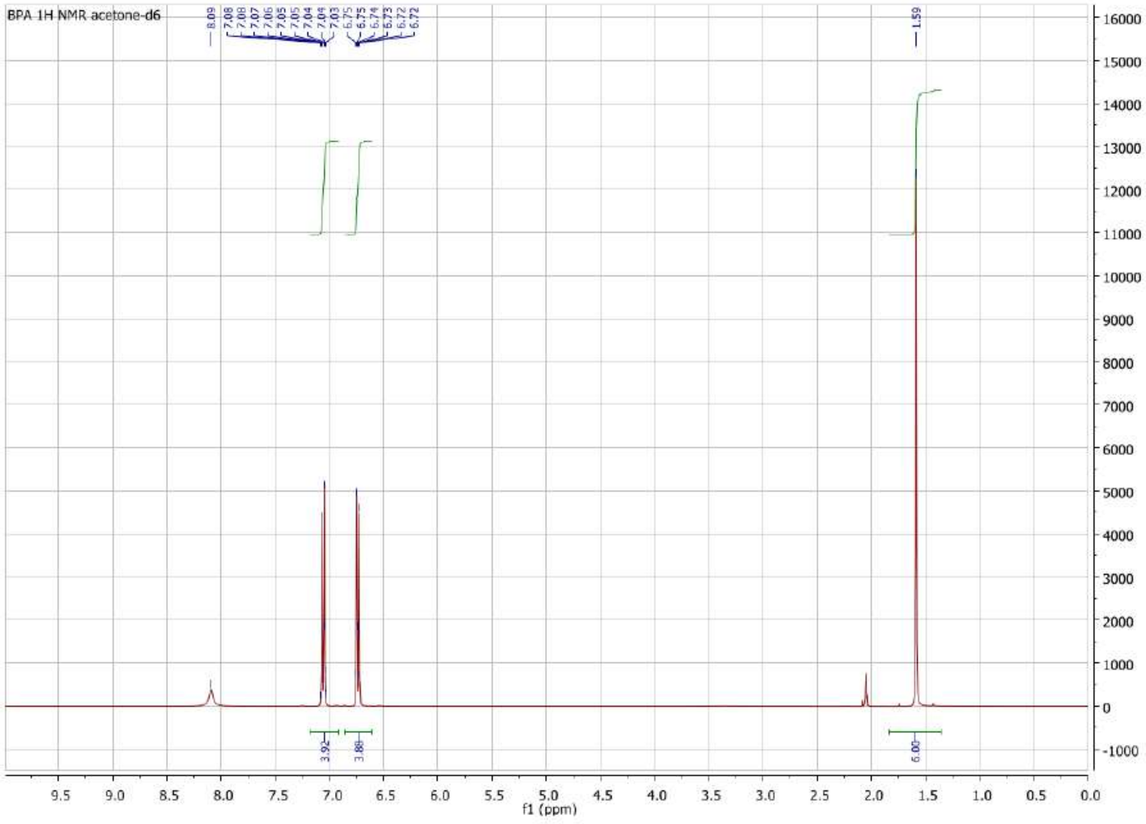
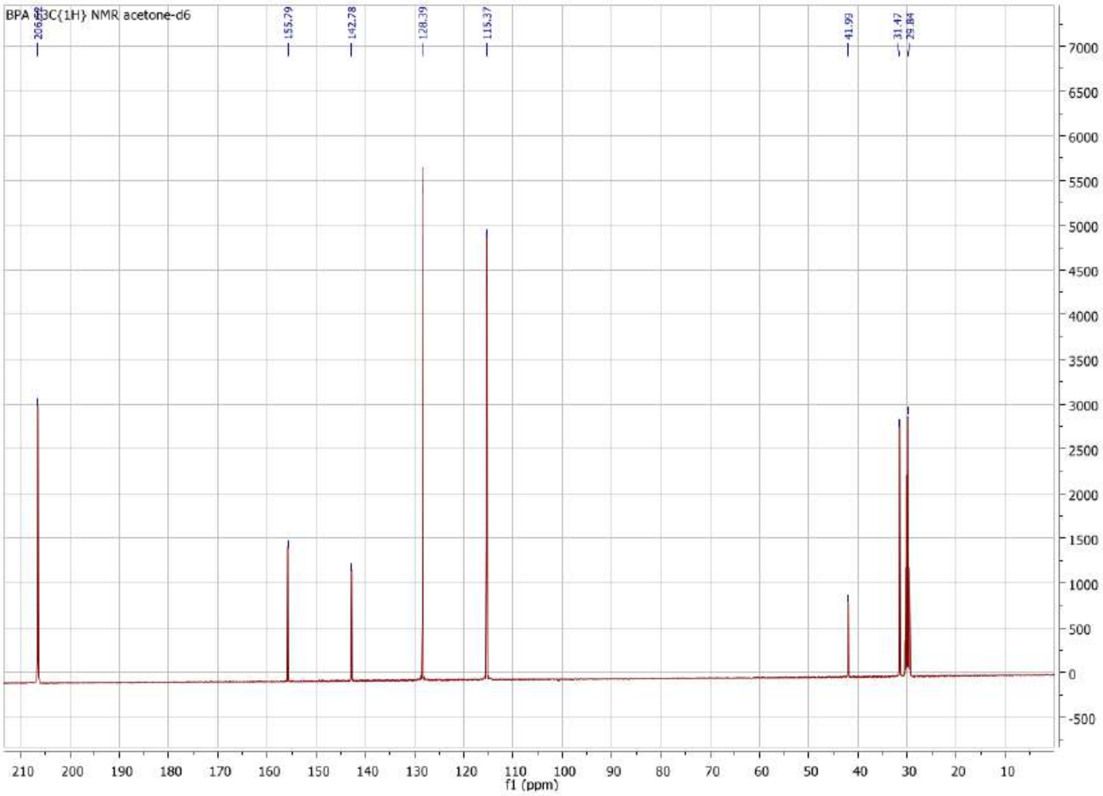
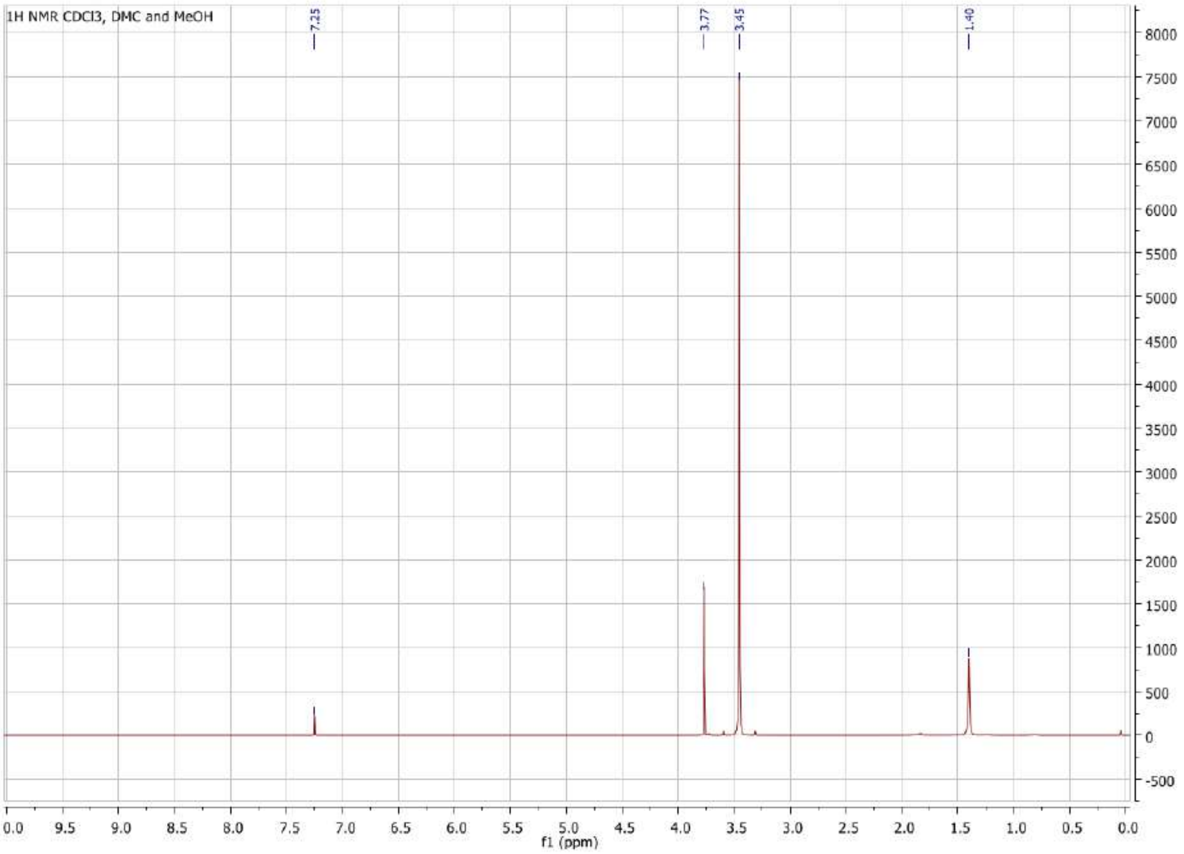


Figure S4. Spectrum of **2** ($^{13}C\{^1H\}$ NMR (125 MHz, acetone-d_6, 25 °C)).



Procedure for the depolymerization of poly(bisphenol A carbonate) 1a: A mixture of commercially available poly(bisphenol A carbonate) (**1a**) (344 mg, 1.35 mmol based on the repeating unit, obtained from Sigma Aldrich), methanol (1.95 g, 62.4 mmol, 46.2 equiv.) and catalytic amounts of 4-dimethylaminopyridine (1.70 mg, 139 µmol, 1.03 mol%) were placed with a stir bar in a vial. The vial was sealed and subjected to microwave irradiation. The reaction was performed for 5 minutes (hold time) at 180 °C and with a stirring rate of 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible) and a pressure of up to 25 bar was created. Afterwards the vial was cooled to room temperature. An aliquot was added to a NMR tube and dissolved in $CDCl_3$ (0.5 mL). The sample was transferred to a 10 mL flask containing a stir bar and was attached to distillation equipment. The mixture was stirred at room temperature and receiving flask was cooled with liquid nitrogen. Methanol and dimethyl carbonate were distilled off under vacuum. After the distillation was finished an oily residue was observed in the reaction flask, which solidifies after standing. The residue was dissolved in hot toluene (15 mL) and stored in a fridge overnight. The colorless crystals were collected by filtration and washed with small amounts of cold toluene. After drying bisphenol A was obtained in 92% yield (286 mg, 1.25 mmol). The NMR spectrum is in accordance to the spectrum for bisphenol A (vide supra). An aliquot of the clear solution in the receiving flask was transferred to a NMR tube and was dissolved in $CDCl_3$. ^{1}H NMR measurements revealed the presence of methanol and dimethyl carbonate.

Figure S5. Spectrum of **3** and methanol ($^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, 25 °C)).



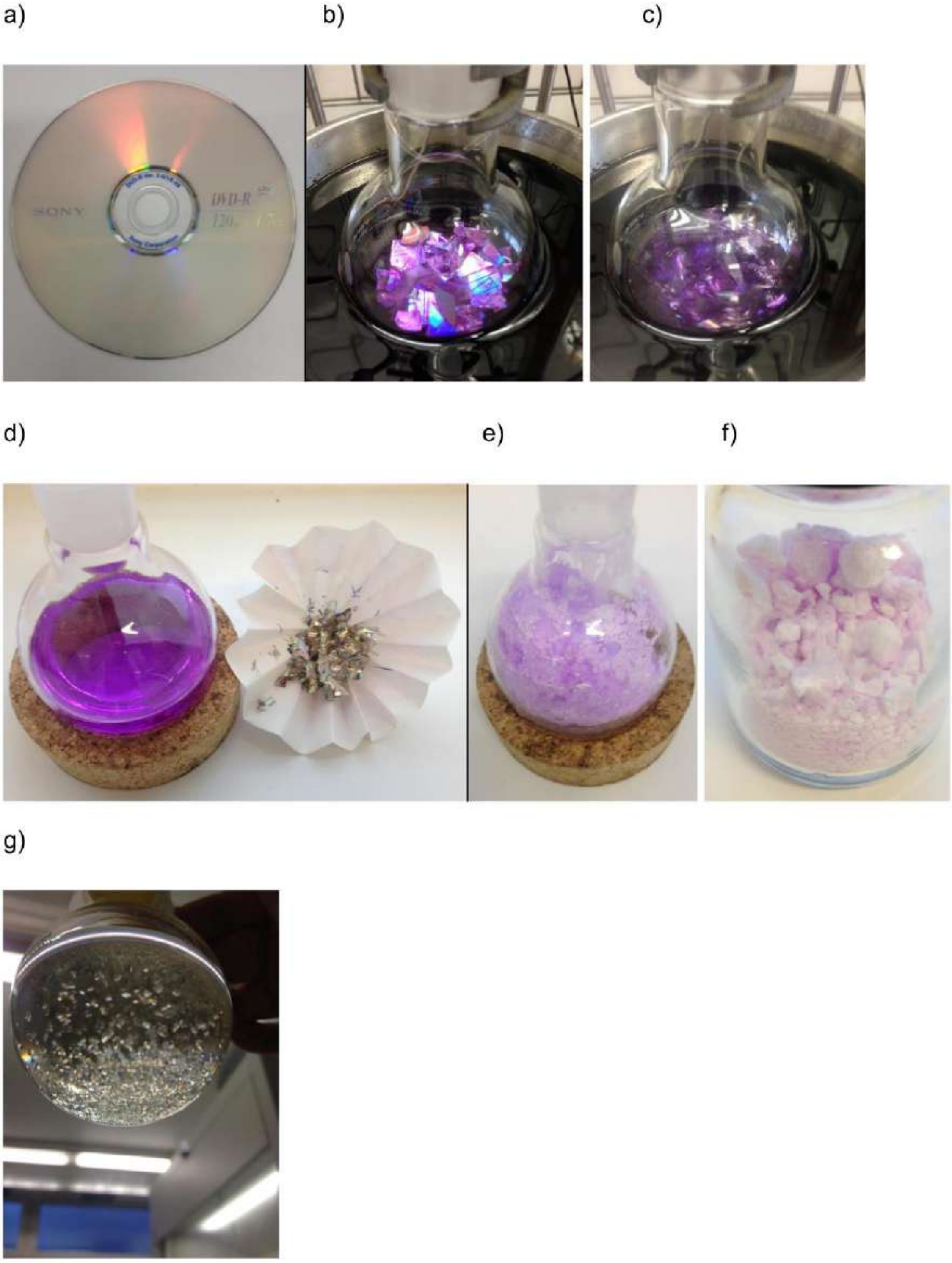
Procedure for the depolymerization of poly(bisphenol A carbonate) starting from DVD:

a) Poly(bisphenol A carbonate) isolation from DVDs

To pieces of a DVD (16.7 g, cut in small pieces) and a stir bar in a 250 mL-flask was added THF (100 mL). A reflux condenser was added and the flask was placed in an oil bath. The mixture was heated at reflux for 30 min. The polycarbonate part of the DVD dissolved, while the aluminum foil and another plastic foil didn´t dissolve. The hot mixture was filtered through a filter paper into a 250 mL flask. The solvent was removed on a rotary evaporator (Note: the collected solvent can be reused for further poly(bisphenol A carbonate) dissolving). The solid residue was added to a frit and was washed with acetone. Afterwards the solid was dried in an oven at 80 °C for 6 hours yielding 13.7 g of poly(bisphenol A carbonate) **1b** (82 wt%

based on the starting DVD) (Note: the color of the poly(bisphenol A carbonate) varies depending on the applied starting DVD).

Figure S6. a) applied DVD; b) mixture of DVD pieces and THF; c) mixture after 30 min at reflux; d) components after filtration; e) poly(bisphenol A carbonate) **1b** after removal of the THF; f) poly(bisphenol A carbonate) **1b** after washing and drying; g) crystals of **2** in toluene.



b) Depolymerization of poly(bisphenol A carbonate) **1b**

A mixture of poly(bisphenol A carbonate) (**1b**) (344 mg, 1.35 mmol based on the repeating unit), methanol (1.95 g, 62.4 mmol, 46.2 equiv.) and catalytic amounts of 4-dimethylaminopyridine (1.70 mg, 139 µmol, 1.03 mol%) were placed with a stir bar in a vial. The vial was sealed and subjected to microwave irradiation. The reaction was performed for 5 minutes (hold time) at 180 °C with a stirring rate of 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible) and a pressure of up to 25 bar was created. Afterwards the vial was cooled to room temperature. An aliquot was added to a NMR tube and dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^1H NMR revealing a NMR yield of >99% (**2**) and 93% (**3**). The reaction mixture was transferred to a flask (50 mL) and all volatiles were removed in vacuum. The residue was dissolved in hot toluene (15 mL) and stored in a fridge overnight. The colorless crystals were collected by filtration and washed with small amounts of cold toluene. After drying bisphenol A was obtained in 85% isolated yield (263 mg, 1.15 mmol).

The NMR spectra are in accordance to the spectra presented for depolymerization of commercially available poly(bisphenol A carbonate) **1a** (vide supra).

Procedure for the depolymerization of poly(bisphenol A carbonate) starting from DVD (conventional heating):

A mixture of poly(bisphenol A carbonate) (**1b**) (obtained from DVD vide supra) (3.44 g, 13.5 mmol based on the repeating unit), methanol (10.0 g, 312 mmol, 23.1 equiv.), THF (20 g) and catalytic amounts of 4-dimethylaminopyridine (17.0 mg, 0.139 mmol, 1.02 mol%) were placed with a stir bar in a flask (100 mL). A condenser was attached and the mixture was heated at reflux (80 °C) for 48 hours. The clear solution was cooled to room temperature and an aliquot was added to a NMR tube and dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^1H NMR revealing a NMR yield of >99% (**2**) and 93% (**3**). Afterwards all volatiles were removed on a rotary evaporator. To the residue was added toluene and the mixture was heated at reflux until the residue dissolved. The mixture was filtered through a filter paper into a flask. The flask was stored overnight in the fridge to yield colorless crystals. The colorless crystals were collected by filtration and washed with small amounts of cold toluene. After drying bisphenol A was obtained in 92% isolated yield (2.82 g, 12.4 mmol).

Procedure for the depolymerization of poly(bisphenol A carbonate) starting from DVD (conventional heating):

A mixture of poly(bisphenol A carbonate) (**1b**) (obtained from DVD vide supra) (1.72 g, 6.75 mmol based on the repeating unit), and catalytic amounts of 4-dimethylaminopyridine (42.5 mg, 0.338 mmol, 5.01 mol%) were placed with a stir bar in a three-neck flask (100 mL). THF (10 g, 138.9 mmol) was added. A condenser was attached and the mixture was heated at reflux (80 °C) until the poly(bisphenol A carbonate) (**1b**) was dissolved and a clear solution occurred. Methanol (10 g, 312 mmol, 46.2 equiv.) was slowly added via a syringe using a syringe pump (overall dosage time: 120 min). During the addition no poly(bisphenol A carbonate) (**1b**) precipitated from the solution. Heating was continued for 22 hours. After cooling to room temperature an aliquot was transferred to a NMR tube and $CDCl_3$ was added. A ^1H NMR revealed a yield of 77% for **2** and 67% for **3**.

Procedure for the phenolysis of poly(bisphenol A carbonate) derived from DVD:

A mixture of poly(bisphenol A carbonate) (**1b**) (344 mg, 1.35 mmol based on the repeating unit), phenol (2.93 g, 31.1 mmol, 23.1 equiv.), THF (2 g) and catalytic amounts of 4-dimethylaminopyridine (8.50 mg, 69.6 µmol, 5.11 mol%) were placed with a stir bar in a vial. The vial was sealed and subjected to microwave irradiation. The reaction was performed for 10 minutes (hold time) at 180 °C and with a stirring rate of 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible) and a pressure of up to 5 bar was created. Afterwards the vial was cooled to room temperature. An aliquot was added to a NMR tube and dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^1H NMR revealing a NMR yield of 77% (**2**). The reaction mixture was transferred to a flask (50 mL) and all volatiles (THF) were removed in vacuum/rotavap. The mixture was subjected to column chromatography using petroleum ether and ethyl acetate as eluent (100:0 → 0:100). Diphenyl carbonate **4** was isolated in 59% (172 mg, 802 µmol) and bisphenol A was isolated in 56% yield (173 mg, 758 µmol) (the NMR spectra are in accordance to earlier measurements (vide supra)).

Figure S7. Spectrum of the reaction mixture of the phenolysis (^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)).

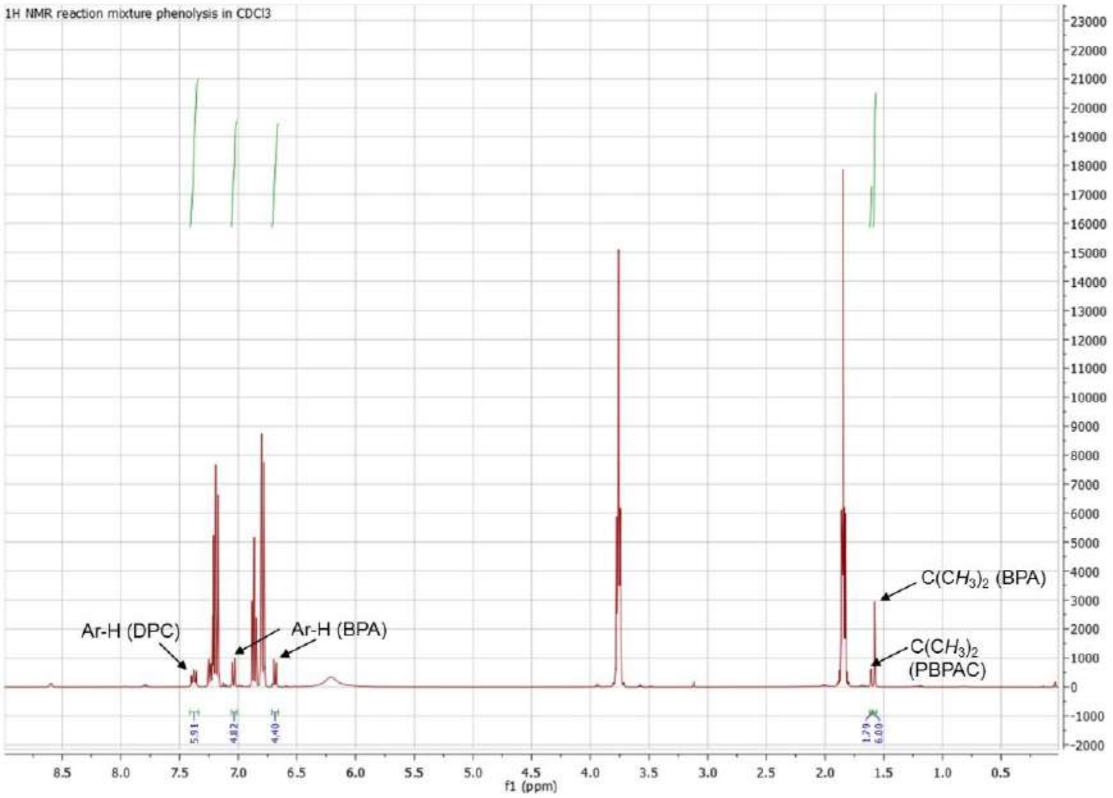
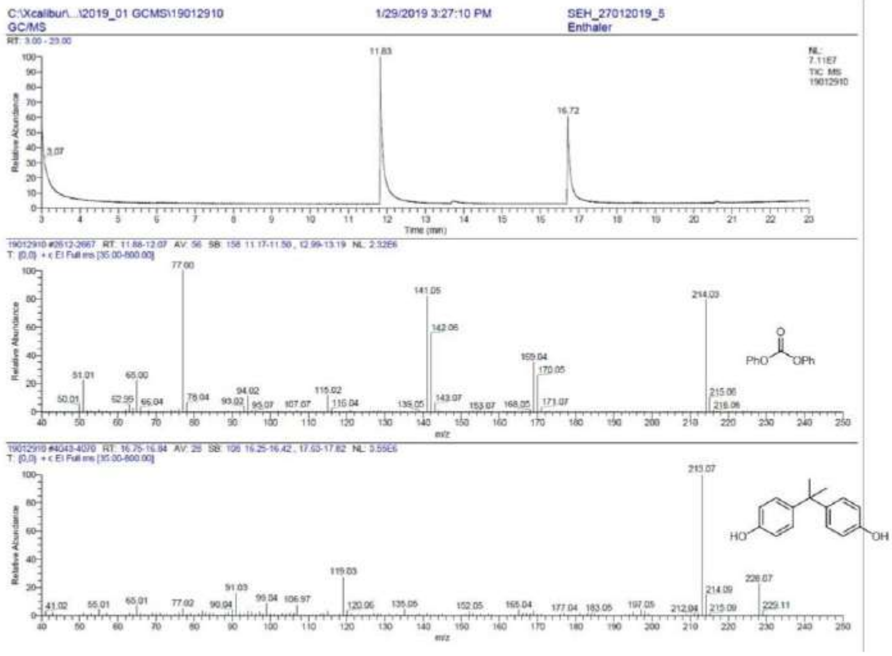


Figure S8. GC-MS spectrum of the depolymerization reaction mixture applying phenol.



Diphenyl carbonate (**3**): ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): δ = 7.32-7.36 (m, 4H), 7.18-7.22 (m, 6H) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, 25 °C): δ = 152.0, 151.0, 129.6, 126.3, 120.9 ppm.

Figure S9. Spectrum of diphenyl carbonate **4** (^{1}H NMR (400 MHz, CDCl$_3$, 25 °C)).

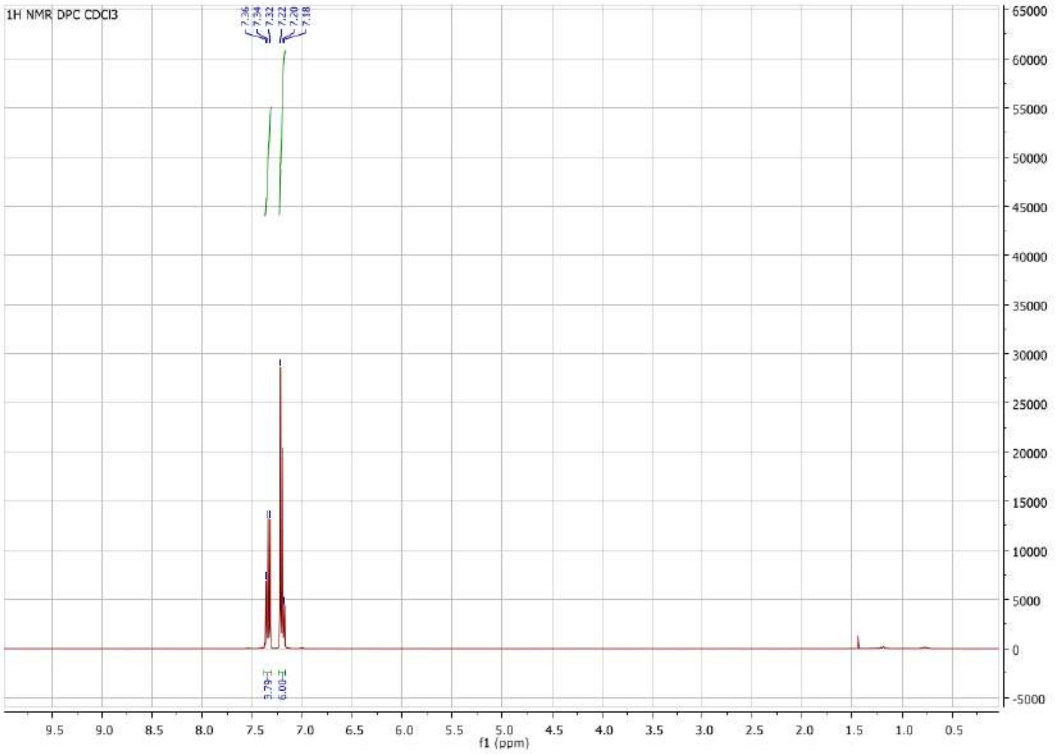
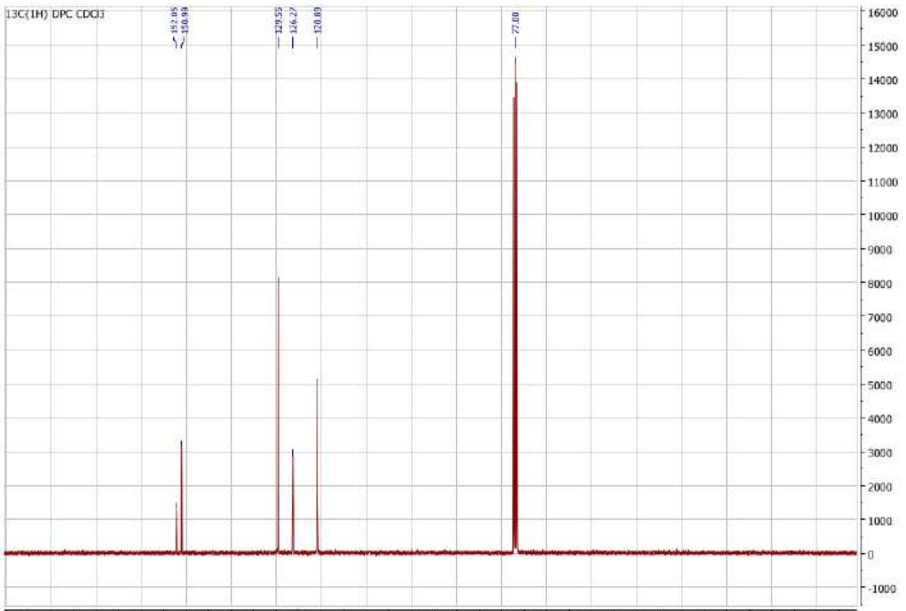


Figure S10. Spectrum of diphenyl carbonate **4** (^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, 25 °C)).



Phenol[3]: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.26-7.30 (m, 2H, *m*-H), 6.96-7.00 (m, 1H), 6.86-6.90 (m, 2H), 5.05 (s, 1H, O*H*) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C): δ = 155.3, 129.7, 120.8, 115.3 ppm.

Figure S11. Spectrum of phenol (^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)).

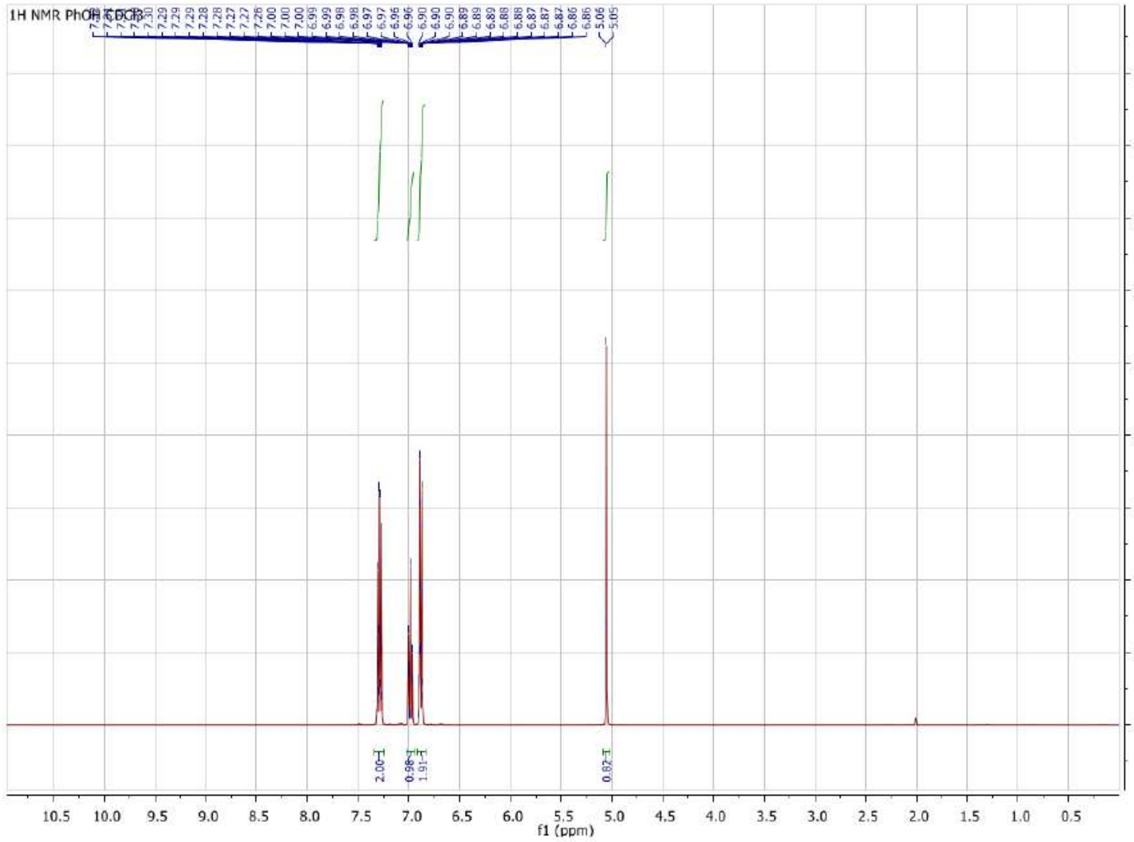
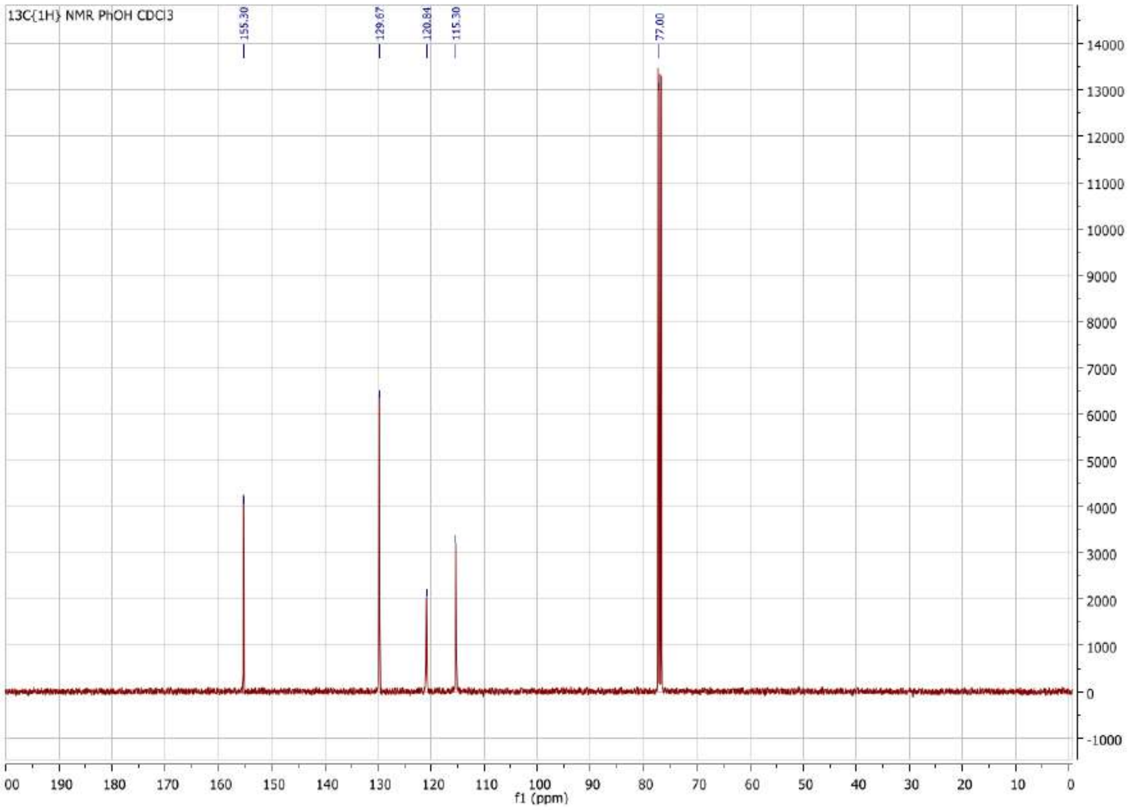


Figure S12. Spectrum of phenol ($^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C)).



Procedure for the phenolysis of poly(bisphenol A carbonate) derived from DVD and subsequent polymerization:

A mixture of poly(bisphenol A carbonate) (**1b**) (344 mg, 1.35 mmol based on the repeating unit), phenol (2.93 g, 31.2 mmol, 23.1 equiv.), THF (2 g) and catalytic amounts of 4-dimethylaminopyridine (8.50 mg, 69.6 µmol, 5.11 mol%) were placed with a stir bar was placed in a vial. The vial was sealed and subjected to microwave irradiation. The reaction was performed for 10 minutes (hold time) at 180 °C and with a stirring rate of 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible) and a pressure of up to 5 bar was created. Afterwards the vial was cooled to room temperature. An aliquot was added to a NMR tube and dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^1H NMR revealing a NMR yield of 77% (**2**). The reaction mixture was transferred to a flask (50 mL) and all volatiles (THF) were removed in vacuum/rotavap. The flask with the residue was attached to a distillation system and a vacuum of 1.1 mbar and a temperature of 70 °C for 1 hour, 80 °C for 1 hour, 90 °C for hour, 100 °C for 1 hour, 140 °C for 1 hour were adjusted. The phenol is distilled off and was collected as colorless crystals. The residue in the reaction flask was washed several times with acetone and was dried in vacuum to give poly(bisphenol A carbonate) as a colorless solid in 44% yield **1c** (152 mg, 0.59 mmol).

Figure S13. poly(bisphenol A carbonate) **1c**.

Figure S14. Spectrum of **1c** (^{1}H NMR (400 MHz, THF-d8, 25 °C)).

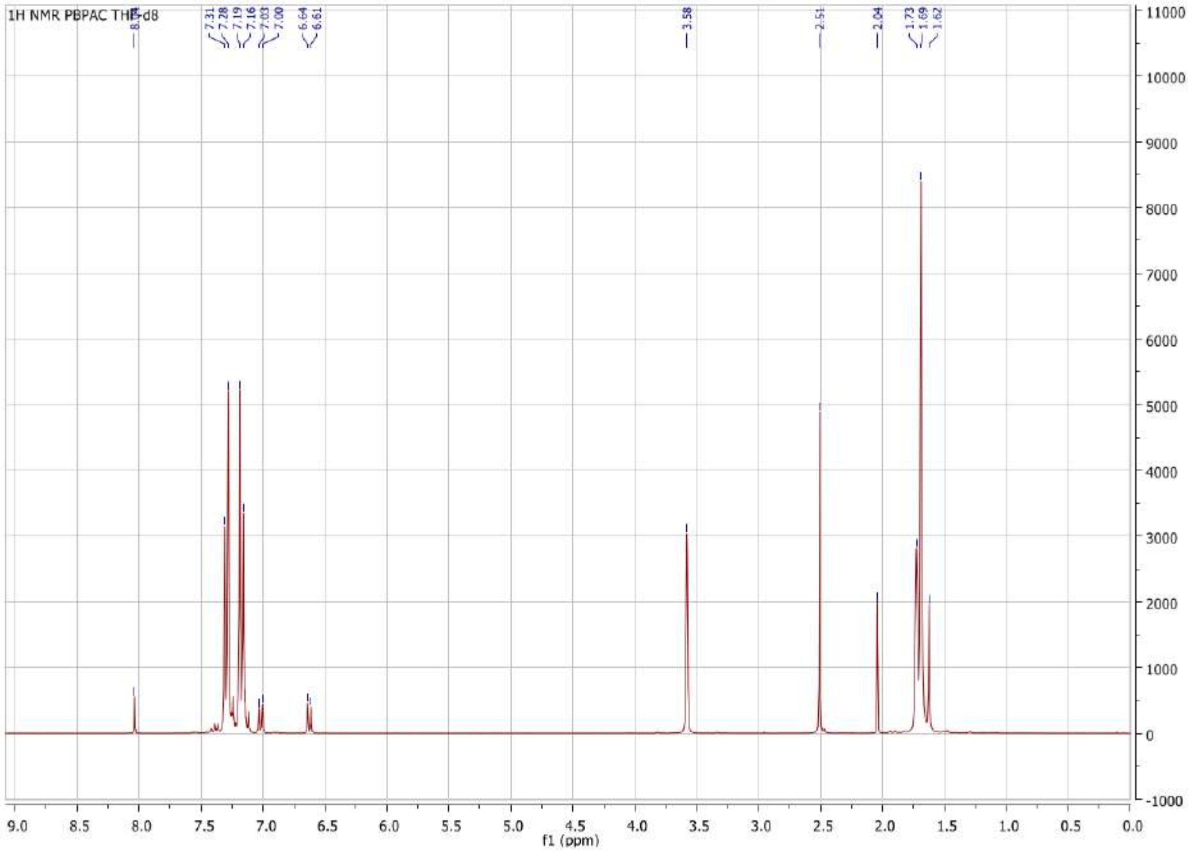
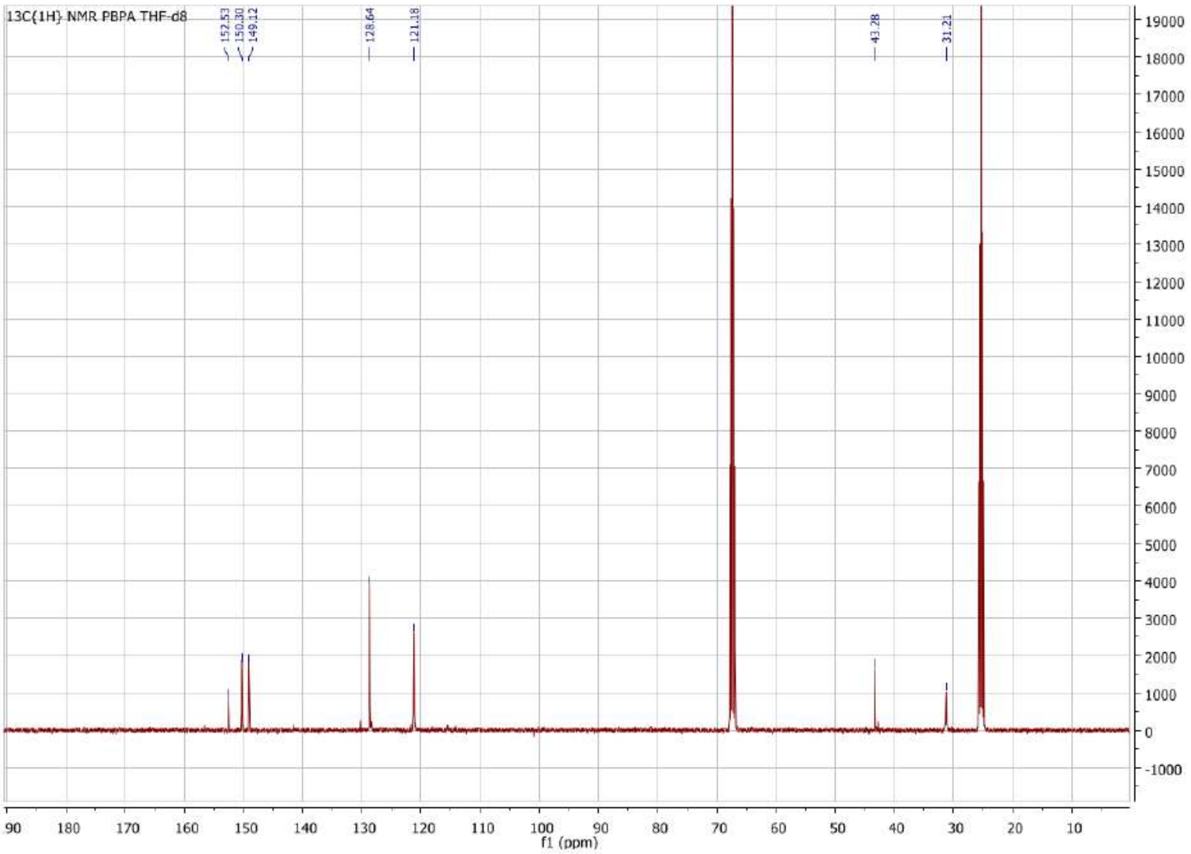


Figure S15. Spectrum of **1c** ($^{13}C\{^1H\}$ NMR (125 MHz, THF-d8, 25 °C)).



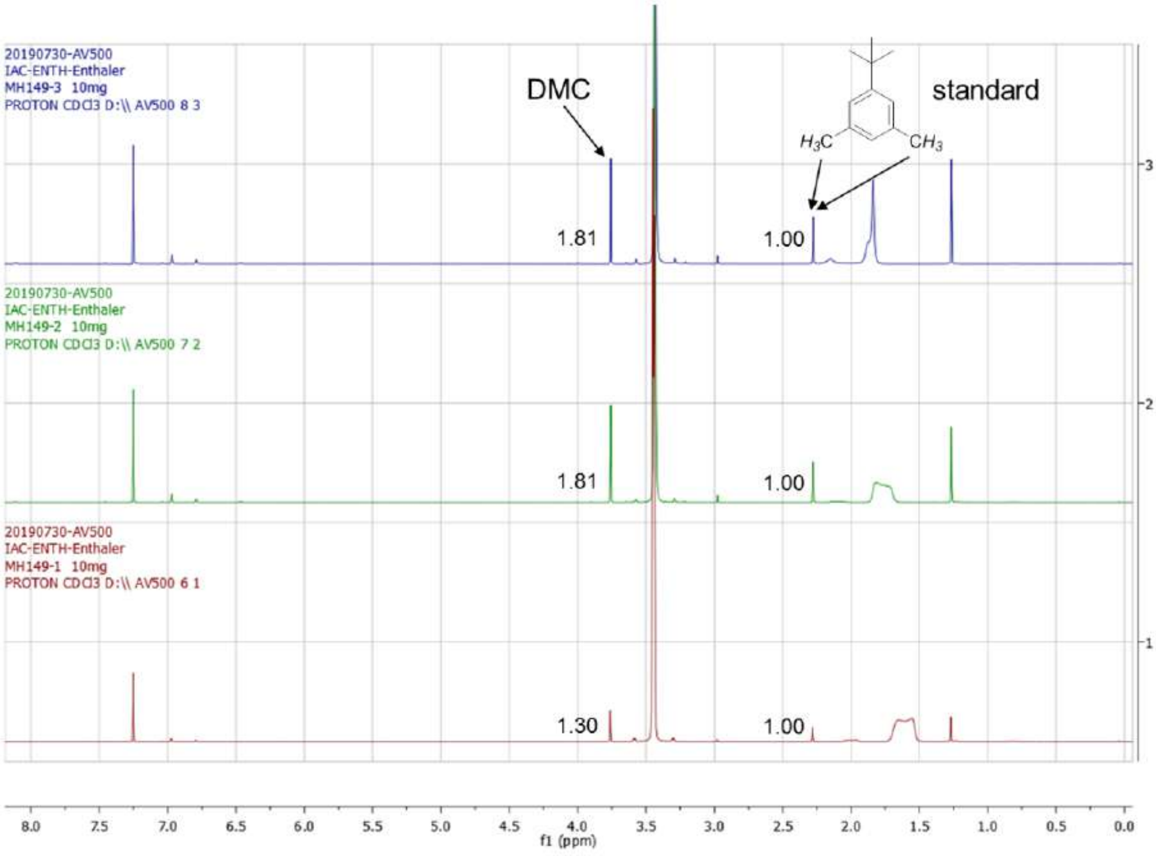
GPC analysis of a THF of **1c** (calibration curve based on narrow polydispersity polystyrene standards): Mn~3289 g/mol, Mw~7319 g/mol, polydispersity 2.23

Procedure for the decomposition of dimethyl carbonate:

A mixture of dimethyl carbonate (**3**) (122 mg, 1.35 mmol), methanol (1.95 g, 62.4 mmol, 46.2 equiv.), 3,5-dimethyl-1-*tert*-butylbenzene (as standard, 100 mg, 0.62 mmol) and catalytic amounts of 4-dimethylaminopyridine (1.70 mg, 139 µmol, 1.0 mol%) were placed with a stir bar in a vial. A aliquot of the solution was added to a NMR tube and a ^{1}H NMR was measured, revealing a **3**:3,5-dimethyl-1-*tert*-butylbenzene ratio of 1.81:1.0. The vial was sealed and subjected to microwave irradiation. The reaction was performed for 10 minutes (hold time) at 160 °C with a stirring rate of 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible) and a pressure of up to 25 bar was created. Afterwards the vial was cooled to room temperature. An aliquot was added to a NMR tube and dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^{1}H NMR revealing a NMR

3:3,5-dimethyl-1-*tert*-butylbenzene ratio of 1.81:1.0. To the reaction mixture water was added (49 mg, 2.70 mmol). The vial was sealed and subjected to microwave irradiation. The reaction was performed for 10 minutes (hold time) at 160 °C with a stirring rate of 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible) and a pressure of up to 25 bar was created. Afterwards the vial was cooled to room temperature. An aliquot was added to a NMR tube and dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^1H NMR revealing a NMR **3**:3,5-dimethyl-1-*tert*-butylbenzene ratio of 1.30:1.0.

Figure S16. Spectrum of the reaction mixture of dimethyl carbonate decomposition (^1H NMR (125 MHz, $CDCl_3$, 25 °C)).



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[1] Kiran, S., James, N. R., Joseph, R., Jayakrishnan, A.: Synthesis and characterization of iodinated polyurethane with inherent radiopacity. Biomaterials **30**, 5552–5559 (2009)

[2] Campion, C. L., Li, W., Lucht, B. L.: Thermal Decomposition of $LiPF_6$-Based Electrolytes for Lithium-Ion Batteries. J. Electrochem. Soc. **152**, A2327–A2334 (2005)

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[3] Abraham, R. J., Reid, M.: ^{1}H chemical shifts in NMR. Part 18. Ring currents and -electron effects in hetero-aromatics. J. Chem. Soc., Perkin Trans. 2 1081–1091 (2002)

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Supporting Information

Depolymerization of End-of-Life Poly(bisphenol A carbonate) via Alkali-Metal-Halide-Catalyzed Methanolysis

Christoph Alberti and Stephan Enthaler*This manuscript is part of a special issue on Earth-Abundant Metals in Catalysis. .

General: All chemicals were used as received without further manipulations. ^{1}H and ^{13}C{^{1}H}NMR spectra were recorded on a *Fourier 300 MHz* (^{1}H: 300 MHz, ^{13}C: 75 MHz) or *Avance I-400* (^{1}H: 400 MHz, ^{13}C: 101 MHz) by Bruker, using the proton signals of the deuterated solvents as reference or external standards. Mass spectrometry was performed using a *Thermo ISQ LT EI* by Thermo Fisher Scientific. TLC was performed on *ALUGRAM XTRA SIL G/UV$_{254}$* cards from *Macherey-Nagel* GmbH & Co. KG with a thickness of 0.20 mm. Detection succeeded with UV-light (254 nm). For preparative column chromatography silica gel 60 (particle size 40 – 63 µm) from *Fluka* was used. For microwave heating experiments a Microwave Synthesis Reactor Monowave 400 (Anton Parr GmbH) was used. GC-MS was measured with Agilent Technologies 5977B GC/MSD.

General procedure for the depolymerization of poly(bisphenol A carbonate) 1a (optimization of reaction conditions): A mixture of commercially available poly(bisphenol A carbonate) (**1a**) (344 mg, 1.35 mmol based on the repeating unit, obtained from Sigma Aldrich), methanol (0.125-2.00 g, 3.90-62.4 mmol, 11.6-46.3 equiv. based on the repeating unit of **1a**) and catalytic amounts of potassium fluoride (0-10 mol%, 0-0.135 mmol based on the repeating unit of **1a**) were placed with a stir bar in a vial. In some cases THF was added as solvent (1.5 g). The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 5-60 minutes (hold time) at 120-180 °C and stirring with 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible) and a pressure of up to 25 bar was created. Afterwards the vial was cooled to room temperature. An aliquot of the clear solution was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.6 mL). The sample was subjected to ^{1}H NMR to determine the yield and the ratio of bisphenol A (**2**) and dimethyl carbonate (**3**). [The yield of **2** was calculated on the basis of the Ar-H or $C(CH_3)_2$ and the Ar-H or $C(CH_3)_2$ leftover signals of the polymer/oligomer. The yield of **3** was calculated on the ratio of the Ar-H of **2** to $(CH_3O)_2C{=}O$.]

Bisphenol A (**2**):[1] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.03-7.07 (m, 4H, Ar-*H*), 6.68-6.71 (m, 4H, Ar-*H*), 1.60 (s, 6H, $(CH_3)_2C$-) ppm. (The signal for 2xOH was not observed).

Dimethyl carbonate (**3**):[2] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.75 (s, 6H, $(CH_3O)_2C{=}O$) ppm.

Figure S1. a) Microwave Synthesis Reactor Monowave 400 (Anton Parr GmbH); b) reaction mixture before microwave heating; c) reaction mixture after microwave heating.

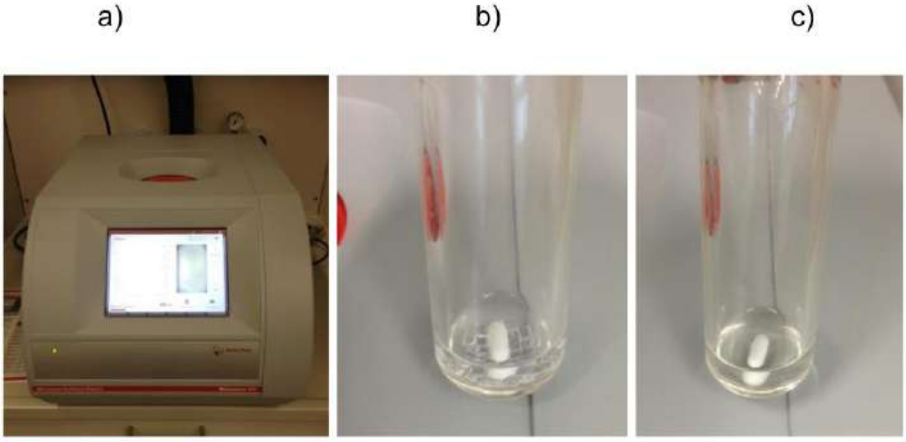
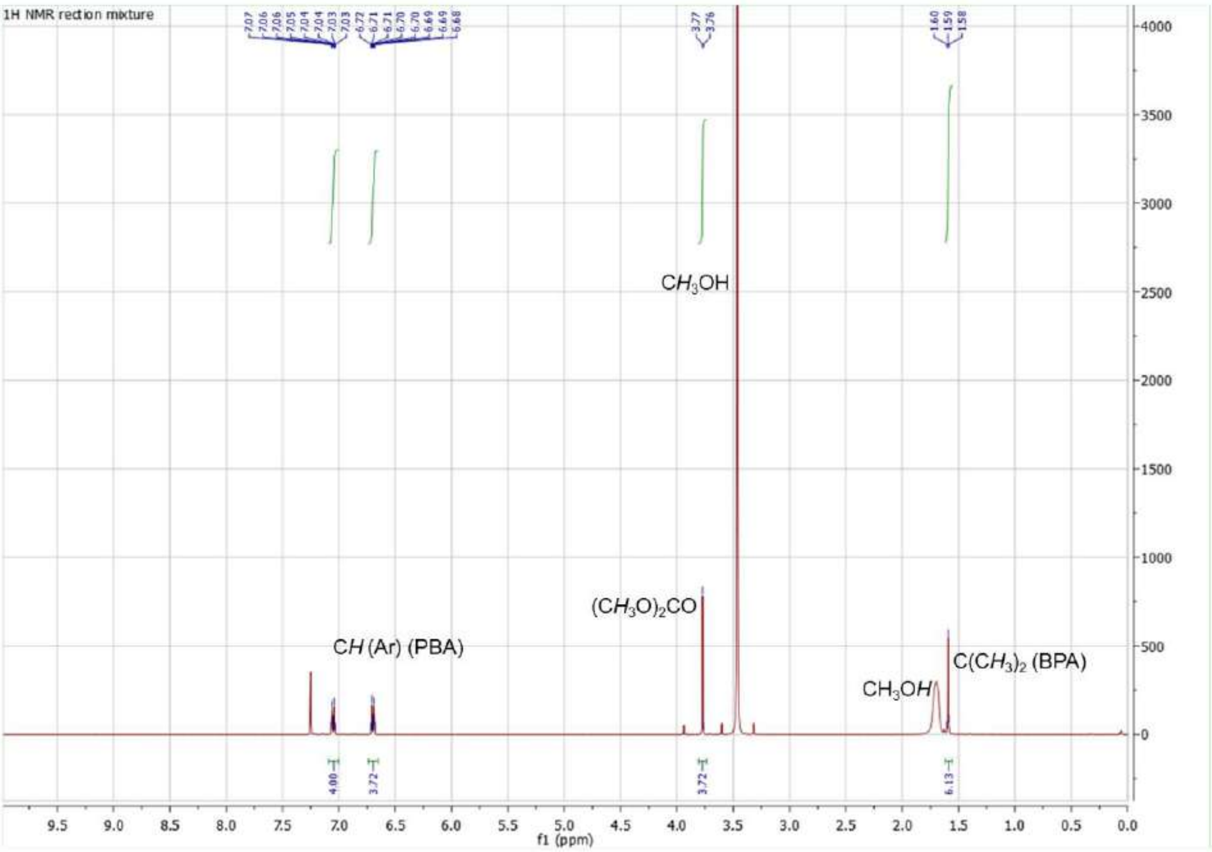


Figure S2. Spectrum of a reaction mixture (10 mol% KF, 46.3 equiv. MeOH, 180 °C, 10 min) (^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)).



Procedure for the depolymerization of poly(bisphenol A carbonate) 1a: A mixture of commercially available poly(bisphenol A carbonate) (**1a**) (1.032 g, 4.05 mmol based on the repeating unit, obtained from Sigma Aldrich), methanol (3 g, 93.6 mmol, 23.1 equiv.) and catalytic amounts of potassium fluoride (2.4 mg, 0.0405 mmol, 1.0 mol%) were placed with a stir bar in a vial. The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 5 minutes (hold time) at 180 °C and stirring with 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible) and a pressure of up to 25 bar was created. Afterwards the vial was cooled to room temperature. An aliquot was added to a NMR tube and was dissolved in $CDCl_3$ (0.6mL). The sample was subjected to ^1H NMR revealing a NMR yield of 98% (**2**) and 72% (**3**). The sample was transferred to a 10 mL flask containing a stir bar and was attached to distillation equipment. The mixture was stirred at room temperature and receiving flask was cooled with liquid nitrogen. Methanol and dimethyl carbonate were distilled off under vacuum. ^1H NMR measurements revealed the presence of methanol and dimethyl carbonate. After the distillation was finished an oily residue was observed in the reaction flask, which solidifies after standing. The residue was dissolved in hot toluene (15 mL) and stored in a fridge overnight. The colorless crystals were collected by filtration and washed with small amounts of cold toluene. After drying bisphenol A was obtained in 79% yield (730 mg, 3.20 mmol).

Bisphenol A (**2**): ^1H NMR (400 MHz, acetone-d_6, 25 °C): $\delta = 8.09$ (s, 2H, -O*H*), 7.03-7.08 (m, 4H, Ar-*H*), 6.72-6.75 (m, 4H, Ar-*H*), 1.59 (s, 6H, $(CH_3)_2C$-) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, acetone-d6, 25 °C): $\delta = 155.8, 142.8, 128.4, 115.4, 42.0, 31.5$ ppm.

Figure S3. Spectrum of **2** (^{1}H NMR (400 MHz, acetone-d_6, 25 °C)).

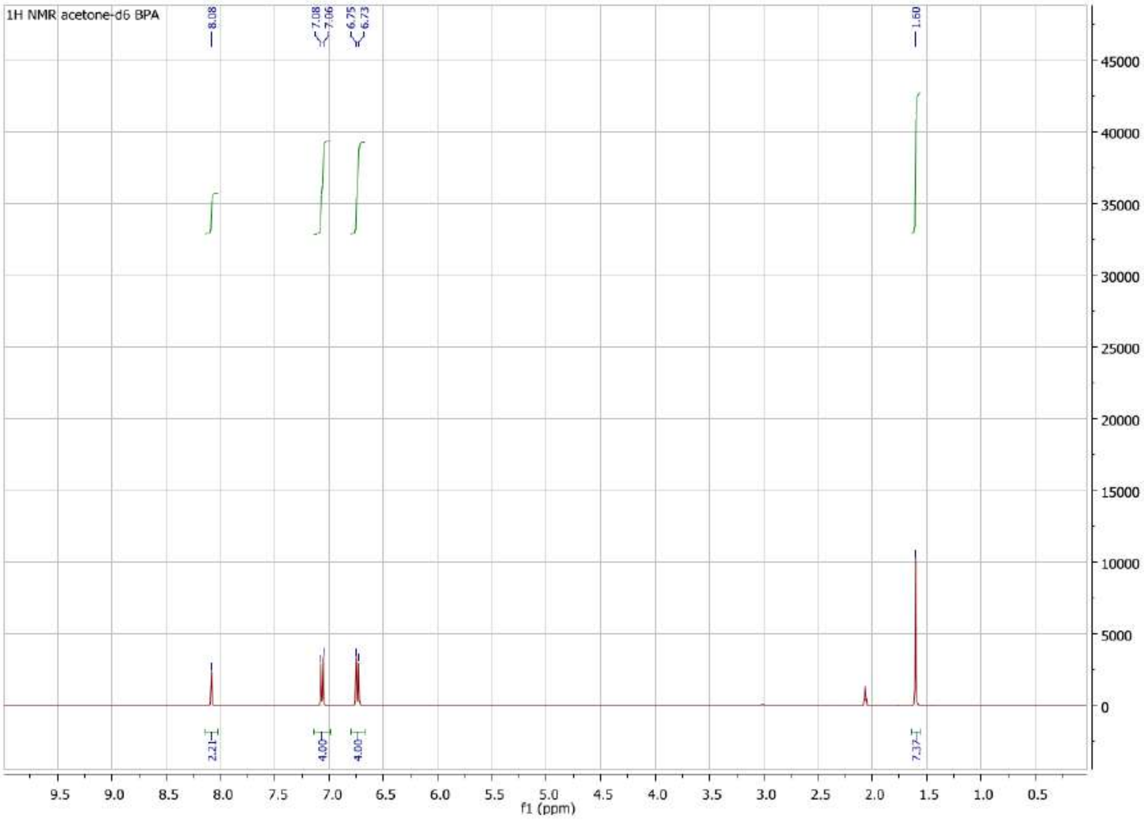


Figure S4. Spectrum of **2** (^{13}C{^{1}H} NMR (125 MHz, acetone-d_6, 25 °C)).

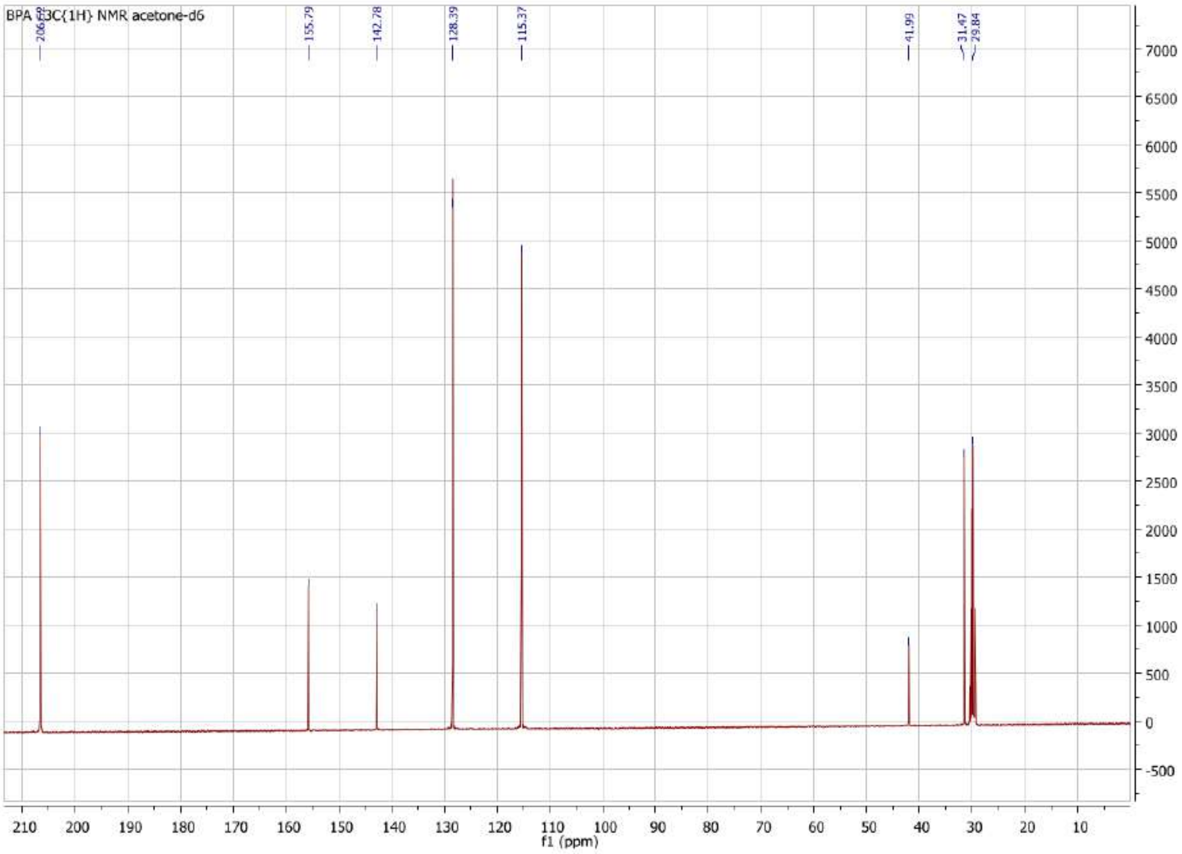
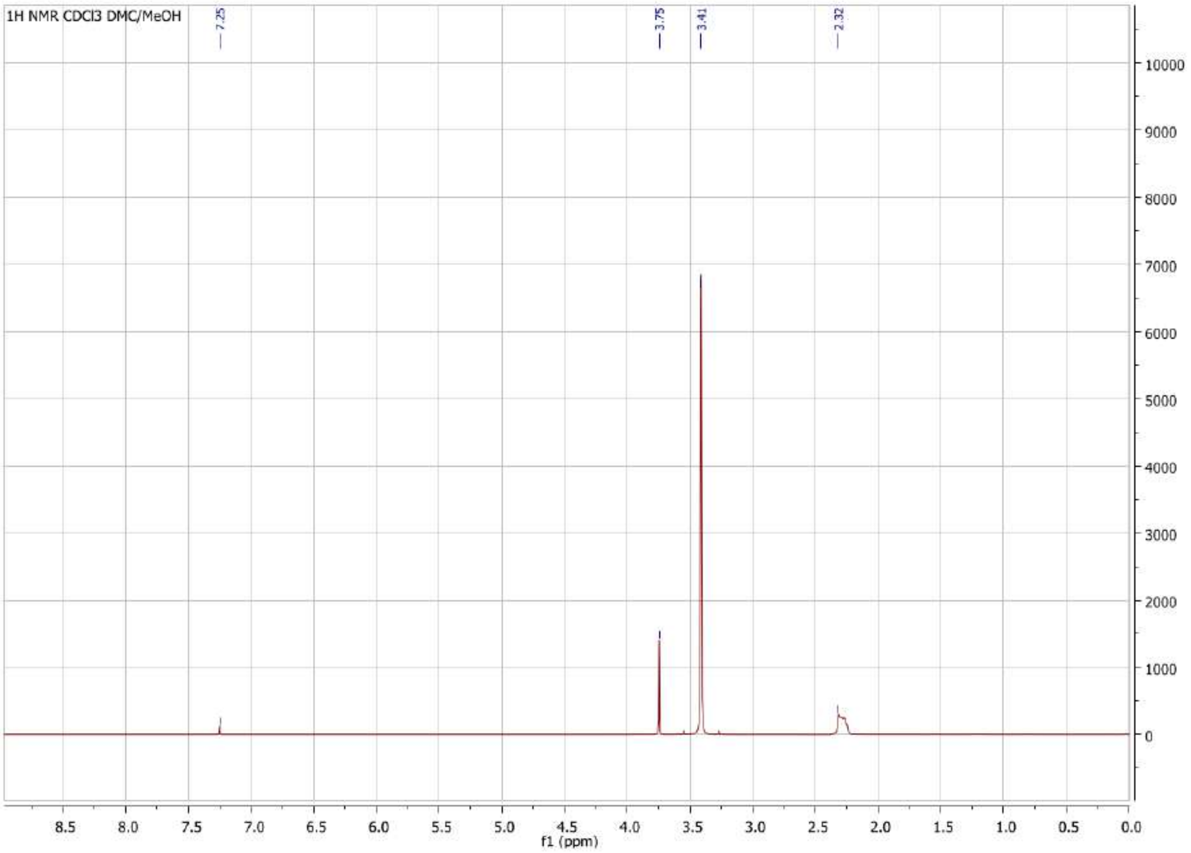


Figure S5. Spectrum of **3** and methanol (^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)).

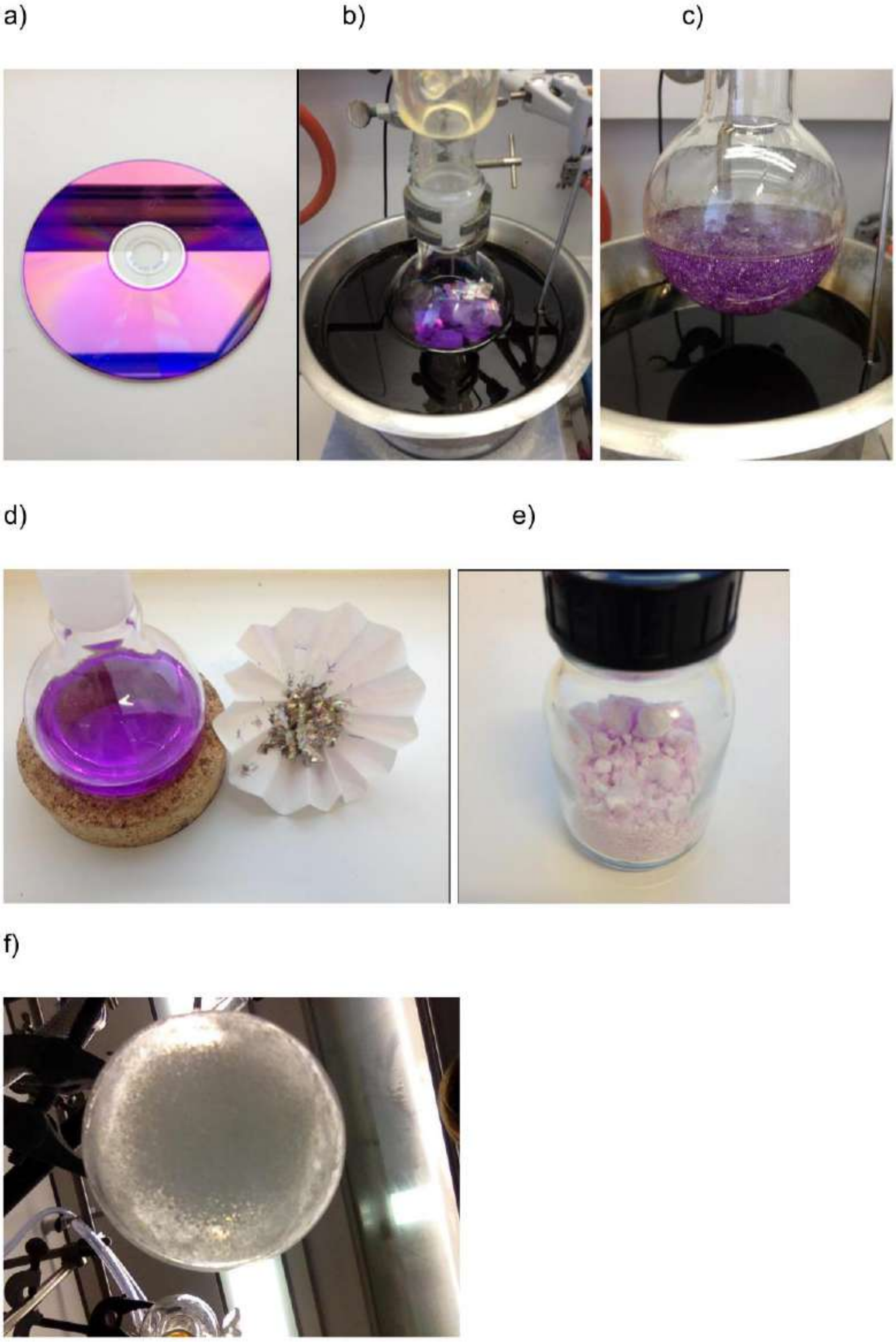


Procedure for the depolymerization of poly(bisphenol A carbonate) starting from DVD:

a) Poly(bisphenol A carbonate) isolation from DVDs

To pieces of a DVD (16.67 g, cut in small pieces) and a stir bar in a 250 mL-flask was added THF (100 mL). A reflux condenser was added and the flask was placed in an oil bath. The mixture was heated under reflux for 30 min. The polycarbonate part of the DVD dissolved, while the aluminum foil and another plastic foil didn´t dissolve. The hot mixture was filtered through a filter paper into a 250 mL flask. The solvent was removed on a rotary evaporator (Note: the collected solvent can be reused for further poly(bisphenol A carbonate) dissolving). The solid residue was added to a frit and was washed with acetone. Afterwards the solid was dried in an oven at 80 °C for 6 hours yielding 13.74 g of poly(bisphenol A carbonate) **1b** (82 wt% based on the starting DVD) (Note: the color of the poly(bisphenol A carbonate) varies depending on the applied starting DVD).

Figure S6. a) applied DVD; b) mixture of DVD pieces and THF; c) mixture after 30 min under reflux; d) components after filtration; e) poly(bisphenol A carbonate) **1b** after washing and drying; f) Crystal of **2** in toluene.



b) Depolymerization of poly(bisphenol A carbonate) **1b** (*option A*)

To pieces of a DVD (400 mg, cut in small pieces) and a stir bar in a 10 mL-flask was added THF (3.56 g). A reflux condenser was added and the flask was placed in an oil bath. The mixture was heated under reflux for 30 min. The polycarbonate part of the DVD dissolved, while the aluminum foil and another plastic foil didn´t dissolve. The hot mixture was filtered through a filter paper into a microwave reactor vial. Potassium fluoride (2.5 wt%, 10 mg, 0.172 mmol), methanol (25 weight equiv., 10 g, 0.31 mol) and a stir bar were added. The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 5 minutes (hold time) at 180 °C and stirring with 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible) and a pressure of up to 25 bar were created. Afterwards the vial was cooled to room temperature. An aliquot was added to a NMR tube and was dissolved in $CDCl_3$ (0.6 mL). The sample was subjected to ^1H NMR revealing a NMR yield of >99% (**2**) and >99% (**3**).

The NMR spectra are in accordance to the spectra presented for depolymerization of commercially available poly(bisphenol A carbonate) **1a** (vide supra).

c) Depolymerization of poly(bisphenol A carbonate) **1b** (*option B*)

A mixture of poly(bisphenol A carbonate) (**1b**) (344 mg, 1.35 mmol based on the repeating unit), methanol (2 g, 62.4 mmol, 46.3 equiv.) and catalytic amounts of potassium fluoride (2.0 mg, 0.0338 mmol, 2.5 mol%) were placed with a stir bar was placed in a vial. The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 5 minutes (hold time) at 180 °C and stirring with 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible) and a pressure of up to 25 bar was created. Afterwards the vial was cooled to room temperature. An aliquot was added to a NMR tube and was dissolved in $CDCl_3$ (0.6 mL). The sample was subjected to ^1H NMR revealing a NMR yield of 99% (**2**) and 79% (**3**). The reaction mixture was transferred to a flask (50 mL) and all volatiles were removed in vacuum. The residue was dissolved in hot toluene (15 mL) and stored in a fridge overnight. The colorless crystals were collected by filtration and washed with small amounts of cold toluene. After drying bisphenol A was obtained in 87% isolated yield (268 mg, 1.17 mmol).

The NMR spectra are in accordance to the spectra presented for depolymerization of commercially available poly(bisphenol A carbonate) **1a** (vide supra).

Procedure for the depolymerization of poly(bisphenol A carbonate) starting from DVD (conventional heating):

A mixture of poly(bisphenol A carbonate) (**1b**) (obtained from DVD vide supra) (3.44 g, 13.5 mmol based on the repeating unit), methanol (10 g, 312 mmol, 23.1 equiv.), THF (20 g, 277.8 mmol) and catalytic amounts of potassium fluoride (20 mg, 0.338 mmol, 2.5 mol%) were placed with a stir bar in a flask (100 mL). A condenser was attached and the mixture was heated under reflux (80 °C) for 48 hours. The clear solution was cooled to room temperature and an aliquot was added to a NMR tube and was dissolved in $CDCl_3$ (0.6 mL). The sample was subjected to ^1H NMR revealing a NMR yield of >99% (**2**) and 67% (**3**). Afterwards all volatiles were removed on a rotary evaporator. To the residue was added toluene and the mixture was heated under reflux until the residue dissolved. The mixture was filtered through a filter paper into a flask. The flask was stored overnight in the fridge to yield colorless crystals. The colorless crystals were collected by filtration and washed with small amounts of cold toluene. After drying bisphenol A was obtained in 86% isolated yield (2.67 g, 1.17 mmol).

Procedure for the depolymerization of poly(bisphenol A carbonate) starting from DVD (conventional heating):

A mixture of poly(bisphenol A carbonate) (**1b**) (obtained from DVD vide supra) (1.72 g, 6.75 mmol based on the repeating unit), and catalytic amounts of potassium fluoride (20 mg, 0.338 mmol, 2.5 mol%) were placed with a stir bar in a three-neck flask (100 mL). THF (10 g, 138.9 mmol) was added. A condenser was attached and the mixture was heated under reflux (80 °C) until the poly(bisphenol A carbonate) (**1b**) was dissolved and a clear solution occurred. Methanol (10 g, 312 mmol, 46.2 equiv.) was slowly added via a syringe using a syringe pump (overall dosage time: 120 min). During the addition no poly(bisphenol A carbonate) (**1b**) precipitated from the solution. Heating was continued for 22 hours. After cooling to room temperature an aliquot was transferred to a NMR tube and $CDCl_3$ was added. A ^1H NMR revealed a yield of 75% for **2** and 58% for **3**.

References

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[2] C. L. Campion, W. Li, B. L. Lucht, *J. Electrochem. Soc.* **2005**, *152*, A2327-A2334.

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Supporting Information

Recycling of End-of-Life Poly(bisphenol A carbonate) via Alkali Metal Halide-Catalyzed Phenolysis

Christoph Alberti, Felix Scheliga, and Stephan Enthaler*

General: All chemicals were used as received without further manipulations. ^{1}H and ^{13}C{^{1}H}NMR spectra were recorded on a *Fourier 300 MHz* (^{1}H: 300 MHz, ^{13}C: 75 MHz) or *Avance I-400* (^{1}H: 400 MHz, ^{13}C: 101 MHz) by Bruker, using the proton signals of the deuterated solvents as reference or external standards. Mass spectrometry was performed using a *Thermo ISQ LT EI* by Thermo Fisher Scientific. TLC was performed on *ALUGRAM XTRA SIL G/UV$_{254}$* cards from *Macherey-Nagel* GmbH & Co. KG with a thickness of 0.20 mm. Detection succeeded with UV-light (254 nm). For preparative column chromatography silica gel 60 (particle size 40 – 63 µm) from *Fluka* was used. For microwave heating experiments a Microwave Synthesis Reactor Monowave 400 (Anton Paar GmbH) was used. GC-MS was measured with Agilent Technologies 5977B GC/MSD. Vacuum distillation was performed with a Kugelrohr distillation apparatus (Büchi Labortechnik AG). Ball milling was performed with a Retsch MM400 ball mill (Retsch GmbH). SEC analysis was performed using a "mixed bed" linear SEC-column (5 µm porous styrene-divinylbenzene particles, separation range 200-1000k g/mol) at a flow rate of 1 ml/min in tetrahydrofuran as eluent. Molecular weights refer to a so called relative calibration based on narrow polystyrene samples supplied by Agilent Technologies. The SEC system was equipped with a Shimadzu LC-10ATvP pump, an AS1000 autosampler from Thermo Separation Products and a RI2012 refractive index detector from Schambeck SFD GmbH.

General procedure for the depolymerization of poly(bisphenol A carbonate) 1a (optimization of reaction conditions): A mixture of commercially available poly(bisphenol A carbonate) (**1a**) (344 mg, 1.35 mmol based on the repeating unit, obtained from Sigma Aldrich), phenol (0.500−6.00 g, 5.31−63.8 mmol, 3.93−47.3 equiv. based on the repeating unit of **1a**), THF (2.00-6.00 g, 27.7-83.4 mmol, 20.5-61.6 equiv. based on the repeating unit of **1a**) and catalytic amounts of alkali metal halides (0.00−8.25 mg, 0.00−0.135mmol, 0−10 mol% based on the repeating unit of **1a**) were placed with a stir bar in a vial. The vial was sealed and subjected to microwave irradiation. The reaction was performed for 5−30 minutes (hold time) at 140−200 °C and with a stirring rate of 600 rpm. The reaction temperature was reached within 1−2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature. An aliquot of the clear solution was transferred to a NMR tube and dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^{1}H NMR to determine the yield and the ratio of bisphenol A (**2**) and diphenyl carbonate (**3**). [The yield of **2** was calculated on the basis of the Ar-H or $C(CH_3)_2$ and the Ar-H or $C(CH_3)_2$ leftover signals of the polymer/oligomer. The yield of **3** was calculated on the ratio of the *o*-H-Ar (4H) of **2** to

$(C_6H_5O)_2C{=}O$. Furthermore, the existence of **2** and **3** were verified by the addition of authentic samples of **2** and **3** to the NMR sample of the reaction mixture]

Figure S1. a) Microwave Synthesis Reactor Monowave 400 (Anton Paar GmbH); b) reaction mixture before microwave heating; c) reaction mixture after microwave heating.

a) b) c)

Figure S2. Spectrum of a reaction mixture (1 mol% KF, 47.3 equiv. PhOH, 180 °C, 15 min) (^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)).

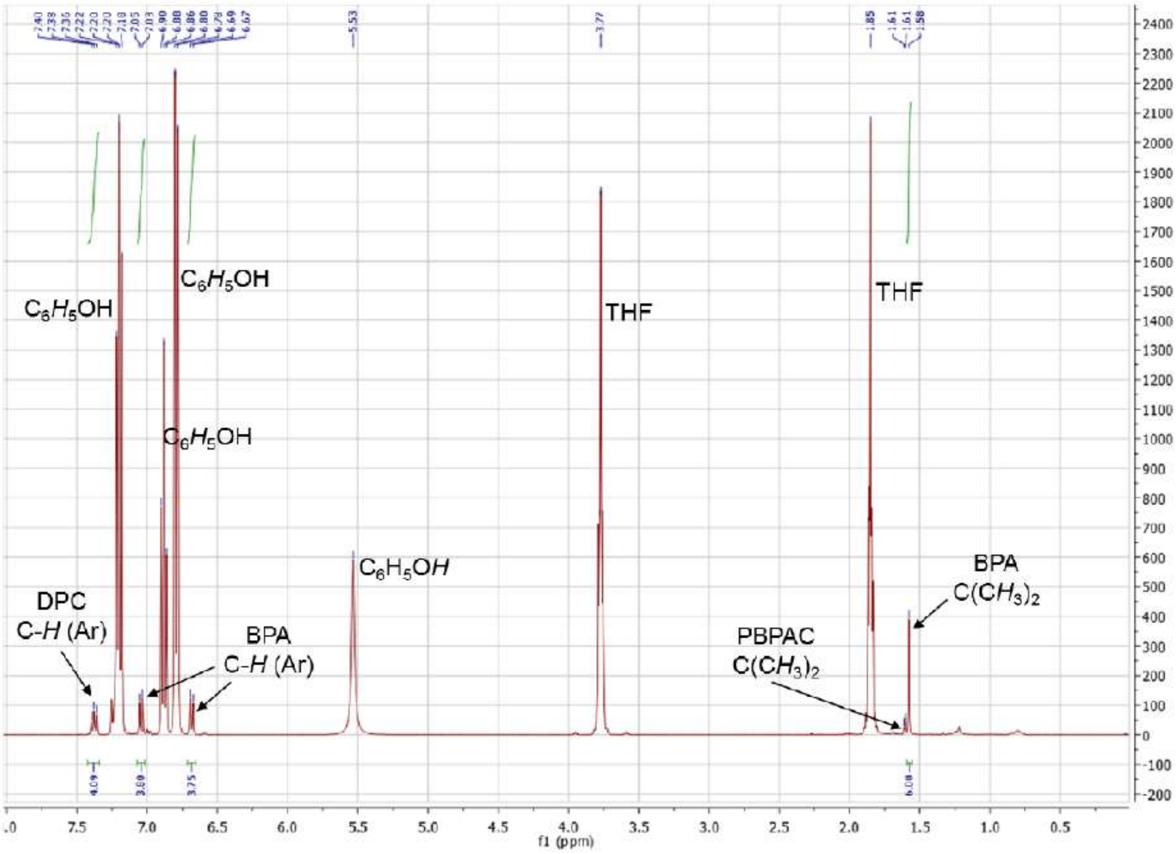
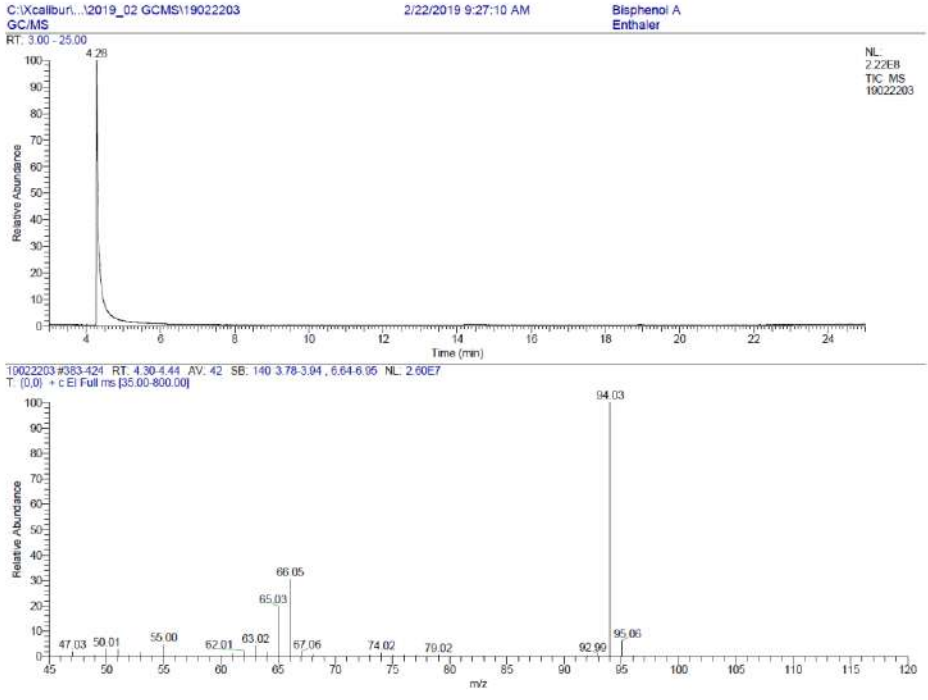
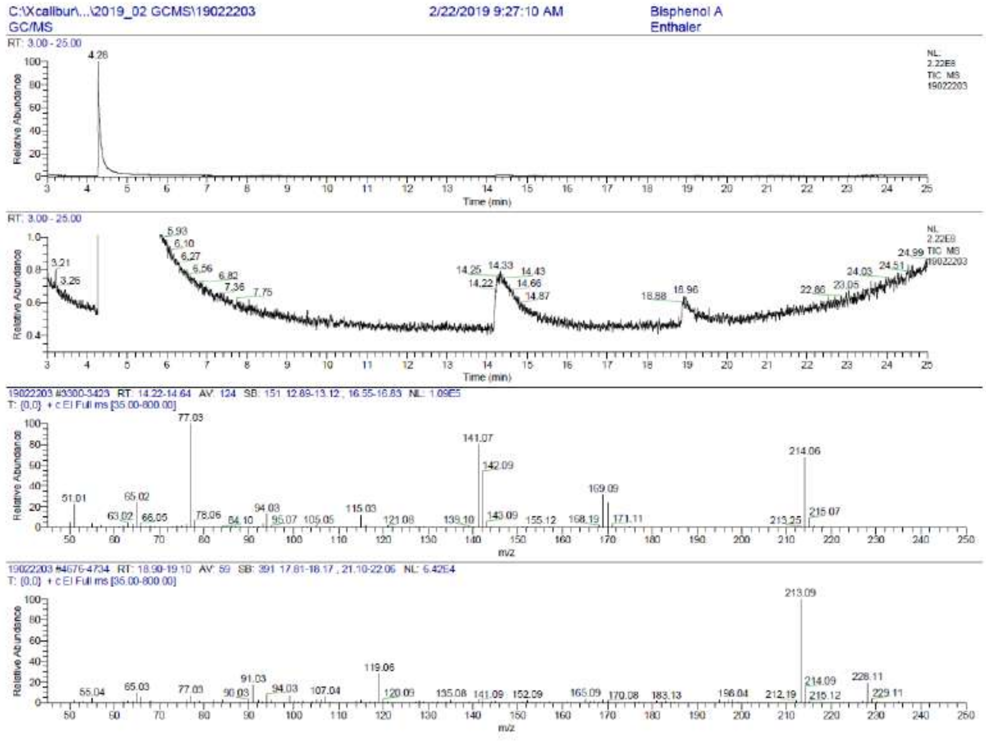


Figure S3. GC-chromatogram of the reaction mixture. Retention time phenol: 4.28 min (MS (EI) m/z = 94.0, 66.1); Retention time (**3**): 14.22-14.64 min (MS (EI) m/z = 214.6, 169.1, 141.07, 77.0); Retention time (**2**): 18.90-19.10 min (MS (EI) m/z = 228.1, 213.1, 119.1).





Procedure for the depolymerization of poly(bisphenol A carbonate) 1a: A mixture of poly(bisphenol A carbonate) (**1a**) (344 mg, 1.35 mmol based on the repeating unit), phenol (6.00 g, 63.8 mmol, 47.3 equiv. based on the repeating unit of **1a**), THF (2.00 g, 27.8 mmol, 20.6 equiv. based on the repeating unit of **1a**) and catalytic amounts of potassium fluoride (4.6 mg, 0.071 mmol, 5 mol%) were placed with a stir bar in a vial. The vial was sealed and subjected to microwave irradiation. The reaction was performed for 15 minutes (hold time) at 180 °C and with a stirring rate of 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible. Afterwards the vial was cooled to room temperature. An aliquot was added to a NMR tube and dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^1H NMR revealing a NMR yield of 86% (**2**) and 86% (**3**). The reaction mixture was transferred to a flask (50 mL) and all volatiles (THF) were removed in vacuum/rotavap. The mixture was subjected to column chromatography using petroleum ether and ethyl acetate as eluent (100:0 → 0:100). Bisphenol A **2** was isolated in 69% yield (212.4 mg, 0.93 mmol) and diphenyl carbonate **3** was isolated in 71% (205.2 mg, 0.96 mmol).

Bisphenol A (**2**)[1]: ^1H NMR (400 MHz, acetone-d_6, 25 °C): δ = 8.04 (s, 2H, O*H*), 7.04−7.06 (m, 4H, Ar-*H*), 6.71−6.73 (m, 4H, Ar-*H*), 1.58 (s, 6H, $(CH_3)_2C$-) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, acetone-d6, 25 °C): δ = 155.8, 142.8, 128.4, 115.4, 42.0, 31.5 ppm.

Diphenyl carbonate (**3**)[2]: ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.32-7.36 (m, 4H), 7.18-7.22 (m, 6H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C): δ = 152.0, 151.0, 129.6, 126.3, 120.9 ppm.

Phenol[3]: ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.25-7.30 (m, 2H, *m*-H), 6.94-7.00 (m, 1H), 6.84-6.89 (m, 2H), 4.75 (s, 1H, O*H*) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C): δ = 155.3, 129.7, 120.8, 115.3 ppm.

Figure S3. Spectrum of bisphenol A **2** (^{1}H NMR (400 MHz, acetone-d_6, 25 °C)).

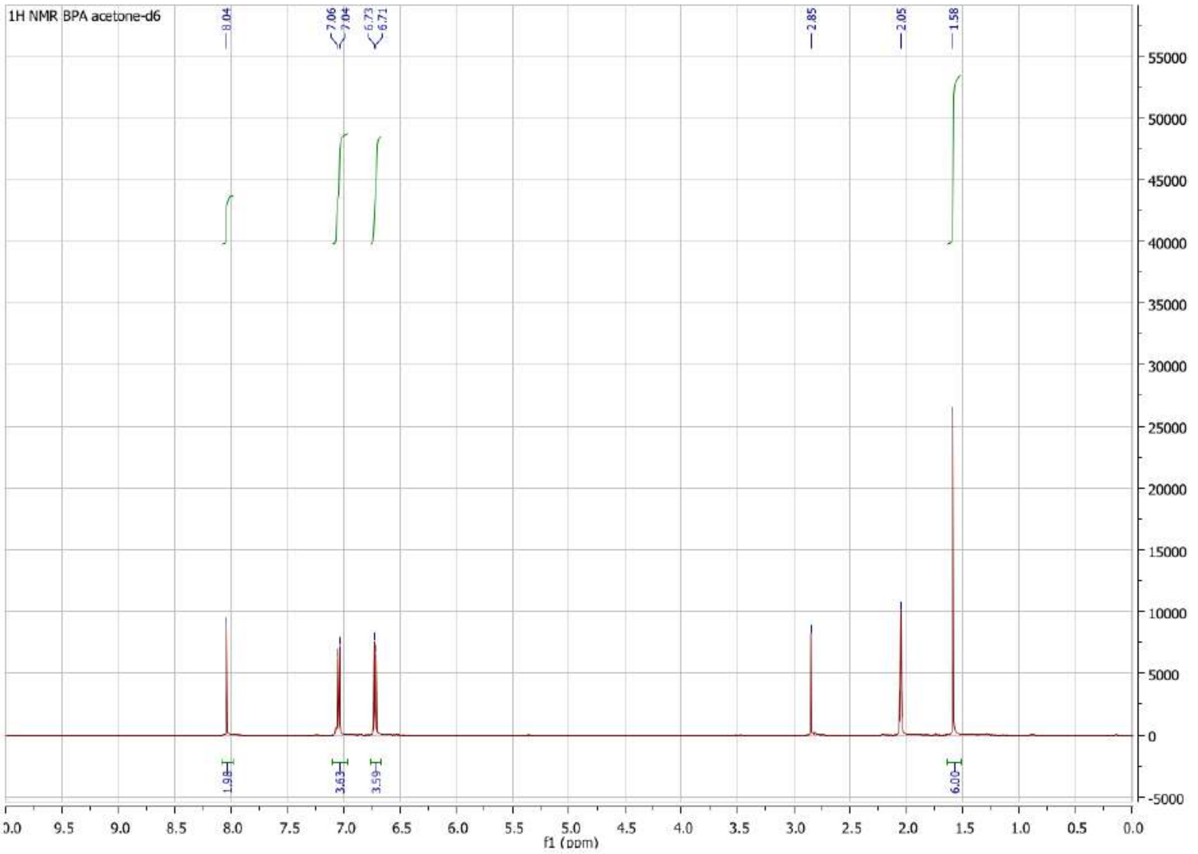


Figure S4. Spectrum of bisphenol A **2** (^{13}C{ ^{1}H} NMR (400 MHz, acetone-d_6, 25 °C)).

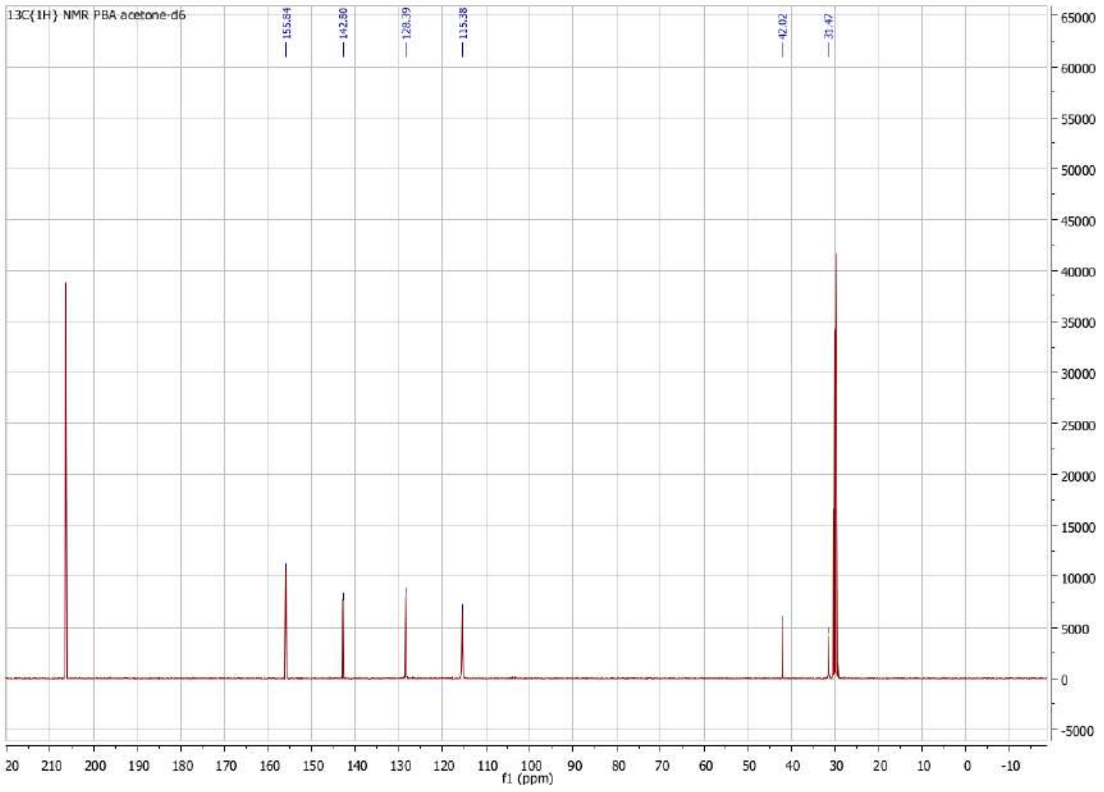


Figure S5. Spectrum of diphenyl carbonate **3** (^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)).

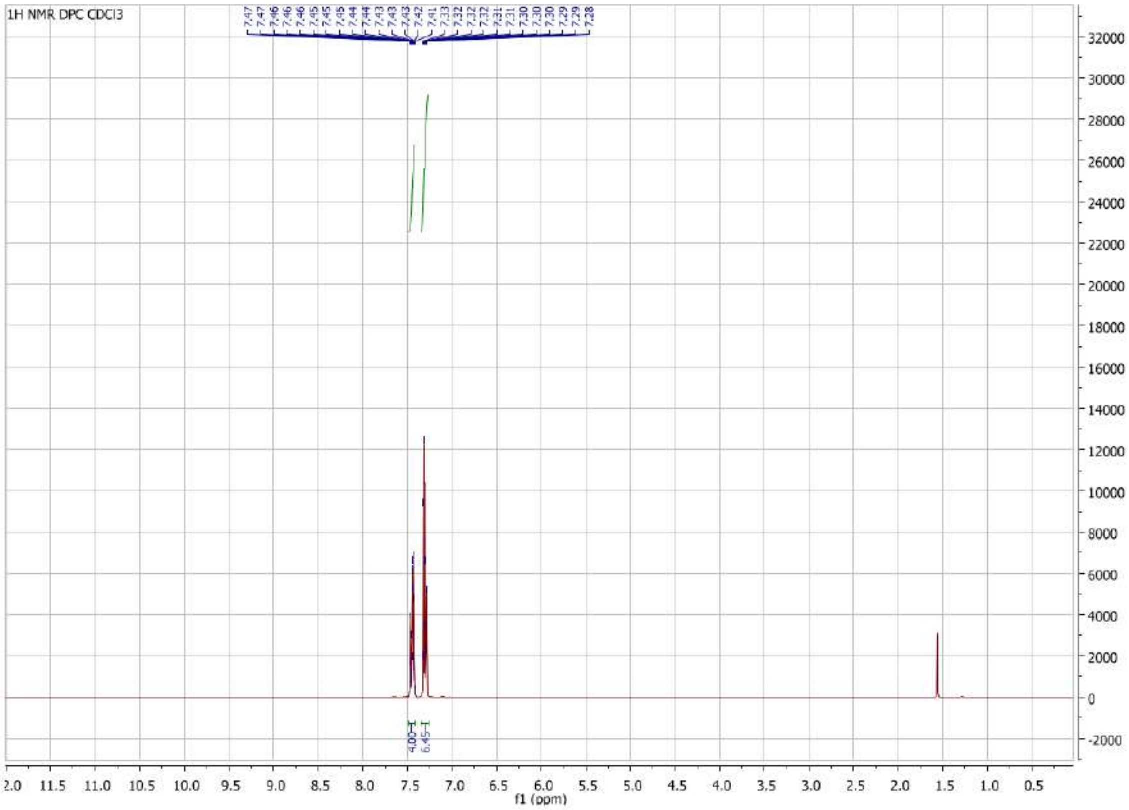


Figure S6. Spectrum of diphenyl carbonate **3** ($^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, 25 °C)).

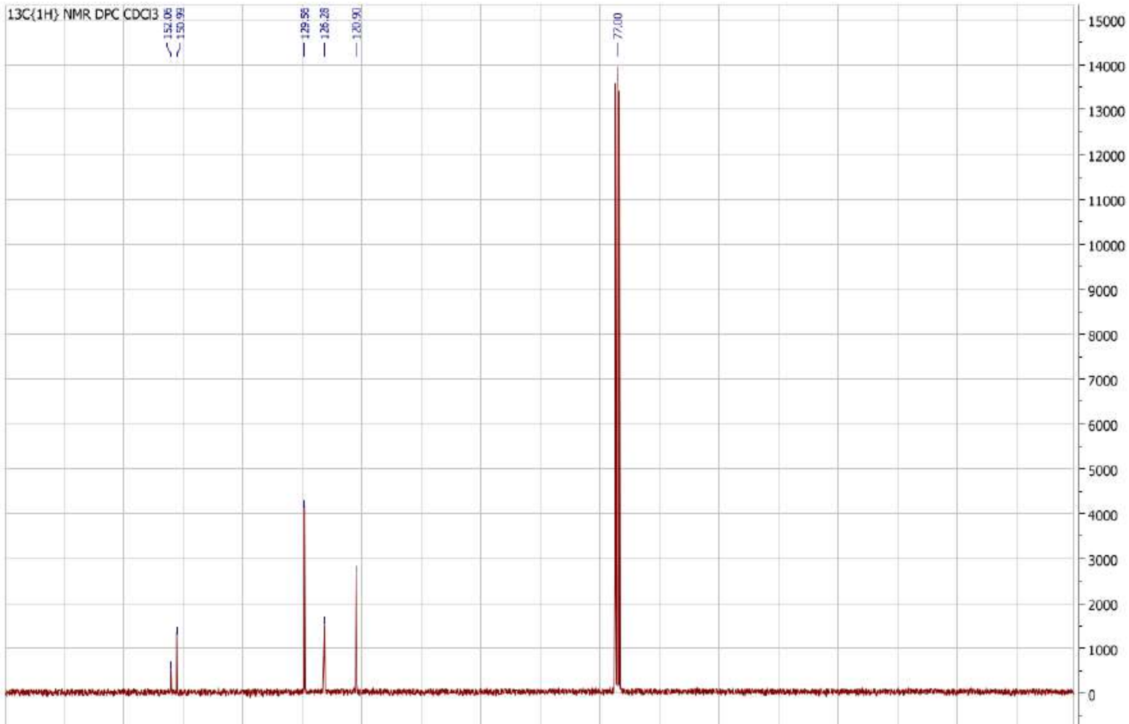


Figure S7. Spectrum of phenol (^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)).

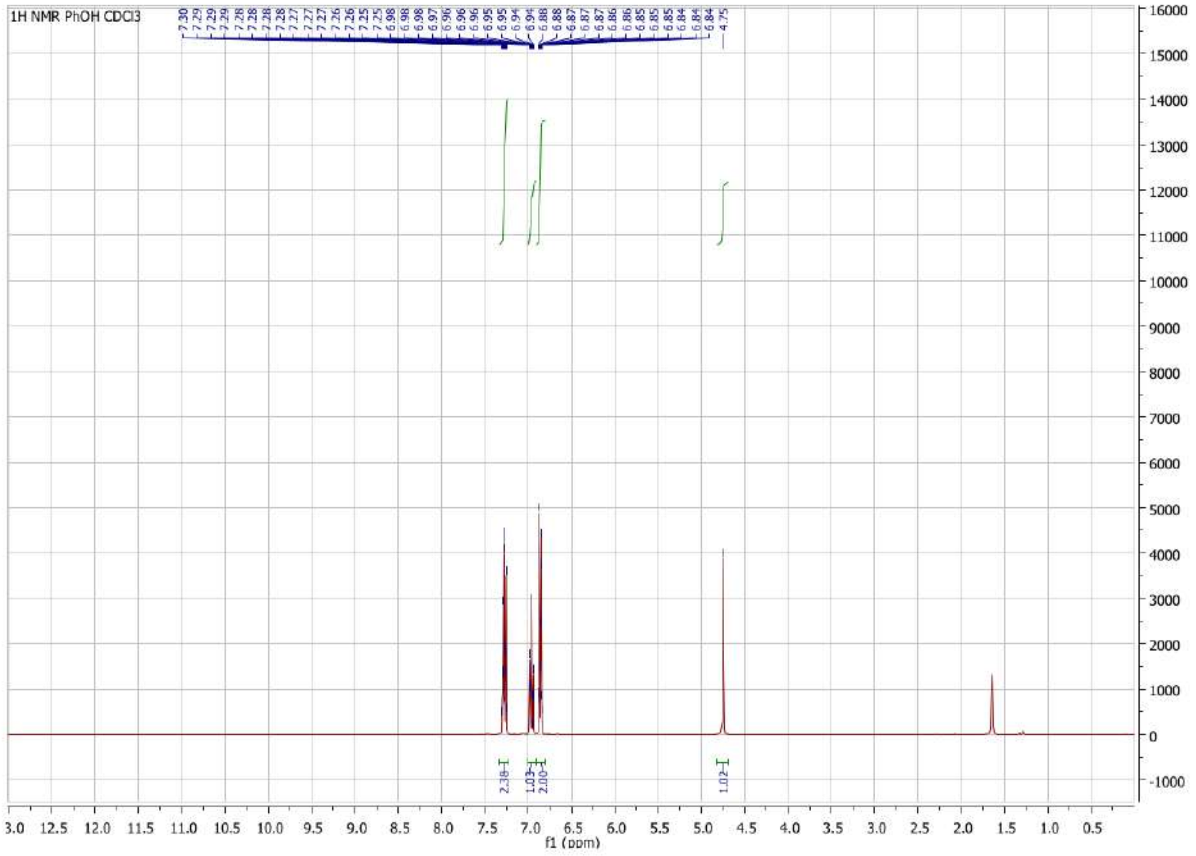
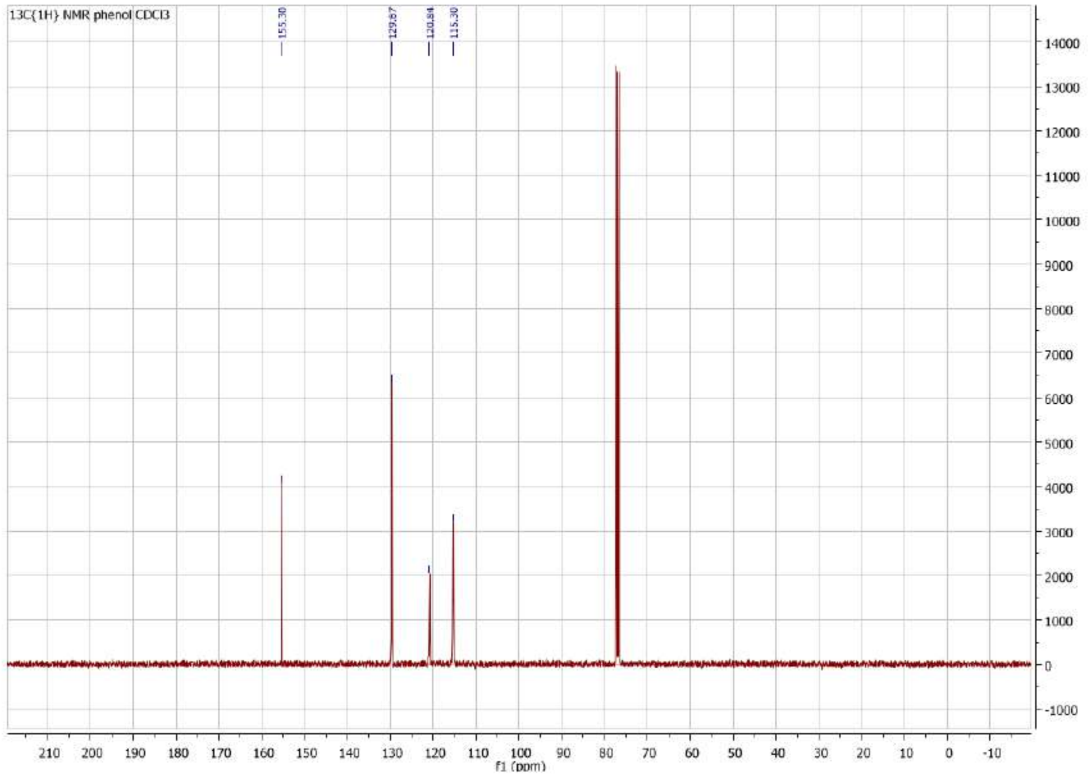


Figure S8. Spectrum of phenol ($^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C)).

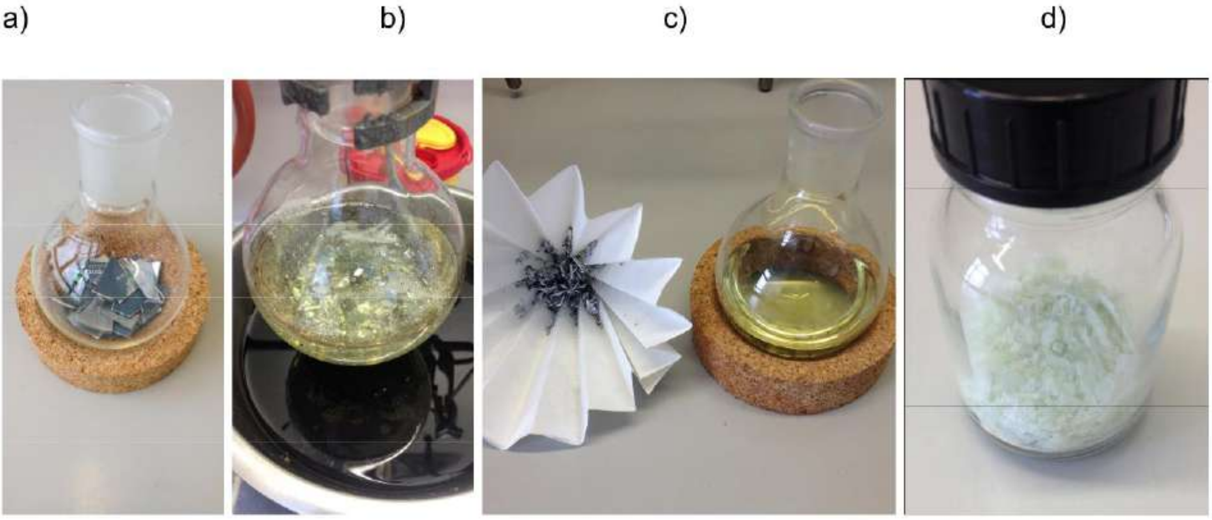


Procedure for the depolymerization of poly(bisphenol A carbonate) starting from DVD:

Pathway A: Poly(bisphenol A carbonate) **1b** isolation from DVDs

a) Poly(bisphenol A carbonate) isolation: To pieces of a DVD (16.7 g, cut in small pieces) and a stir bar in a 250 mL-flask was added THF (100 mL). A reflux condenser was added and the flask was placed in an oil bath. The mixture was heated at reflux for 30 min. The polycarbonate part of the DVD dissolved, while the aluminum foil and another plastic foil didn´t dissolve. The hot mixture was filtered through a filter paper into a 250 mL flask. The solvent was removed on a rotary evaporator (Note: the collected solvent can be reused for further poly(bisphenol A carbonate) dissolving). The solid residue was added to a frit and was washed with acetone. Afterwards the solid was dried in an oven at 80 °C for 6 hours yielding 13.7 g of poly(bisphenol A carbonate) **1b** (82 wt% based on the starting DVD) (Note: the color of the poly(bisphenol A carbonate) varies depending on the applied starting DVD).

Figure S9. a) applied DVD; b) mixture of DVD pieces and THF after mixture after 30 min at reflux; c) components after filtration; d) **1b** after THF removal, washing and drying.



b) Depolymerization of poly(bisphenol A carbonate) ***1b***

A mixture of poly(bisphenol A carbonate) **1b** (344 mg, 1.35 mmol based on the repeating unit), phenol (6.00 g, 63.8 mmol, 47.3 equiv. based on the repeating unit of **1b**) and THF (2.00 g, 27.8 mmol, 20.6 equiv. based on the repeating unit of **1b**) was placed with a stir bar in a flask (10 mL) and a reflux condenser was connected. The mixture was stirred and heated to 180 °C in an oil bath. After holding the mixture for 5 min at 180 °C (oil bath temperature, internal temperature 125-130 °C) catalytic amounts of potassium fluoride (1.60 mg, 0.0275 mmol, 2 mol%) were added to start the depolymerization. The reaction was performed for 30 minutes at 180 °C. Afterwards the vial was cooled to room temperature. An aliquot was added to a NMR tube and dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^1H NMR revealing a NMR yield of 90% (**2**) and 90% (**3**). Afterwards the THF and the phenol were carefully removed by vacuum distillation apparatus (Kugelrohr) in vacuum (50-55 °C, 1.1 mbar). Importantly, at higher temperature polymerization starts to form new poly(bisphenol A carbonate). Same observation was found if the amounts of phenol in the reaction mixture getting low. At a ratio of bisphenol:phenol of 1:~3 the yield of **2** decrease to 85% (Figure S11). Increasing the temperature to 200 °C (1.1 mbar) revealed the formation of poly(bisphenol A carbonate), which was isolated in 54% yield (m = 186 mg) as off-white powder after washing the residue with acetone and drying (Figure S12).

Figure S10. poly(bisphenol A carbonate) **1ba.**

Figure S11. Spectrum of **1b** depolymerization reaction mixture (^1H NMR (400 MHz, $CDCl_3$, 25 °C)).

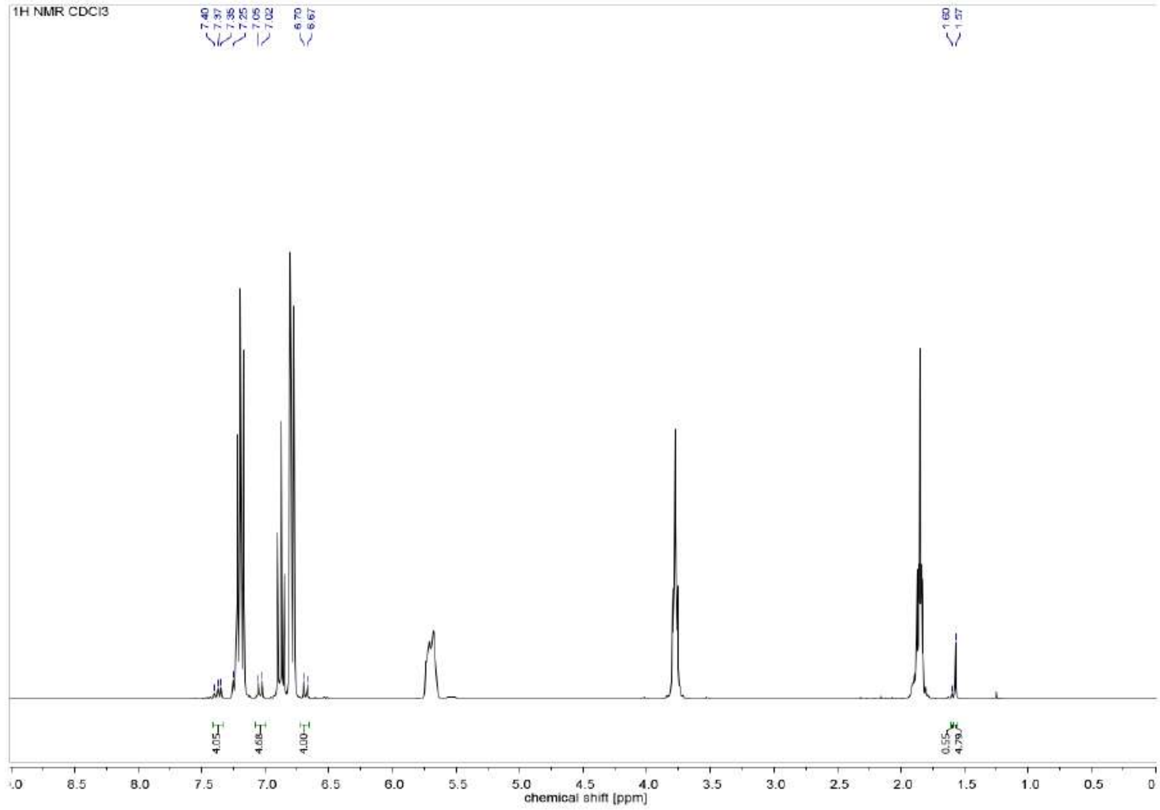


Figure S12. Spectrum of **1b** depolymerization after removal of THF and partial removal of phenol (ca. 3 equiv. leftover) (^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)).

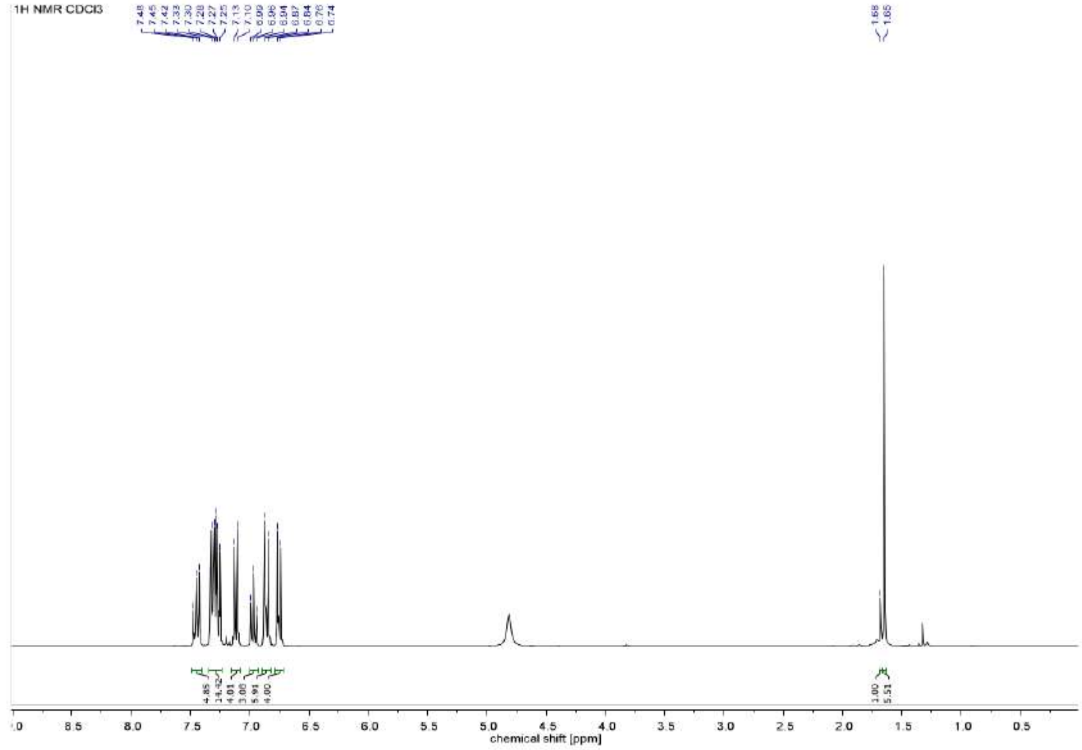
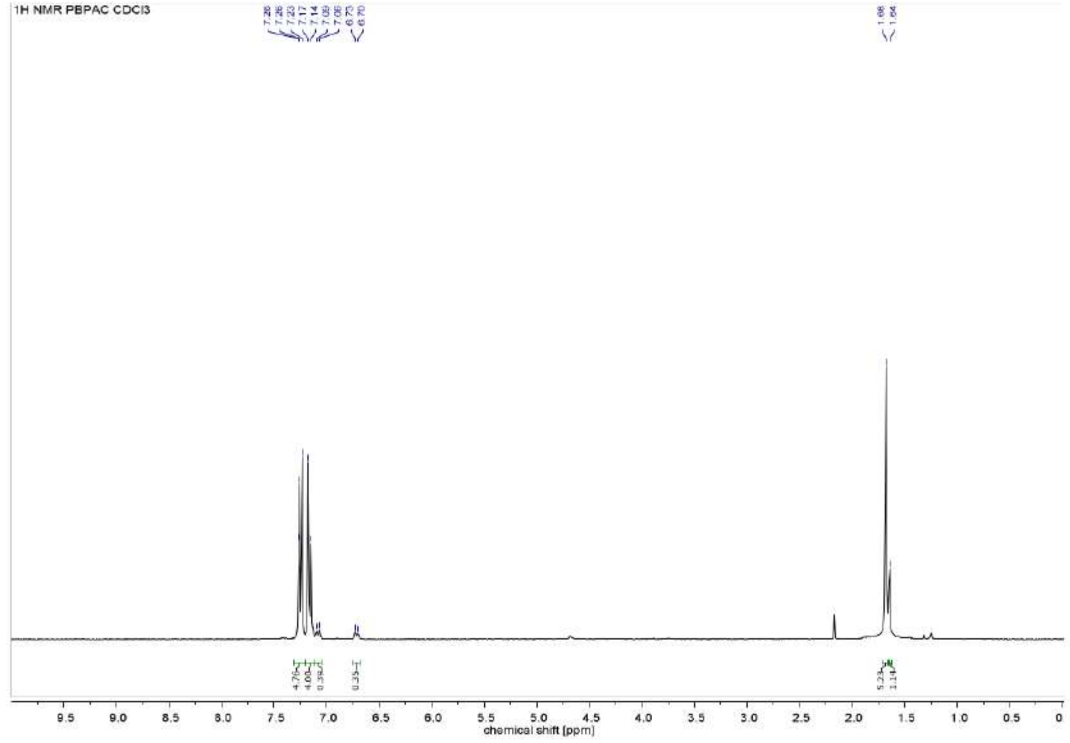


Figure S13. Spectrum of **1ba** obtained from **1b** depolymerization and removal of phenol (^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)).



GPC analysis of a THF of **1ba** (calibration curve based on narrow polydispersity polystyrene standards): Mn~4162 g/mol, Mw~6412 g/mol, polydispersity 1.54.

c) Depolymerization of poly(bisphenol A carbonate) ***1b*** *– scale-up*

A mixture of poly(bisphenol A carbonate) **1b** (5.00 g, 19.7 mmol based on the repeating unit) and phenol (48.2 g, 512 mmol, 26.1 equiv. based on the repeating unit of **1b**) was placed with a stir bar in a flask (250 mL) and a reflux condenser was connected. The mixture was stirred and heated to 180 °C in an oil bath (oil bath temperature). After holding the mixture for 5 min at 180 °C catalytic amounts of potassium fluoride (5.70 mg, 0.098 mmol, 0.5 mol% based on the repeating unit of **1b**) were added to start the depolymerization. The reaction was performed for 60 minutes at 180 °C. Afterwards the vial was cooled to room temperature. An aliquot was added to a NMR tube and dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^{1}H NMR revealing a NMR yield of 84% (**2**) and 84% (**3**). Afterwards the phenol was partially removed by vacuum distillation apparatus in vacuum (50-55 °C, 1.1 mbar). At a certain point a precipitate is formed. The precipitate was isolated by filtration and recrystallized from chloroform to yield after filtration, washing ($CHCl_3$) and drying colorless crystals of bisphenol A (m = 0.653 g, yield: 15% (100% = 4.47 g) in high purity. The first crop of crystals was harvested after storing the solution at room temperature (m = 400 mg) and the second one after storing the solution in the fridge (m = 253 mg). To the reaction residue was added chloroform and the mixture was heated and subsequently filtered. After storing at room temperature colorless crystals were formed and isolated (after filtration, washing with $CHCl_3$ and drying) of bisphenol A/phenol (m = 0.722 g, ratio: 1:1). After storing in the fridge colorless crystals of bisphenol A/phenol/diphenyl carbonate were formed (m = 0.528 g, ratio: 1:1.26:0.4). After storing in the fridge colorless crystals of bisphenol A/phenol/diphenyl carbonate were formed (1. crop: m = 0.491 g, ratio: 1:1:0.2; 2. crop: 0.260 g, ratio: 1:1.2:0.57). In the leftover a bisphenol A/phenol/diphenyl carbonate ratio of 1:11:5.9 was observed alongside with some PBPAC (Figure S16).

Figure S14. Spectrum of **1b** depolymerization (scale-up) reaction mixture (^{1}H NMR (400 MHz, CDCl$_3$, 25 °C)).

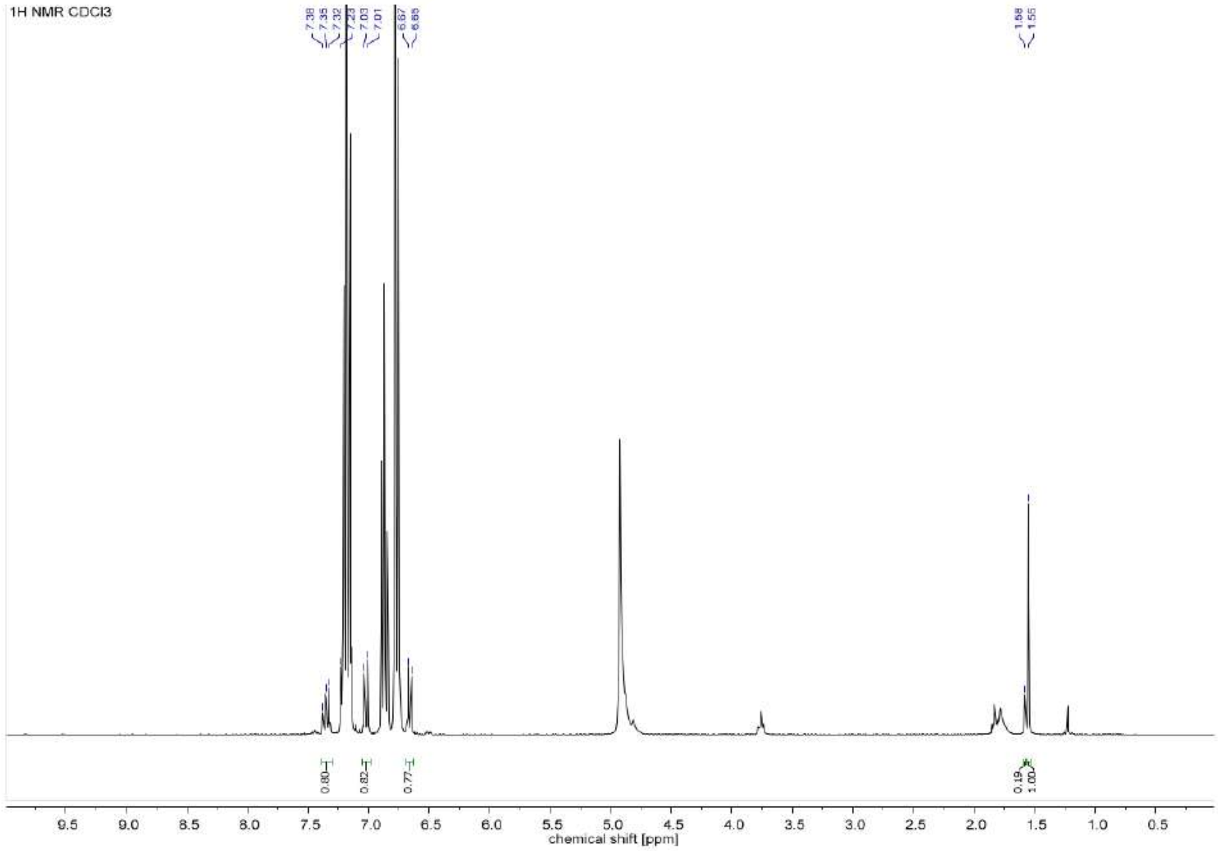


Figure S15. Spectrum of **1b** depolymerization (scale-up) after partial removal of phenol and filtration of precipitate (^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)). Ratio BPA:PBPAC(leftover) 1:0.45; ratio BPA:DPC 1:1.45.

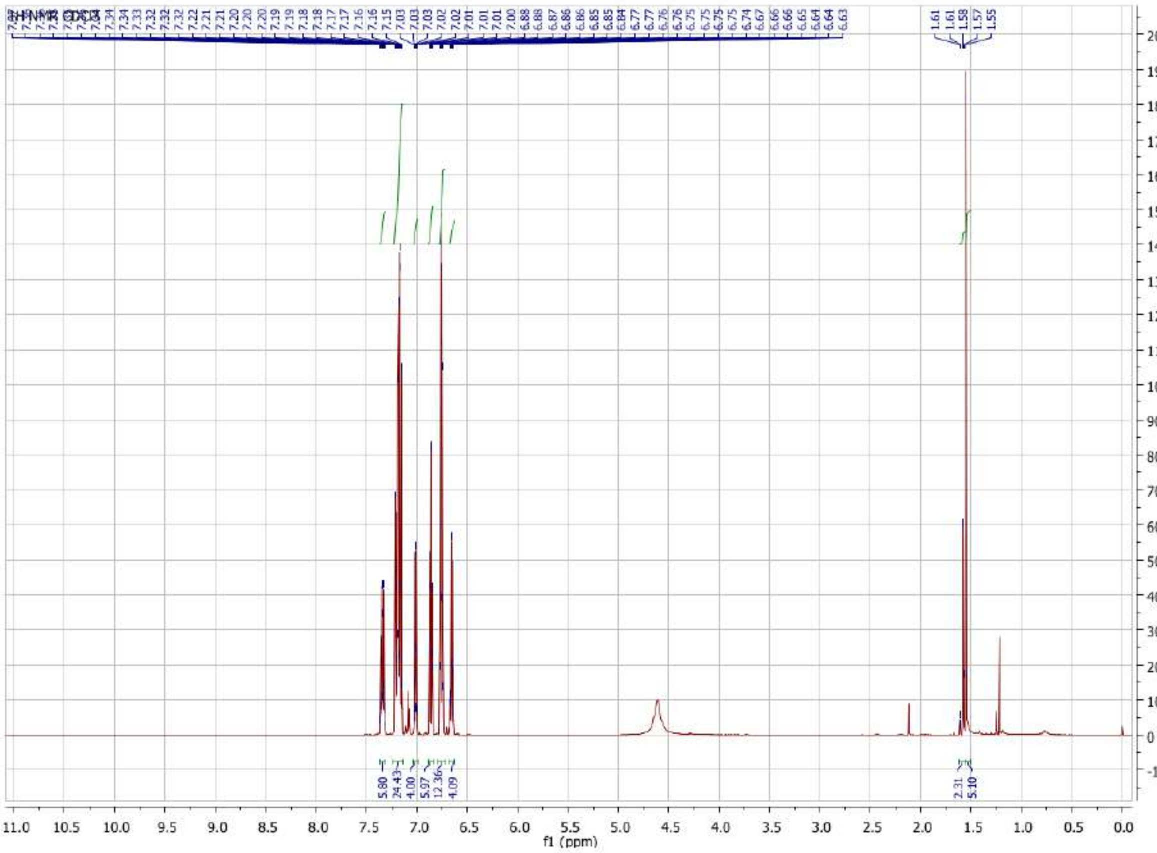
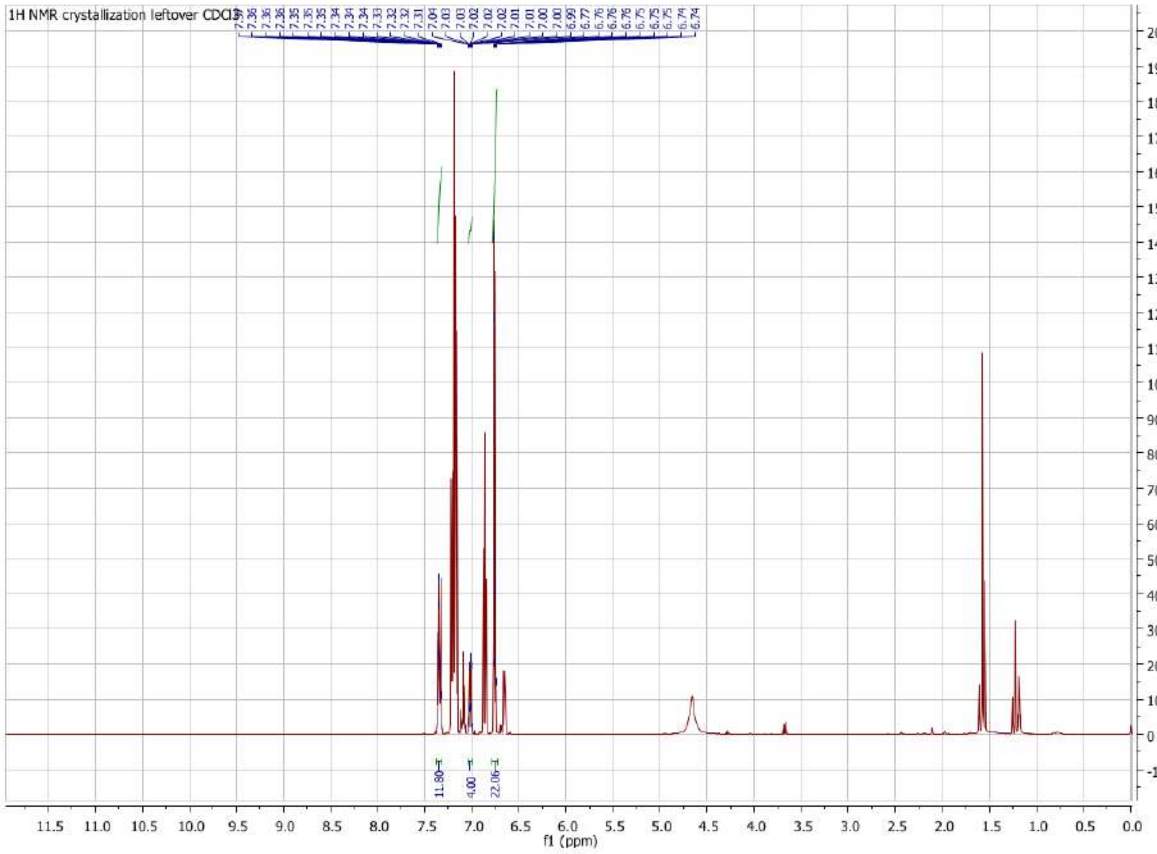


Figure S16. Spectrum of **1b** depolymerization (scale-up) after partial removal of phenol and partial removal of PBA by crystallization (^{1}H NMR (400 MHz, CDCl$_3$, 25 °C)).



Pathway B: Depolymerization of DVD-powder containg poly(bisphenol A carbonate) **1c**

a) Depolymerization of poly(bisphenol A carbonate) ***1c***

A mixture of poly(bisphenol A carbonate) based DVD powder **1c** (assumption DVD powder contains 100% **1c**: 344 mg, 1.35 mmol based on the repeating unit; assumption DVD powder contains 87wt%[4] **1c**: 299 mg, 1.17 mmol based on the repeating unit) [The DVD was cut into small pieces and were placed in a ball mill steel cylinder with a steel ball. The cylinder was cooled in liquid nitrogen. Afterwards it was attached to the ball bill and was ball milled for 20 min with a rate of 30 s^{-1}], phenol (6.00 g, 63.8 mmol, 47.3 equiv. (100% **1c**) or 52.5 equiv. (87 wt% **1c**) based on the repeating unit of **1c**) and THF (2 g, 27.8 mmol, 20.6 equiv. (100% **1c**) or 23.7 equiv. (87 wt% **1c**) based on the repeating unit of **1c**) was placed with a stir bar in a flask (10 mL) and a reflux condenser was connected. The mixture was stirred and heated to 180 °C in an oil bath (oil bath temperature). After holding the mixture for 5 min at 180 °C catalytic amounts of potassium fluoride (1.6 mg, 0.0271 mmol, 2 mol% (100% **1c**) or 2 mol%

(87 wt% **1c**)) were added to start the depolymerization. The reaction was performed for 30 minutes at 180 °C. Afterwards the vial was cooled to room temperature. An aliquot was added to a NMR tube and dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^1H NMR revealing a NMR yield of 76% (**2**) and 76% (**3**). Afterwards the THF and the phenol (partially) were carefully removed by vacuum distillation apparatus (Kugelrohr) in vacuum (50-55 °C, 1.1 mbar). Importantly, at higher temperature polymerization starts to form new poly(bisphenol A carbonate). Same observation was found if the amounts of phenol in the reaction mixture getting low (vide supraIncreasing the temperature to 200 °C (1.1 mbar) revealed the formation of poly(bisphenol A carbonate), which was isolated in 35% yield (100% **1c**) or 40% (87 wt% **1c**) (m = 121 mg) as off-white powder after washing the residue with acetone and drying.

Figure S17. Spectrum of **1c** depolymerization reaction mixture (^1H NMR (400 MHz, $CDCl_3$, 25 °C)).

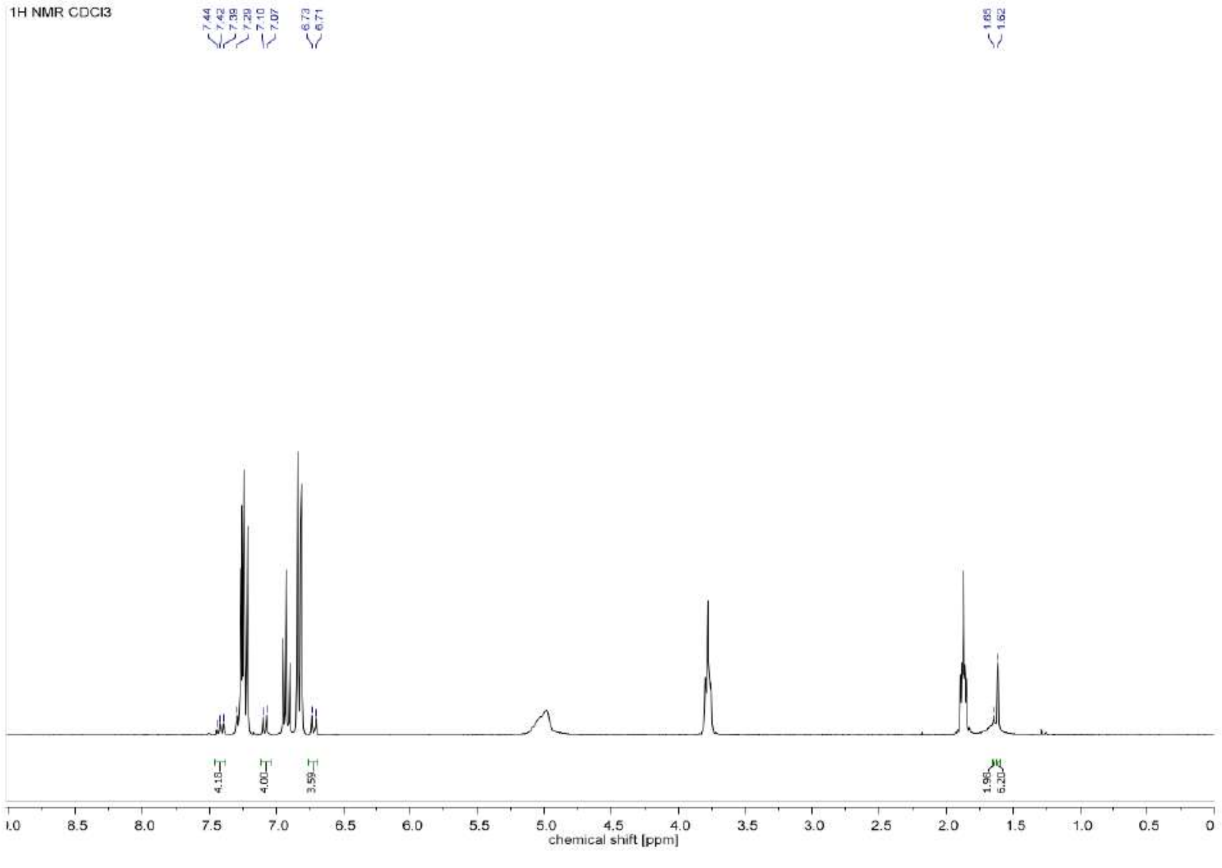
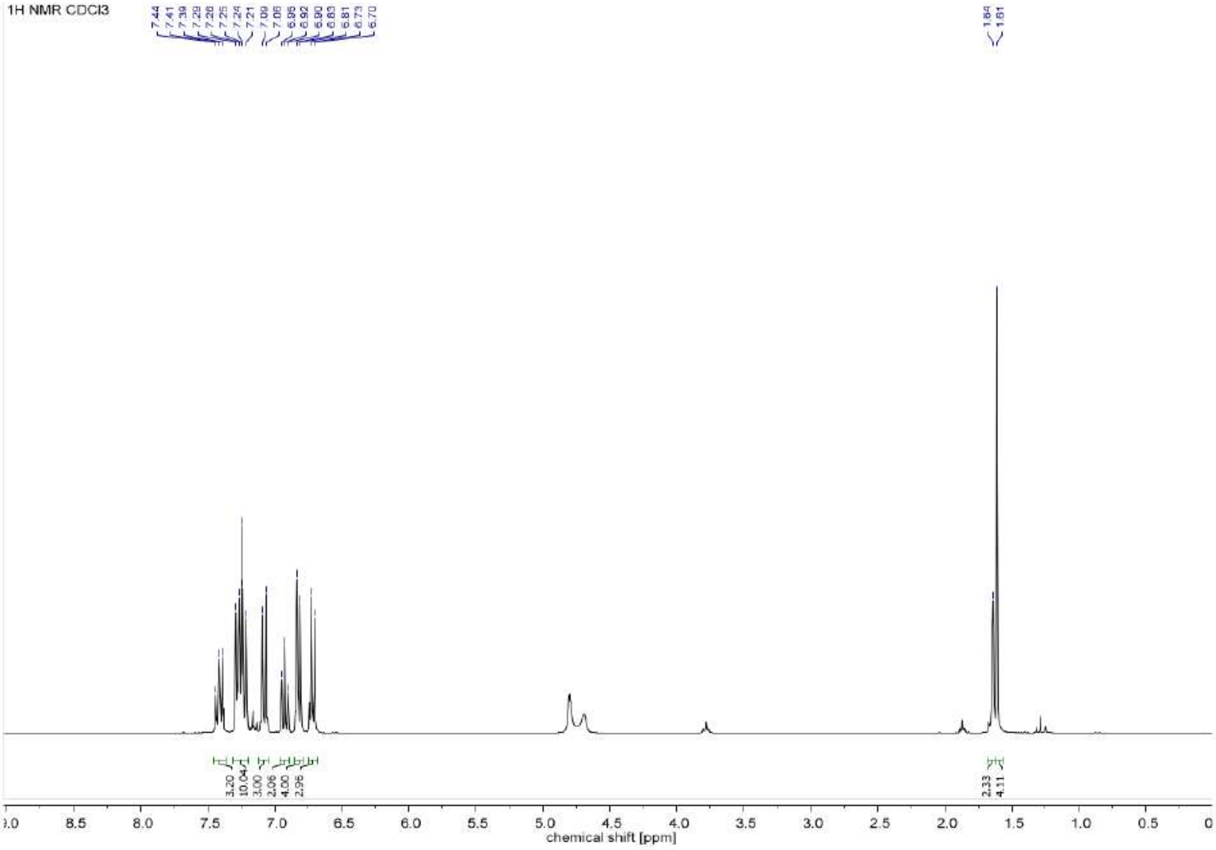


Figure S18. Spectrum of **1c** depolymerization after removal of THF and partial removal of phenol (ca. 3 equiv. leftover) (^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)).



GPC analysis of a THF of **1ca** (calibration curve based on narrow polydispersity polystyrene standards): Mn~8304 g/mol, Mw~24606 g/mol, polydispersity 2.96.

b) Depolymerization of poly(bisphenol A carbonate) ***1c*** *– scale up*

A mixture of poly(bisphenol A carbonate) based DVD powder **1c** (assumption DVD powder contains 100% **1b**: 5.00 g, 19.6 mmol based on the repeating unit; assumption DVD powder contains 87wt%[4] **1c**: 4.35 g, 17.0 mmol based on the repeating unit) and phenol (48.2 g, 512mmol, 26.1 equiv. based on the repeating unit of **1c** (100% **1c**) or 30.1 equiv. (87 wt% **1c**) based on the repeating unit of **1c**) was placed with a stir bar in a flask (10 mL) and a reflux condenser was connected. The mixture was stirred and heated to 180 °C in an oil bath (oil bath temperature). After holding the mixture for 5 min at 180 °C catalytic amounts of potassium fluoride (22.8 mg, 0.392 mmol, 2 mol% based on the repeating unit of **1b**, assumption DVD powder contains 100% **1c**; 0.888 mmol, 2.3 mol%) were added to start the depolymerization. The reaction was performed for 30 minutes at 180 °C. Afterwards the vial was cooled to room temperature. An aliquot was added to a NMR tube and dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^1H NMR revealing a NMR yield of 73% (**2**) and 71% (**3**). Afterwards, the phenol was carefully removed (partially) by vacuum distillation apparatus (Kugelrohr) in vacuum (50-55 °C, 1.1 mbar). At a certain point a precipitate is formed. The precipitate was isolated by filtration and recrystallized from chloroform to yield after filtration, washing ($CHCl_3$) and drying colorless crystals of bisphenol A/phenol/diphenyl carbonate (m = 0.956 g, ratio: 1:1.13:0.16) in high purity. In the leftover a bisphenol A/phenol/diphenyl carbonate ratio of 1:8.7:5.1 was observed alongside with some PBPAC.

Figure S19. Spectrum of **1c** depolymerization reaction mixture – scale up (^1H NMR (400 MHz, $CDCl_3$, 25 °C)).

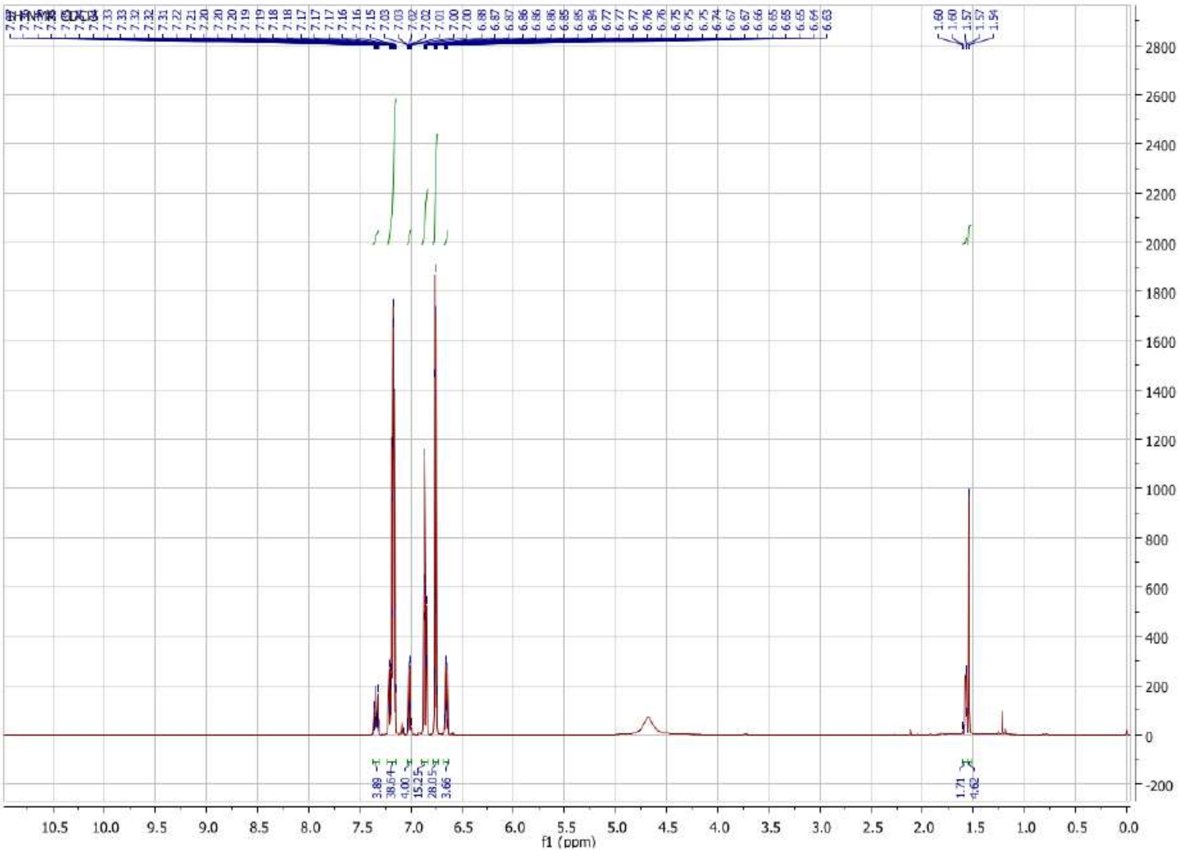
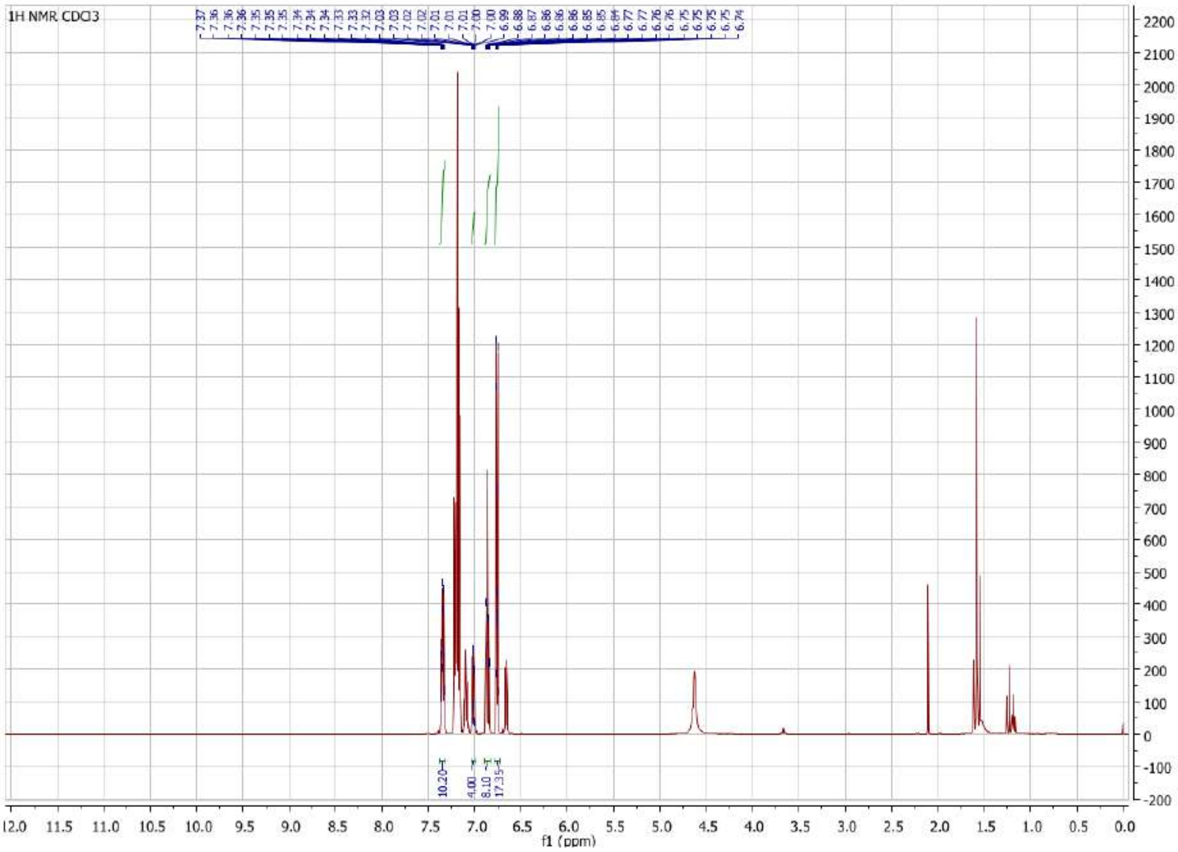


Figure S20. Spectrum of **1c** depolymerization reaction mixture – after partial removal of phenol by distillation and partial removal of PBA by crystallization (^1H NMR (400 MHz, $CDCl_3$, 25 °C)).



References

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[3] R. J. Abraham, M. Reid, *J. Chem. Soc., Perkin Trans.* **2002**, 1081–1091.

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ChemistrySelect

Supporting Information

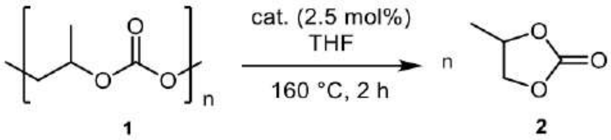
Depolymerization of Poly(1,2-propylene carbonate) via Ring Closing Depolymerization and Methanolysis

Christoph Alberti, Desiree Rijono, Moritz Wehrmeister, Even Cheung, and Stephan Enthaler*

General: All chemicals were used as received without further manipulations. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a *Fourier 300 MHz* (^1H: 300 MHz, ^{13}C: 75 MHz) or *Avance I-400* (^1H: 400 MHz, ^{13}C: 101 MHz) by Bruker, using the proton signals of the deuterated solvents as reference or external standards. Mass spectrometry was performed using a *Thermo ISQ LT EI* by Thermo Fisher Scientific. For microwave experiments a Microwave Synthesis Reactor Monowave 400 (Anton Paar GmbH) was used. The methanolysis on a large scale was performed in a Parr autoclave (model: 4774) (Parr Instrument Company).

General procedure for the methanolysis of poly(propylene carbonate) (1) (optimization of the reaction conditions): A mixture of poly(propylene carbonate) (**1**) (138 mg, 1.35 mmol based on the repeating unit), methanol (1.03-8.05 g, 32.0-251 mmol, 23.7-186 equiv. based on the repeating unit of **1**) and catalytic amount of a catalyst (0-5 mol%, 0-0.0675 mmol based on the repeating unit of **1**) were placed in a vial with a stir bar. When no methanol was applied, CH_2Cl_2 or THF were used as solvent (5.2 mL). The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 10-180 minutes (hold time) at 120-160 °C and stirring with 400 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature. An aliquot of the solution was transferred to a flask to remove MeOH in vacuum. The residue was dissolved in $CDCl_3$ (0.6 mL) and transferred to an NMR tube. The sample was subjected to ^1H NMR to determine the yield of propylene carbonate (**2**) and propane-1,2-diol (**3**) [The yield of **2** and **3** was calculated on the basis of the C*H* function of **2** and **3** and the leftover signals of the C*H* function of the polymer/oligomer].

Table S1: Application of zinc(II) salts for the RCD of **1**.



Entry[a]	Catalyst [mol%]	Ratio[b] (**1**:**2**)
1	$Zn(OAc)_2$ [2.5]	69:31
2	$ZnCl_2$ [2.5]	96:4
3	$ZnBr_2$ [2.5]	96:4
4	$Zn(OTf)_2$ [2.5]	94:6
5	zinc(II)methacrylate [2.5]	67:33
6[c]	$Zn(OAc)_2$ [2.5]	76:24

[a] Reaction conditions: **1** (1.35 mmol, based on repeating unit of **1**), catalyst (2.55 mol%, 0-33.8 µmol based on the repeating unit of **1**), THF (5.2 mL). [b] The yield was determined by ^{1}H NMR assuming that the polymer contains 100% carbonate linkages. [c] The reaction time was 3 h.

Figure S1: ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 25°C) of reaction solution (2.5 mol% $Zn(OPiv)_2$, 93.2 equiv. MeOH, 160 °C, 10 min).

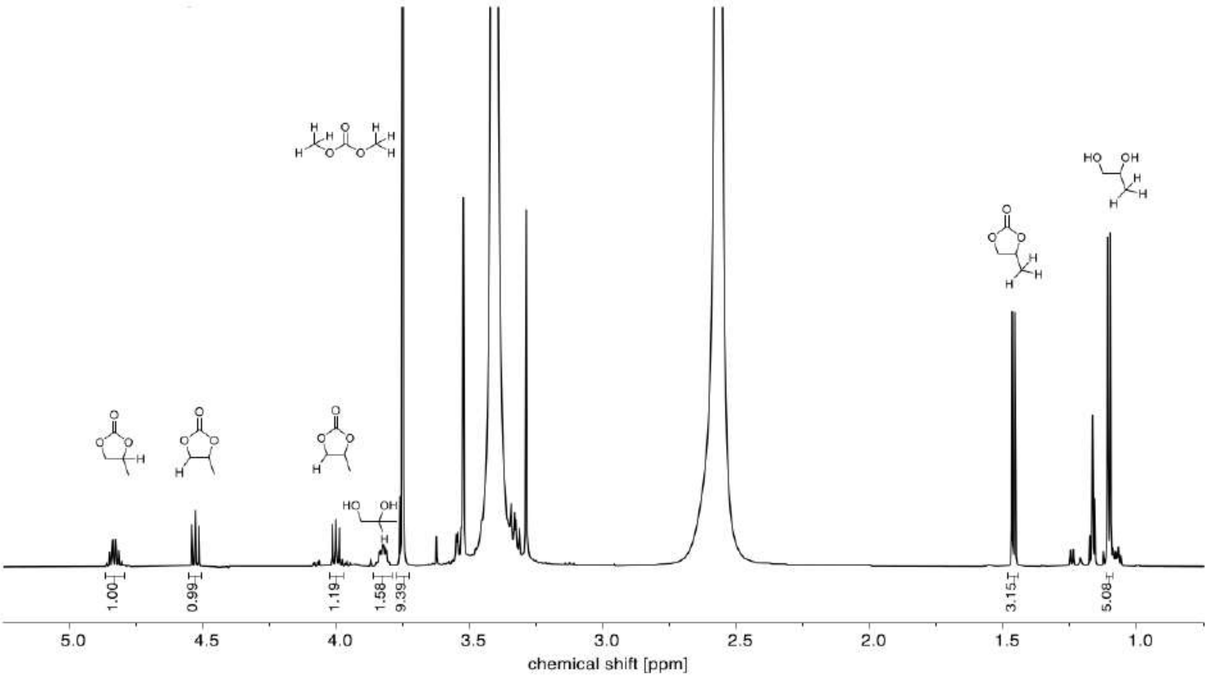
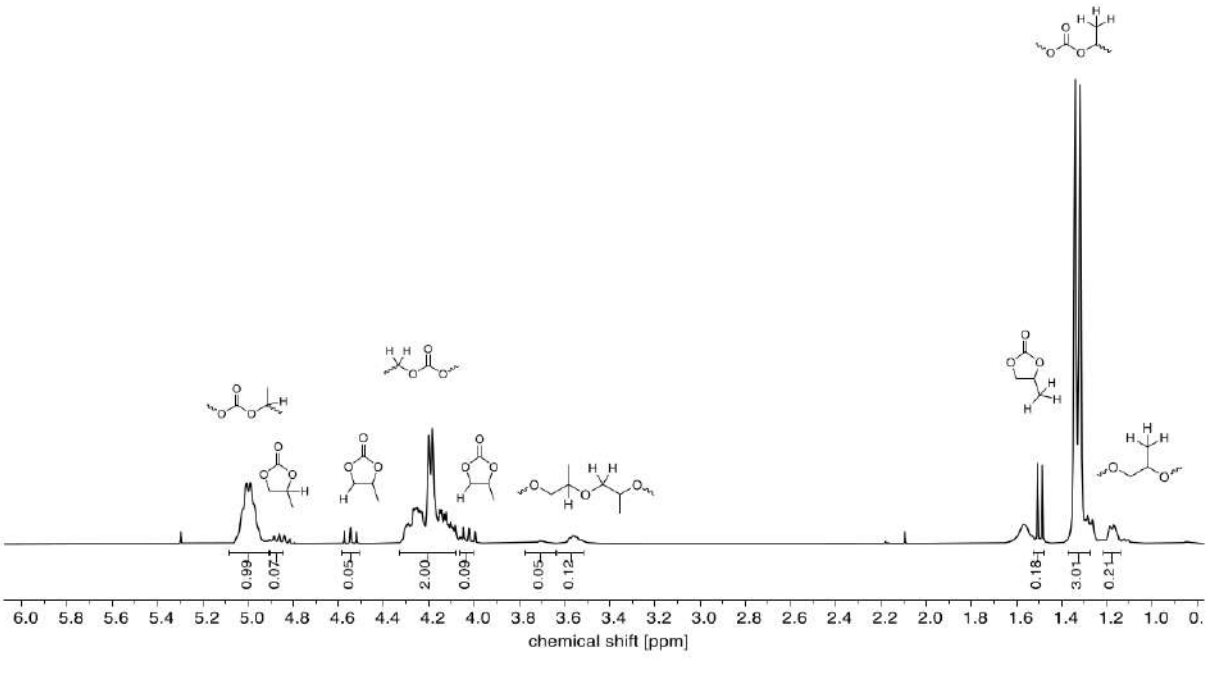


Figure S2: ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25°C) of a poly(propylene carbonate) sample.



Procedure for studying the influence of the amount of methanol on the degradation of poly(propylene carbonate) (1): A mixture of poly(propylene carbonate) (**1**) (138 mg, 1.35 mmol based on the repeating unit), methanol (0.433 g-4.76 g, 13.5-251 mmol, 10-110 equiv. based on the repeating unit of **1**) and catalytic amounts of $Zn(OAc)_2$ (2.5 mol%, 33.8 µmol based on the repeating unit of **1**) were placed in a vial with a stir bar. The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 10 minutes (hold time) at 160 °C and stirring with 400 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature. An aliquot of the solution was transferred to a flask to remove the solvent in vacuum. The residue was dissolved in $CDCl_3$ (0.6 mL) and transferred to an NMR tube. The sample was subjected to ^{1}H NMR to determine the yield of propylene carbonate (**2**) and propane-1,2-diol (**3**) [The yield of **2** and **3** was calculated on the basis of the C*H* function of **2** and **3** and the leftover signals of the C*H* function of the polymer/oligomer].

Procedure for time-yield-plot of the degradation of poly(propylene carbonate) (1): A mixture of poly(propylene carbonate) (**1**) (138 mg, 1.35 mmol based on the repeating unit), methanol (4.03 g, 126 mmol, 93.2 equiv. based on the repeating unit of **1**) and catalytic amounts of $Zn(OAc)_2$, $Zn(OOC\textit{t}Bu)_2$ or NaOAc (2.5 mol%, 33.8 µmol based on the repeating unit of **1**) were placed in a vial with a stir bar. The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 10-180 minutes (hold time) at 120 °C and stirring with 400 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature. An aliquot of the solution was transferred to a flask to remove MeOH in vacuum. The residue was dissolved in $CDCl_3$ (0.6 mL) and transferred to an NMR tube. For the following datapoints the same sample was submitted to reaction.

Figure S3: yield vs. time plot (2.5 mol% Zn(OOC*t*Bu)$_2$, 93.2 equiv. MeOH, 120 °C).

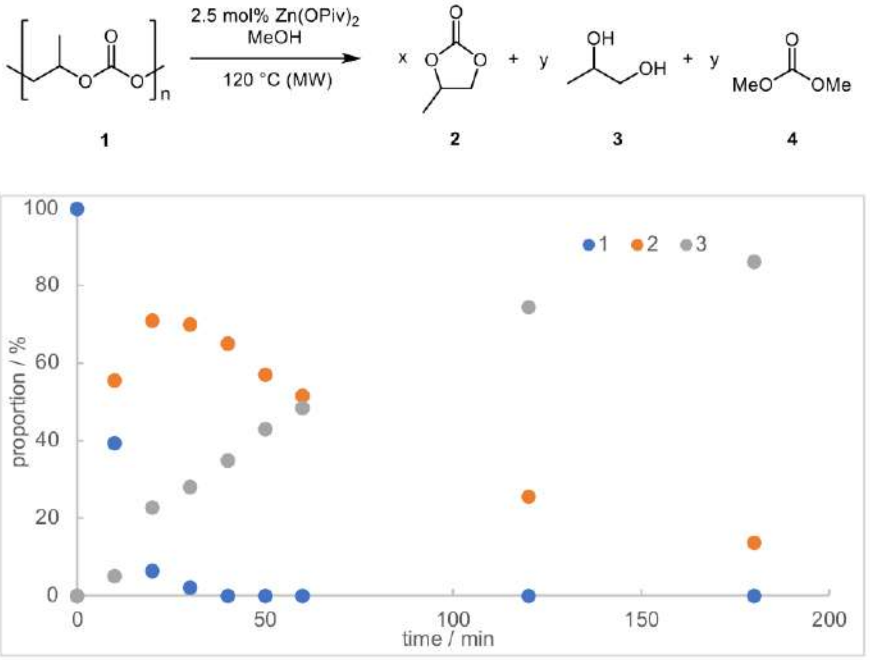


Figure S4: ESI-MS of oligomer sample after removal of volatiles from the reaction solution (2.5 mol% Zn(OOC*t*Bu)$_2$, 93.2 equiv. MeOH, 120 °C, 10 min).

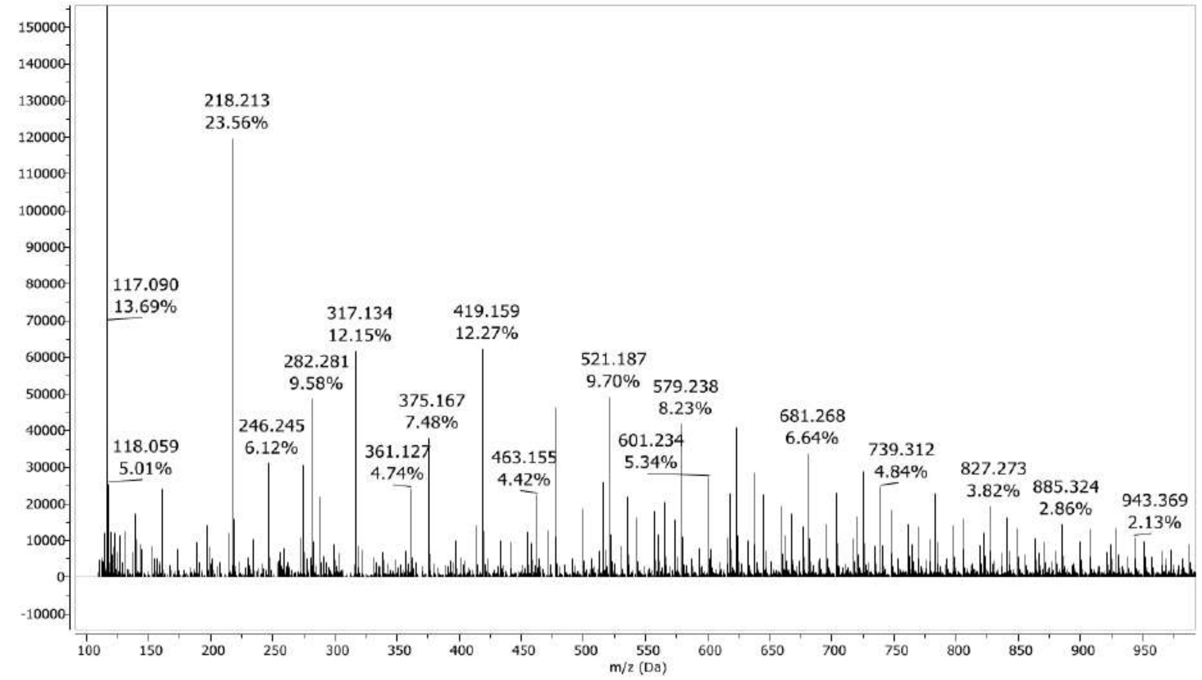
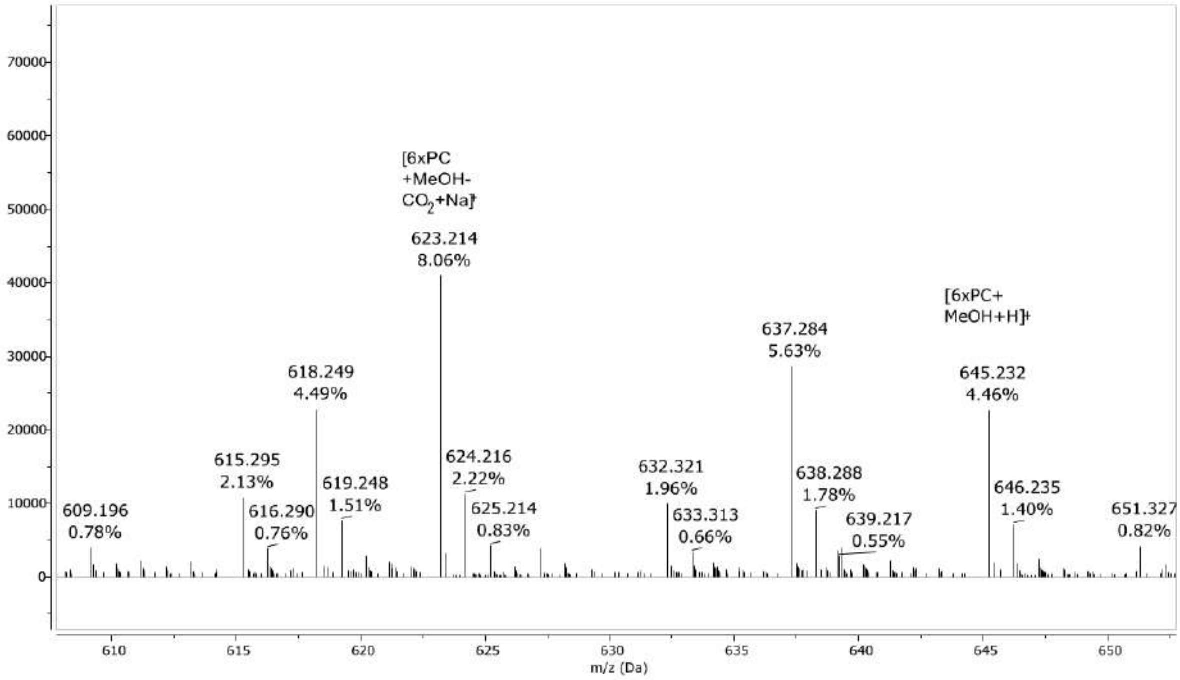


Figure S5: Section of ESI-MS (Fig. S4) of oligomer sample after removal of volatiles from the reaction solution (2.5 mol% Zn(OOC*t*Bu)$_2$, 93.2 equiv. MeOH, 120 °C, 10 min) (PC = carbonate unit of the polycarbonate).



Procedure for the methanolysis of poly(propylene carbonate) (1) using an autoclave with 23.7 equiv. MeOH: Pellets of poly(propylene carbonate) (**1b**) (11.8 g, 115 mmol, based on the repeating unit of **1**), and catalytic amounts of the NaOAc (235 mg, 2.88 µmol, 2.5 mol%, based on the repeating unit of **1**) were placed with a stir bar in a steal autoclave. Subsequently, MeOH (110 mL, 87.3 g, 2.73 mol, 23.7 equiv.) was added and the autoclave was sealed and heated to the desired temperature (160 °C). The temperature was hold for 24 hours, while stirring the reaction mixture. Afterwards the autoclave was cooled to room temperature and the dimethyl carbonate **4** and methanol were carefully distilled off. The yield of carbonate **4** in the distillate (84.5 g) was determined by addition of mesitylene as standard (162.5 mg) to a sample of the distillate (m = 1.05 g). A yield of 72% yield was calculated using ^{1}H NMR analysis. The residue was purified by Kugelrohr distillation under vacuum. In the distillate 1,2-propane diol (**3**, 82% yield, m = 7.22 g, assuming that **1** contains 100% carbonate linkages) and propylene carbonate (**2**, 6% yield, m = 0.73 g, assuming that **1** contains 100% carbonate linkages) were collected.

1,2-propane diol (3)[1]: ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): δ [ppm] = 4.04-3.85 (m, -C*H*OH, 1H), 3.62-3.59 (m, -C*H*$_2$OH, 1H), 3.40-3.35 (m, -C*H*$_2$OH, 1H), 1.14 (d, *J* = 6.3 Hz, -C*H*$_3$, 3H).

$^{13}C\{^1H\}$ NMR (500 MHz, $CDCl_3$, 25 °C): δ [ppm] = 68.3 (HOCH-), 67.9 (HOCH_2-), 18.7 (-CHCH_3).

Figure S6: ^1H NMR spectrum (300 MHz, $CDCl_3$, 25°C) of the mixture of **2** and **3**.

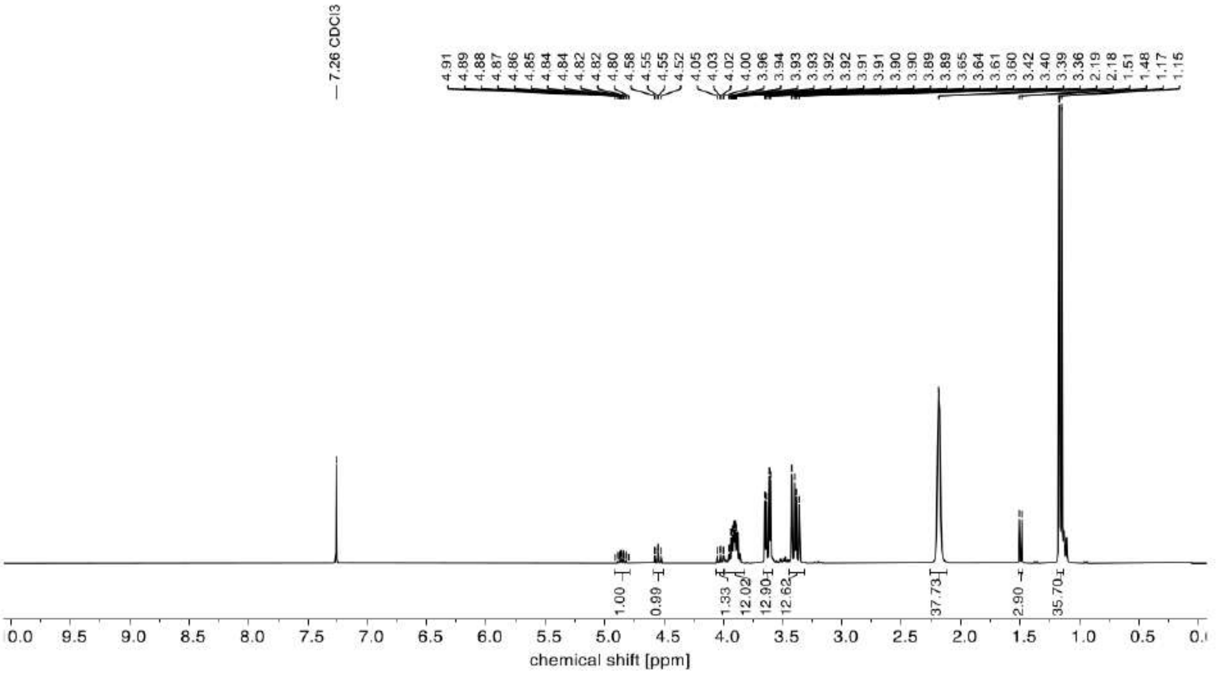


Figure S7: $^{13}C\{^1H\}$ NMR spectrum (500 MHz, $CDCl_3$, 25°C) of the distillate.

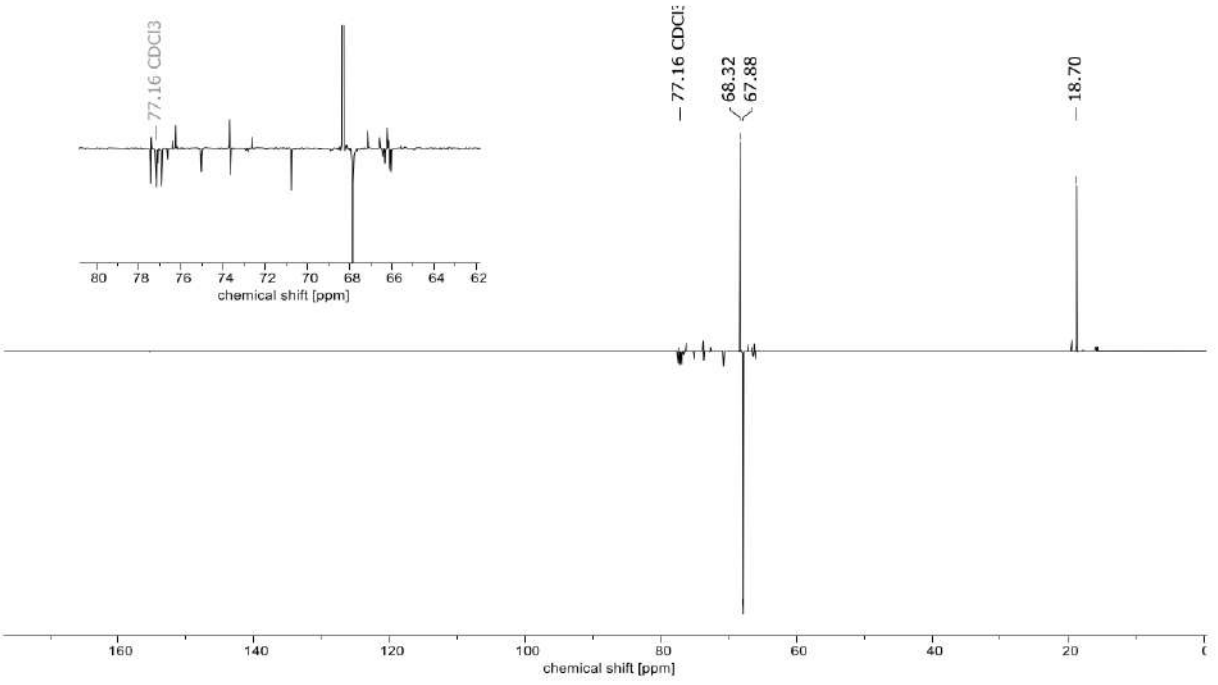
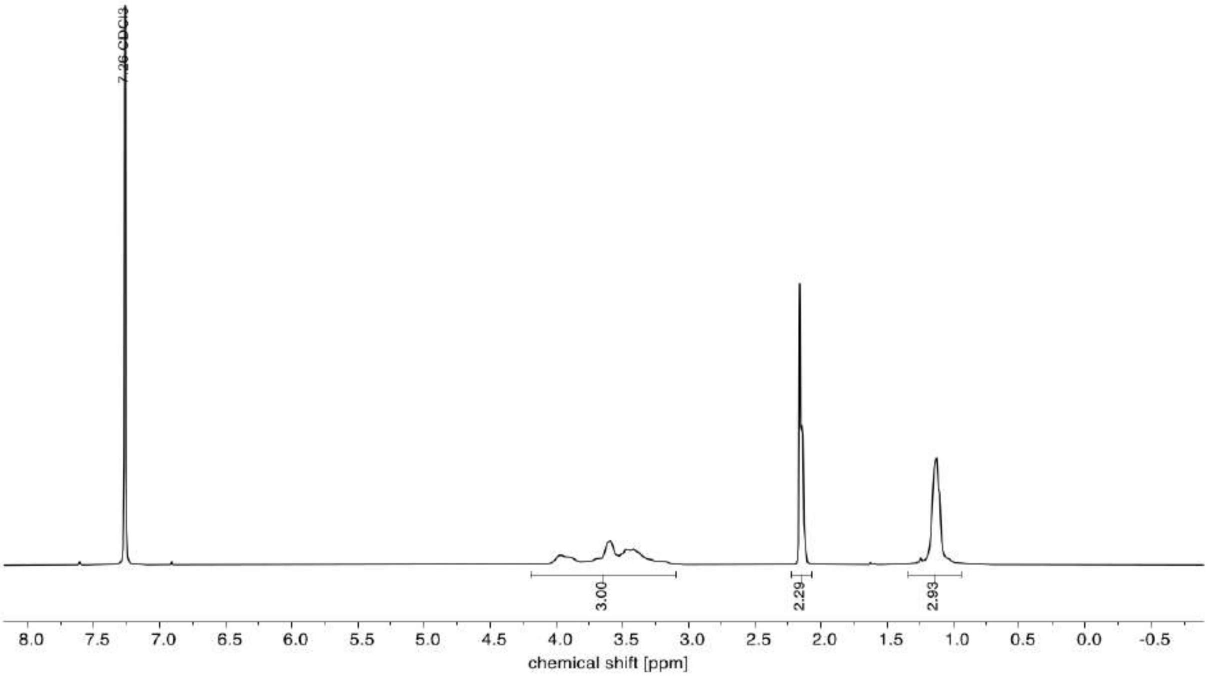
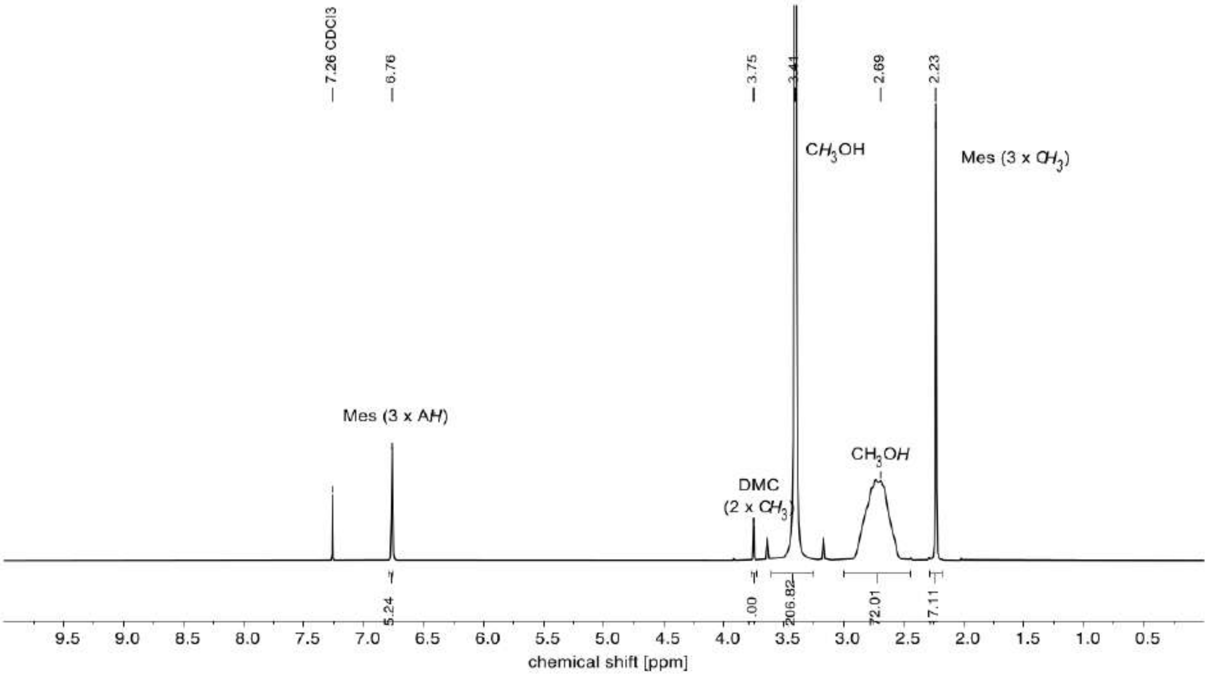


Figure S8: ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25°C) of the oligomeric residue after distillation.



Procedure for the methanolysis of poly(propylene carbonate) (1) using an autoclave with 373 equiv. MeOH: Pellets of poly(propylene carbonate) (**1b**) (617 mg, 6.00 mmol, based on the repeating unit of **1**), and catalytic amounts of the NaOAc (12.3 mg, 150 µmol, 2.5 mol%, based on the repeating unit of **1**) were placed with a stir bar in a steal autoclave. Subsequently, MeOH (90 mL, 71.5 g, 2.23 mol, 373 equiv.) was added and the autoclave was sealed and heated to the desired temperature (160 °C). The temperature was hold for 2 hours, while stirring the reaction mixture. Afterwards the autoclave was cooled to room temperature and the dimethyl carbonate **4** and methanol were carefully distilled off. The yield of carbonate **4** in the distillate (59.0 g) was determined by addition of mesitylene as standard (49.0 mg) to a sample of the distillate (483 mg). A yield of 79% yield was calculated using ^{1}H NMR analysis. The residue was purified by Kugelrohr distillation under vacuum. In the distillate 1,2-propane diol (**3**, 58% yield, m = 265 mg, assuming that **1** contains 100% carbonate linkages) was collected.

Figure S9: ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25°C) of the distillate containing MeOH and carbonate **4** after addition of mesitylene as standard.



1,2-propane diol (3)[1]: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ [ppm] = 3.90-3.84 (m, -C*H*OH, 1H), 3.62-3.59 (m, -CH_2OH, 1H), 3.43-3.33 (m, -CH_2OH, 1H), 1.13 (d, *J* = 6.3 Hz, -CH_3, 3H). ^{13}C{^{1}H} NMR (500 MHz, $CDCl_3$, 25 °C): δ [ppm] = 68.5 (HO*C*H-), 68.1 (HOCH_2-), 18.8 (-CHCH_3).

Figure S10: ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25°C) of **3**.

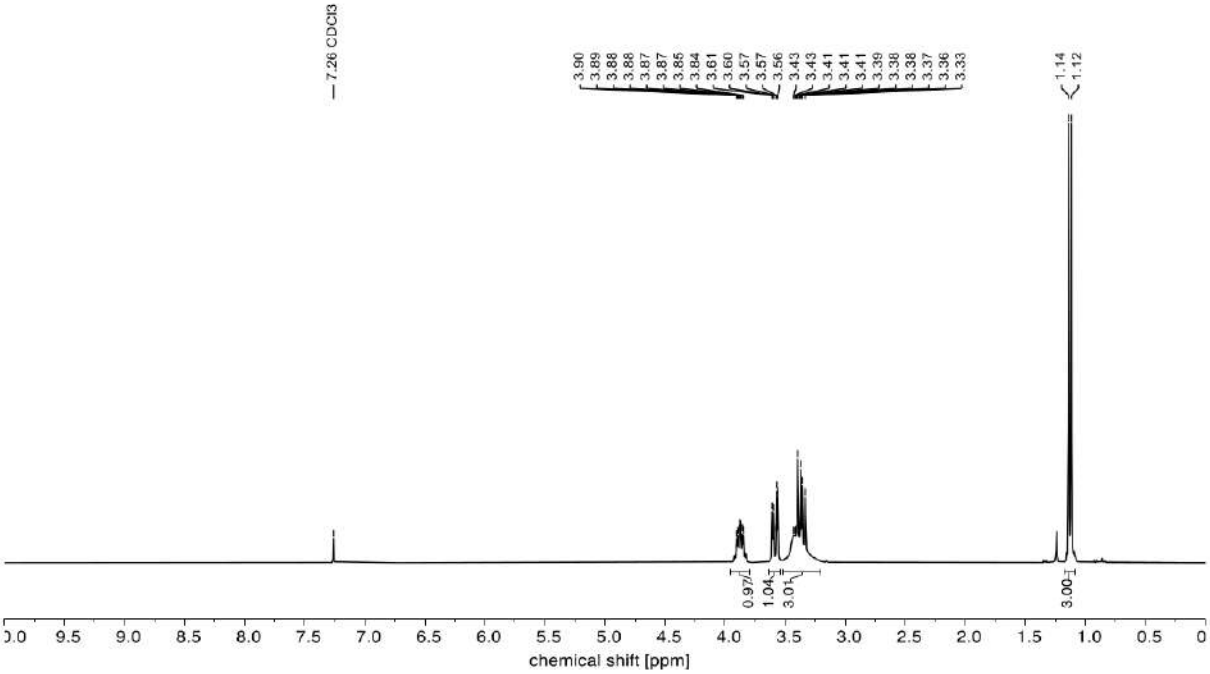
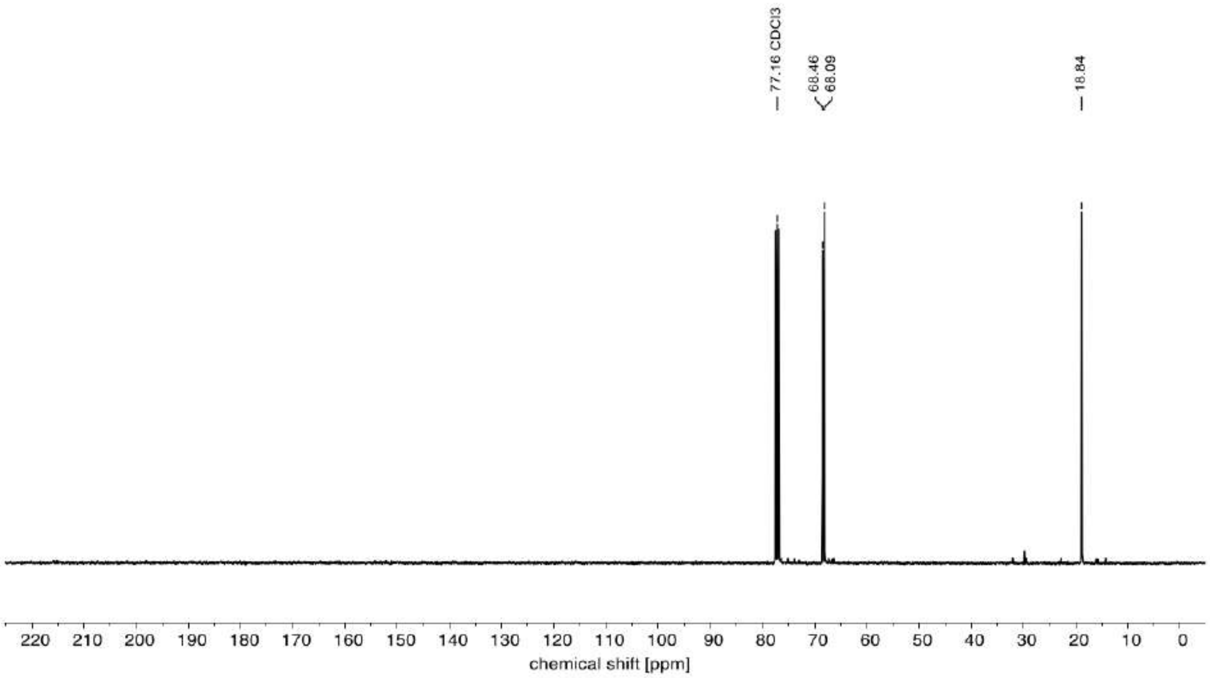


Figure S11: $^{13}C\{^1H\}$ NMR spectrum (100.6 MHz, $CDCl_3$, 25°C) of **3**.



Procedure for the degradation of poly(propylene carbonate) (1b) using reactive distillation: Pellets of poly(propylene carbonate) (**1b**) (2.50 g, 9.84 mmol, based on the repeating unit of **1**), and catalytic amounts of the $Zn(OAc)_2$ (111 mg, 607 µmol, 2.5 mol%, based on the repeating unit of **1**) were placed in a Kugelrohr distillation apparatus. The temperature was increased to 180 °C and the pressure was reduced to 180 mbar, collecting all volatiles. After 1 h propylene carbonate (**2**) (yield = 85%, m = 2.10 g) was collected.

Propylene carbonate (2)[2]: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ [ppm] = 4.90-4.81 (m, -C*H*O, 1H), 4.58-4.52 (m, -C*H*$_2$O, 1H), 4.04-3.99 (m, -C*H*$_2$O, 1H), 1.49 (d, *J* = 6.3 Hz, -C*H*$_3$, 3H). ^{13}C{^{1}H} NMR (500 MHz, $CDCl_3$, 25 °C): δ [ppm] = 155.1 (-*C*O$_3$), 73.7 (-*C*H), 70.7 (-*C*H$_2$), 19.3 (-*C*H$_3$).

Figure S12: ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25°C) of propylene carbonate (**2**).

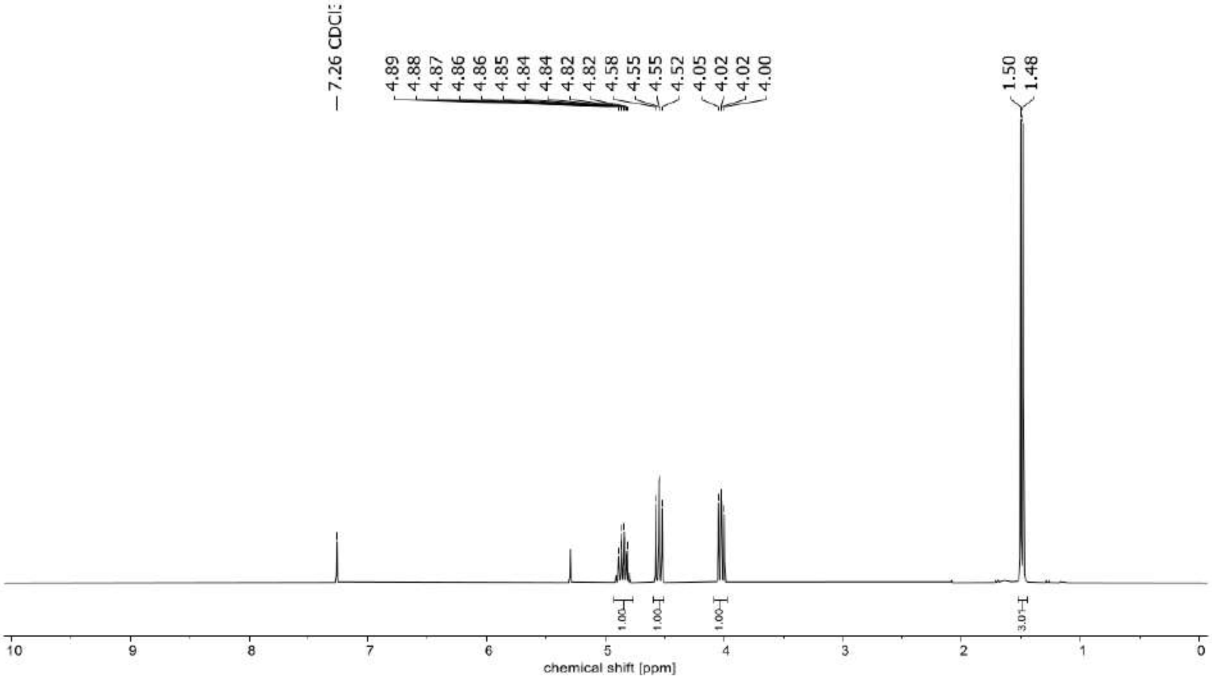
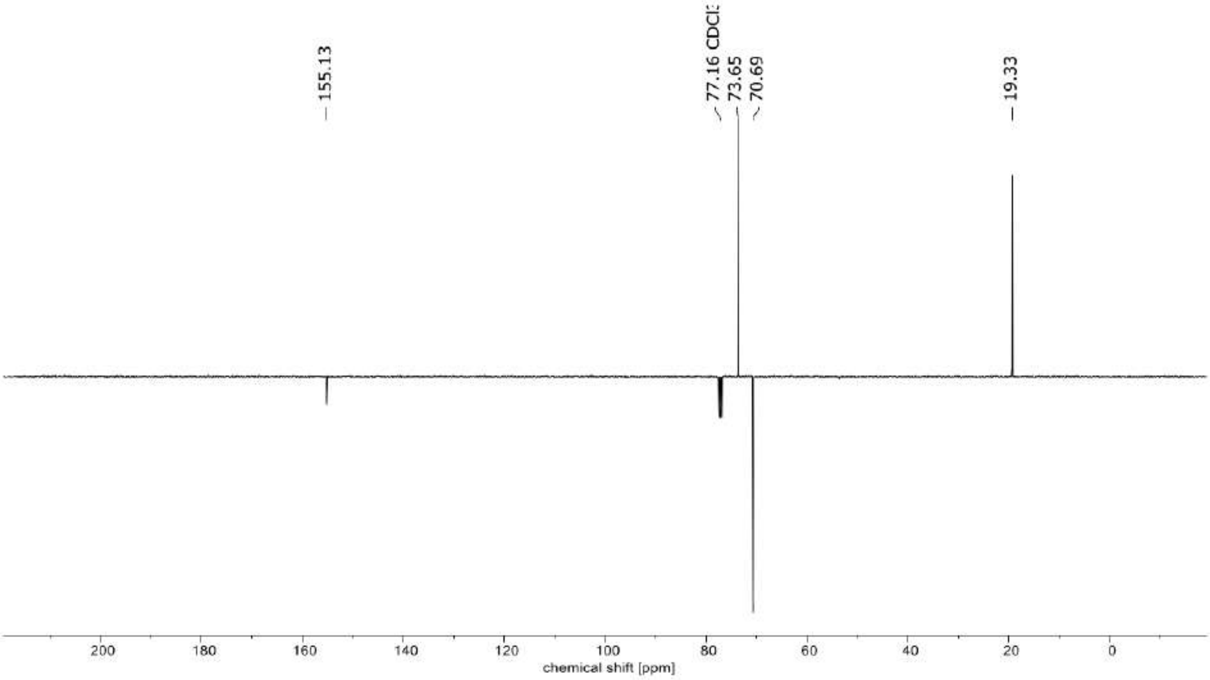
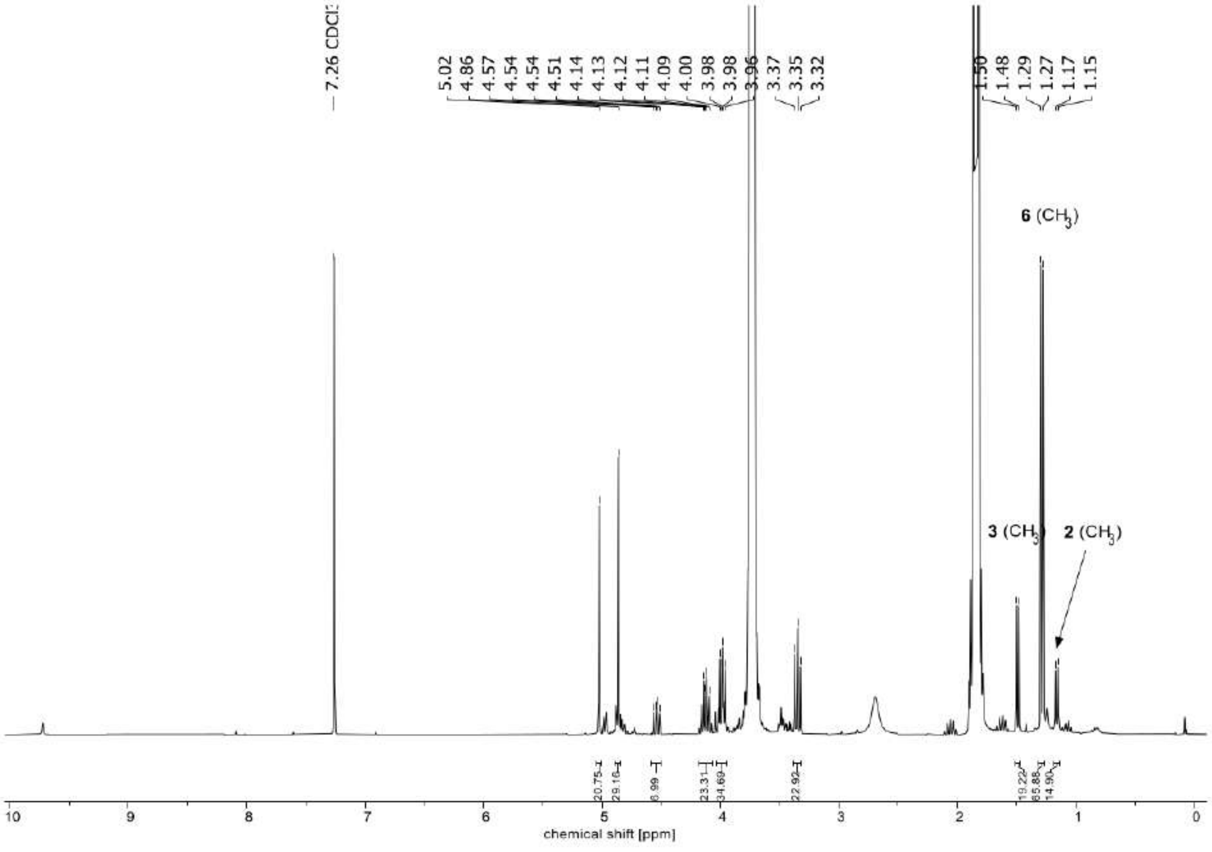


Figure S13: $^{13}C\{^1H\}$ NMR spectrum (500 MHz, $CDCl_3$, 25°C) of propylene carbonate (**2**).



Procedure for the methanolysis of poly(propylene carbonate) (1) with subsequent degradation of poly(oxymethylene): A mixture of poly(propylene carbonate) (**1**) (138 mg, 1.35 mmol based on the repeating unit), methanol (4.03 g, 126 mmol, 93.2 equiv. based on the repeating unit of **1**) and catalytic amounts of a $Zn(OAc)_2$ (6.2 mg, 2.5 mol%, 33.8 µmol based on the repeating unit of **1**) were placed in a vial with a stir bar. The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 120 minutes (hold time) at 160 °C and stirring with 400 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature. The MeOH and dimethyl carbonate was carefully distilled off and to the residue was added $Bi(OTf)_3$ (44.2 mg, 33.7 µmol, 5 mol%, based on the repeating unit of **1**)), poly(oxymethylene) (40.5 mg, 1.35 mmol, 1.0 equiv., based on the repeating unit of **1**) and THF (4 mL) and the mixture was heated to 70 °C for 3 h. After cooling, an aliquot of the reaction mixture was dissolved in $CDCl_3$ (0.6 mL) and transferred to an NMR tube. The sample was subjected to ^1H NMR to determine the yield of 4-methyl-1,3-dioxolane (**6**)[3]. The yield of **6**, **2** and **3** was calculated on the basis of the -CH_3 function of **6**, **2** and **3**.

Figure S14: ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25°C) of reaction mixture after degradation of poly(oxymethylene).



Grocedure for the depolymerization of poly(bisphenol A carbonate) 7: A mixture of commercially available poly(bisphenol A carbonate) (**7**) (344 mg, 1.35 mmol based on the repeating unit, obtained from Sigma Aldrich), methanol (4.00 g, 125.8 mmol, 93.2 equiv. based on the repeating unit of **7**) and catalytic amounts of $Zn(OAc)_2$ (6.2 mg, 2.5 mol%, 0.034 mmol based on the repeating unit of **7**) or NaOAc (2.8 mg, 2.5 mol%, 0.034 mmol based on the repeating unit of **7**) were placed with a stir bar in a vial. The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 10 minutes (hold time) at 160 and stirring with 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature. An aliquot of the clear solution was transferred to an NMR tube and was dissolved in $CDCl_3$ (0.6 mL). The sample was subjected to ^{1}H NMR to determine the yield and the ratio of bisphenol A (**8**) and dimethyl carbonate (**4**). [The yield of **8** was calculated on the basis of the Ar-H or $C(CH_3)_2$ and the Ar-H or $C(CH_3)_2$ leftover signals of the polymer/oligomer. The yield of **4** was calculated on the ratio of the Ar-H of **8** to $(CH_3O)_2C{=}O$.]

Bisphenol A (**2**)[4]: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.00-7.02 (m, 4H, Ar-*H*), 6.66-6.67 (m, 4H, Ar-*H*), 1.56 (s, 6H, $(CH_3)_2C$-) ppm. (The signal for 2xOH was not observed).

Dimethyl carbonate (**3**)[5]: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.75 (s, 6H, $(CH_3O)_2C{=}O$) ppm.

Figure S15: ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25°C) of reaction mixture after degradation of poly(bisphenol A carbonate) with $Zn(OAc)_2$.

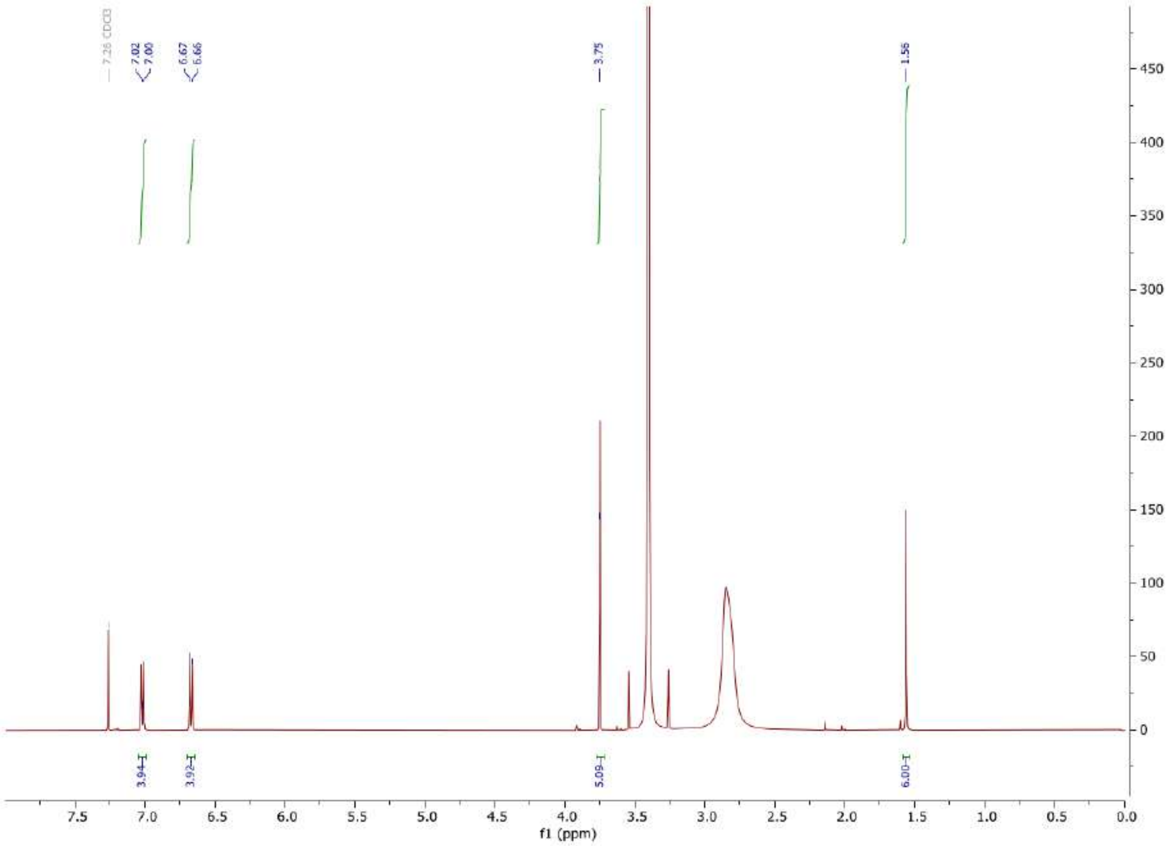
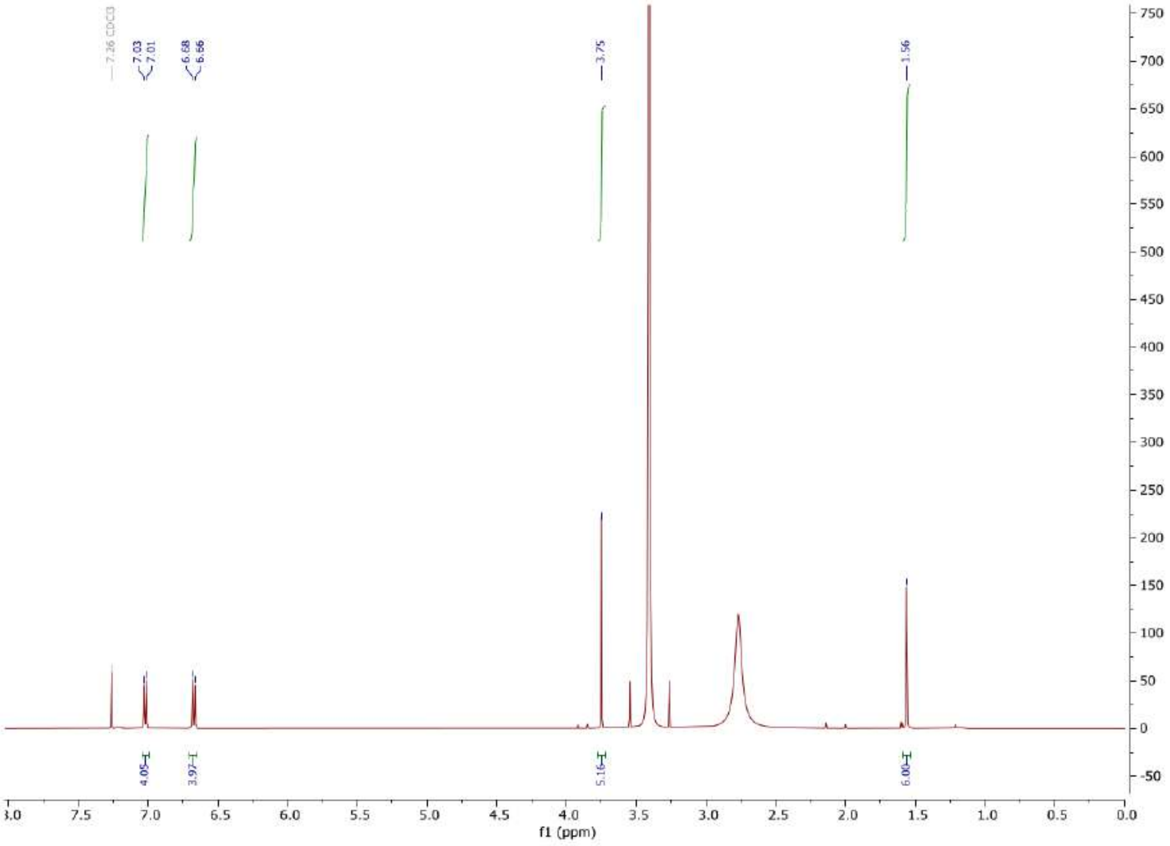


Figure S16: ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25°C) of reaction mixture after degradation of poly(bisphenol A carbonate) with NaOAc.



References

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Chemistry
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Supporting Information

Depolymerization of End-of-Life Poly(lactide) via 4-Dimethylaminopyridine-Catalyzed Methanolysis

Christoph Alberti, Nicole Damps, Roderich R. R. Meißner, and Stephan Enthaler*

General: All chemicals were used as received without further manipulations. ^{1}H and ^{13}C{^{1}H}NMR spectra were recorded on a *Fourier 300 MHz* (^{1}H: 300 MHz, ^{13}C: 75 MHz) or *Avance I-400* (^{1}H: 400 MHz, ^{13}C: 101 MHz) by Bruker, using the proton signals of the deuterated solvents as reference or external standards. Mass spectrometry was performed using a *Thermo ISQ LT EI* by Thermo Fisher Scientific. For microwave heating experiments a Microwave Synthesis Reactor Monowave 400 (Anton Paar GmbH) was used. GC-MS was measured with Agilent Technologies 5977B GC/MSD.

General procedure for the depolymerization of polylactide (1a) (optimization of the reaction conditions): A mixture of polylactide (**1a**, transparent plastic cup from Prodana GmbH) (97.2 mg, 1.35 mmol based on the repeating unit), methanol (0.125-2.00 g, 2.89-31.2 mmol, 2.9-46.3 equiv. based on the repeating unit of **1a**) and catalytic amounts of 4-dimethylaminopyridine (0-5 mol%, 0-0.0675 mmol based on the repeating unit of **1a**) were placed with a stir bar in a vial. In case of <23.1 equiv. of methanol THF was added as solvent (1 g). The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 5-60 minutes (hold time) at 100-180 °C and with a stirring of600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature. An aliquot of the clear solution was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.6 mL). The sample was subjected to ^{1}H NMR to determine the yield of methyl lactate (**2**) [The yield of **2** was calculated on the basis of the C*H* function of **2** and the leftover signals of the C*H* function of the polymer/oligomer.

Methyl lactate[1] (**2**): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 4.26$ (q, $J = 6.91$ Hz, 1H, CH_3CH), 3.76 (s, 3H, CH_3O-), 1.39 (d, $J = 6.91$ Hz, 3H, CH_3CH-) ppm.

Figure S1. a) Microwave Synthesis Reactor Monowave 400 (Anton Paar GmbH); b) reaction mixture before microwave heating; c) reaction mixture after microwave heating.

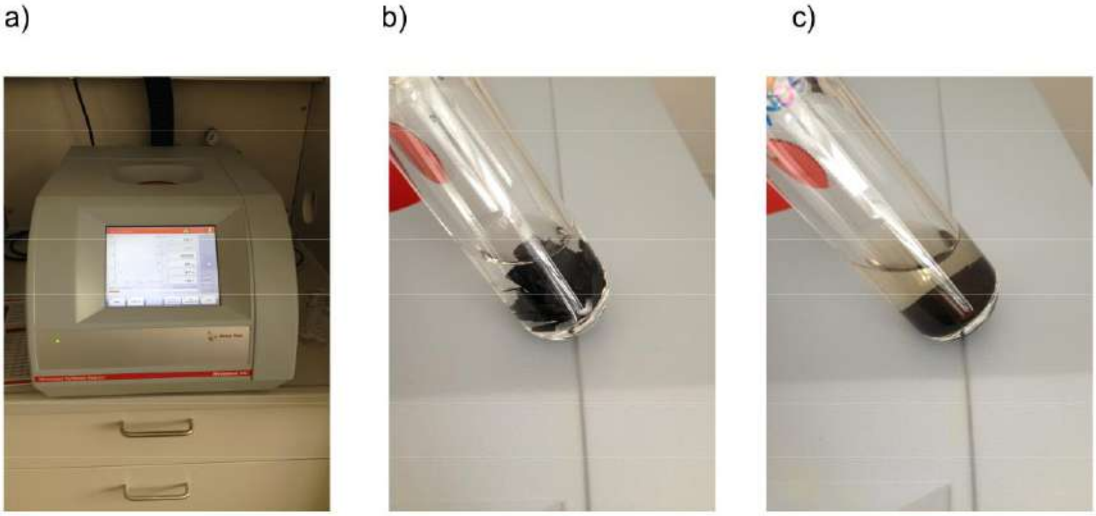
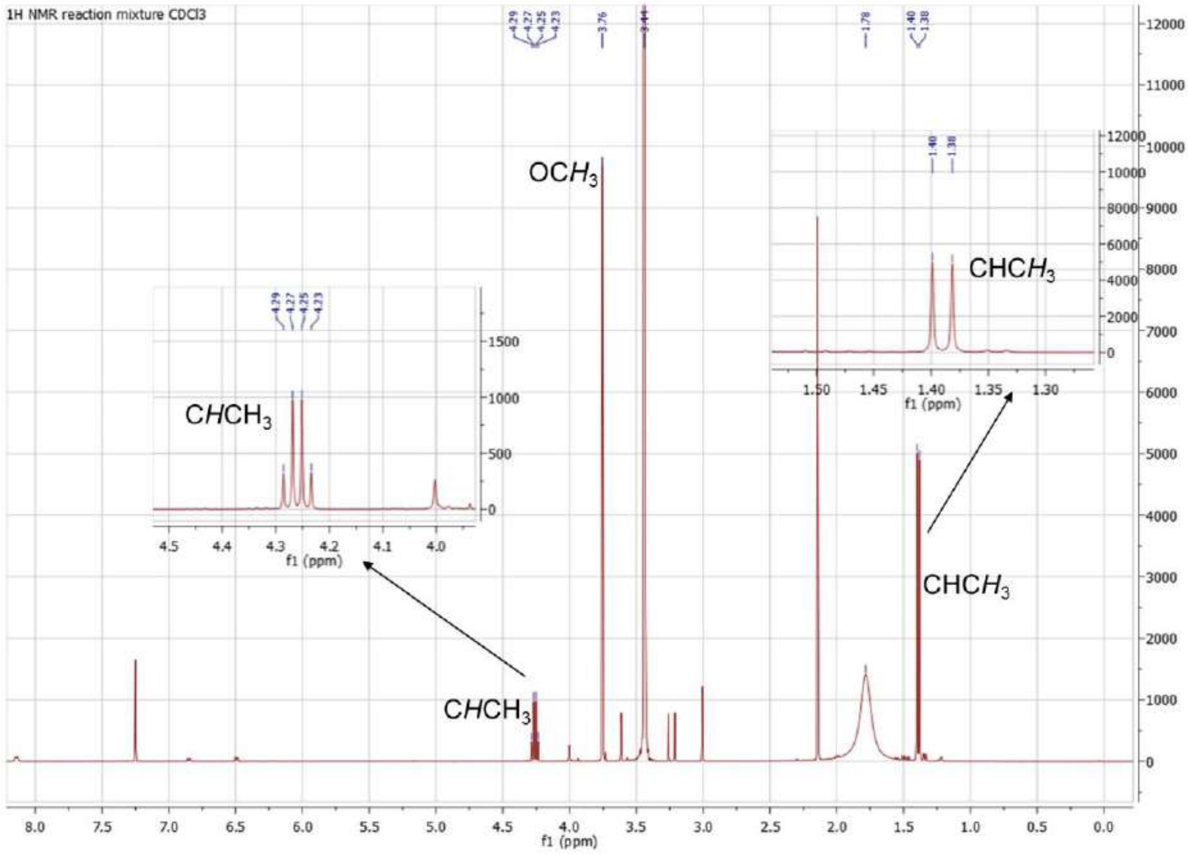


Figure S2. Spectrum of a reaction mixture (5 mol% DMAP, 23.1 equiv. MeOH, 180 °C, 10 min) (^{1}H NMR (400 MHz, CDCl$_3$, 25 °C)).



General procedure for the depolymerization of polylactide (1a): A mixture of polylactide-goods (**1a**) (583.2 mg, 8.1 mmol based on the repeating unit, for simplification we insinuate that the PLA-product is composed of 100% of PLA), methanol (6 g, 187.2 mmol, 23.1 equiv. based on the repeating unit of **1**), and catalytic amounts of 4-dimethylaminopyridine (49.2 mg, 5 mol%, 0.405 mmol based on the repeating unit of **1**) were placed with a stir bar in a vial. The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 20 minutes (hold time) at 180 °C and stirring with 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature. To remove insolubly compounds the mixture was passed through a funnel containing filter paper into a 50 mL flask. The flask was attached to distillation equipment. The receiving flask (50 mL) was cooled with liquid nitrogen. The volatile compounds (methanol, methyl lactate) were removed in vacuum and were collected in the receiving flask. Afterwards the receiving flask was attached to a rotary evaporator and the methanol was carefully removed in vacuum. The amount of the liquid residue was determined and an aliquot was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.6 mL).

Methyl lactate (**2**): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.26 (dq, *J* = 6.91 Hz, *J* = 5.20 Hz 1H, CH_3CH-), 3.76 (s, 3H, CH_3O-), 2.79 (d, *J* = 5.20 Hz, 1H, -CHO*H*), 1.39 (d, *J* = 6.91 Hz, 3H, CH_3CH-) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C): δ = 176.1, 66.7, 52.5, 20.4 ppm.

Figure S3. Spectrum of **2** (^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)).

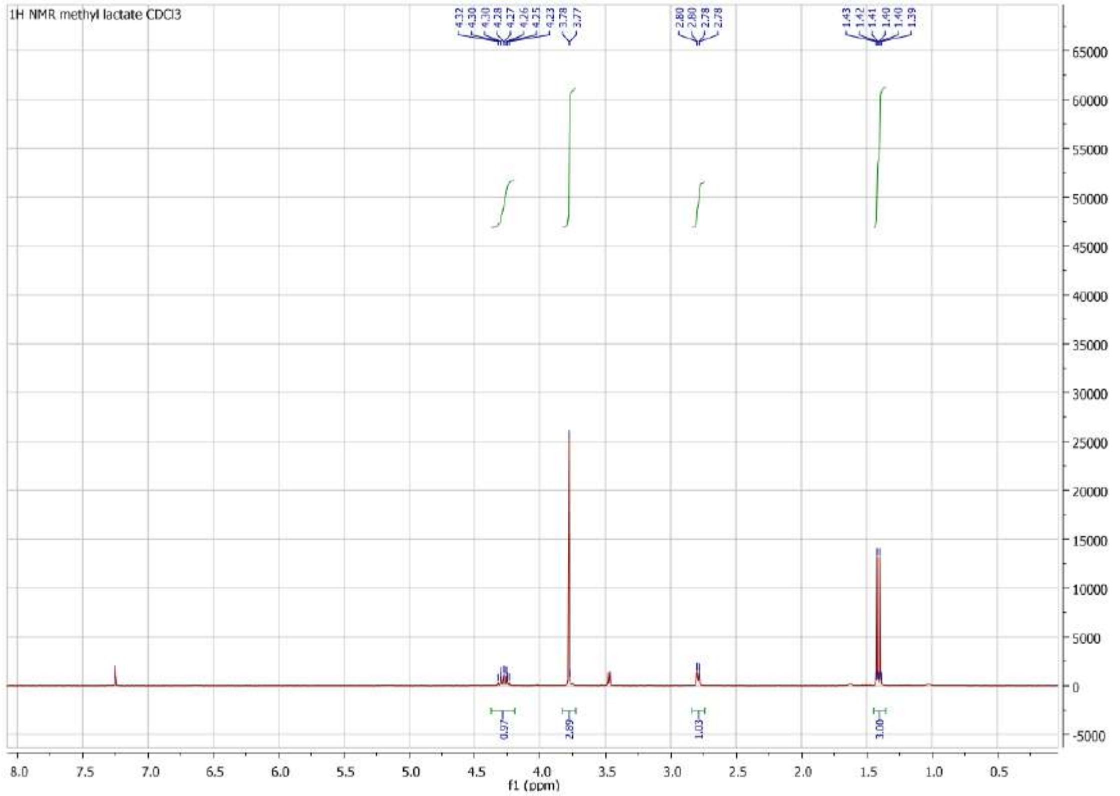


Figure S4. Spectrum of **2** ($^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C)).

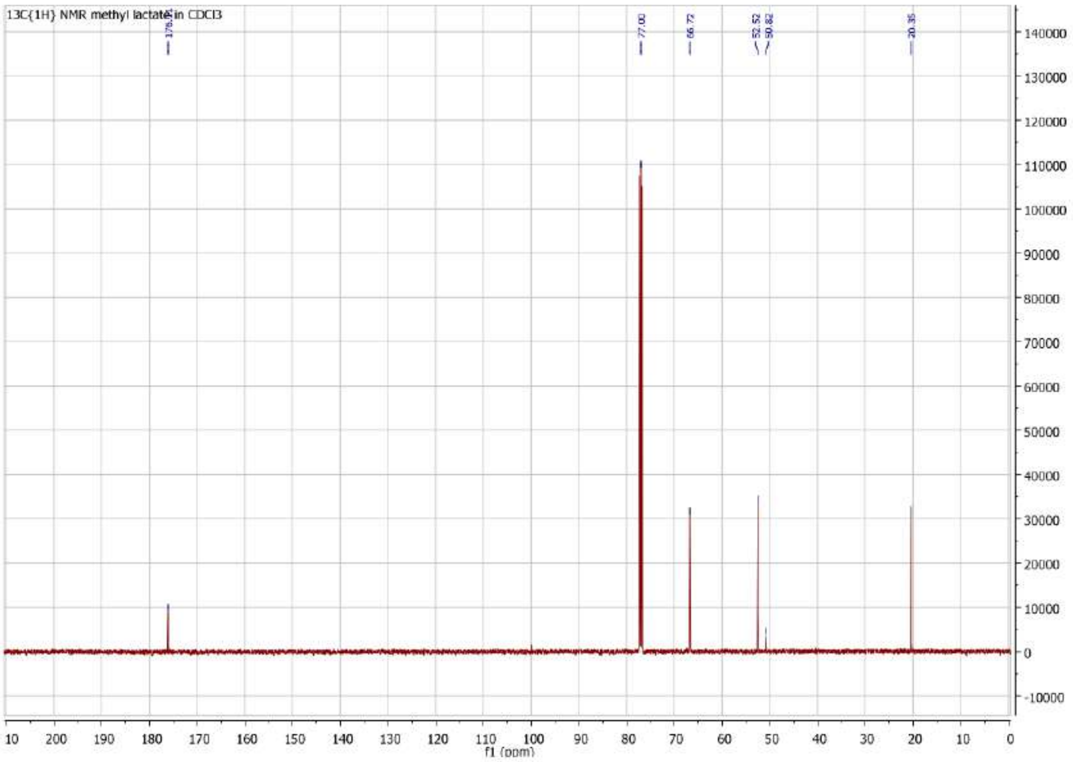
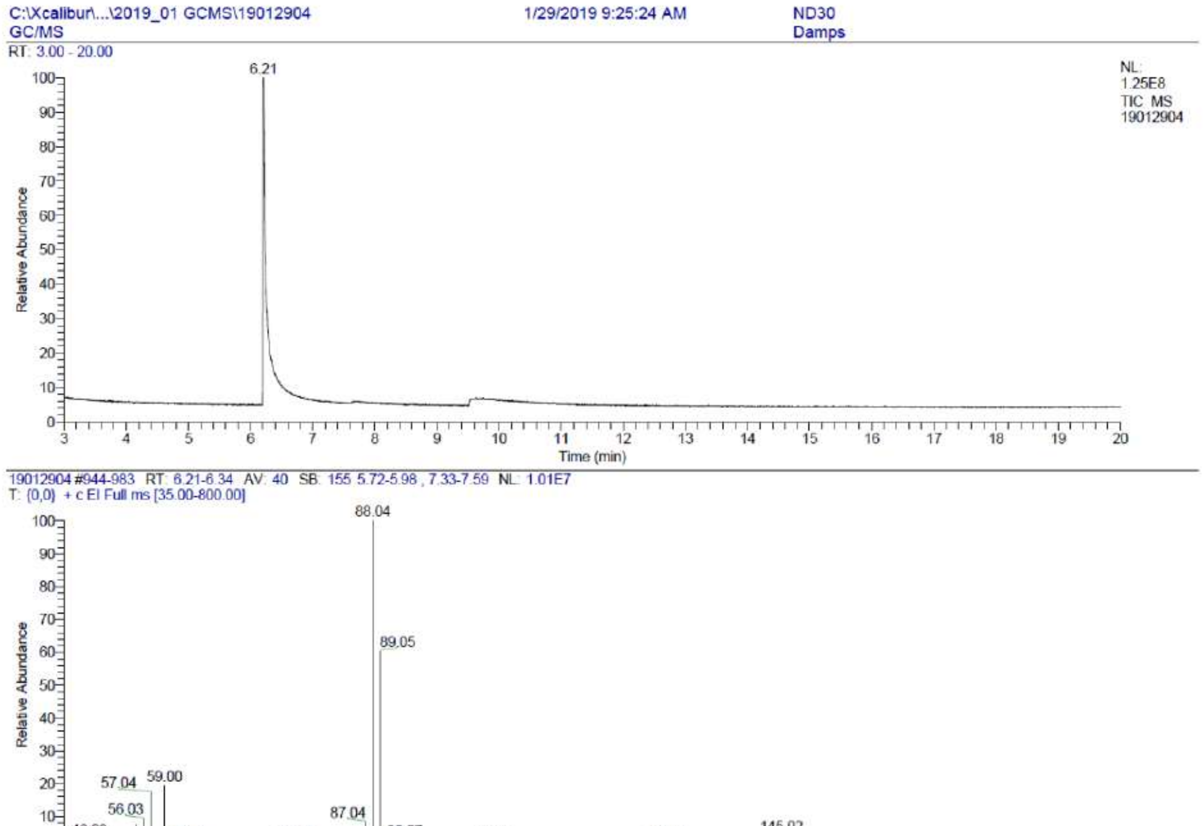


Figure S5. GC-MS spectrum of **2**.



General procedure for the depolymerization of polylactide-products (1): A mixture of polylactide-products (**1**) (583.2 mg, 8.1 mmol based on the repeating unit, for simplification we insinuated that the PLA-product is composed of 100% of PLA), methanol (6 g, 187.2 mmol, 23.1 equiv. based on the repeating unit of **1**), and catalytic amounts of 4-dimethylaminopyridine (49.2 mg, 5 mol%, 0.405 mmol based on the repeating unit of **1**) were placed with a stir bar in a vial. The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 20 minutes (hold time) at 180 °C with a stirring rate of 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature. To remove insolubly compounds the mixture was passed through a funnel containing filter paper into a 50 mL flask. The flask was attached to distillation equipment. The receiving flask (50 mL) was cooled with liquid nitrogen. The volatile compounds (methanol, methyl lactate) were removed in vacuum and were collected in the receiving flask. Afterwards the receiving flask was attached to a rotary evaporator and the methanol was carefully removed in vacuum. The amount of the liquid residue was determined and an aliquot was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.6 mL). The mass of isolated **2** was related to the mass of the starting PLA-product. The amount of substance of **2** was related to the amount of substance of the starting PLA-product insinuating that the PLA-product is composed of 100% of PLA.

The NMR spectra are in accordance to the NMR spectra obtained for depolymerization of **1a** (vide supra).

Table S1. Polylactide products (the PLA-products were obtained from Prodana GmbH and were used as received).

Entry	PLA-Product	Item number
1	transparent plastic cup (**1a**)	Huhtamaki
2	drinking straw with green strips (**1b**)	VSS05GS-Mu
3	lid for espresso mugs with talcum powder (~20-30%) (**1c**)	VLID62A1-Mu
4	transparent disposable food box (**1d**)	VHD08-Mu
5	red ice cream spoon (**1e**)	VSP3C-Mu
6	black lid for coffee mugs (**1f**)	VLID89SB-Mu
7	transparent cover of a disposable Sushi box (**1g**)	VSU02-Mu
8	black base of a disposable Sushi box (**1h**)	VSU02-Mu
9	blue disposable glove (**1i**)	VGLBS-Mu
10	disposable fork with talcum powder (**1j**)	VWKFSWN-Mu
11	transparent disposable serving cup (**1k**)	VWPP05-Mu
12	transparent plastic sheet (**1l**)	VGNSH2-Mu
13	coffee mug with PLA coating on the inside (**1m**)	VKV08-Mu
14	transparent bottle (**1n**)	NAFL250-Mu

Table S2. Appearance after depolymerzation reaction.

Entry	PLA-Product	Appearance
1	transparent plastic cup (**1a**)	Clear colorless solution
2	drinking straw with green strips (**1b**)	Green solution with precipitate
3	lid for espresso mugs with talcum powder (~20-30%) (**1c**)	Colorless solution with colorless precipitate
4	transparent disposable food box (**1d**)	Clear colorless solution
5	red ice cream spoon (**1e**)	Clear colorless solution with red precipitate
6	black lid for coffee mugs (**1f**)	Clear colorless solution with black precipitate
7	transparent cover of a disposable Sushi box (**1g**)	Clear colorless solution
8	black base of a disposable Sushi box (**1h**)	Clear colorless solution with black precipitate
9	blue disposable glove (**1i**)	Clear colorless solution with blue precipitate
10	disposable fork with talcum powder (**1j**)	Clear colorless solution with colorless precipitate
11	transparent disposable serving cup (**1k**)	Clear colorless solution with colorless precipitate
12	transparent plastic sheet (**1l**)	Clear colorless solution
13	coffee mug with PLA coating on the inside (**1m**)	Clear yellow solution and pieces of paper (shape unchanged). The inside surface of the

		pieces of paper changed from plain (before depolymerization) to rough (after depolymerization)
14	transparent bottle (**1n**)	Clear colorless solution

Table S3. Appearance after depolymerzation reaction – used PLA-products.

Entry	PLA-Product	Appearance
1	Yellow ice cream spoon (**1e**). Used for stirring a mixture of coffee, sugar and milk. The PLA-product was not cleaned before depolymerization.	Clear colorless solution with yellow precipitate
2	Black lid for coffee mugs (**1f**). Used with coffee, milk and sugar. The PLA-product was not cleaned before depolymerization.	Clear colorless solution with black precipitate

References

[1] a) M. Liu, J. Guo, Y. Gu, J. Gao, F. Liu, *ACS Sustainable Chem. Eng.* **2018**, *6*, 15127−15134; b) X. Y. Song, X. J. Zhang, H. Wang, F. S. Liu, S. T. Yu, S. W. Liu, *Polym. Degrad. Stab.* **2013**, *98*, 2760−2764.

ADVANCED
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SYSTEMS

Supporting Information

for *Adv. Sustainable Syst.,* DOI: 10.1002/adsu.201900081

Selective Degradation of End-of-Life Poly(lactide) via Alkali-Metal-Halide Catalysis

*Christoph Alberti, Nicole Damps, Roderich R. R. Meißner, Melanie Hofmann, Desiree Rijono, and Stephan Enthaler**

General: All chemicals were used as received without further manipulations. ^{1}H and ^{13}C{^{1}H}NMR spectra were recorded on a *Fourier 300 MHz* (^{1}H: 300 MHz, ^{13}C: 75 MHz) or *Avance I-400* (^{1}H: 400 MHz, ^{13}C: 101 MHz) by Bruker, using the proton signals of the deuterated solvents as reference or external standards. Mass spectrometry was performed using a *Thermo ISQ LT EI* by Thermo Fisher Scientific. For microwave heating experiments a Microwave Synthesis Reactor Monowave 400 (Anton Paar GmbH) was used. GC-MS was measured with Agilent Technologies 5977B GC/MSD. SEC analysis was performed using a "mixed bed" linear SEC-column (5 µm porous styrene-divinylbenzene particles, separation range 200-1000k g/mol) at a flow rate of 1 ml/min in tetrahydrofuran as eluent. Molecular weights refer to a so called relative calibration based on narrow polystyrene samples supplied by Agilent Technologies. The SEC system was equipped with a Shimadzu LC-10ATvP pump, an AS1000 autosampler from Thermo Separation Products and a RI2012 refractive index detector from Schambeck SFD GmbH. The specific rotation was measured with machine from Krüss Optronic Germany.

General procedure for the depolymerization of poly(lactide) (1a) (optimization of the reaction conditions): A mixture of poly(lactide) (**1a**, transparent plastic cup from Prodana GmbH) (97.2 mg, 1.35 mmol based on the repeating unit), methanol (0.043-1.00 g, 1.35-31.2 mmol, 1.0-23.1 equiv. based on the repeating unit of **1a**) and catalytic amounts of a alkali metal halide (0-5 mol%, 0-0.0675 mmol based on the repeating unit of **1a**) were placed with a stir bar in a vial. In case of <11.6 equiv. of methanol THF was added as solvent (1-2 g). The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 5-60 minutes (hold time) at 120-180 °C and stirring with 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature. An aliquot of the clear solution was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.6 mL). The sample was subjected to ^{1}H NMR to determine the yield of methyl lactate (**2**) [The yield of **2** was calculated on the basis of the C*H* function of **2** and the leftover signals of the C*H* function of the polymer/oligomer.

Methyl lactate[1] (**2**): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.26 (q, *J* = 6.91 Hz, 1H, CH_3CH), 3.76 (s, 3H, CH_3O-), 1.39 (d, *J* = 6.91 Hz, 3H, CH_3CH-) ppm. MS (EI) m/z = 104 (M^+).

Figure S1. Spectrum of a reaction mixture (5.0 mol% KF, 23.1 equiv. MeOH, 180 °C, 10 min) (^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)).

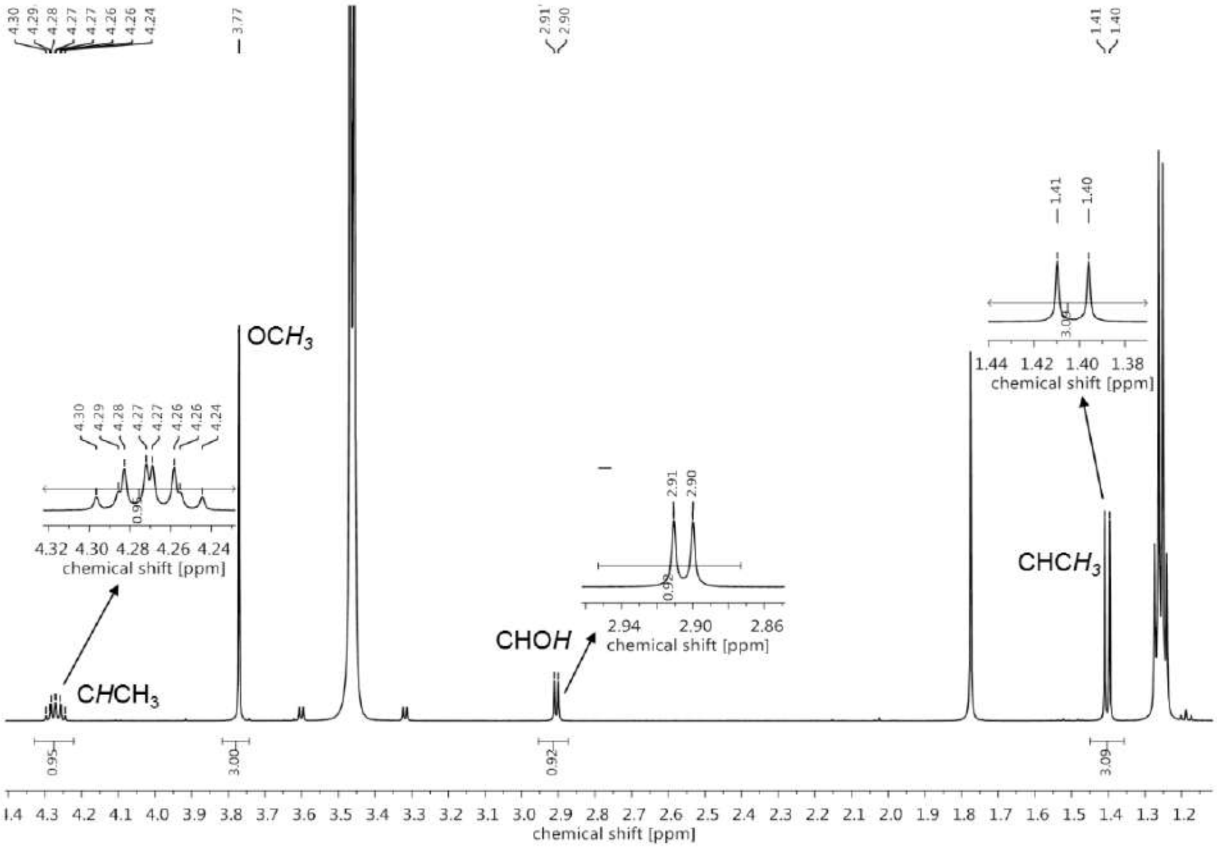


Figure S2. Spectrum of the PLA plastic cup (^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)).

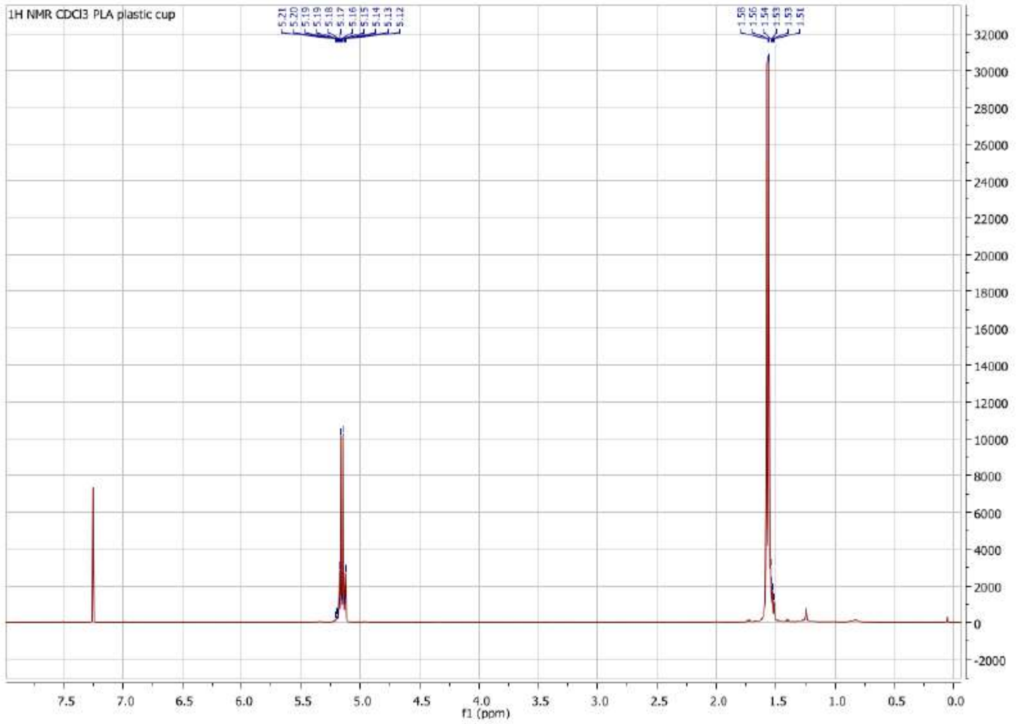
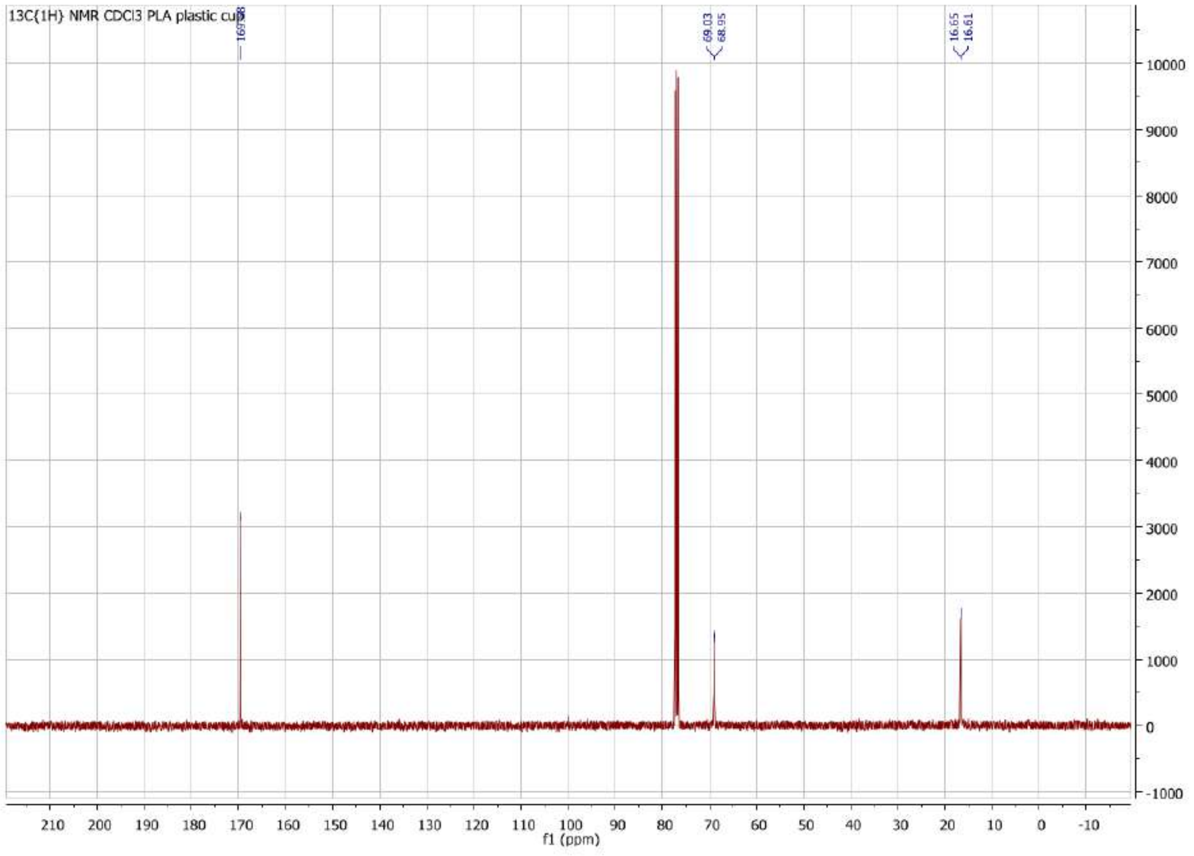


Figure S3. Spectrum of the PLA plastic cup ($^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, 25 °C)).



General procedure for the depolymerization of poly(lactide) (1a): A mixture of poly(lactide)-goods (**1a**) (583.2 mg, 8.1 mmol based on the repeating unit, for simplification we insinuate that the PLA-product is composed of 100% of PLA), methanol (6 g, 187.2 mmol, 23.1 equiv. based on the repeating unit of **1**), and catalytic amounts of potassium fluoride (12.0 mg, 2.5 mol%, 0.203 mmol based on the repeating unit of **1**) were placed with a stir bar in a vial. The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 20 minutes (hold time) at 180 °C and stirring with 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature and the reaction mixture was transferred to a flask (50 mL). The flask was attached to distillation equipment. The receiving flask (50 mL) was cooled with liquid nitrogen. The volatile compounds (methanol, methyl lactate) were removed in vacuum and were collected in the receiving flask. Afterwards the receiving flask was attached to a rotary evaporator and the methanol was carefully removed in vacuum. The amount of the liquid residue was determined and an aliquot was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.6 mL). The mass of isolated **2** was related to the mass of the starting PLA-product. The amount of substance of **2** was related to the amount of substance of the starting PLA-product insinuating that the PLA-product is composed of 100% of PLA.

Methyl lactate (**2**): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.27 (dq, J = 6.91 Hz, J = 5.20 Hz 1H, CH_3CH-), 3.77 (s, 3H, CH_3O-), 2.87 (br, 1H, -CHOH), 1.40 (d, J = 6.91 Hz, 3H, CH_3CH-) ppm. $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, 25 °C): δ = 176.1, 66.7, 52.5, 20.4 ppm.

Figure S4. Spectrum of **2** (^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)).

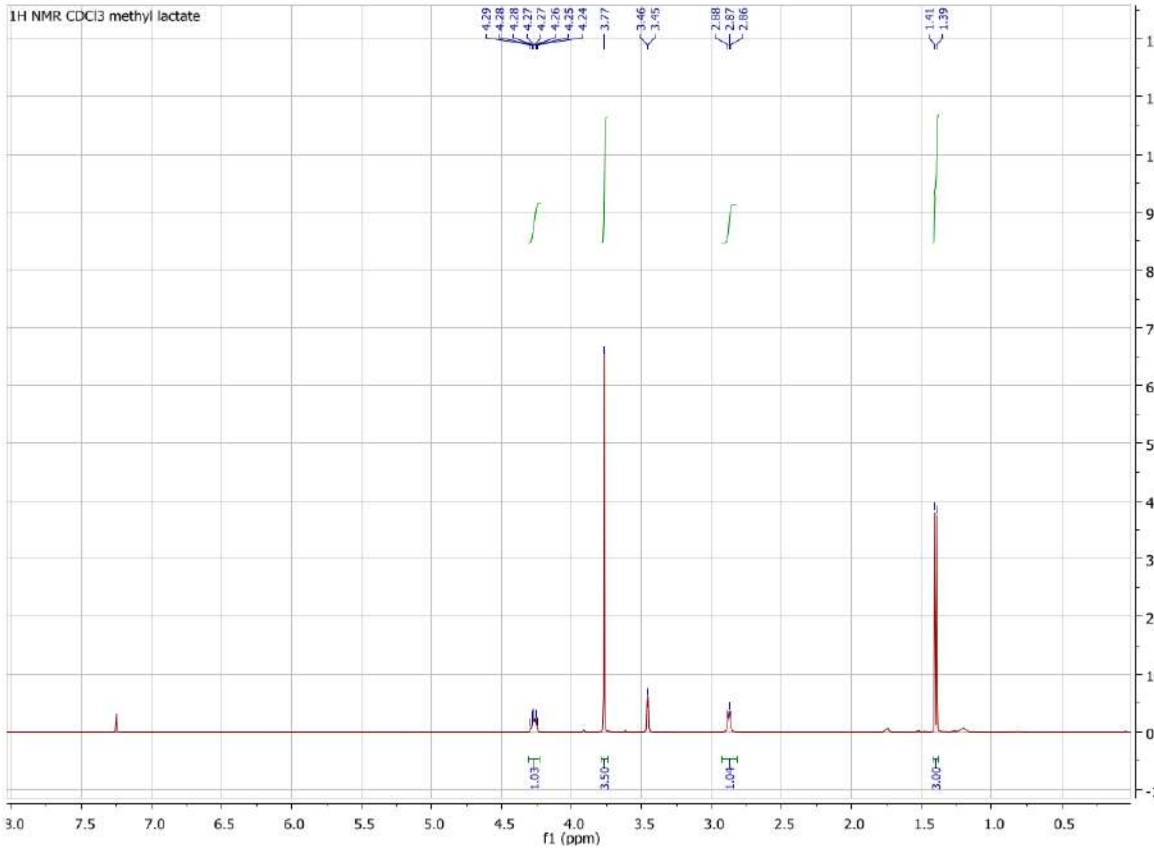


Figure S5. Spectrum of **2** ($^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, 25 °C)).

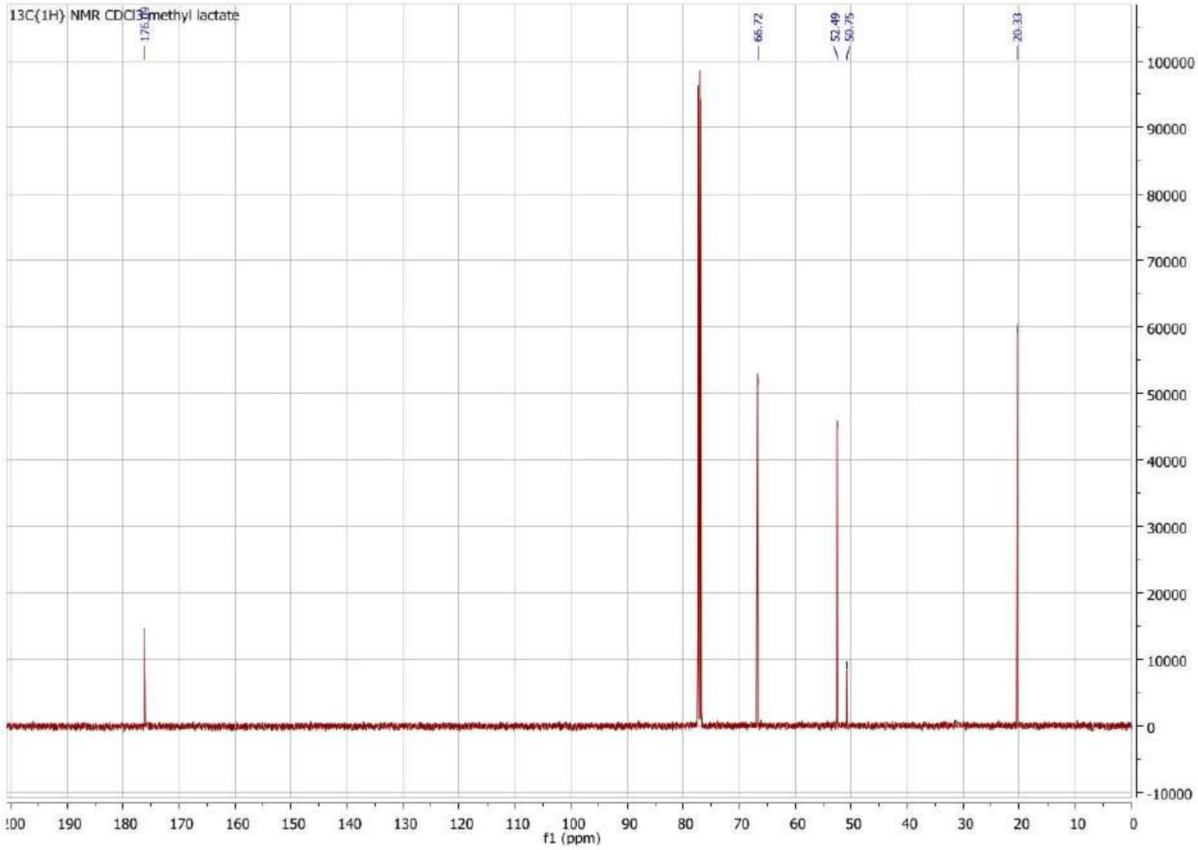
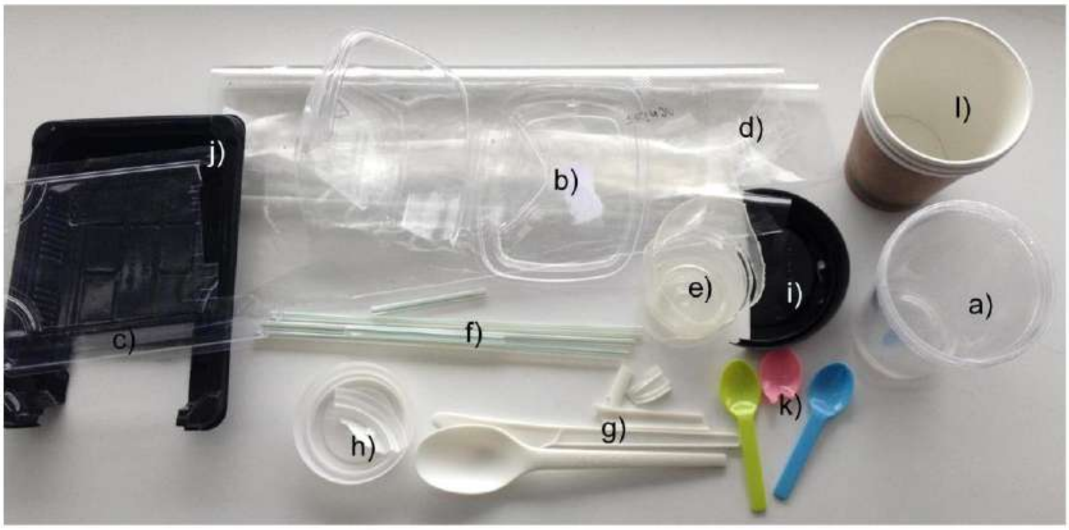


Table S1. polylactide products (the PLA-products were obtained from Prodana GmbH and were used as received).



Entry[a]	Product	item number
1	transparent plastic cup (**1a**)	Huhtamaki
2	transparent disposable food box (**1b**)	VHD08-Mu
3	transparent cover of a disposable Sushi box (**1c**)	VSU02-Mu
4	transparent plastic sheet (**1d**)	VGNSH2-Mu
5	transparent bottle (**1e**)	NAFL250-Mu
6	drinking straw with green strips (**1f**)	VSS05GS-Mu
7	disposable fork with talcum powder (**1g**)	VWKFSWN-Mu
8	lid for espresso mugs with talcum powder (~20-30%) (**1h**)	VLID62A1-Mu
9	black lid for coffee mugs (**1i**)	VLID89SB-Mu
10	used black lid for coffee mugs (**1i**)	VLID89SB-Mu
11	black base of a disposable Sushi box (**1j**)	VSU02-Mu
12	pink ice cream spoon (**1k**)	VSP3C-Mu
13	used yellow ice cream spoon (**1k**)	VSP3C-Mu
14	coffee mug with PLA coating on the inside (**1l**)	VKV08-Mu

Table S2. Appearance after depolymerzation reaction.

Entry	PLA-Product	Appearance
1	transparent plastic cup (**1a**)	clear colorless solution
2	transparent disposable food box (**1b**)	clear colorless solution
3	transparent cover of a disposable Sushi box (**1c**)	clear colorless solution
4	transparent plastic sheet (**1d**)	clear colorless solution
5	transparent bottle (**1e**)	clear colorless solution
6	drinking straw with green strips (**1f**)	green solution with precipitate
7	disposable fork with talcum powder (**1g**)	clear colorless solution with colorless precipitate
8	lid for espresso mugs with talcum powder (~20-30%) (**1h**)	colorless solution with colorless precipitate
9	black lid for coffee mugs (**1i**)	clear colorless solution with black precipitate
11	black base of a disposable Sushi box (**1j**)	clear colorless solution with black precipitate
12	pink ice cream spoon (**1k**)	Clear colorless solution with pink precipitate
14	coffee mug with PLA coating on the inside (**1l**)	clear yellow solution and pieces of paper (shape unchanged). The inside surface of the pieces of paper changed from plain (before depolymerization) to rough (after depolymerization)

Table S3. Specific rotation of PLA goods (path length = 0.5 dm).

Entry	PLA-Product
1	transparent plastic cup (**1a**) $[\alpha]_D$ = -150.1° mL/(dm*g) 23.6 °C, 42.6 mg/4 mL ($CHCl_3$)[2]
2	transparent disposable food box (**1b**) $[\alpha]_D$ = -89.6° mL/(dm*g) 24.4 °C, 47.4 mg/4 mL ($CHCl_3$)
3	transparent cover of a disposable $[\alpha]_D$ = -140.1° mL/(dm*g) 24.4 °C, 43.1 mg/4 mL ($CHCl_3$)e Sushi box (**1c**)
4	transparent plastic sheet (**1d**) $[\alpha]_D$ = -144.3° mL/(dm*g) 24.5 °C, 26.0 mg/4 mL ($CHCl_3$)
5	transparent bottle (**1e**) $[\alpha]_D$ = -90.3° mL/(dm*g) 24.4 °C, 44.3 mg/4 mL ($CHCl_3$)
6	drinking straw with green strips (**1f**)
7	disposable fork with talcum powder (**1g**)
8	lid for espresso mugs with talcum powder (~20-30%) (**1h**)
9	black lid for coffee mugs (**1i**)
11	black base of a disposable Sushi box (**1j**)
12	pink ice cream spoon (**1k**)
14	coffee mug with PLA coating on the inside (**1l**)

Table S4. Appearance after depolymerzation reaction – used PLA-products.

Entry	PLA-Product	Appearance
1	Yellow ice cream spoon (**1k**). Used for stirring a mixture of coffee, sugar and milk. The PLA-product was not cleaned before depolymerization.	clear colorless solution with yellow precipitate
2	Black lid for coffee mugs (**1i**). Used with coffee, milk and sugar. The PLA-product was not cleaned before depolymerization.	clear colorless solution with black precipitate

General procedure for the depolymerization of poly(lactide) (1a) – catalyst recycling: A mixture of poly(lactide) (**1a**) (583.2 mg, 8.1 mmol based on the repeating unit, for simplification we insinuate that the PLA-product is composed of 100% of PLA), methanol (6 g, 187.2 mmol, 23.1 equiv. based on the repeating unit of **1**), and catalytic amounts of potassium fluoride (12.0 mg, 2.5 mol%, 0.203 mmol based on the repeating unit of **1**) were placed with a stir bar in a vial. The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 20 minutes (hold time) at 180 °C and stirring with 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature. An aliquot of the clear solution was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.6 mL). The sample was subjected to ^1H NMR to determine the yield of methyl lactate (**2**) [The yield of **2** was calculated on the basis of the C*H* function of **2** and the leftover signals of the C*H* function of the polymer/oligomer. The reaction mixture was transferred to a flask (50 mL). The flask was attached to distillation equipment. The receiving flask (50 mL) was cooled with liquid nitrogen. The volatile compounds (methanol, methyl lactate) were removed in vacuum and were collected in the receiving flask. The residue of the reaction mixture was dissolved in methanol (6 g) and was transferred to a vial, which contains a new portion of PLA. The run was performed in accordance. 5 runs have been performed.

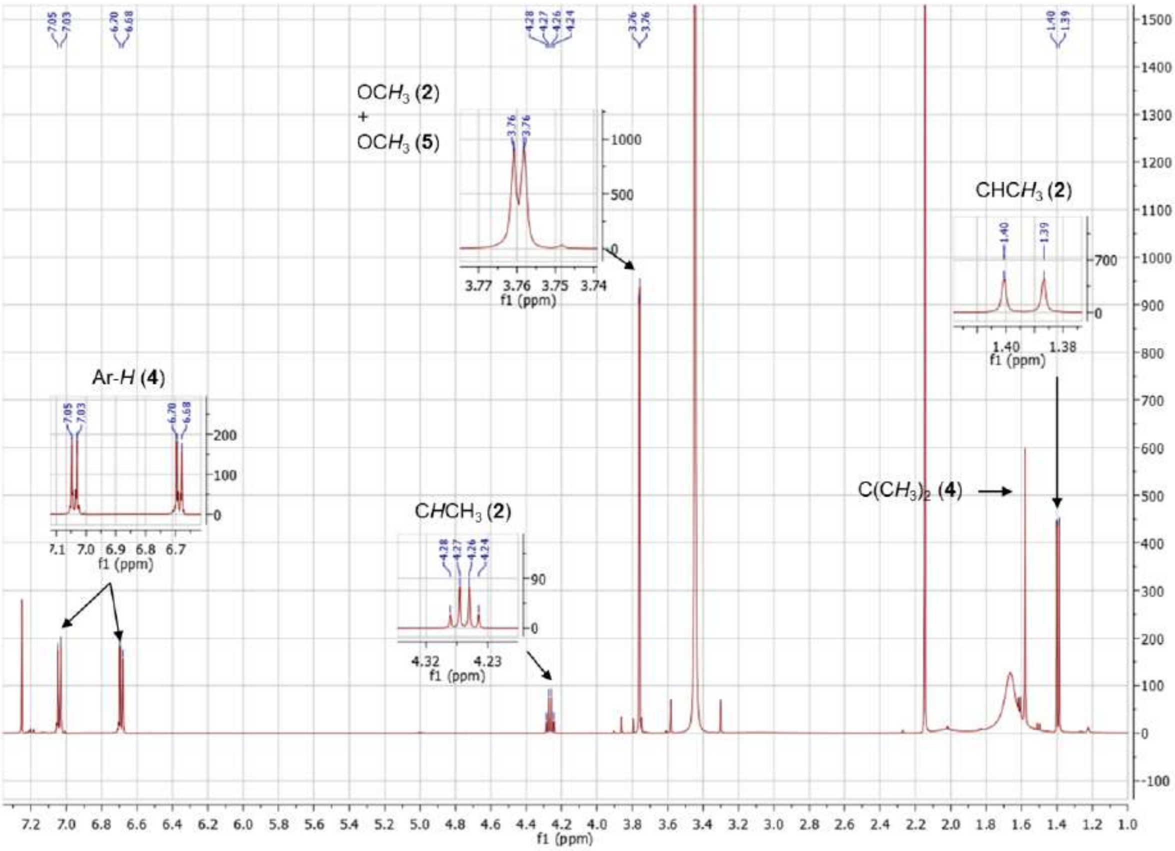
Procedure for the depolymerization of poly(lactide) (1a) using a 160 mL autoclave: A mixture of poly(lactide) (**1a**, transparent plastic cup from Prodana GmbH) (7.40 g, 102.7 mmol based on the repeating unit), methanol (79.0 g, 2.47 mol, 24.0 equiv. based on the repeating unit of **1a**) and potassium fluoride (298 mg, 5.13 mmol, 5 mol% based on the repeating unit of **1a**) was placed in an autoclave. Within 30 minutes the reaction mixture was heated to 140 °C and stirred for 60 minutes at this temperature. Afterwards the mixture was cooled to room temperature and methanol was removed under reduced pressure. The residue was distilled in vacuum at 60 °C to yield methyl lactate **2** (8.63 g, 82.9 mmol, 81% based on the repeating unit of **1a**) as a colorless liquid. The NMR spectra are in accordance to the data of **2** (*vide supra*). The optical rotation was measured: $[\alpha]_D$ = -7.5° (neat) 23.0 °C (literature[3]: $[\alpha]_D$ = -8.1° (neat) 18.0 °C), which corresponds to 93%ee of (-)-methyl L-lacate.

General procedure for the depolymerization of poly(lactide) (1a) – time yield plot: A mixture of poly(lactide) (**1a**) (583.2 mg, 8.1 mmol based on the repeating unit, for simplification we insinuate that the PLA-product is composed of 100% of PLA), methanol (6 g, 187.2 mmol, 23.1 equiv. based on the repeating unit of **1**), and catalytic amounts of potassium fluoride (12.0 mg, 2.5 mol%, 0.203 mmol based on the repeating unit of **1**) were placed with a stir bar in a vial. The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed 10 times at 140 °C and stirring with 600 rpm and was stopped after different reaction times. Afterwards the vial was cooled to room temperature. An aliquot of the clear solution was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.6 mL). The sample was subjected to ^1H NMR to determine the yield of methyl lactate (**2**) [The yield of **2** was calculated on the basis of the C*H* function of **2** and the leftover signals of the C*H* function of the polymer/oligomer.

General procedure for the depolymerization of poly(lactide) (1a) and poly(bisphenol A carbonate) (3): A mixture of poly(lactide) (**1a**, transparent plastic cup from Prodana GmbH) (388.8 mg, 5.4 mmol based on the repeating unit), poly(bisphenol A carbonate) (**3**) (688 mg, 2.7 mmol based on the repeating unit, obtained from Sigma Aldrich), methanol (4.0 g, 124.9 mmol, 23.1 equiv. with respect to the repeating unit of **1a**, 46.3 equiv. with respect to the repeating unit of **3**) and catalytic amounts of potassium fluoride (7.9 mg, 0.135 mmol, 2.5

mol% with respect to the repeating unit of **1a**, 5.0 mol% with respect to the repeating unit of **3**) were placed with a stir bar in a vial. The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 20 minutes (hold time) at 160 °C and stirring with 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature. An aliquot of the clear solution was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.6 mL). The sample was subjected to ^1H NMR to determine the yield of methyl lactate (**2**) [The yield of **2** was calculated on the basis of the C*H* function of **2** and the leftover signals of the C*H* function of the polymer/oligomer. [The yield of **4** was calculated on the basis of the Ar-H or $C(CH_3)_2$ and the Ar-H or $C(CH_3)_2$ leftover signals of the polymer/oligomer. The yield of **5** was not calculated, because of overlap with the signal of OCH_3 of **2**.]

Figure S6. Spectrum of the reaction mixture of depolymerization of **1a** and **3** (^1H NMR (400 MHz, $CDCl_3$, 25 °C)).



Afterwards the reaction mixture was transferred to a flask (50 mL). The flask was attached to distillation equipment. The receiving flask (50 mL) was cooled with liquid nitrogen. The volatile compounds (methanol, methyl lactate, dimethyl carbonate) were removed in vacuum and were collected in the receiving flask. The oily residue was recrystallized from chloroform yielding colorless crystals of bisphenol A (m = 434.2 mg, yield = 70%). Later the receiving flask was attached to distillation equipment and methanol and dimethyl carbonate were distilled off (due to formation of an azeotrope the mixture of methanol and dimethyl carbonate was not separated) (m = 3.41 g, containing 2% of dimethyl carbonate). On the other hand, the distillation leftover was isolated, yielding m = 511.3 mg, yield 91% of methyl lactate (NMR data in accordance to earlier parts of the study).

Bisphenol A[4] (**2**): ^{1}H NMR (400 MHz, acetone-d_6, 25 °C): δ = 8.08 (s, br, -O*H*), 7.03-7.06 (m, 4H, Ar-*H*), 6.71-6.74 (m, 4H, Ar-*H*), 1.58 (s, 6H, $(CH_3)_2C$-) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, acetone-d6, 25 °C): δ = 155.9, 142.8, 128.4, 115.4, 42.0, 31.5 ppm.

Dimethyl carbonate[5] (**3**): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.76 (s, 6H, $(CH_3O)_2C{=}O$) ppm.

Figure S7. Spectrum of **4** (^{1}H NMR (400 MHz, acetone-d_6, 25 °C)).

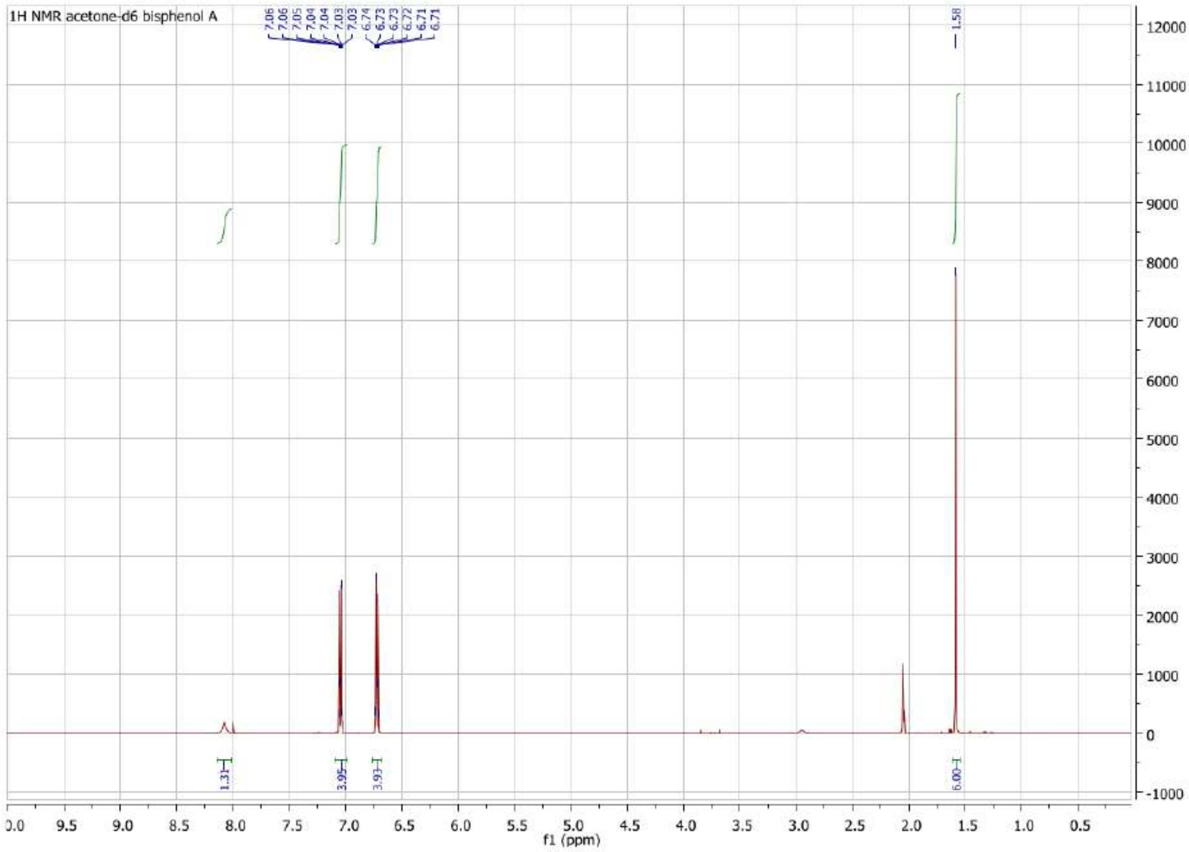


Figure S8. Spectrum of **4** (^{13}C{^{1}H} NMR (125 MHz, acetone-d_6, 25 °C)).

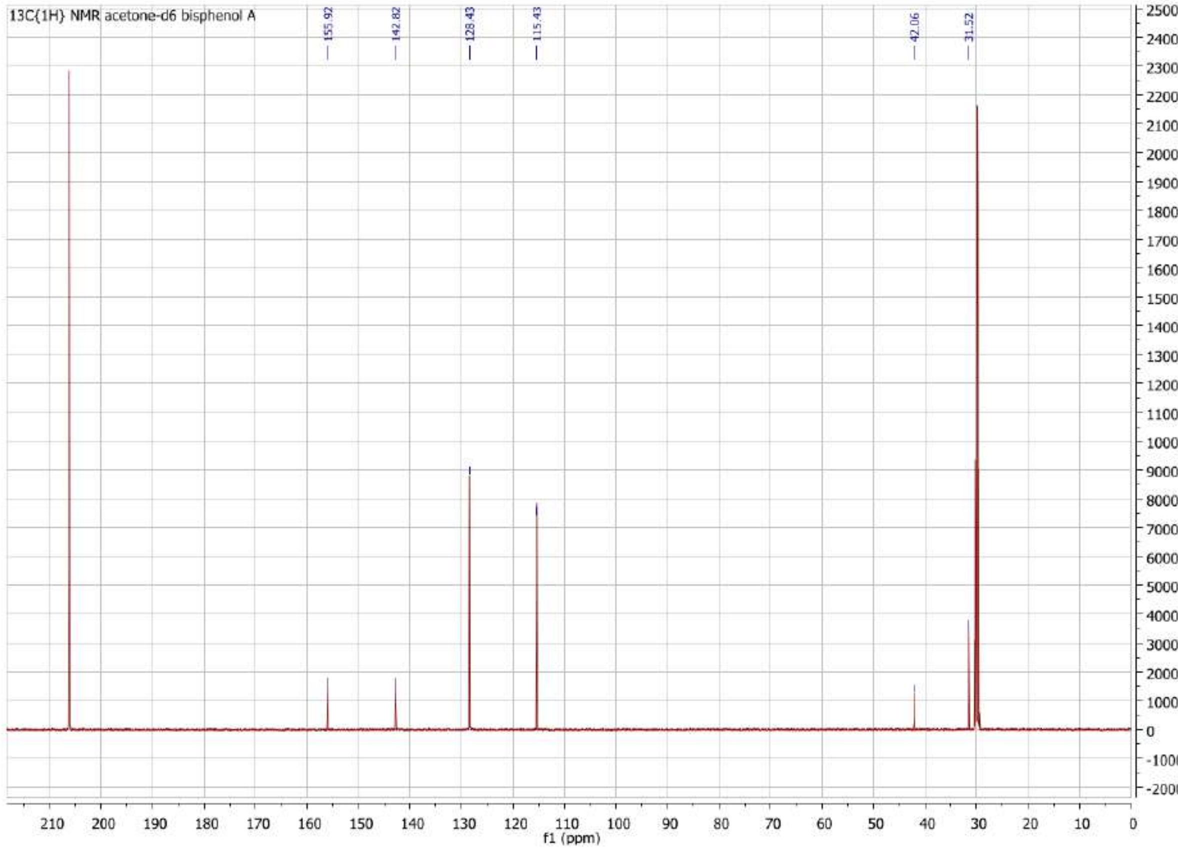
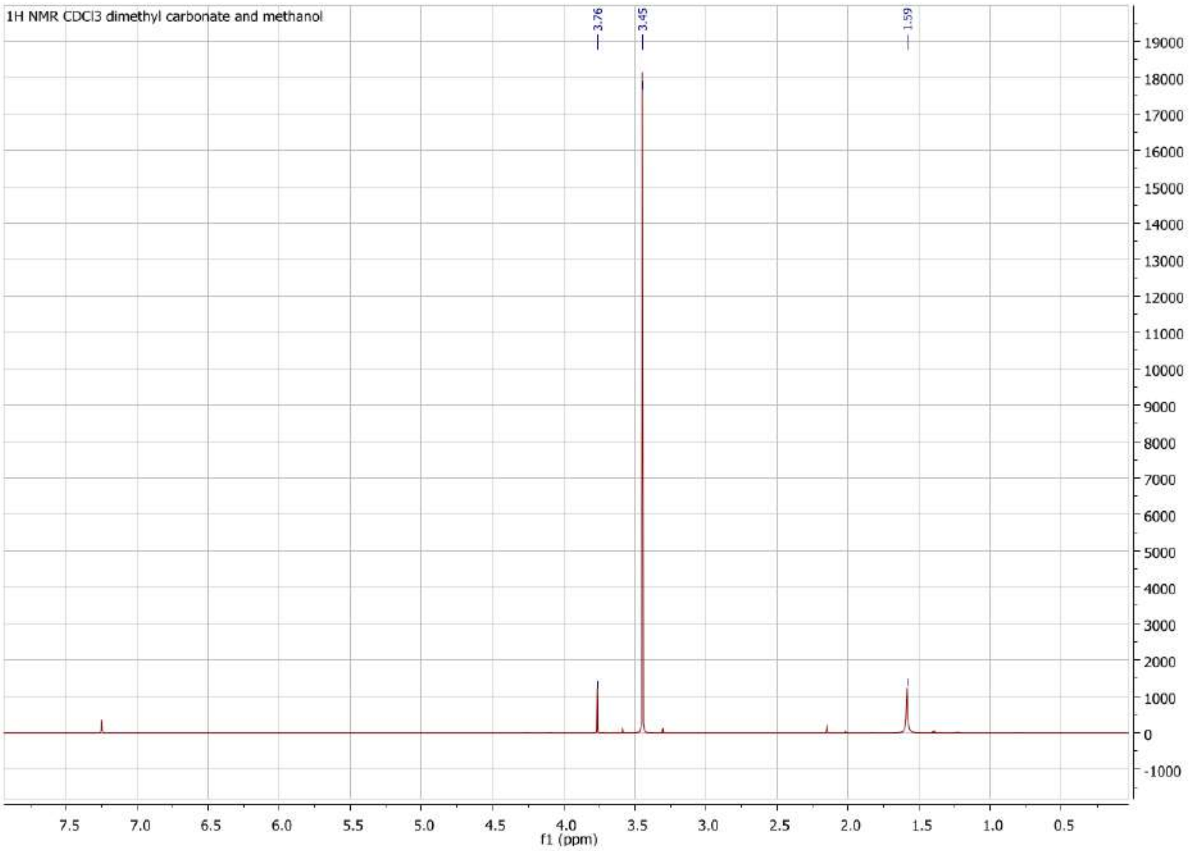


Figure S9. Spectrum of dimethyl carbonate and methanol (^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)).



General procedure for the depolymerization of poly(lactide) (1a) and poly(ethylene terephthalate) (6): Experiment was carried out in accordance to the experiment using **3**, using **6** instead of **3**. After depolymerization process a suspension was obtained. The methyl lactate and methanol were distilled off in vacuum. In the residue no dimethyl phthalate or ethylene glycol was detected.

General procedure for the depolymerization of poly(lactide) (1a) and nylon 6 (7): Experiment was carried out in accordance to the experiment using **3**, using **7** instead of **3**. After depolymerization process a suspension was obtained. The methyl lactate and methanol were distilled off in vacuum. In the residue no methyl 6-aminohexanoate was detected.

References

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[1] a) M. Liu, J. Guo, Y. Gu, J. Gao, F. Liu, *ACS Sustainable Chem. Eng.* **2018**, *6*, 15127−15134; b) X. Y. Song, X. J. Zhang, H. Wang, F. S. Liu, S. T. Yu, S. W. Liu, *Polym. Degrad. Stab.* **2013**, *98*, 2760−2764.

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[2] In accordance to the specific rotation of PLLA (Sigma Aldrich) we assume that the PLA of the PLA plastic cup is PLLA.

[3] a) Charles Edmund Wood, John Edward Such, Frank Scarf**,** *J. Chem. Soc., Trans.* **1923**, *123*, 600-616; b) See Sigma Aldrich.

[4] S. Kiran, N. R. James, R. Joseph, A. Jayakrishnan, *Biomaterials* **2009**, *30*, 5552-5559.

[5] C. L. Campion, W. Li, B. L. Lucht, *J. Electrochem. Soc.* **2005**, *152*, A2327-A2334.

ChemistrySelect

Supporting Information

Application of Bismuth Catalysts for the Methanolysis of End-of-Life Poly(lactide)

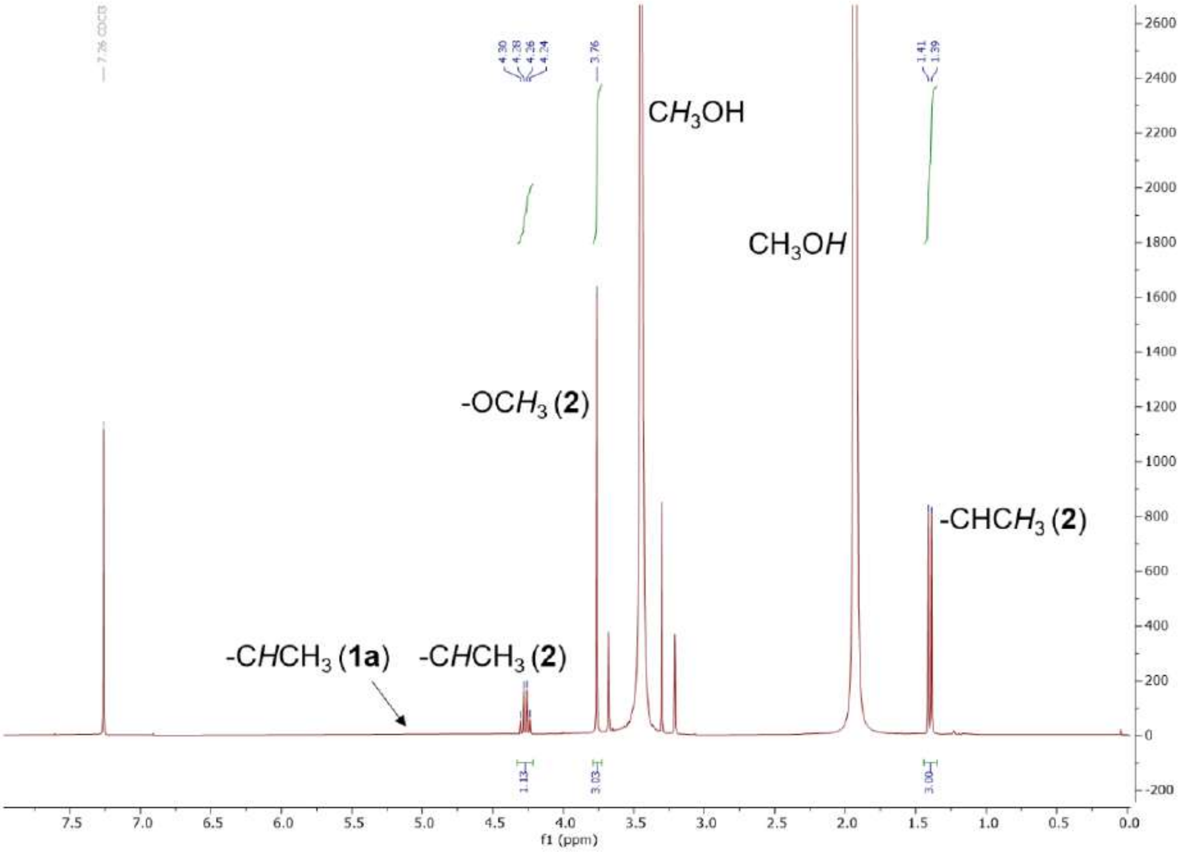
Christoph Alberti, Hans Rytger Kricheldorf, and Stephan Enthaler*

General: All chemicals were used as received without further manipulations. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a *Fourier 300 MHz* (^{1}H: 300 MHz, ^{13}C: 75 MHz), *Avance I-400* (^{1}H: 400 MHz, ^{13}C: 101 MHz) or *Avance I 500* (^{1}H: 500 MHz, ^{13}C: 126 MHz) by Bruker, using the signals of the deuterated solvents as reference or external standards. Mass spectrometry was performed using a *Thermo ISQ LT EI* by Thermo Fisher Scientific. For microwave heating experiments a Microwave Synthesis Reactor Monowave 400 (Anton Paar GmbH) was used.

General procedure for the depolymerization of polylactide (1a) (optimization of the reaction conditions): A mixture of polylactide (**1a**, end-of-life transparent plastic cups) (200 mg, 2.78 mmol based on the repeating unit), methanol (4.4-6.0 g, 138.7-187.3 mmol, 50.0-67.5 equiv. equiv. based on the repeating unit of **1a**) and catalytic amounts of bismuth salts (0-1.0 mol%, 0-0.0278 mmol based on the repeating unit of **1a**) was placed with a stir bar in a vial. The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 1-10 minutes (hold time) at 120-180 °C and with a stirring of 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature. An aliquot of the solution was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^{1}H NMR to determine the yield of methyl lactate (**2**) [The yield of **2** was calculated on the basis of the C*H* function of **2** and the leftover signals of the C*H* function of the polymer/oligomers; yield (**2**) = area (CH-**2**)/(area(CH-**2**)+area(CH-**1a**))*100].

Methyl lactate[1] (**2**): ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 4.27 (pseudo-q, J = 6.91 Hz, 1H, CH_3CH-, the coupling to the OH-function was not observed), 3.76 (s, 3H, CH_3O-), 1.40 (d, J = 6.91 Hz, 3H, CH_3CH-) ppm.

Figure S1. Spectrum of a reaction mixture (1.0 mol% $Bi(OTf)_3$, MeOH, 160 °C, 10 min) (^1H NMR (500 MHz, $CDCl_3$, 25 °C)).



General procedure for the depolymerization of polylactide goods (1): A mixture of polylactide (**1**) (200 mg, 2.78 mmol based on the repeating unit, based on the idealized assumption that the good contains 100% PLA), methanol (6.0 g, 187.3 mmol, 67.5 equiv. equiv. based on the repeating unit of **1**) and catalytic amounts of bismuth subsalicylate (1.0 mol%, 0.0278 mmol based on the repeating unit of **1**) was placed with a stir bar in a vial. The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 10 minutes (hold time) at 160 °C and with a stirring of 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature. An aliquot of the solution was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^1H NMR to determine the yield of methyl lactate (**2**) [The yield of **2** was calculated on the basis of the *CH* function of **2** and the leftover signals of the *CH* function of the polymer/oligomers].

Procedure for the depolymerization of polylactide (1a) – catalyst recycling: A mixture of polylactide (**1**) (200 mg, 2.78 mmol based on the repeating unit, based on the idealized assumption that the good contains 100% PLA), methanol (6.0 g, 187.3 mmol, 67.5 equiv. equiv. based on the repeating unit of **1**) and catalytic amounts of bismuth subsalicylate (0.25 mol% or 1.0 mol%, 0.00695 mmol or 0.0278 mmol based on the repeating unit of **1**) was placed with a stir bar in a vial. The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 10 minutes (hold time) at 160 °C and with a stirring of 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature. An aliquot of the solution was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^1H NMR to determine the yield of methyl lactate (**2**) [The yield of **2** was calculated on the basis of the C*H* function of **2** and the leftover signals of the C*H* function of the polymer/oligomers]. The liquid part of the reaction mixture was removed by syringe filter and was collected. The solid residue was washed with methanol and filtered again. New PLA and methanol were added to the catalyst into the vial and the reaction was started. The stated procedure was carried out five times in total. The collected solutions of the product were combined and the methanol was carefully removed in vacuum to obtain a colorless liquid (73%, m = 1.42 g, n = 10.15 mmol).

Methyl lactate (**2**): ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.28 (pseudo-q, J = 6.90 Hz, 1H, CH_3CH-, the coupling to the OH-function was not observed), 3.78 (s, 3H, CH_3O-, the coupling to the CH_3CH-function was not observed), 2.82 (br, 1H, -CHO*H*), 1.41 (d, J = 6.90 Hz, 3H, CH_3CH-) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25 °C): δ = 176.3, 66.1, 52.6, 20.5 ppm.

Figure S2. Spectrum of **2** (^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)).

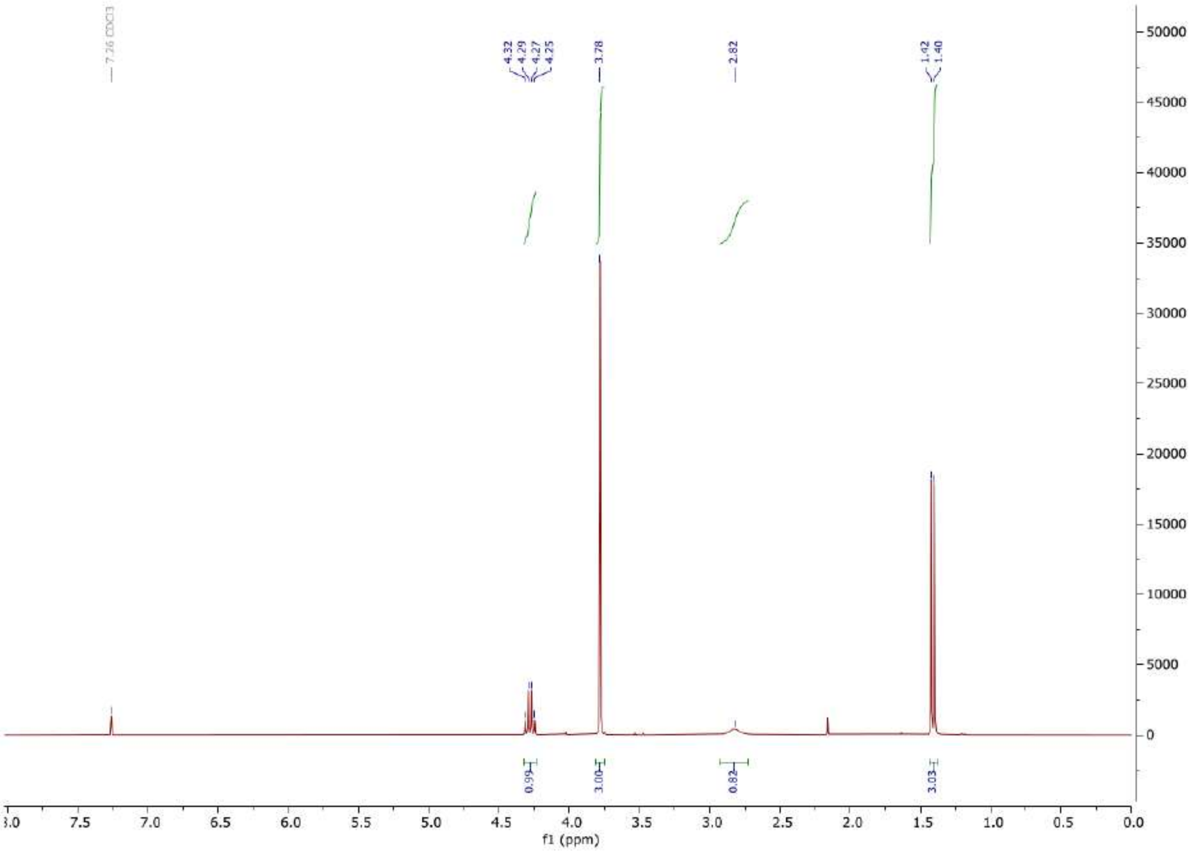
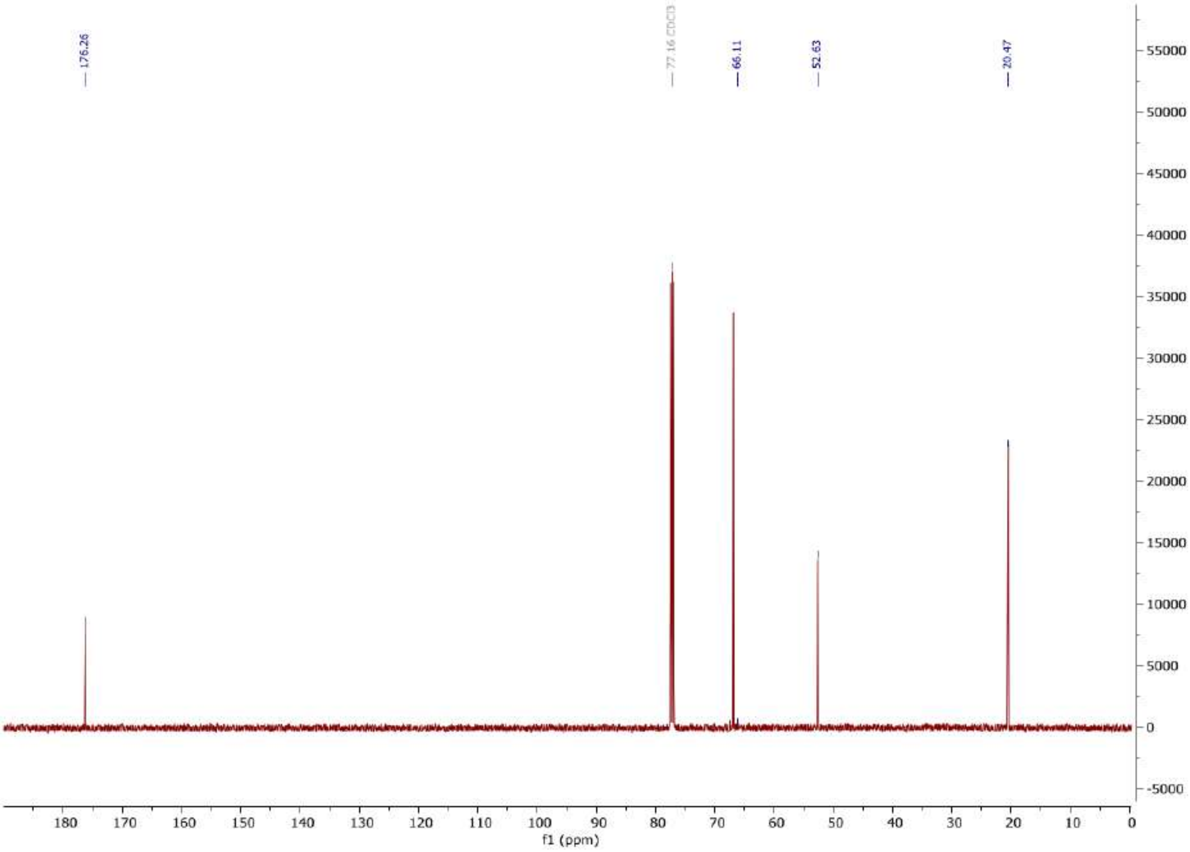


Figure S3. Spectrum of **2** ($^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25 °C)).



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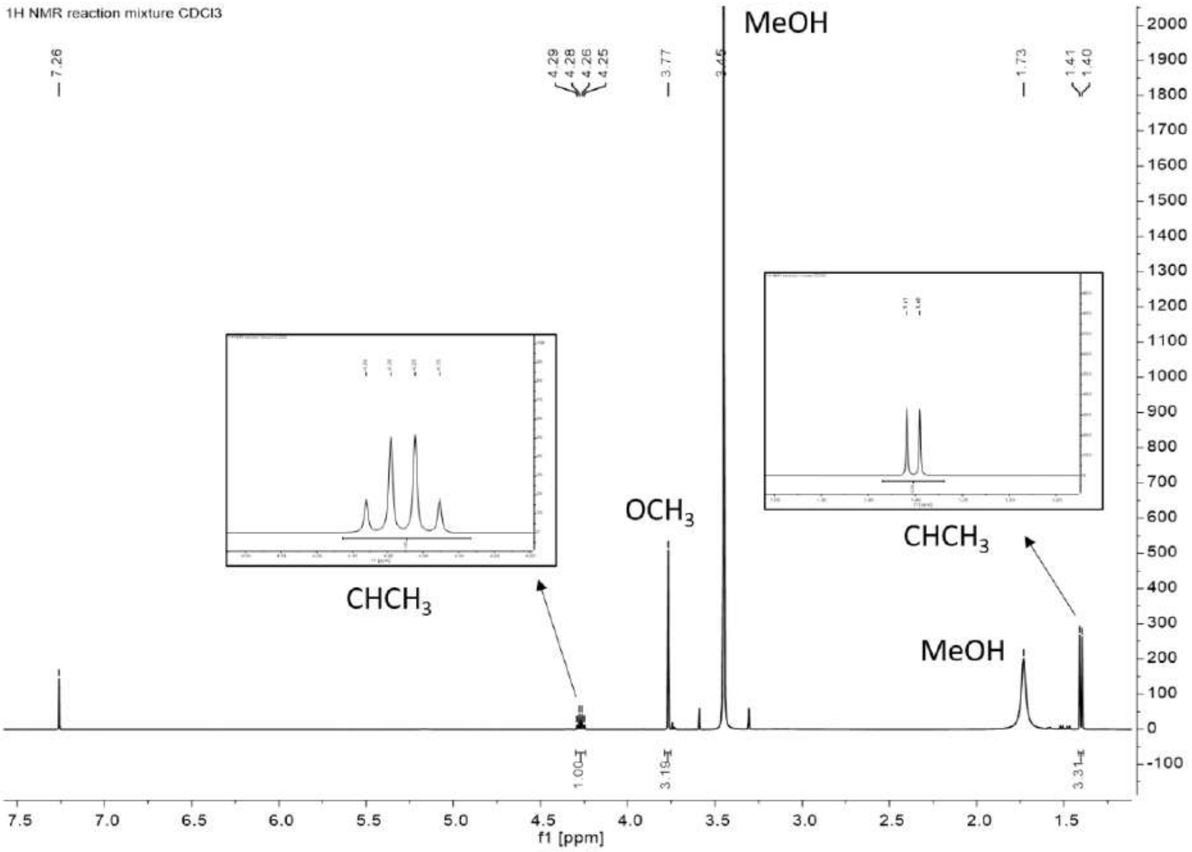
[1] a) M. Liu, J. Guo, Y. Gu, J. Gao, F. Liu, *ACS Sus. Chem. Eng.* **2018**, *6*, 15127−15134; b) X. Y. Song, X. J. Zhang, H. Wang, F. S. Liu, S. T. Yu, S. W. Liu, *Polym. Degrad. Stabil.* **2013**, *98*, 2760−2764.

General: All chemicals were used as received without further manipulations. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a *Fourier 300 MHz* (^{1}H: 300 MHz, ^{13}C: 75 MHz), *Avance I-400* (^{1}H: 400 MHz, ^{13}C: 101 MHz) or *Avance I 500* (^{1}H: 500 MHz, ^{13}C: 126 MHz) by Bruker, using the proton signals of the deuterated solvents as reference or external standards. Mass spectrometry was performed using a *Thermo ISQ LT EI* by Thermo Fisher Scientific. For microwave heating experiments a Microwave Synthesis Reactor Monowave 400 (Anton Paar GmbH) was used. For scale-up experiments a CEM Mars 6 microwave reactor was used. GC-MS was measured with Agilent Technologies 5977B GC/MSD. SEC analysis was performed using a “mixed bed” linear SEC-column (5 µm porous styrene-divinylbenzene particles, separation range 200-1000k g/mol) at a flow rate of 1 mL/min in tetrahydrofuran as eluent. Molecular weights refer to a so-called relative calibration based on narrow polystyrene samples supplied by Agilent Technologies. The SEC system was equipped with a Shimadzu LC-10ATvP pump, an AS1000 autosampler from Thermo Separation Products and a RI2012 refractive index detector from Schambeck SFD GmbH. The scale-up reaction was performed in a Parr autoclave (model: 4774).

General procedure for the depolymerization of polylactide (1a) (optimization of the reaction conditions): A mixture of polylactide (**1a**, transparent plastic cup from Prodana GmbH) (583.2 mg, 8.1 mmol based on the repeating unit), methanol (1.5-6.0 g, 47.0-187.1 mmol, 5.8-23.1 equiv. based on the repeating unit of **1a**) and catalytic amounts of $Sn(Oct)_2$ (0-0.25 mol%, 0-0.0203 mmol based on the repeating unit of **1a**) were placed with a stir bar in a vial. In case of <15.4 equiv. of methanol THF was added as solvent (3.0 g). The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 1-20 minutes (hold time) at 100-180 °C and with a stirring of 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature. An aliquot of the clear solution was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^{1}H NMR to determine the yield of methyl lactate (**2**) [The yield of **2** was calculated on the basis of the C*H* function of **2** and the leftover signals of the C*H* function of the polymer/oligomers].

Methyl lactate[1] (**2**): ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 4.26 (q, *J* = 6.91 Hz, 1H, CH_3CH), 3.77 (s, 3H, CH_3O-), 1.40 (d, *J* = 6.91 Hz, 3H, CH_3CH-) ppm.

Figure S1. Spectrum of a reaction mixture (0.25 mol% $Sn(Oct)_2$, 23.4 equiv. MeOH, 160 °C, 10 min) (^1H NMR (500 MHz, $CDCl_3$, 25 °C)).



General procedure for the depolymerization of polylactide (1): A polylactide-good (**1**) (583.2 mg, 8.1 mmol based on the repeating unit, for simplification we insinuate that the PLA-product is composed of 100% of PLA), methanol (6.0 g, 187.2 mmol, 23.1 equiv. based on the repeating unit of **1**), and catalytic amounts of $Sn(Oct)_2$ (0.25 mol%, 0.0203 mmol based on the repeating unit of **1**) were placed with a stirring bar in a vial. The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 10 minutes (hold time) at 160 °C and stirring with 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature. The reaction mixture was transferred into a 50 mL flask. The flask was attached to distillation equipment. The receiving flask (50 mL) was cooled with liquid nitrogen. The volatile compounds (methanol, methyl lactate) were removed in vacuum and were collected in the receiving flask. Afterwards the receiving flask was attached to a rotary evaporator and the methanol was carefully removed in vacuum. The amount of the liquid residue was determined and an aliquot was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.5 mL). The mass of isolated **2** was related to the mass of the starting

PLA-product. The amount of substance of **2** was related to the amount of substance of the starting PLA-product insinuating that the PLA-product is composed of 100% of PLA.

The NMR spectra are in accordance to the NMR spectra obtained for depolymerization of **1a** (*vide supra*).

Methyl lactate (**2**): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.27 (dq, *J* = 6.91 Hz, *J* = 5.20 Hz 1H, CH_3CH-), 3.77 (s, 3H, CH_3O-), 2.83 (d, *J* = 5.20 Hz, 1H, -CHO*H*), 1.40 (d, *J* = 6.91 Hz, 3H, CH_3CH-) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25 °C): δ = 176.1, 66.7, 52.6, 20.4 ppm.

Figure S2. Spectrum of **2** (^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)).

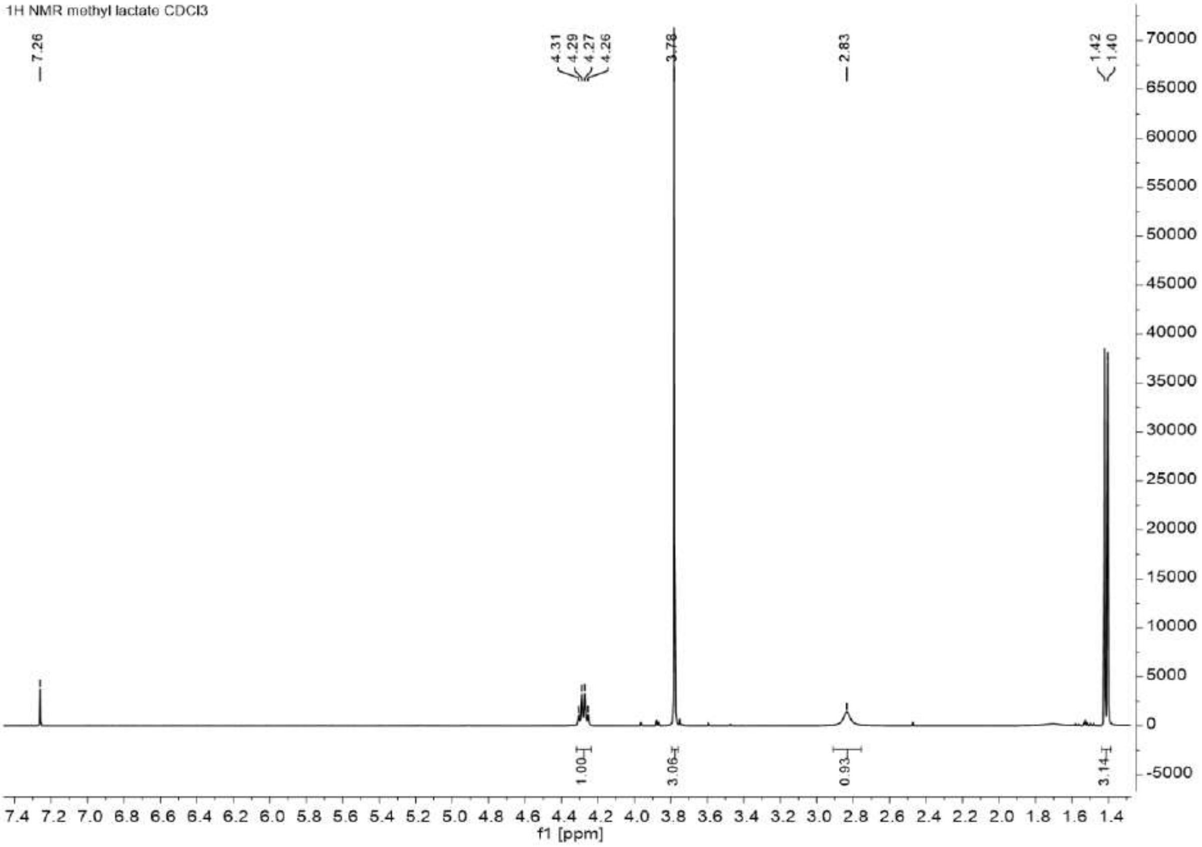


Figure S3. Spectrum of **2** ($^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 25 °C)).

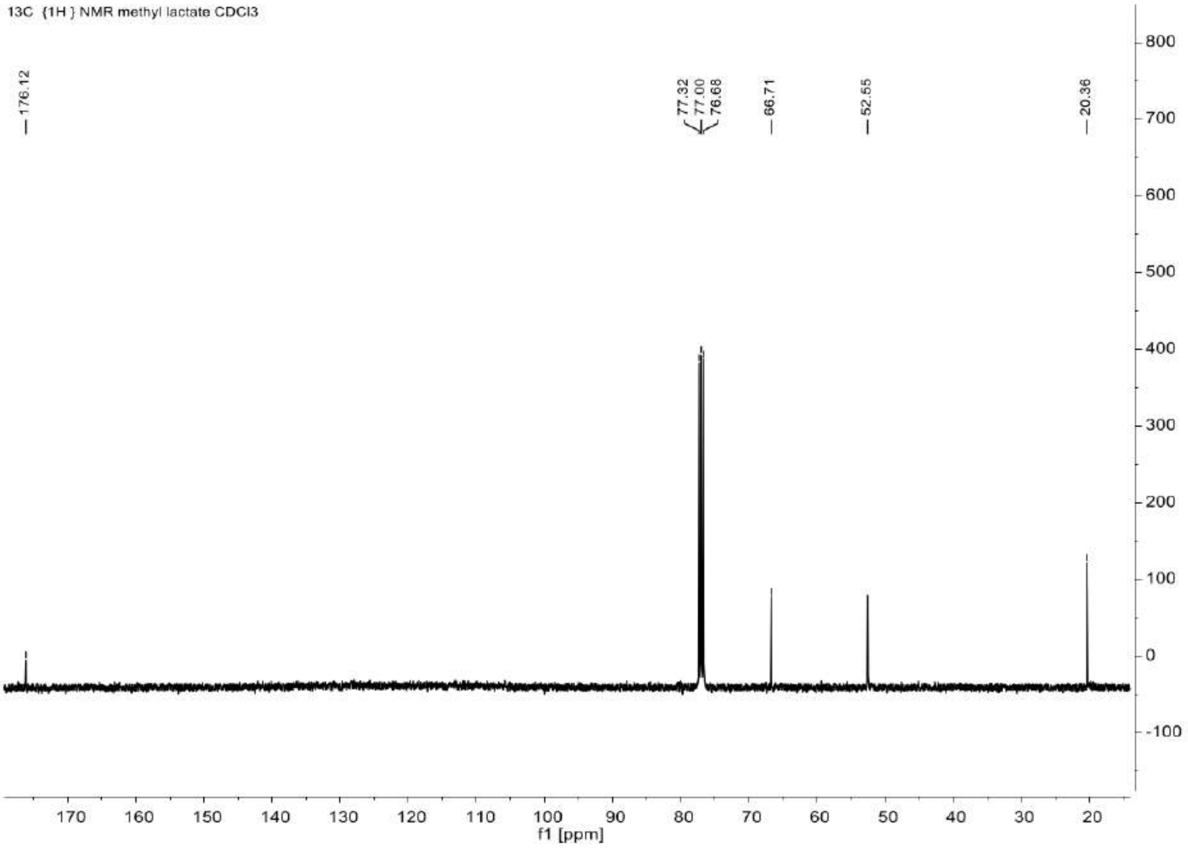


Figure S4. GC-MS spectrum of **2**.

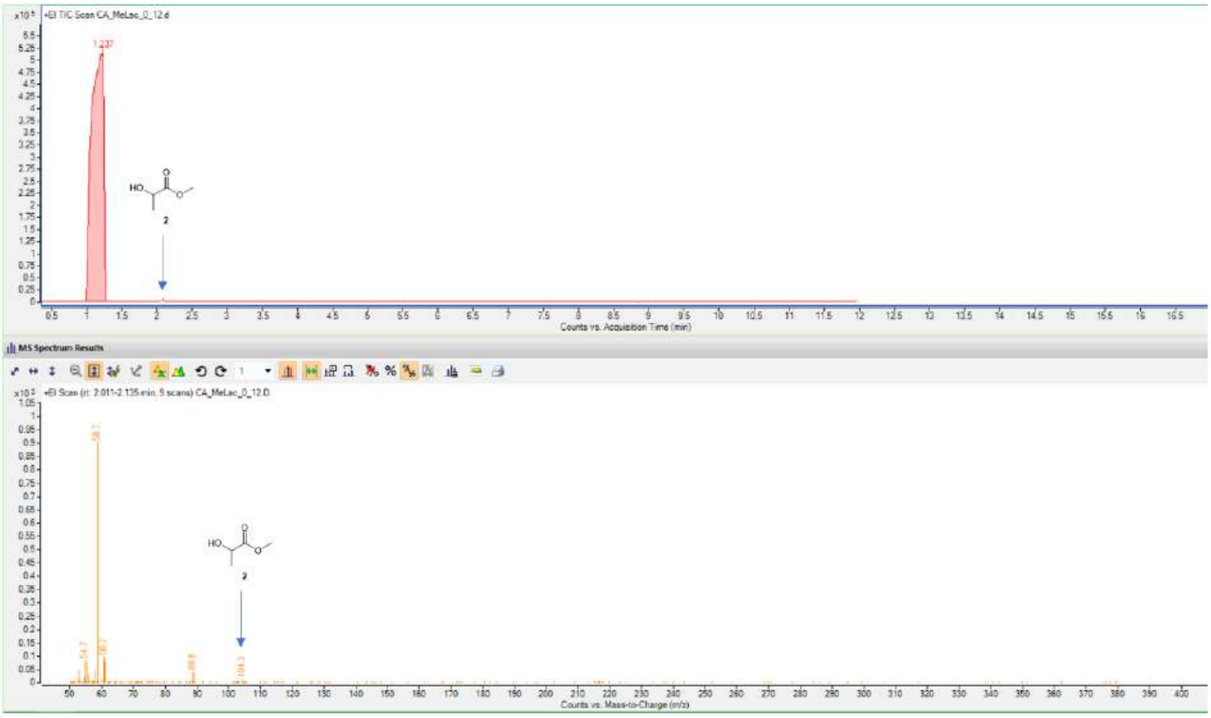
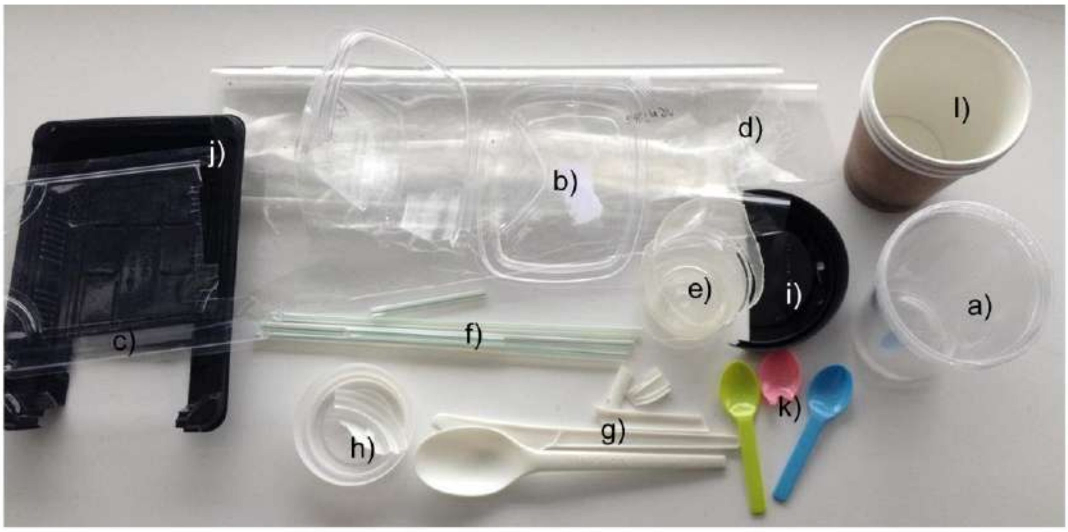


Table S1. Polylactide products (the PLA-products were obtained from Prodana GmbH and were used as received).



Entry	PLA-Product	Item number
1	transparent plastic cup (**1a**)	Huhtamaki
2	transparent disposable food box (**1b**)	VHD08-Mu
3	transparent cover of a disposable Sushi box (**1c**)	VSU02-Mu
4	transparent plastic sheet (**1d**)	VGNSH2-Mu
5	transparent bottle (**1e**)	NAFL250-Mu
6	drinking straw with green strips (**1f**)	VSS05GS-Mu
7	disposable fork with talcum powder (**1g**)	VWKFSWN-Mu
8	lid for espresso mugs with talcum powder (~20-30%) (**1h**)	VLID62A1-Mu
9	black lid for coffee mugs (**1i**)	VLID89SB-Mu
10	black base of a disposable Sushi box (**1j**)	VSU02-Mu
11	pink ice cream spoon (**1k**)	VSP3C-Mu
12	coffee mug with PLA coating on the inside (**1l**)	VKV08-Mu

Table S2. Appearance after depolymerzation reaction.

Entry	Product
1	transparent plastic cup (**1a**) (M_n = 57500 g/mol, M_w = 240800 g/mol, D = 4.2)
2	transparent disposable food box (**1b**) (M_n = 43600 g/mol, M_w = 236000 g/mol, D = 5.4)
3	transparent cover of a disposable Sushi box (**1c**) (M_n = 54700 g/mol, M_w = 212700 g/mol, D = 3.9)
4	transparent plastic sheet (**1d**) (M_n = 150400 g/mol, M_w = 262000 g/mol, D = 1.7)
5	transparent bottle (**1e**) (M_n = 99100 g/mol, M_w = 254900 g/mol, D = 2.6)
6	drinking straw with green strips (**1f**) (M_n = 112100 g/mol, M_w = 239900 g/mol, D = 2.1)
7	disposable fork with talcum powder (**1g**) (M_n = 59000 g/mol, M_w = 124100 g/mol, D = 2.1)
8	lid for espresso mugs with talcum powder (~20-30%) (**1h**) (M_n = 56100 g/mol, M_w = 177500 g/mol, D = 3.2)
9	black lid for coffee mugs (**1i**) (M_n = 75400 g/mol, M_w = 241100 g/mol, D = 3.2)
10	black base of a disposable Sushi box (**1j**) (M_n = 80300 g/mol, M_w = 148400 g/mol, D = 1.8)
11	pink ice cream spoon (**1k**) (M_n = 57600 g/mol, M_w = 133000 g/mol, D = 2.3)
12	coffee mug with PLA coating on the inside (**1l**) (M_n = 86400 g/mol, M_w = 221000 g/mol, D = 2.6)

Table S3. Appearance after depolymerzation reaction.

Entry	**PLA-Product**	**Appearance**
1	transparent plastic cup (**1a**)	Clear colorless solution
2	transparent disposable food box (**1b**)	Clear colorless solution
3	transparent cover of a disposable Sushi box (**1c**)	Clear colorless solution
4	transparent plastic sheet (**1d**)	Clear colorless solution
5	transparent bottle (**1e**)	Clear colorless solution
6	drinking straw with green strips (**1f**)	Green solution with precipitate
7	disposable fork with talcum powder (**1g**)	Clear colorless solution with colorless precipitate
8	lid for espresso mugs with talcum powder (~20-30%) (**1h**)	Colorless solution with colorless precipitate
9	black lid for coffee mugs (**1i**)	Clear colorless solution with black precipitate
10	black base of a disposable Sushi box (**1j**)	Clear colorless solution with black precipitate
11	pink ice cream spoon (**1k**)	Clear colorless solution with pink precipitate
12	coffee mug with PLA coating on the inside (**1l**)	Clear yellow solution and pieces of paper (shape unchanged). The inside surface of the pieces of paper changed from plain (before depolymerization) to rough (after depolymerization)

Table S4. Appearance after depolymerzation reaction – used PLA-products.

Entry	PLA-Product	Appearance
1	Yellow ice cream spoon (**1e**). Used for stirring a mixture of coffee, sugar and milk. The PLA-product was not cleaned before depolymerization.	Clear colorless solution with yellow precipitate
2	Black lid for coffee mugs (**1f**). Used with coffee, milk and sugar. The PLA-product was not cleaned before depolymerization.	Clear colorless solution with black precipitate

Procedure for the depolymerization of polylactide (1m) – scale-up (autoclave): Used PLA-cups were washed with water and dried in air. PLA cups (**1m**, NatureWorks) (5.832 g, 81 mmol based on the repeating unit, for simplification we insinuate that the PLA-product is composed of 100% of PLA), methanol (40 g, 1.2 mol, 15.4 equiv. based on the repeating unit of **1**), and catalytic amounts of $Sn(Oct)_2$ (0.25 mol%, 0.203 mmol based on the repeating unit of **1**) were placed with a stirring bar in an autoclave. The autoclave was sealed and heated to 140 °C (a pressure of 18.1 bar was noticed). The temperature was hold for 2 hours, while stirring the solution. Afterwards the vial was cooled to room temperature. The reaction mixture (clear solution) was transferred into a 250 mL flask. The flask was attached to distillation equipment. The receiving flask (100 mL) was cooled with liquid nitrogen. The volatile compounds (methanol, methyl lactate) were removed in vacuum and were collected in the receiving flask. Afterwards the receiving flask was attached to a rotary evaporator and the methanol was carefully removed in vacuum. The amount of the liquid residue was determined and an aliquot was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.5 mL). The mass of isolated **2** was related to the mass of the starting PLA-product. The amount of substance of **2** was related to the amount of substance of the starting PLA-product insinuating that the PLA-product is composed of 100% of PLA.

The NMR spectra are in accordance to the NMR spectra obtained for depolymerization of **1a** (*vide supra*).

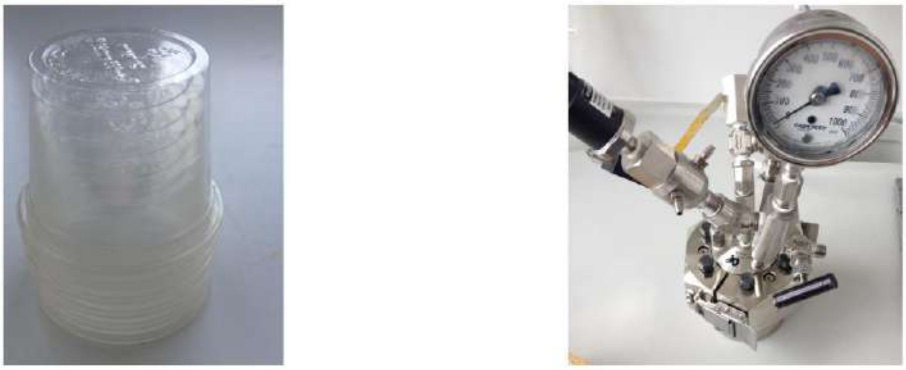
Figure S5. Scale-up experiment (autoclave)

a) PLA-cups after use

b) PLA-cups after washing

c) Applied cups for scale-up experiment

d) Autoclave (160 mL) charged with reagents



e) Isolated methyl lactate

Procedure for the depolymerization of polylactide (1m) – scale-up (autoclave): Used PLA-cups were washed with water and dried in air. PLA cups (**1m**, NatureWorks) (50.8732 g, 705.98 mmol based on the repeating unit, for simplification we insinuate that the PLA-product is composed of 100% of PLA), methanol (277 g, 8.3 mol, 11.8 equiv. based on the repeating unit of **1**), and catalytic amounts of $Sn(Oct)_2$ (0.25 mol%, 1.406 mmol based on the repeating unit of **1**) were placed with a stirring bar in an autoclave. The autoclave was sealed and heated to 140 °C (a pressure of 10.5 bar was noticed). The temperature was hold for 2 hours, while stirring the solution. Afterwards the autoclave was cooled to room temperature. The reaction mixture (clear solution) was transferred into a 500 mL flask. The flask was attached to distillation equipment. The receiving flask (500 mL) was cooled with liquid nitrogen. The volatile compounds (methanol, methyl lactate) were removed in vacuum and were collected in the receiving flask. Afterwards the receiving flask was attached to a rotary evaporator and the methanol was carefully removed in vacuum. The amount of the liquid residue was determined and an aliquot was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.5 mL). The mass of isolated **2** was related to the mass of the starting PLA-product. The amount of substance of **2** was related to the amount of substance of the starting PLA-product insinuating that the PLA-product is composed of 100% of PLA.

The NMR spectra are in accordance to the NMR spectra obtained for depolymerization of **1a** (*vide supra*).

Procedure for the depolymerization of polylactide (1m) – scale-up (microwave): Used PLA-cups were washed with water and dried in air. The following reactions were performed in eight microwave reactor vials (each 100 mL volume), which were treated with microwave irradiation at the same time. PLA cups (**1m**, NatureWorks, ~33 exemplars) (8x5.00 g = 40 g, 8x69.5 mmol = 556.0 mmol based on the repeating unit, for simplification we insinuate that the PLA-product is composed of 100% of PLA), methanol (8x35 g = 280 g, 8x1.05 mol = 8.4 mol, 15.1 equiv. based on the repeating unit of **1**), and catalytic amounts of $Sn(Oct)_2$ (8x0.25 mol%, 8x70.0 mg = 560 mg, 8x0.17 mmol = 1.38 mmol based on the repeating unit of **1**) were placed with a stirring bar in Teflon microwave vials (8x100 mL). The vials were sealed and heated to 140 °C in a microwave reactor. The temperature was hold for 20 min, while stirring the solution. Afterwards the vial was cooled to ambient temperature. The reaction mixtures (clear solutions) were filtered over a paper filter and combined into a 500 mL flask. The flask was attached to distillation equipment. The receiving flask (500 mL) was cooled with liquid nitrogen. The volatile compounds (methanol, methyl lactate) were removed in vacuum and were collected in the receiving flask. Afterwards the receiving flask was attached to a rotary evaporator and the methanol was partially removed in vacuum. The flask containing the liquid residue was attached to distillation equipment and the methanol and the methyl lactate was removed in vacuum and was collected in a flask cooled with liquid nitrogen. Afterwards the collecting flask was attached to a rotary evaporator and the methanol was removed in vacuum. The amount of the remaining liquid was determined and an aliquot was transferred to a NMR tube and dissolved in $CDCl_3$ (0.5 mL). The mass of isolated **2** was related to the mass of the starting PLA-product. The amount of substance of **2** was related to the amount of substance of the starting PLA-product insinuating that the PLA-product is composed of 100% of PLA.

The NMR spectra are in accordance to the NMR spectra obtained for depolymerization of **1a** (*vide supra*).

Figure S6. Scale-up experiment (microwave)

a) Applied cups for scale-up experiment

b) Sealed microwave reactor vial

c) Microwave reactor with samples.

d) Filtration of the reaction mixture

e) Methyl lactate

Procedure for the depolymerization of poly(lactide) (1a), poly(bisphenol A carbonate) (3) and poly(ethylene terephthalate) (4): A mixture of poly(lactide) (**1a**, transparent plastic cup from Prodana GmbH) (194.5 mg, 2.7 mmol based on the repeating unit), poly(bisphenol A carbonate) (**3**) (689 mg, 2.7 mmol based on the repeating unit, obtained from a DVD[2]), poly(ethylene terephthalate) (**4**, transparent water bottle) (518.5 mg, 2.7 mmol based on the repeating unit), methanol (6.0 g, 187.3 mmol, 69.4 equiv. with respect to the repeating unit of **1a**, **3** and **4**) and catalytic amounts of $Sn(Oct)_2$ (17.2 mg, 0.042 mmol, 1.5 mol% with respect to the repeating unit of **1a**, **3** and **4**) were placed with a stir bar in a vial. The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 20 minutes (hold time) at 160 °C and stirring with 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature. The suspension was filtered to remove the unreacted PET. An aliquot of the clear solution was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^1H NMR to determine the yield/conversion of the polymers. A NMR yield of >99% of **2** was detected, since no PLA leftover was observed. A NMR yield of >99% of 5 was detected, since no PC leftover was observed. A NMR yield of >99% of **5** and **6** was detected, since no PC leftover was observed. For PET only traces of the polymer were observed in the $CDCl_3$ by NMR.

For isolation of the monomers the solution was transferred to a flask, which was attached to distillation equipment. All volatiles (methanol, dimethyl carbonate, methyl lactate) were removed in vacuum and were collected in the collecting flask, which was cooled with liquid nitrogen. The collecting flask was attached to distillation equipment. The methanol and dimethyl carbonate were distilled off by heating the mixture to 110 °C. Due to azeotrope formation of methanol and dimethyl carbonate only the quality was checked by ^{1} HNMR. The leftover in the distillation flask was characterized by NMR, revealing the presence of methyl lactate (the ^1H NMR is in accordance as aforementioned). Methyl lactate was isolated in 61% yield (m = 170 mg). The residue of the reaction mixture was dissolved in chloroform and stored in a fridge. Colorless crystals were obtained, which were filtered off and dried in vacuum. Bisphenol A was isolated in 64% yield (m = 394 mg).

Bisphenol A (**2**)[3]: ^1H NMR (400 MHz, acetone-d6, 25 °C): δ = 8.09 (s, 2H, -O*H*), 7.03-7.08 (m, 4H, Ar-*H*), 6.72-6.75 (m, 4H, Ar-*H*), 1.59 (s, 6H, $(CH_3)_2C$-) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, acetone-d6, 25 °C): δ = 155.9, 142.8, 128.4, 115.4, 42.1, 31.5 ppm.

Dimethyl carbonate (**3**):[4] ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.76 (s, 6H, $(CH_3O)_2C=O$) ppm.

Figure S7. Left: PLA transparent cup; 4 isolated from a DVD; PET transparent bottle. Middle: Reaction mixture before microwave heating. Right: Reaction mixture after microwave heating.

Figure S8. Spectrum of the reaction mixture (^{1}H NMR (500 MHz, $CDCl_3$, 25 °C)).

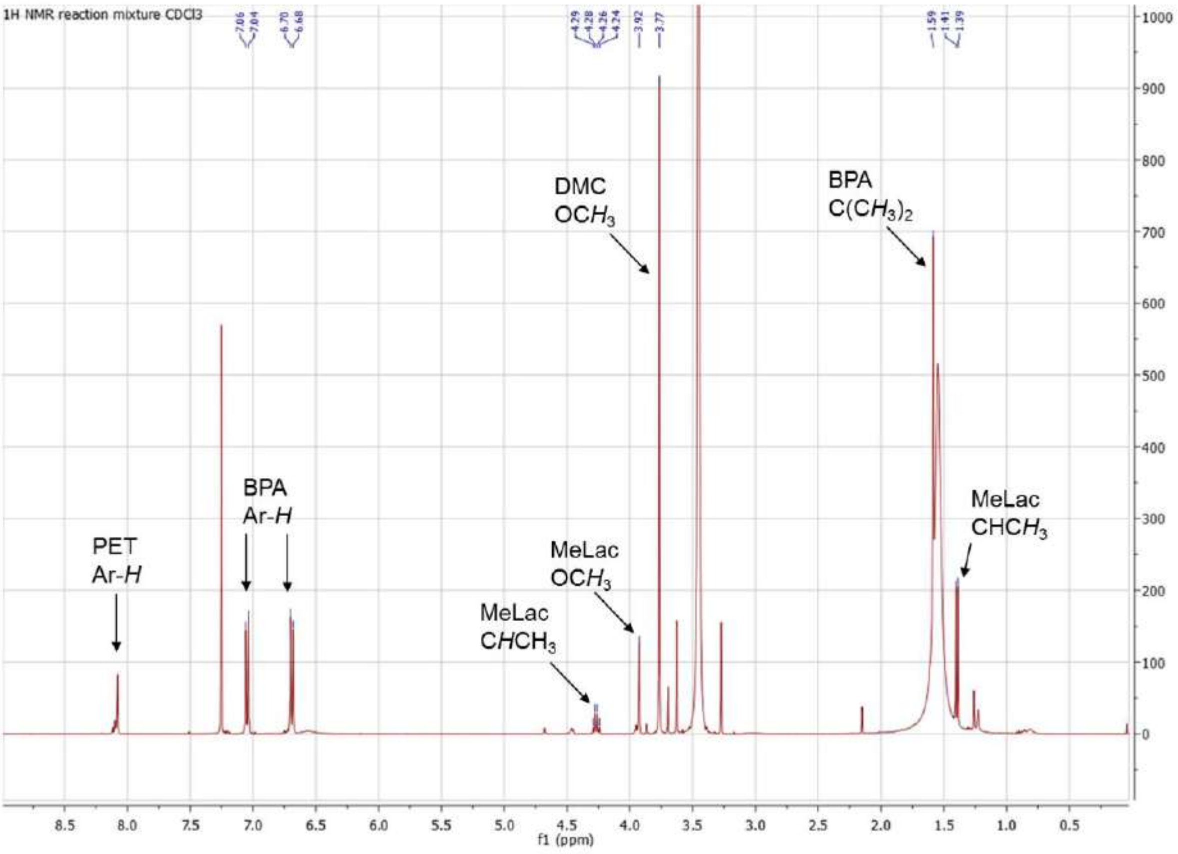


Figure S9. Spectrum of dimethyl carbonate/methanol (^{1}H NMR (500 MHz, CDCl$_3$, 25 °C)).

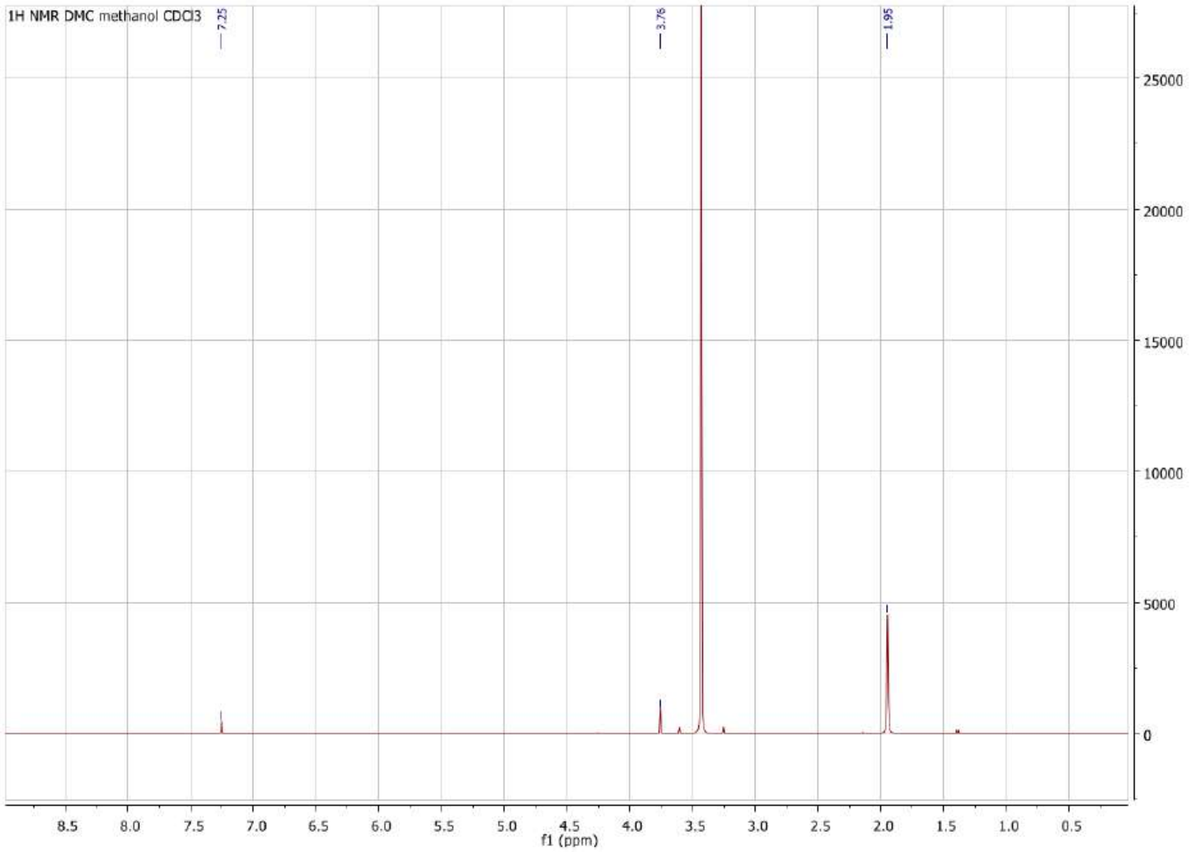


Figure S10. Spectrum of bisphenol A (^{1}H NMR (500 MHz, acetone-d6, 25 °C)).

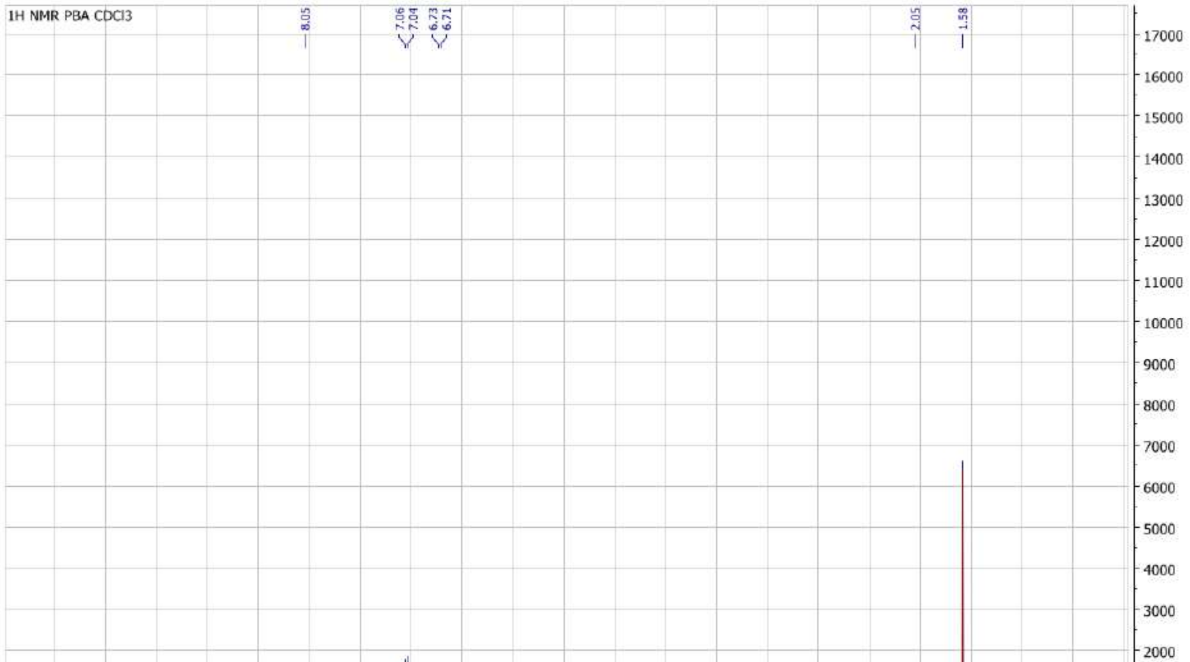
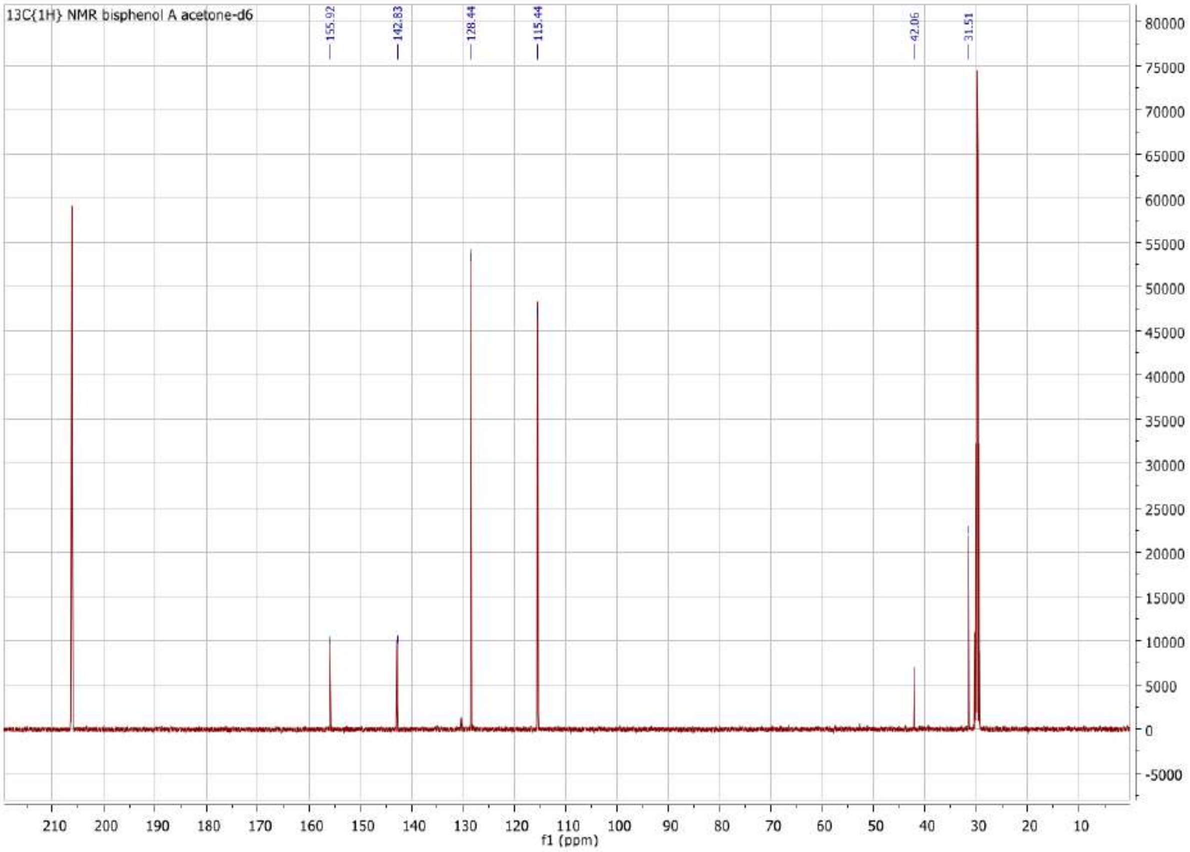


Figure S11. Spectrum of bisphenol A ($^{13}C\{^{1}H\}$ NMR (101 MHz, acetone-d6, 25 °C)).



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[1] a) M. Liu, J. Guo, Y. Gu, J. Gao, F. Liu, *ACS Sustainable Chem. Eng.* **2018**, *6*, 15127−15134; b) X. Y. Song, X. J. Zhang, H. Wang, F. S. Liu, S. T. Yu, S. W. Liu, *Polym. Degrad. Stab.* **2013**, *98*, 2760−2764.

[2] For the isolation of poly(bisphenol A carbonate) (**3**) from a DVD see for instance: a) C. Alberti, F. Scheliga, S. Enthaler, *ChemistrySelect* **2019**, *4*, 2639–2643; b) C. Alberti, S. Enthaler, *Asian J. Org. Chem.* **2019**, DOI: 10.1002/ajoc.201900242R1; c) C. Alberti, F. Scheliga, S. Enthaler, *ChemistryOpen* **2019**, DOI: 10.1002/open.201900149.

[3] S. Kiran, N. R. James, R. Joseph, A. Jayakrishnan, *Biomaterials* **2009**, *30*, 5552-5559.

[4] C. L. Campion, W. Li, B. L. Lucht, *J. Electrochem. Soc.* **2005**, *152*, A2327-A2334.

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Supporting Information

Depolymerization of End-of-Life Poly(lactide) to Lactide via Zinc-Catalysis

Christoph Alberti and Stephan Enthaler*

General: All chemicals were used as received without further manipulations. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a *Fourier 300 MHz* (^{1}H: 300 MHz, ^{13}C: 75 MHz), *Avance I-400* (^{1}H: 400 MHz, ^{13}C: 101 MHz) or *Avance I 500* (^{1}H: 500 MHz, ^{13}C: 126 MHz) by Bruker, using the signals of the deuterated solvents as reference or external standards.

General procedure for the depolymerization of polylactide (1a) (optimization of the reaction conditions): A mixture of polylactide (**1a**, end-of-life transparent plastic cups) (5.0 g, 69.39 mmol based on the repeating unit), catalytic amounts of catalyst (0-0.40 mol%, 0-0.278 mmol based on the repeating unit of **1a**) and a stir bar was placed in a flask. Distillation equipment was attached. The reaction mixture was heated at 200 °C and 6 mbar for 1-6 hours, while stirring. Afterwards the mass of the colorless solid in the collected flask was determined. An aliquot of the clear solution was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.5 mL).

L-Lactide[1] (**2a**): ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 5.03 (q, *J* = 6.70 Hz, 2H, $CH_3C\mathit{H}$), 1.67 (d, *J* = 6.70 Hz, 3H, $C\mathit{H}_3CH$-) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ = 167.5, 72.6, 16.0 ppm.

meso-Lactide (**2b**): ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 5.06 (q, *J* = 7.15 Hz, 2H, $CH_3C\mathit{H}$), 1.71 (d, *J* = 7.15 Hz, 3H, $C\mathit{H}_3CH$-) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ = 166.3, 73.0, 17.6 ppm.

Figure S1. Spectrum of the condensate (0.4 mol% Zn(OAc)$_2$, 140 °C, 5 mbar, 1 h) (^{1}H NMR (500 MHz, CDCl$_3$, 25 °C)).

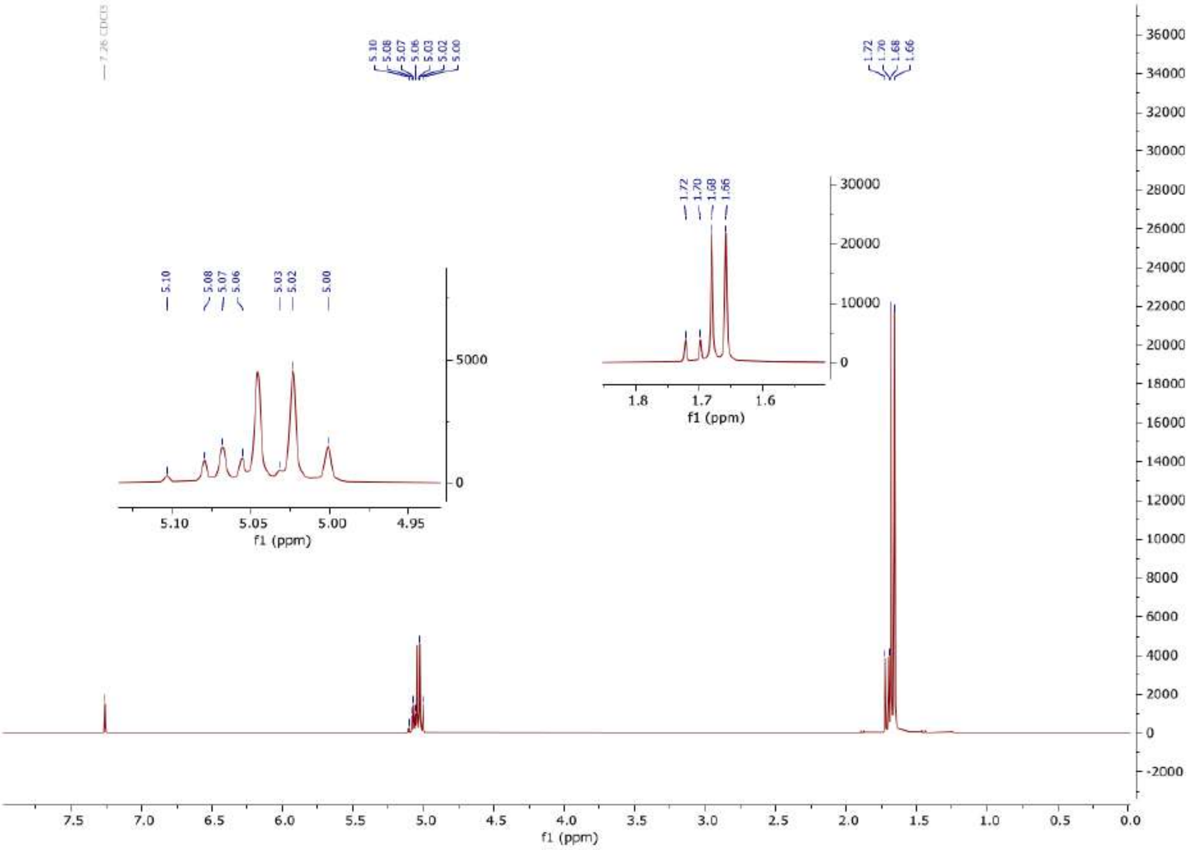


Figure S2. Spectrum of **2** ($^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25 °C)).

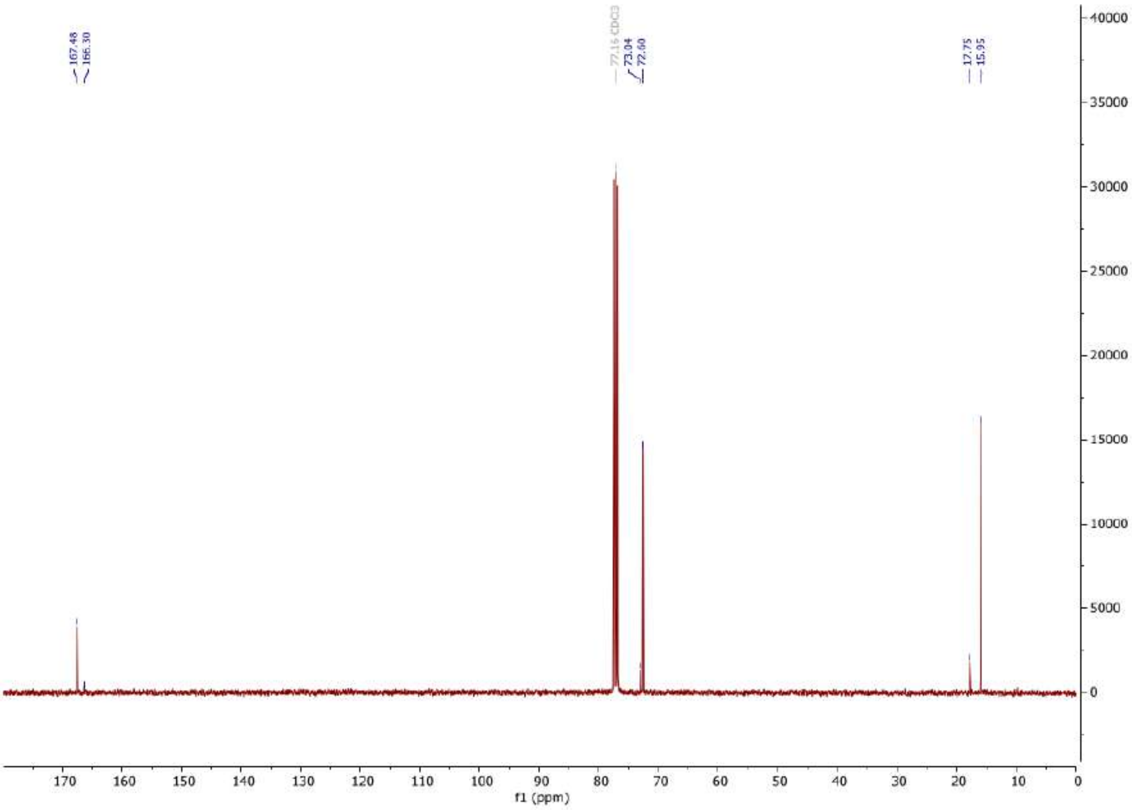
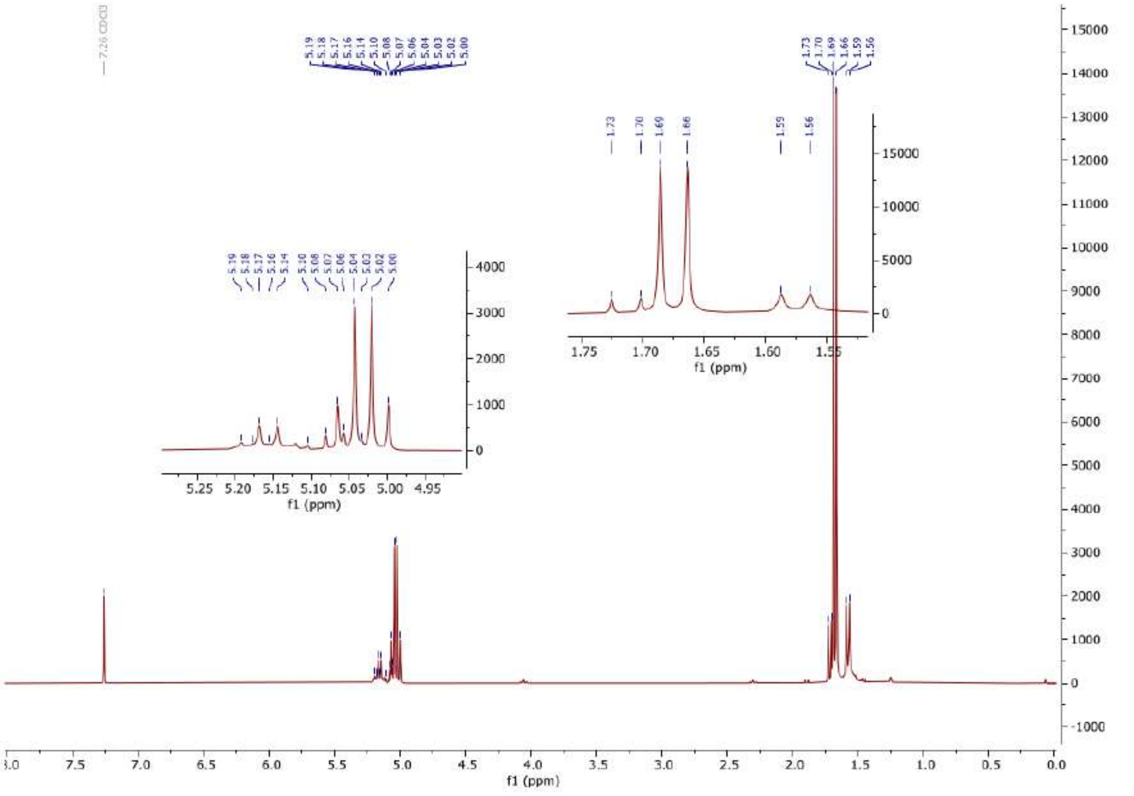


Figure S3. Spectrum of the reaction mixture residue (0.4 mol% $Zn(OAc)_2$, 140 °C, 5 mbar, 1 h) (^1H NMR (500 MHz, $CDCl_3$, 25 °C)).



Procedure for the depolymerization of polylactide (1a) – scale-up: Used PLA-cups were washed with water and dried in air. PLA cups (**1a**, NatureWorks, 100 exemplars) (123.5 g, 1.7 mol based on the repeating unit, for simplification we insinuate that the PLA-product is composed of 100% of PLA) and catalytic amounts of $Zn(OAc)_2$ (0.4 mol%, 1.26 g, 6.85 mmol based on the repeating unit of **1a**) were placed with a stirring bar in flask (2000 mL), which was equipped with distillation equipment. The mixture was heated at 200-210 °C at 6 mbar for 24 hours. Afterwards the mass of the colorless solid in the collected flask was determined. An aliquot of the clear solution was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.5 mL).

Lactide: yield: 79%, m = 97.6 g, n = 0.68 mol, proportion of L-lactide of **2**: 83%

Figure S4. Applied PLA cups and $Zn(OAc)_2$.

Figure S5. Reaction set-up.

Figure S6. Lactide.

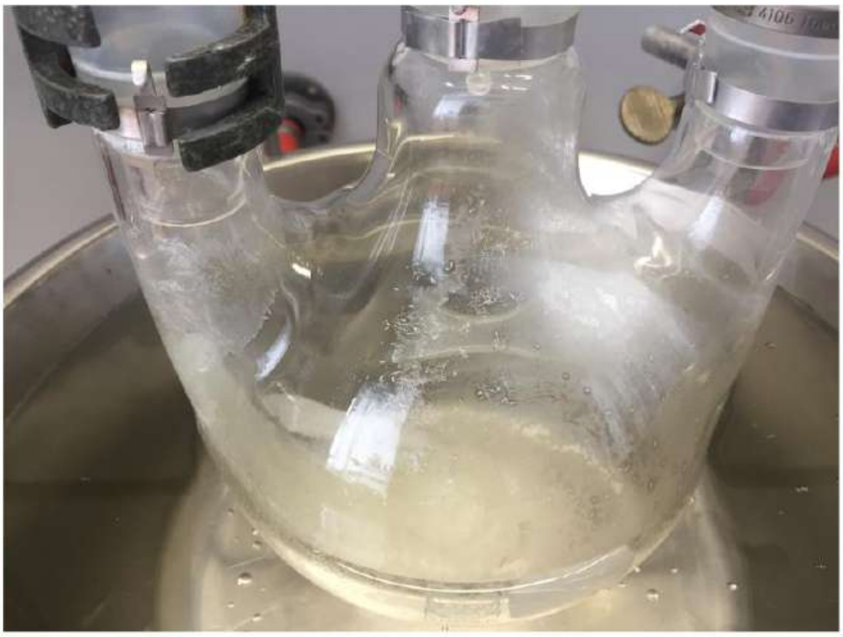


Figure S7. Reaction leftover.

Procedure for the depolymerization of a mixture of polylactide (1c): A mixture of polylactide (**1b**, mixture of end-of-life PLA) (5.0 g, 69.39 mmol based on the repeating unit) and catalytic amounts of $Zn(OAc)_2$ (0.40 mol%, 50.92 mg, 0.278 mmol based on the repeating unit of **1b**) were placed in a flask. Distillation equipment was attached. The reaction mixture was heated at 200-210 °C and 6 mbar for 6 hours, while stirring. Afterwards the mass of the colorless solid in the collected flask was determined. An aliquot of the clear solution was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.5 mL).

Lactide: yield: 48%, m = 2.39 g, n = 16.66 mmol, proportion of L-lactide of **2**: 87%

Figure S8. Mixture of PLA goods.

Figure S9. Product **2**.

Figure S10. Residue in the reaction flask.

Procedure for the depolymerization of a mixture of polylactide (1a), Nylon 6 (3) and poly(ε-caprolactone) (4): A mixture of polylactide (**1a**) (5.0 g, 69.39 mmol based on the repeating unit), Nylon 6 (**3**) (grey dowels, 7.9 g, 69.39 mmol based on the repeating unit) and poly(ε-caprolactone) (**4**) (M_n ~14000 g/mol, 7.9 g, 69.39 mmol based on the repeating unit) and catalytic amounts of $Zn(OAc)_2$ (0.40 mol%, 50.92 mg, 0.278 mmol based on the repeating unit of **1a** + 0.40 mol%, 50.92 mg, 0.278 mmol based on the repeating unit of **3** + 0.40 mol%, 50.92 mg, 0.278 mmol based on the repeating unit of **4**) were placed in a flask. Distillation equipment was attached. The reaction mixture was heated at 200-210 °C and 6 mbar for 6 hours, while stirring. Afterwards 1-*tert*-butyl-3,5-dimethylbenzene was added as standard to the collecting flask. An aliquot of the solution was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.5 mL).

Lactide: yield: 73%, proportion of L-lactide of **2**: 78%

ε-caprolactam (**3a**): <1%

ε-caprolactone (**4a**): 5%

Figure S11. Spectrum of the reaction mixture (^{1}H NMR (500 MHz, $CDCl_3$, 25 °C)).

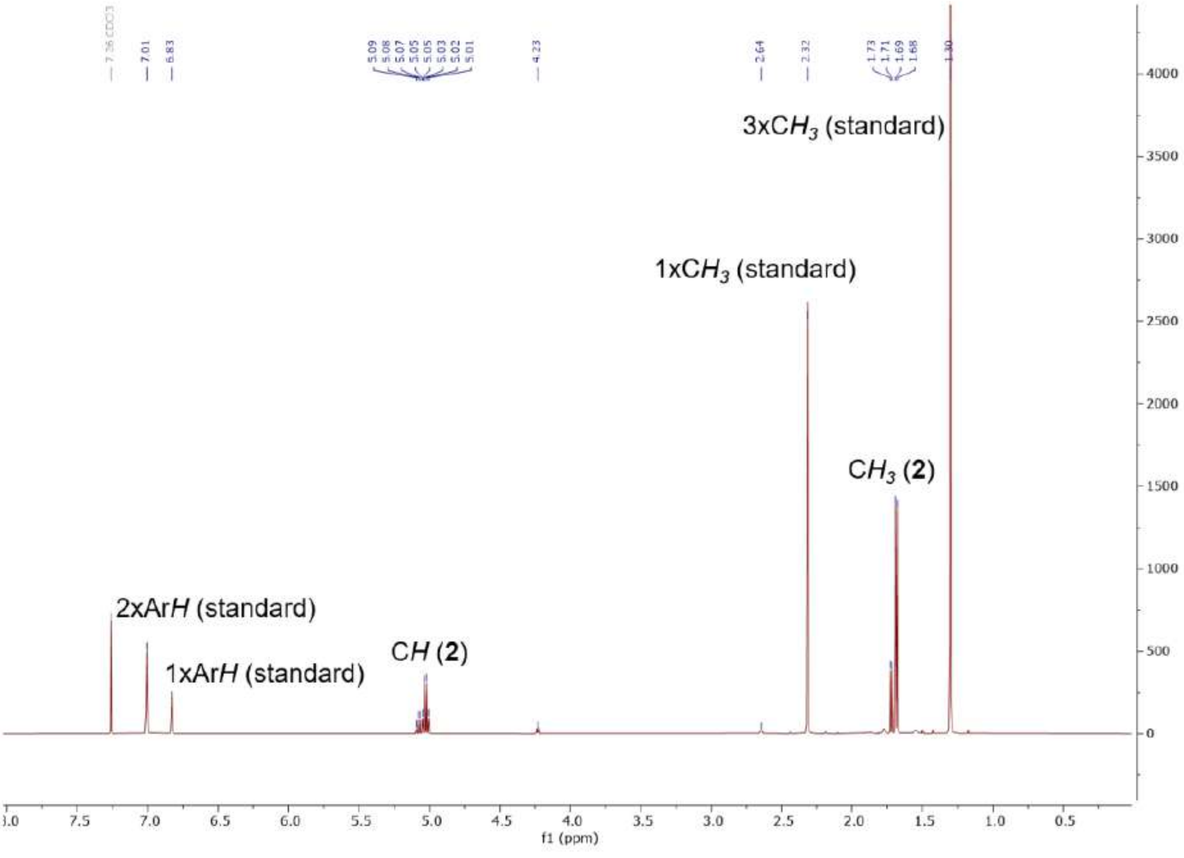


Figure 12. Mixture of polymers.

Figure 12. Reaction mixture leftover.

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[1] Compared with an authentic sample.

ChemistrySelect

Supporting Information

Zinc(II) acetate Catalyzed Depolymerization of Poly (ethylene terephthalate)

Melanie Hofmann, Jannis Sundermeier, Christoph Alberti, and Stephan Enthaler*

General: All chemicals were used as received without further manipulations. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a *Fourier 300 MHz* (^{1}H: 300 MHz, ^{13}C: 75 MHz) or *Avance I-400* (^{1}H: 400 MHz, ^{13}C: 101 MHz) by Bruker, using the proton signals of the deuterated solvents as reference or external standards. Mass spectrometry was performed using a *Thermo ISQ LT EI* by Thermo Fisher Scientific. For microwave heating experiments a Microwave Synthesis Reactor Monowave 400 (Anton Paar GmbH) was used. For scale-up experiments a CEM Mars 6 microwave reactor was used. GC-MS was measured with Agilent Technologies 5977B GC/MSD. Zinc(II) acetate was received from Sigma Aldrich. All catalytic hydrogenation set-ups were prepared in a glovebox under argon. Ru-MACHO®-BH: Carbonylhydrido(tetrahydroborato)[bis(2-diphenylphosphinoethyl)amino]ruthenium(II) (CAS Number: 1295649-41-0) was received from TCI Deutschland GmbH. THF was dried over sodium-benzophenone, was distilled off and stored over molecular sieves 4 Å under a nitrogen atmosphere. The hydrogenations were performed in a Parr autoclave (model: 4774) (Parr Instrument Company).

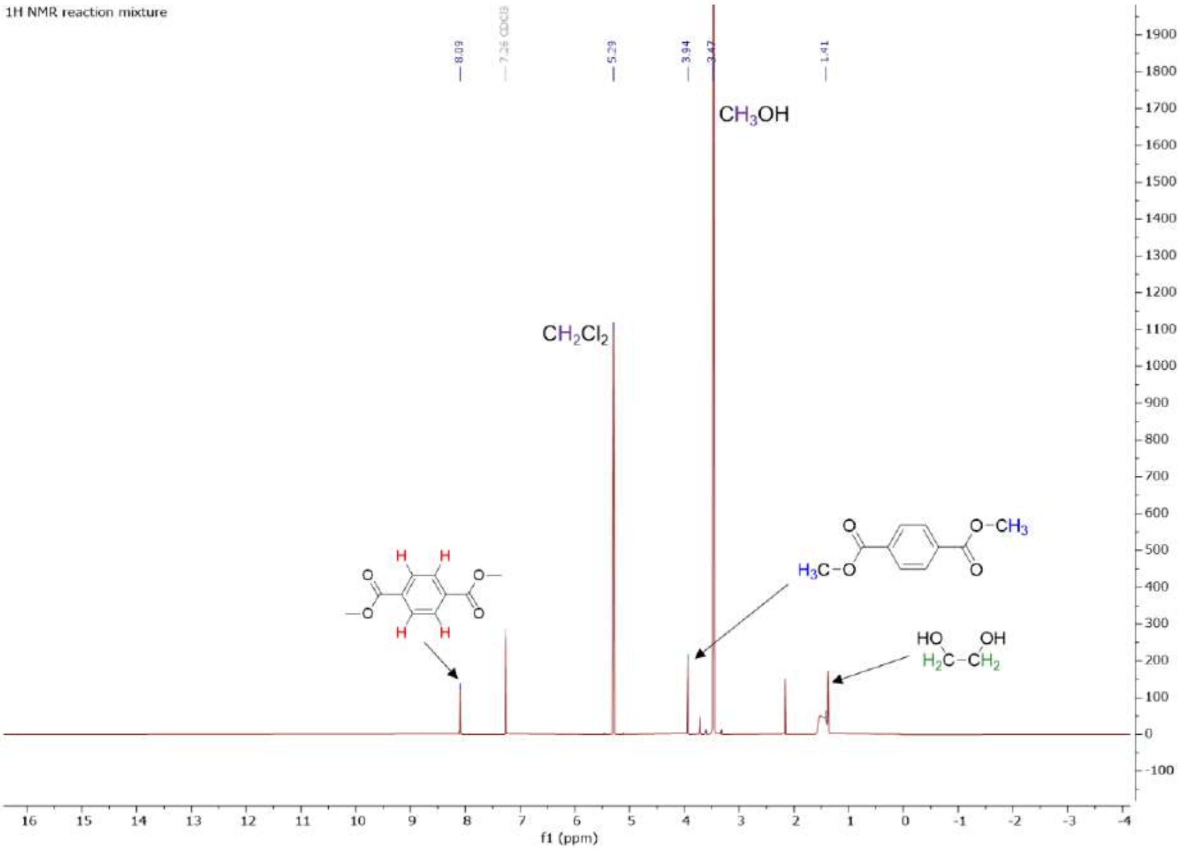
Depolymerization of PET

General procedure for the depolymerization of poly(ethylene terephthalate) (1a) (optimization of the reaction conditions): A mixture of poly(ethylene terephthalate) (**1a**, transparent plastic bottle) (259.4 mg, 1.35 mmol based on the repeating unit), methanol (2.0-3.0 g, 62.4-93.7 mmol, 46.2-69.4 equiv. based on the repeating unit of **1a**), dichloromethane (1.0-3.0 g, 11.7-35.4 mmol, 8.7-26.2 equiv. based on the repeating unit of **1a**) and catalytic amounts of zinc(II) acetate (0-2.5 mg, 0-1 mol%, 0-0.0135 mmol based on the repeating unit of **1a**) was placed with a stir bar in a vial. The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 10-60 minutes (hold time) at 120-160 °C and stirring with 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature. An aliquot of the clear solution was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.6 mL). The sample was subjected to ^{1}H NMR to determine the yield of dimethyl terephthalate (**2**) (The yield of **2** was calculated on the basis of the aromatic C*H* functions of **2** and the leftover signals of the aromatic C*H* function of the polymer/oligomer) and ethylene glycol (in various cases an overlap with the signal of methanol was observed).

Dimethyl terephthalate[1,2] (**2**): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.09 (s, 4H, Ar-*H*), 3.94 (s, 6H, CH_3O-) ppm.

Ethylene glycol[3]: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.41 (s, 4H, CH_2O-) ppm.

Figure S1. Spectrum of a reaction mixture (1.0 mol% $Zn(OAc)_2$, 46.2 equiv. MeOH, 17.4 equiv. CH_2Cl_2, 160 °C, 20 min) (^1H NMR (400 MHz, $CDCl_3$, 25 °C)).



General procedure for the depolymerization of poly(ethylene terephthalate) (1): A mixture of poly(ethylene terephthalate) (**1**) (259.4 mg, 1.35 mmol with respect to the monomeric unit, for simplification we insinuate that the PET-product is composed of 100% of PET), methanol (2.0 g, 62.4 mmol, 46.2 equiv. based on the repeating unit of **1a**), dichloromethane (2.0 g, 23.5 mmol, 17.4 equiv. based on the repeating unit of **1a**) and catalytic amounts of zinc(II) acetate (2.5 mg, 1 mol%, 0.0135 mmol based on the repeating unit of **1a**) was placed with a stir bar in a vial. The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 20 minutes (hold time) at 160 °C and stirring with 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature and the reaction mixture was transferred to a flask (50 mL). The methanol and dichloromethane were removed in vacuum. The residue was dissolved in a mixture of methanol and dichloromethane under reflux. The hot solution was filtered through filter paper. The filtrate was stored in a fridge. The colorless crystals were filtered off and were washed with cold methanol and dried in vacuum.

Dimethyl terephthalate (**2**): ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 8.10 (s, 4H, Ar-*H*), 3.95 (s, 6H, C*H*$_3$O-) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, 25 °C): δ = 166.3 (*C*=O), 134.0 (Ar*C*), 129.6 (Ar*C*-H), 53.2 (*C*H$_3$O-) ppm.

Figure S2. Spectrum of isolated **2** (^{1}H NMR (400 MHz, CDCl$_3$, 25 °C)).

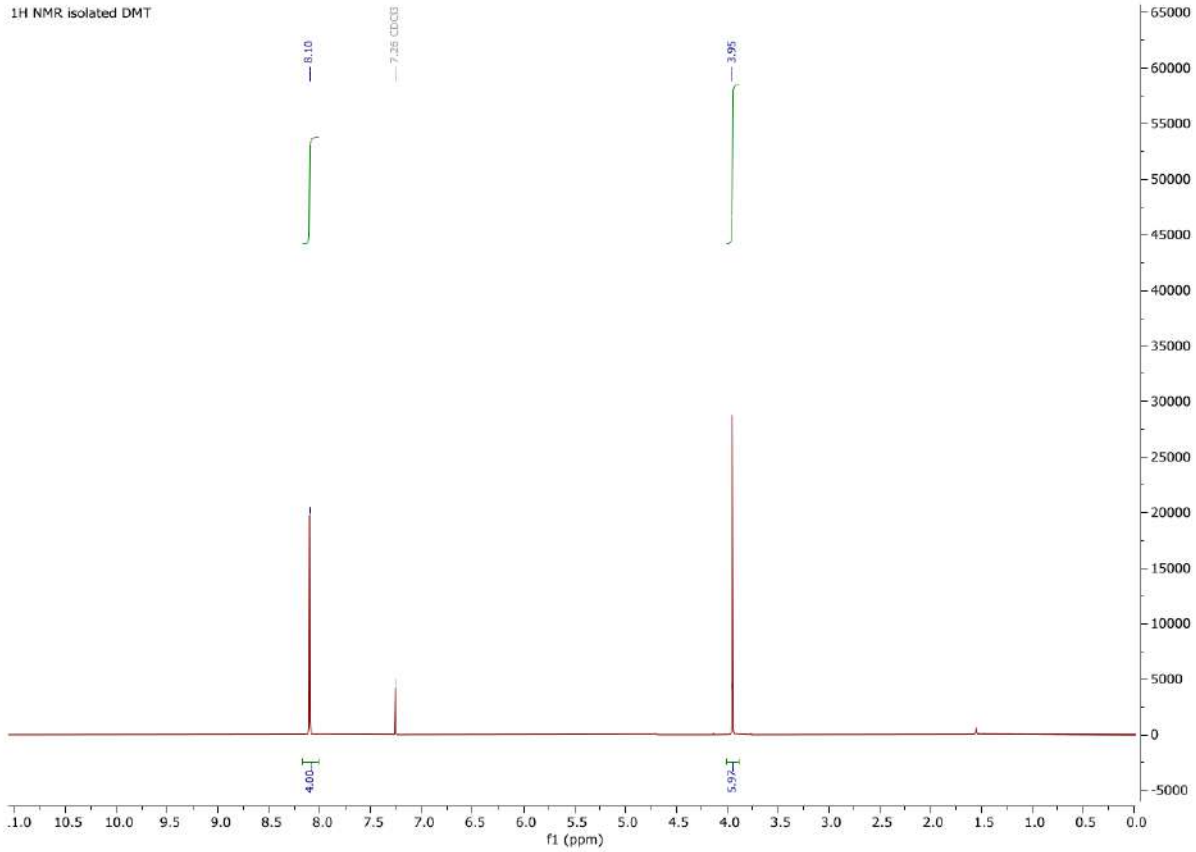


Figure S3. Spectrum of **2** ($^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C)).

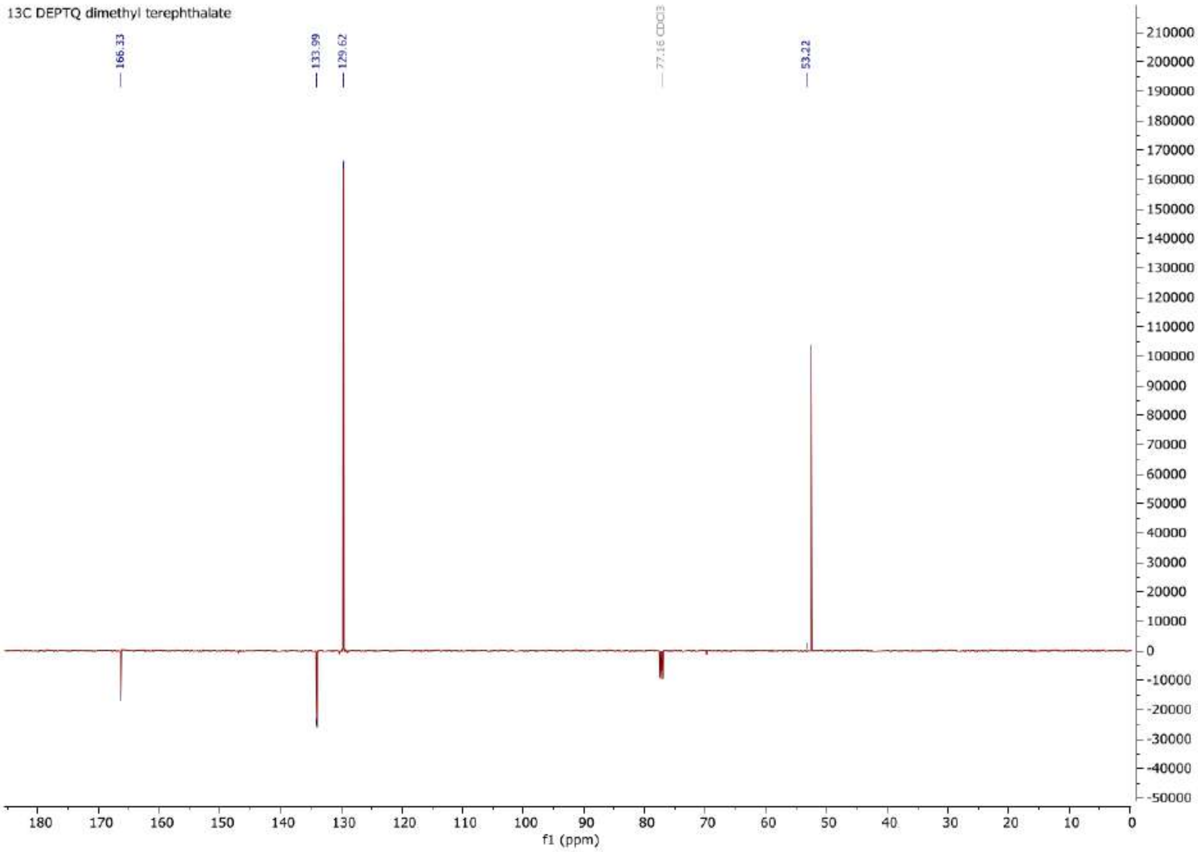


Table S1. Poly(ethylene terephthalate) products.

Entry[a]	**Product**
1	Transparent bottle (colourless) **1a**
2	Used transparent Cola bottle **1b**
3	Transparent bottle (green) **1c**
4	Dish detergent bottle **1d**
5	Dish detergent bottle with glue contamination **1e**
6	Soap dispenser **1f**
7	Soap dispenser with label contamination **1g**
8	Detergent bottle **1h**
9	Transparent food box **1i**
10	Transparent shampoo bottle **1j**
11	Toothbrush packaging colourless **1k**
12	Filling material colourless **1l**
13	Shampoo bottle (grey) **1m**
14	Softener bottle (purple) **1n**

Depolymerization of poly(ethylene terephthalate) – scale-up (microwave): A mixture of poly(ethylene terephthalate) (**1a**) (10.5 g, 0.055 mol based on the repeating unit, for simplification we insinuate that the PET-product is composed of 100% of PET), methanol (80.5 g, 2.53 mol, 45.7 equiv. based on the repeating unit of **1**), dichloromethane (81.3 g, 0.94 mol, 17.4 equiv. based on the repeating unit of **1**) and catalytic amounts of zinc(II) acetate (101.8 mg, 1.0 mol%, 0.55 mmol based on the repeating unit of **1**) was divided into eight portions and placed in eight vials in a microwave. The vials were sealed and heated at 140 °C for 2 hours. Afterwards the vials were cooled to room temperature and the reaction mixture was transferred to a flask (500 mL). The flask was attached to a rotary evaporator and the methanol and dichloromethane were removed in vacuum. The residue was dissolved in a mixture of methanol and dichloromethane under reflux. The hot solution was filtered through filter paper. The filtrate was stored in a fridge. The colorless crystals were filtered off and were washed with cold methanol and dried in vacuum.

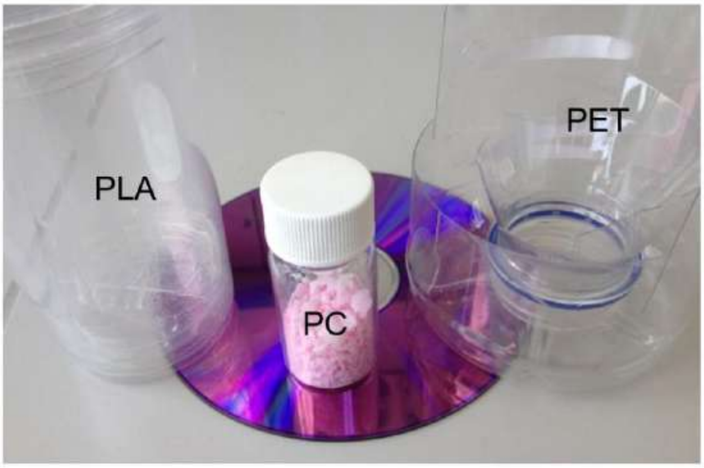
Yield (**2**) = 7.4 g (69%). The NMR data of **2** are in accordance to experiments shown before.

Depolymerization of poly(ethylene terephthalate) – scale-up (autoclave): A mixture of poly(ethylene terephthalate) (**1a**) (26.0 g, 0.135 mol based on the repeating unit, for simplification we insinuate that the PET-product is composed of 100% of PET), methanol (197.5 g, 6.2 mol, 45.7 equiv. based on the repeating unit of **1**), dichloromethane (199.5 g, 2.3 mol, 17.4 equiv. based on the repeating unit of **1**) and catalytic amounts of zinc(II) acetate (249.8 mg, 1.0 mol%, 1.35 mmol based on the repeating unit of **1**) was placed with a stir bar in an autoclave. The autoclave was sealed and heated at 140 °C for 2 hours. Afterwards the autoclave was cooled to room temperature and the reaction mixture was transferred to a flask (500 mL). The flask was attached to a rotary evaporator and the methanol and dichloromethane were removed in vacuum. The residue was dissolved in a mixture of methanol and dichloromethane under reflux. The hot solution was filtered through filter paper. The filtrate was stored in a fridge. The colorless crystals were filtered off and were washed with cold methanol and dried in vacuum.

Yield (**2**) = 15.4 g (59%). The NMR data of **2** are in accordance to experiments shown before.

Procedure for the depolymerization of poly(ethylene terephthalate) (1a), poly(bisphenol A carbonate) (6) and poly(lactide) (7): A mixture of poly(ethylene terephthalate) (**1a**) (259.4 mg, 1.35 mmol with respect to the monomeric unit, for simplification we insinuate that the PET-product is composed of 100% of PET), poly(bisphenol A carbonate) (**6**) (343.3 mg, 1.35 mmol with respect to the monomeric unit, isolated from a DVD[4]), poly(lactide) (**7**) (97.3 mg, 1.35 mmol with respect to the monomeric unit, transparent plastic cup from Prodana GmbH, for simplification we insinuate that the PLA-product is composed of 100% of PLA), methanol (2.0 g, 62.4 mmol, 46.2 equiv. based on the repeating unit of **1a**), dichloromethane (2.0 g, 23.5 mmol, 17.4 equiv. based on the repeating unit of **1a**) and catalytic amounts of zinc(II) acetate (2.5 mg, 1 mol%, 0.0135 mmol based on the repeating unit of **1a**) was placed with a stir bar in a vial. The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 20 minutes (hold time) at 160 °C and stirring with 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature. An aliquot of the clear solution was transferred to an NMR tube and was dissolved in $CDCl_3$ (0.6 mL). The sample was subjected to ^1H NMR to determine the yield of dimethyl terephthalate (**2**) (The yield of **2** was calculated on the basis of the aromatic C*H* functions of **2** and the leftover signals of the aromatic C*H* function of the polymer/oligomer), ethylene glycol, bisphenol A (**8**) (The yield of **8** was calculated on the basis of the aromatic C*H* functions of **8** and the leftover signals of the aromatic C*H* function of the polymer/oligomer), dimethyl carbonate (**9**) (The yield of **9** was calculated on the basis of the aromatic C*H* functions of **8**) and methyl lactate (**10**) (The yield of **10** was calculated on the basis of the C*H* functions of **10** and the leftover signals of the C*H* function of the polymer/oligomer). Afterwards the vial was cooled to room temperature and the reaction mixture was transferred to a flask (50 mL). The flask was attached to distillation equipment. The receiving flask (50 mL) was cooled with liquid nitrogen. First dichloromethane was removed and collected. Afterwards methanol and dimethyl carbonate were collected in the receiving flask. Methanol and dimethyl carbonate were not separated due to azeotrope formation. Afterwards the temperature was increased and methyl lactate was collected in 59% yield (m = 83.0 mg). To the leftover of the reaction mixture was added chloroform to dissolve dimethyl terephthalate. The mixture was filtered and the colorless solid (bisphenol A) was washed with small amounts of cold chloroform. To the bisphenol A chloroform was added and the mixture was heated to reflux until the bisphenol was dissolved. The mixture was filtered and solution was stored in a fridge to obtain colorless crystals, which were recrystallized again. After filtration and drying bisphenol A was obtained in 73% yield (m = 225.0 mg). From the dimethyl terephthalate-chloroform solution the chloroform was removed in vacuum and the solid residue was recrystallized twice from methanol-dichloromethane. After filtration and drying dimethyl terephthalate was obtained in 47% yield (m = 123.2 mg).

Figure S4. Polymer mixture **1a**, **6** and **7**.



Dimethyl carbonate (**9**)[5]: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.78 (s, 6H, $(CH_3O)_2C=O$) ppm.

Methyl lactate (**10**)[6]: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.28 (dq, *J* = 6.91 Hz, *J* = 5.20 Hz 1H, CH_3CH-), 3.77 (s, 3H, CH_3O-), 2.93 (d, *J* = 5.20 Hz, 1H, -CHO*H*), 1.40 (d, *J* = 6.91 Hz, 3H, CH_3CH-) ppm.

Bisphenol A (**8**)[7]: ^{1}H NMR (400 MHz, acetone-*d*$_6$, 25 °C): δ = 8.09 (s, 2H, -O*H*), 7.03-7.08 (m, 4H, Ar-*H*), 6.72-6.75 (m, 4H, Ar-*H*), 1.58 (s, 6H, $(CH_3)_2C$-) ppm.

Figure S5. Spectrum of the reaction mixture of depolymerization of **1a**, **6** and **7** (^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)).

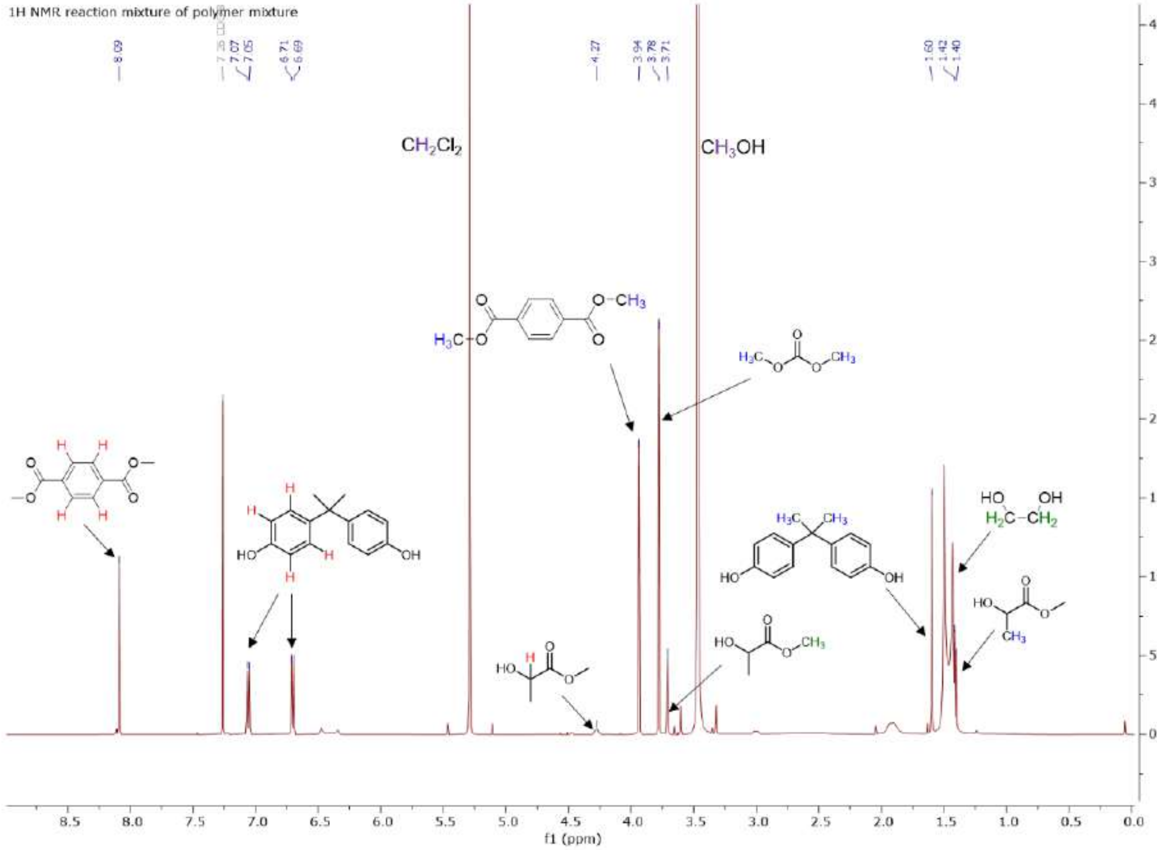


Figure S6. Spectrum of dimethyl carbonate and methanol (^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)).

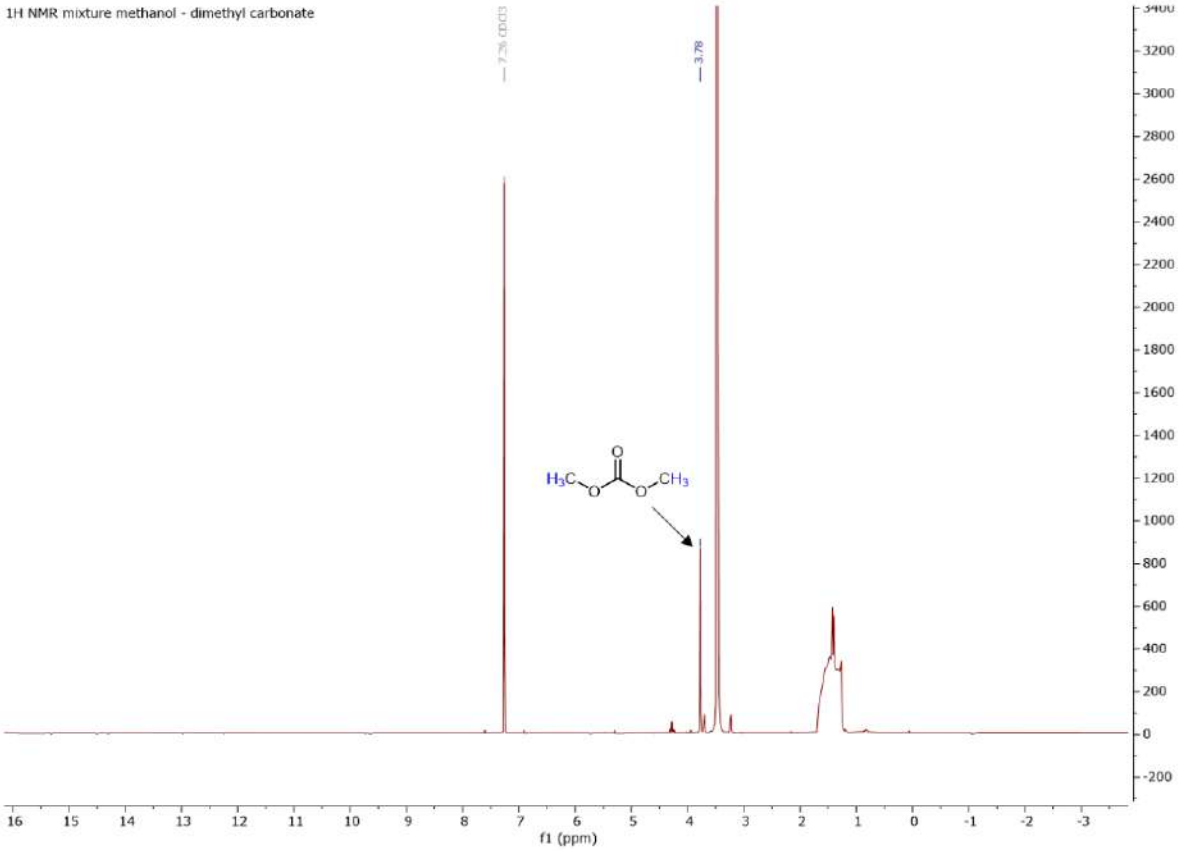


Figure S7. Spectrum of methyl lactate (^1H NMR (400 MHz, $CDCl_3$, 25 °C)).

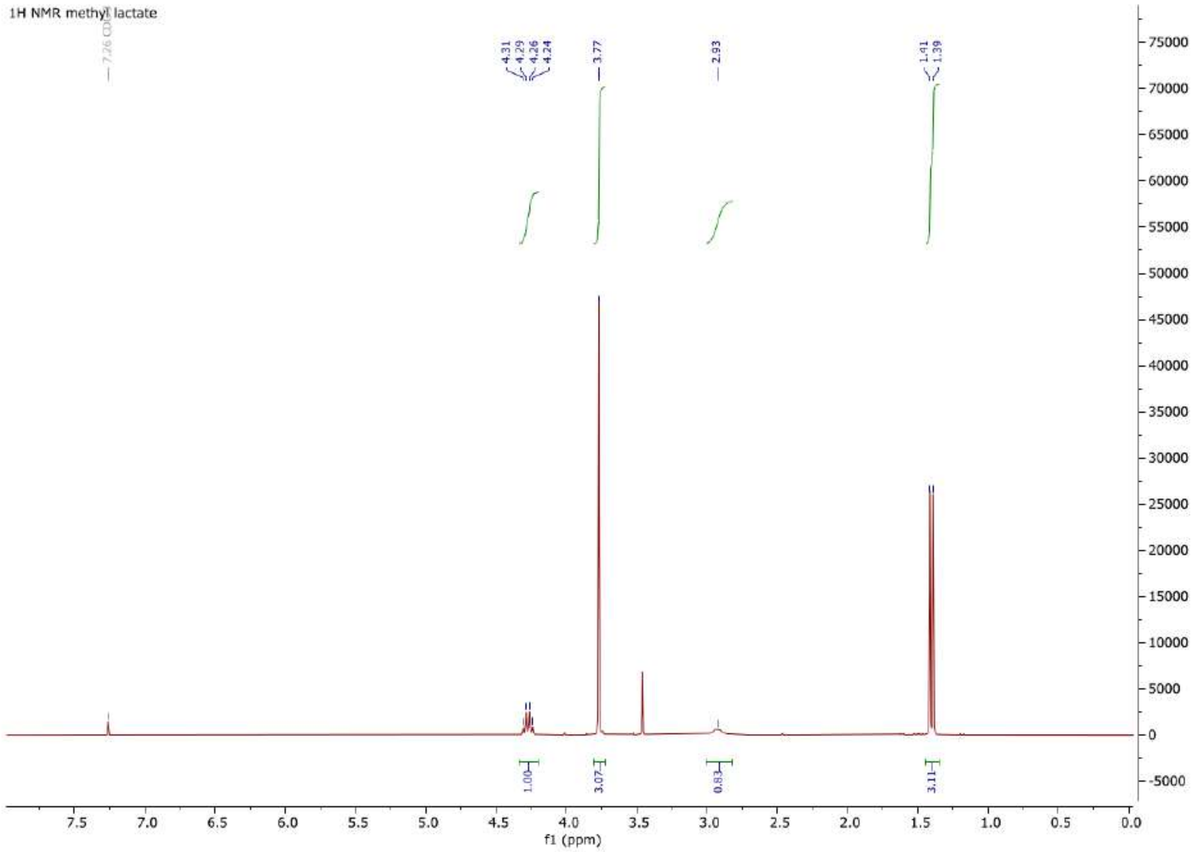
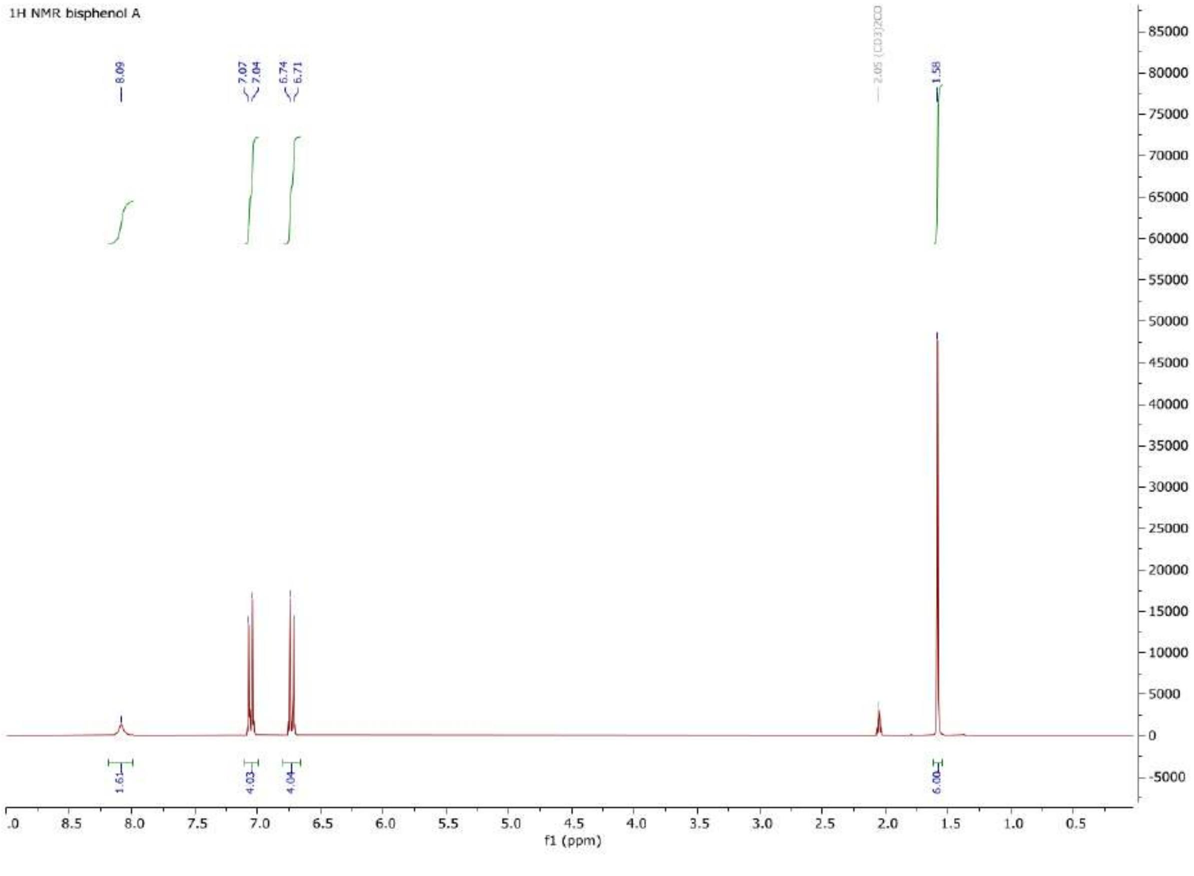


Figure S8. Spectrum of bisphenol A (^1H NMR (400 MHz, $CDCl_3$, 25 °C)).



Hydrogenation of dimethyl terephthalate (2)

General procedure for hydrogenation of the aromatic unit of dimethyl terephthalate (2) (optimization of reaction conditions): A mixture of dimethyl terephthalate (**2**) (13.1 mg, 0.068 mmol) and ruthenium (5 wt%)/C or palladium (5 wt%)/C (1-5 mol%, 0.00068-0.0034 mmol based on the metal) was placed with a stir bar in a vial. THF (2.0 mL) was added. The vial was placed in an autoclave, which was sealed and purged with hydrogen (5 times). Afterwards the desired hydrogen pressure was adjusted (5-45 bar) the autoclave was heated to the desired temperature (60-140 °C). The temperature was hold for 3-6 hours, while stirring the reaction mixture. Afterwards the autoclave was cooled to room temperature and the hydrogen pressure was carefully released. An aliquot of the solution was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.6 mL). The sample was subjected to ^1H NMR to determine the conversion of **2**. The yield of **2** was calculated on the basis of the ester functionalities of **2** and **3**.

Dimethyl 1,4-cyclohexanedicarboxylate[8,9] (**3**): ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.66 (s, 6H, $-OCH_3$), 3.65 (s, 6H, $-OCH_3$), 1.43-2.45 (m, 10H, C_6H_{10}) ppm. A mixture of isomers was detected. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C): δ = 176.1, 175.6, 51.7, 42.5, 40.4, 22.7, 26.1 ppm.

Figure S9. Spectrum of a reaction mixture (5.0 mol% Ru (5 wt%)/C, THF, 45 bar H_2, 80 °C, 6 h) (^1H NMR (400 MHz, $CDCl_3$, 25 °C)).

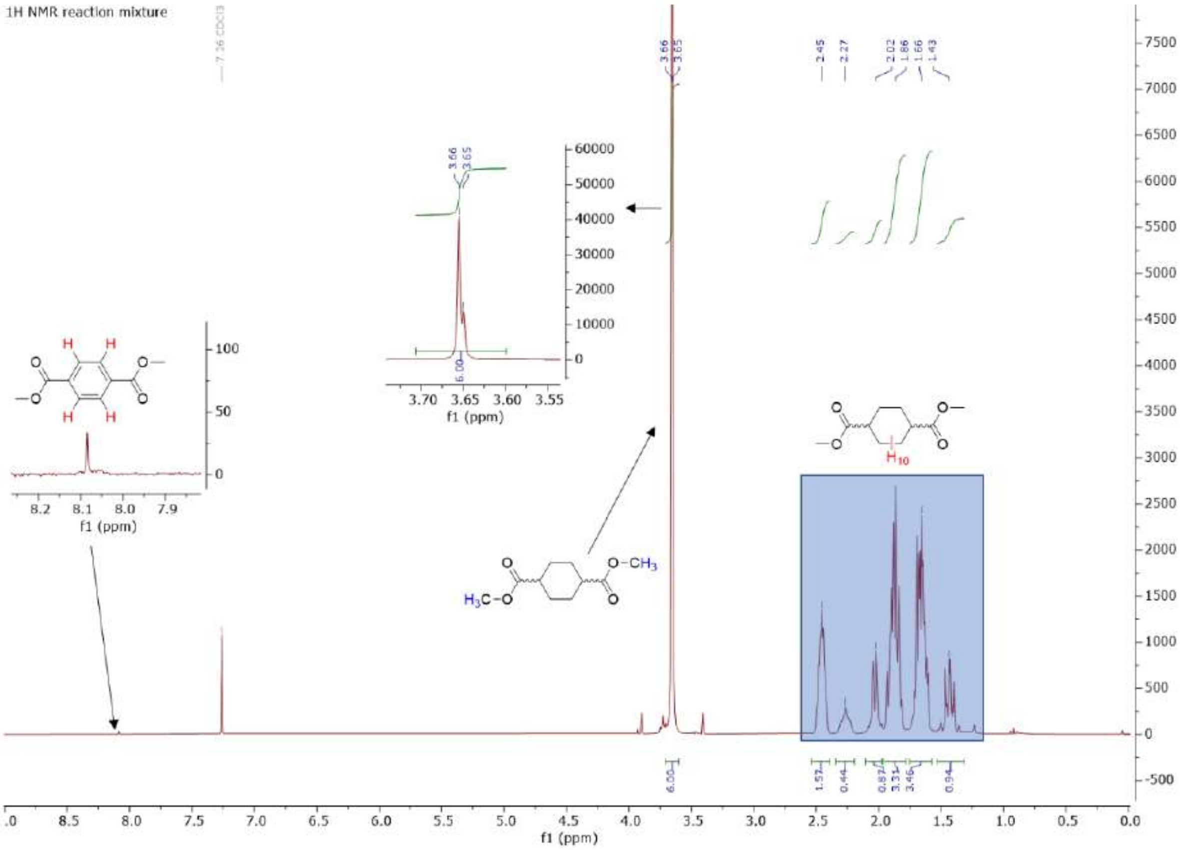
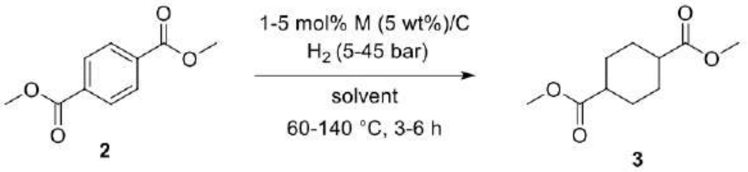


Table S2. Hydrogenation of DMT – optimization of the reaction conditions.



Entry	Catalyst loading [mol%]	T [°C]	p [bar]	t [h]	Yield 4 [%]
1	Ru (5 wt%)/C [5]	140	45	6	86
2	Ru (5 wt%)/C [5]	120	45	6	>99
3	Ru (5 wt%)/C [5]	100	45	6	>99
4	Ru (5 wt%)/C [5]	80	45	6	>99
5	Ru (5 wt%)/C [5]	60	45	6	>99
6	Ru (5 wt%)/C [5]	140	22.5	6	>99
7	Ru (5 wt%)/C [5]	120	22.5	6	98
8	Ru (5 wt%)/C [5]	100	22.5	6	>99
9	Ru (5 wt%)/C [5]	100	10	6	98
10	Ru (5 wt%)/C [5]	100	5	6	63
11	Ru (5 wt%)/C [5]	140	45	3	98
12	Ru (5 wt%)/C [5]	100	45	3	99
13	Ru (5 wt%)/C [5]	140	5	6	43
14	Ru (5 wt%)/C [2.5]	140	22.5	6	87
15	Ru (5 wt%)/C [1]	140	22.5	6	83
16	Ru (5 wt%)/C [2.5]	120	22.5	6	99
17	Ru (5 wt%)/C [1]	120	22.5	6	99
18	Ru (5 wt%)/C [2.5]	100	22.5	6	40
19	Ru (5 wt%)/C [1]	100	22.5	6	10
20	Ru (5 wt%)/C [5]	60	10	6	94
21	Pd (5 wt%)/C [5]	140	45	6	99
22	Pd (5 wt%)/C [5]	120	45	6	91
23	Pd (5 wt%)/C [5]	100	45	6	90

24	Pd (5 wt%)/C [5]	80	45	6	40
25	Pd (5 wt%)/C [5]	60	45	6	40
26	Pd (5 wt%)/C [5]	140	22.5	6	96
27	Pd (5 wt%)/C [5]	120	22.5	6	94
28	Pd (5 wt%)/C [5]	100	22.5	6	61
29	Pd (5 wt%)/C [5]	140	45	3	50
30	Pd (5 wt%)/C [5]	140	5	6	36
31	Pd (5 wt%)/C [2.5]	120	22.5	6	95
32	Pd (5 wt%)/C [1]	120	22.5	6	70
33	Pd (5 wt%)/C [5]	60	10	6	12

Table S3. Hydrogenation of DMT – solvent screening.

Entry	Solvent	Catalyst loading [mol%]	T [°C]	p [bar]	t [h]	Yield 4 [%]
1	THF	Ru (5 wt%)/C [5]	100	6	22.5	>99
2	MeOH	Ru (5 wt%)/C [5]	100	6	22.5	99
3	MeOH/ CH_2Cl_2 (1:1)	Ru (5 wt%)/C [5]	100	6	22.5	2
4	THF	Ru (5 wt%)/C [5]	100	6	22.5	61
5	MeOH	Ru (5 wt%)/C [5]	100	6	22.5	56
6	MeOH/ CH_2Cl_2 (1:1)	Ru (5 wt%)/C [5]	100	6	22.5	9

Hydrogenation of the aromatic unit of dimethyl terephthalate (2)- isolation: A mixture of dimethyl terephthalate (**2**) (260.1 mg, 1.35 mmol) and Ruthenium (5 wt%)/C (6.8 mg, 5 mol%, 0.0675 mmol based on the metal) was placed with a stir bar in a vial. THF (2.0 mL) was added. The vial was placed in an autoclave, which was sealed and purged with hydrogen (5 times). Afterwards the desired hydrogen pressure was adjusted (45 bar) the autoclave was heated to the desired temperature (120 °C). The temperature was hold for 24 hours, while stirring the reaction mixture. Afterwards the autoclave was cooled to room temperature and the hydrogen pressure was carefully released. The mixture was filtered over a plug of silica to remove the Ru/C, which was washed with dichloromethane. The solvent was removed in vacuum. Chemical **3** was obtained in 44% yield (m = 120 mg).

Figure S11. ^{1}H NMR spectrum of **3** (^{1}H NMR (400 MHz, CDCl$_3$, 25 °C)).

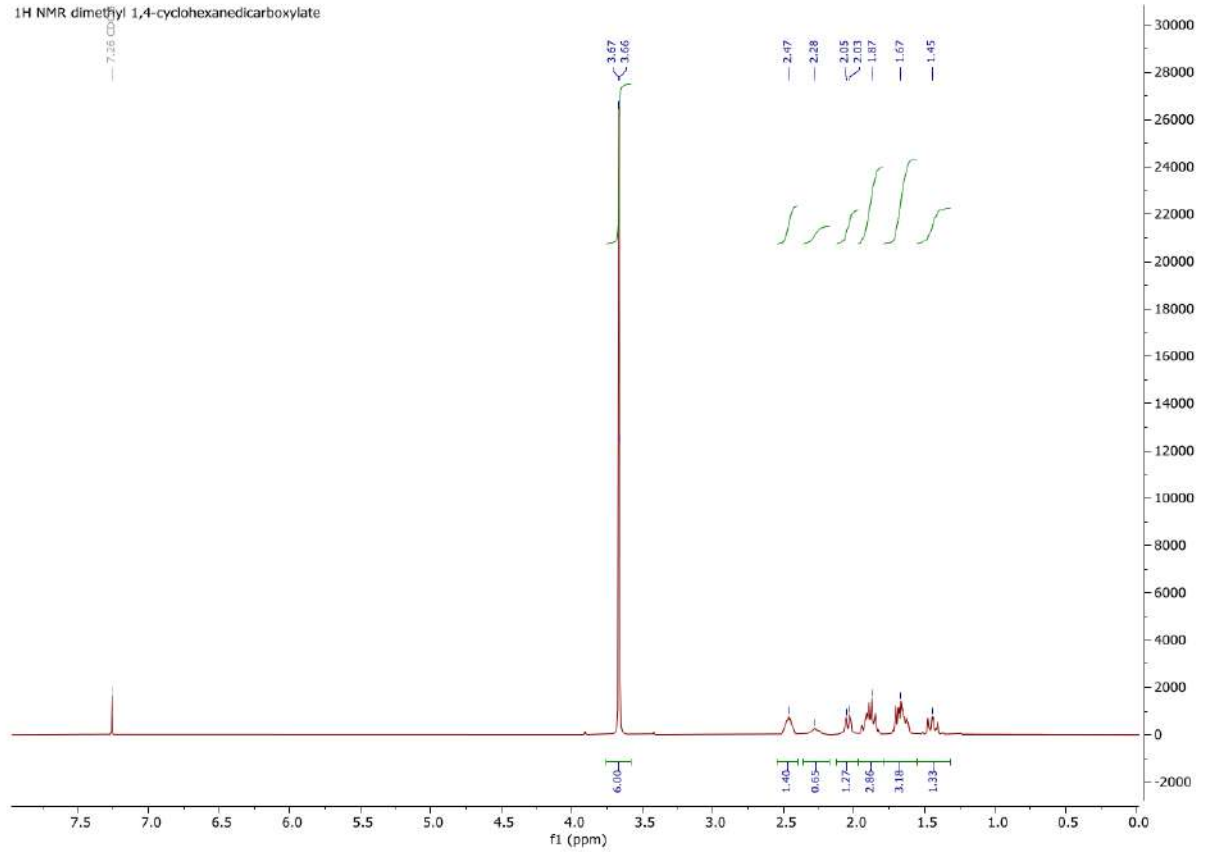
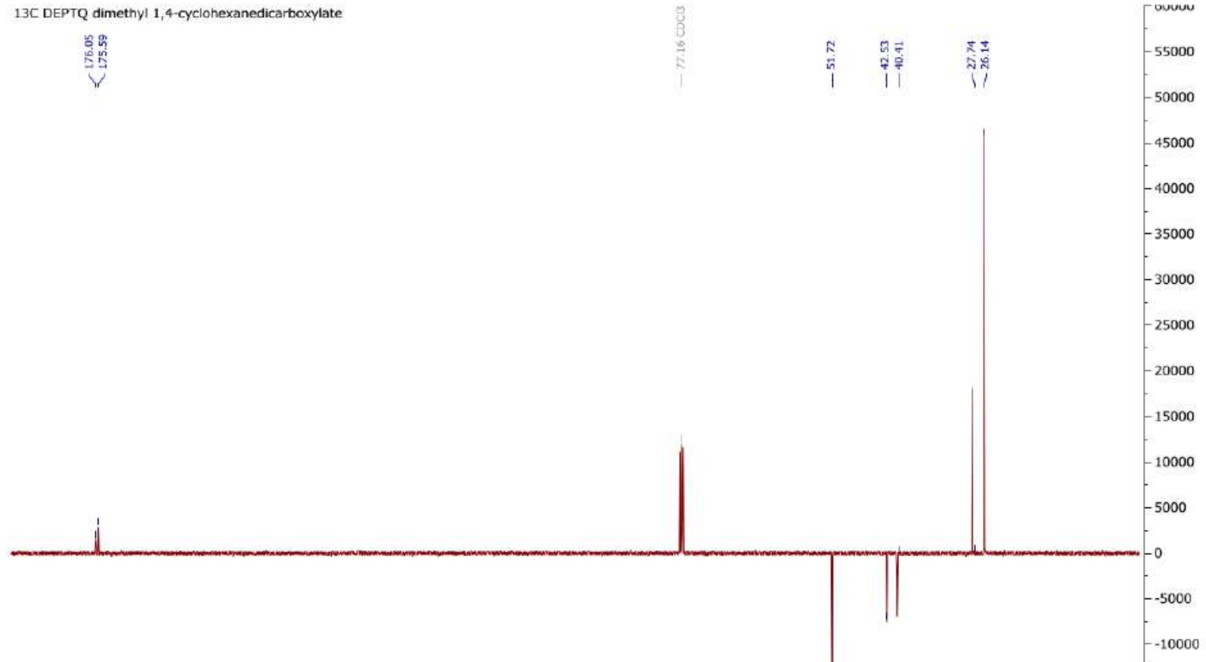


Figure S12. ^{13}C{^{1}H} NMR spectrum of **3** (^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, 25 °C)).



Procedure for hydrogenation of the ester functionalities of dimethyl terephthalate (2): A mixture of dimethyl terephthalate (**2**) (260.1 mg, 1.35 mmol) and Ruthenium-MACHO-BH (7.9 mg, 1.0 mol%, 0.0135 mmol) were placed with a stir bar in a vial. THF (2.0 mL) was added. The vial was placed in an autoclave, which was sealed and purged with hydrogen (5 times). Afterwards the desired hydrogen pressure was adjusted (45 bar) the autoclave was heated to the desired temperature (120 °C). The temperature was hold for 24 hours, while stirring the reaction mixture. Afterwards, the autoclave was cooled to room temperature and the hydrogen pressure was carefully released. An aliquot of the solution was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.6 mL). The sample was subjected to ^1H NMR to determine the conversion of **2**. The yield of **4** was calculated on the basis of the ester functionalities of **2** and the methylene units of **4**. Afterwards, the reaction mixture was filtered over a plug of silica, which was washed with acetone. The solvents were removed in vacuum. Compound **4** was obtained in 82% yield (m = 153 mg).

1,4-Benzenedimethanol (**4**): ^1H NMR (400 MHz, acetone-d6, 25 °C): δ = 7.31 (s, 4H, Ar*H*), 4.61 (d, *J* = 5.8 Hz, 4H, -C*H*$_2$OH), 4.12 (t, *J* = 5.8 Hz, 2H, -CH$_2$O*H*) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, acetone-d6, 25 °C): δ = 142.0, 127.3, 65.1 (-*C*H$_2$O-) ppm.

Figure S13. Spectrum of the reaction mixture (^1H NMR (400 MHz, acetone-d6, 25 °C)).

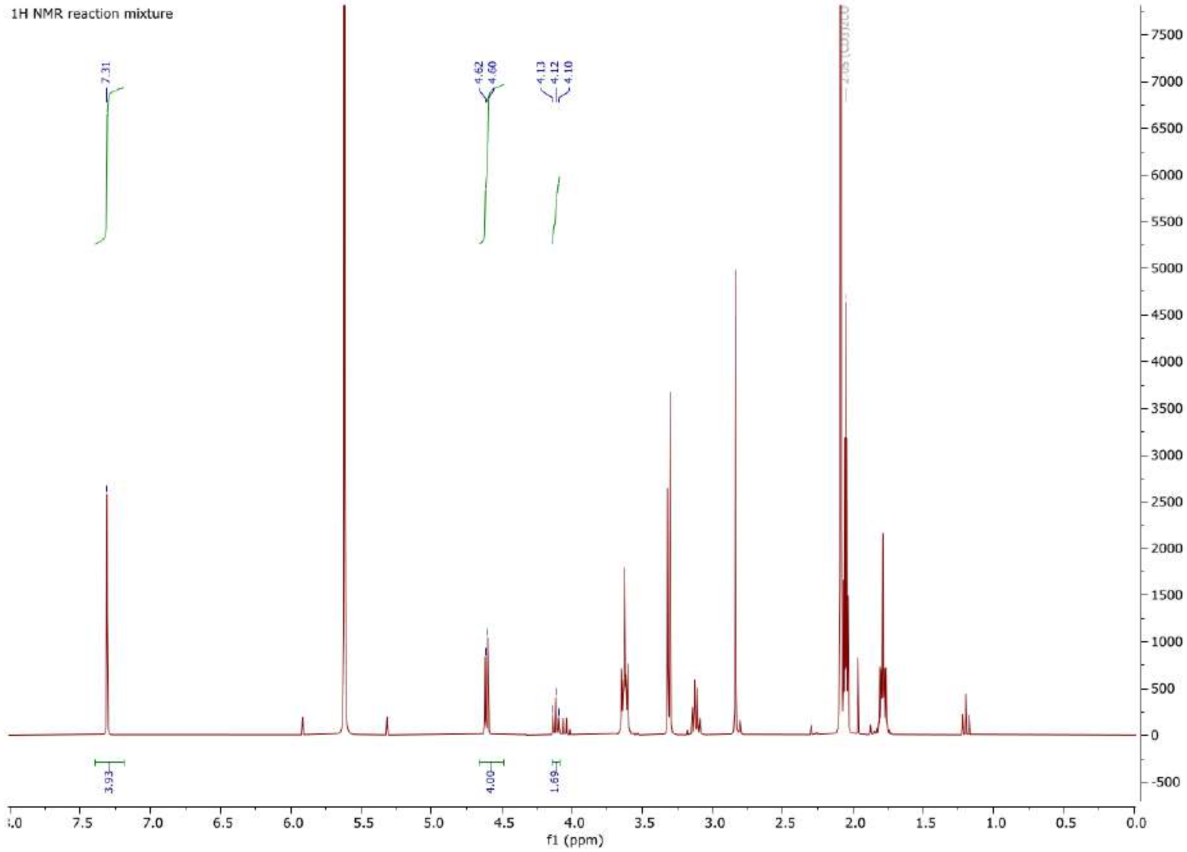


Figure S14. ^{1}H NMR spectrum of **4** (^{1}H NMR (400 MHz, acetone-d6, 25 °C)).

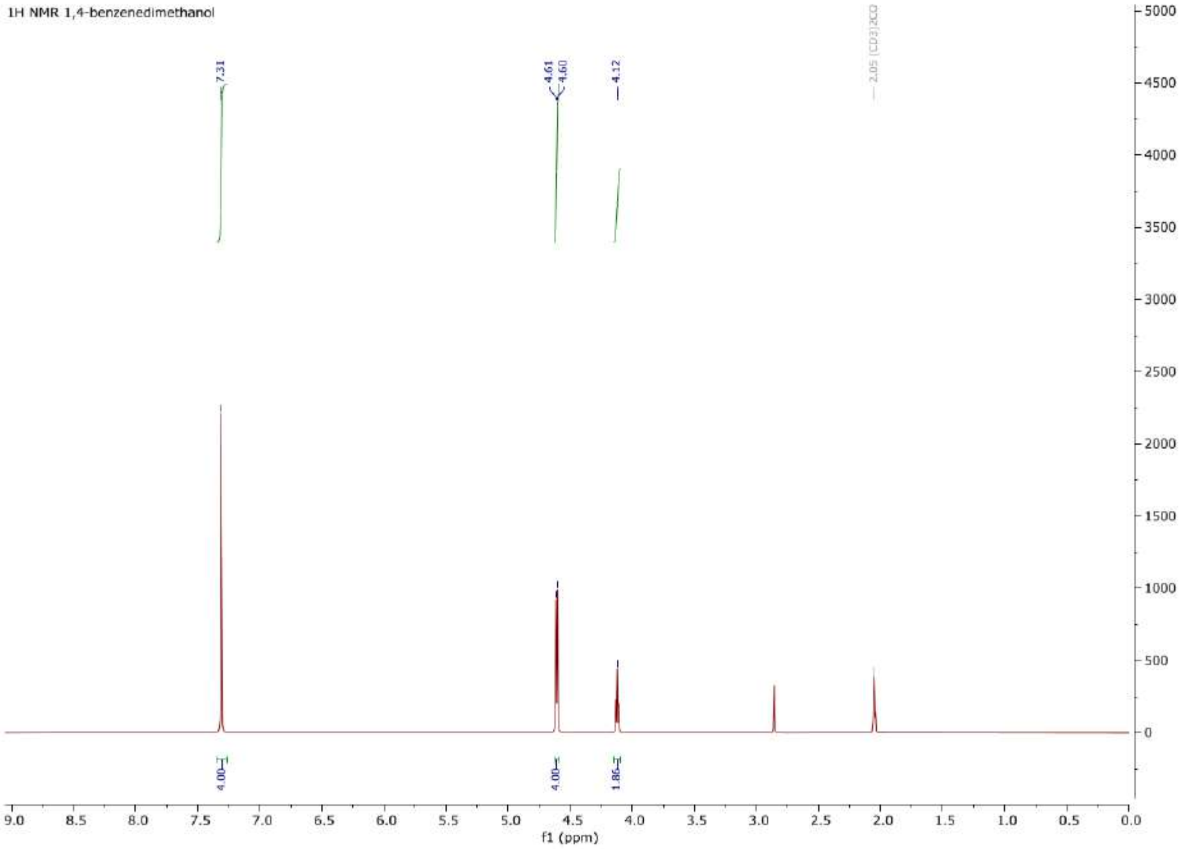
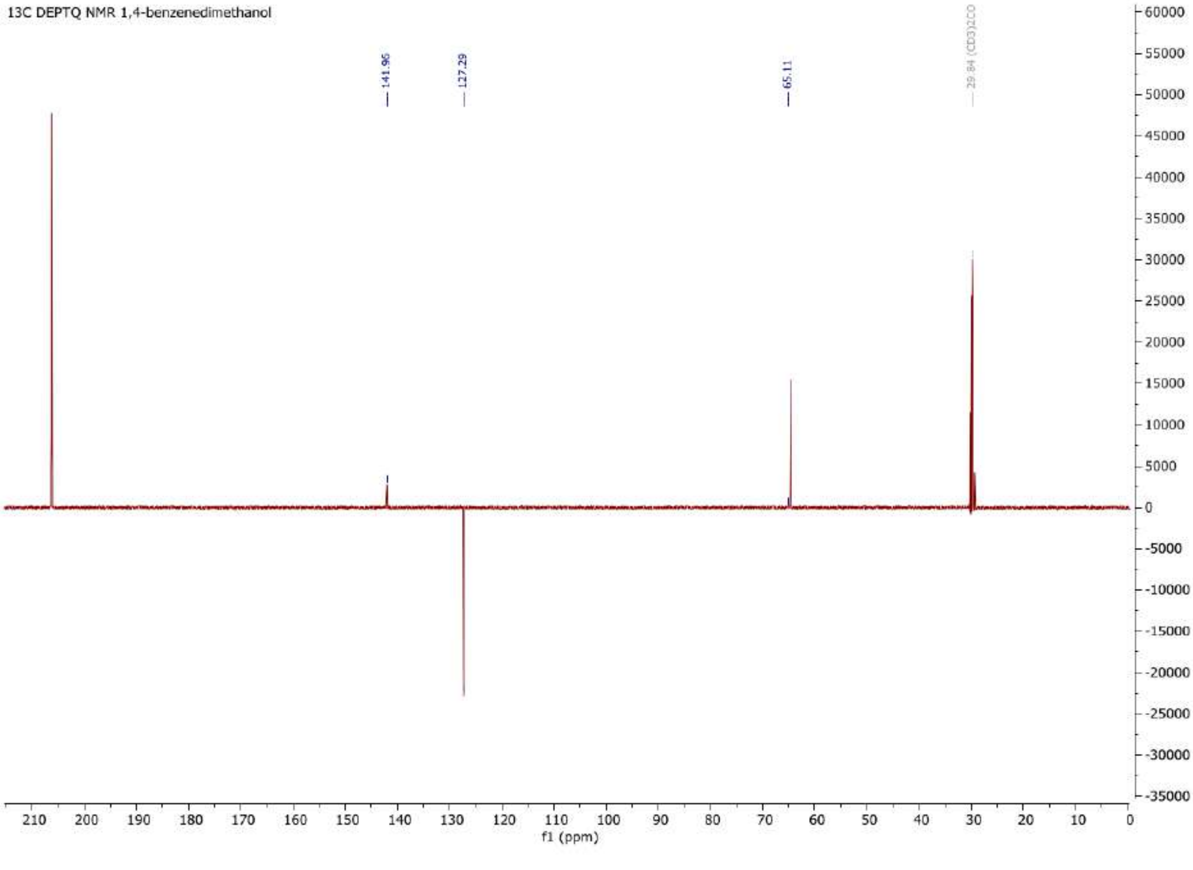


Figure S15. ^{13}C{^{1}H} NMR spectrum of **4** (^{13}C{^{1}H} NMR (125 MHz, acetone-d6, 25 °C)).



Procedure for hydrogenation of the ester functionalities of dimethyl 1,4-cyclohexanedicarboxylate (3): A mixture of dimethyl 1,4-cyclohexanedicarboxylate (**3**) (270.3 mg, 1.35 mmol) and Ruthenium-MACHO-BH (7.9 mg, 1.0 mol%, 0.0135 mmol) were placed with a stir bar in a vial. THF (2.0 mL) was added. The vial was placed in an autoclave, which was sealed and purged with hydrogen (5 times). Afterwards the desired hydrogen pressure was adjusted (45 bar) the autoclave was heated to the desired temperature (120 °C). The temperature was hold for 24 hours, while stirring the reaction mixture. Afterwards the autoclave was cooled to room temperature and the hydrogen pressure was carefully released. An aliquot of the solution was transferred to an NMR tube and was dissolved in $CDCl_3$ (0.6 mL). The sample was subjected to ^{1}H NMR to determine the conversion of **3**. The yield of **5** was calculated on the basis of the ester functionalities of **3** and the methylene units of **5**. Afterwards, the reaction mixture was filtered over a plug of silica, which was washed with acetone. The solvents were removed in vacuum. Compound **5** was obtained in 91% yield (m = 177 mg).

1,4-Cyclohexanedimethanol (**5**): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.45-3.56 (m, 4H, -O*CH₂*), 0.92-1.88 (m, 12H) ppm. A mixture of isomers was detected. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C): δ = 68.6, 66.1, 40.7, 38.1, 29.0, 25.4 ppm.

Figure S16. Spectrum of the reaction mixture (^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)).

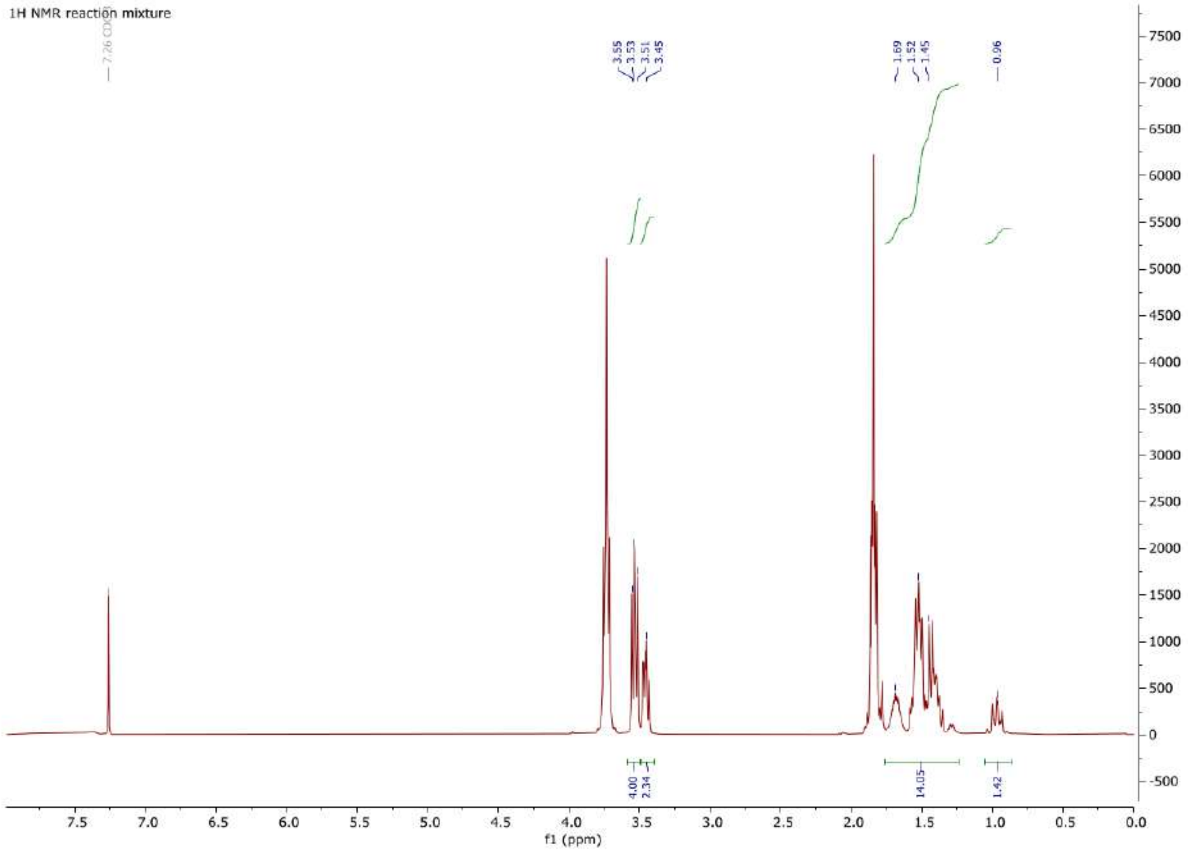


Figure S17. ^{1}H NMR spectrum of **5** (^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)).

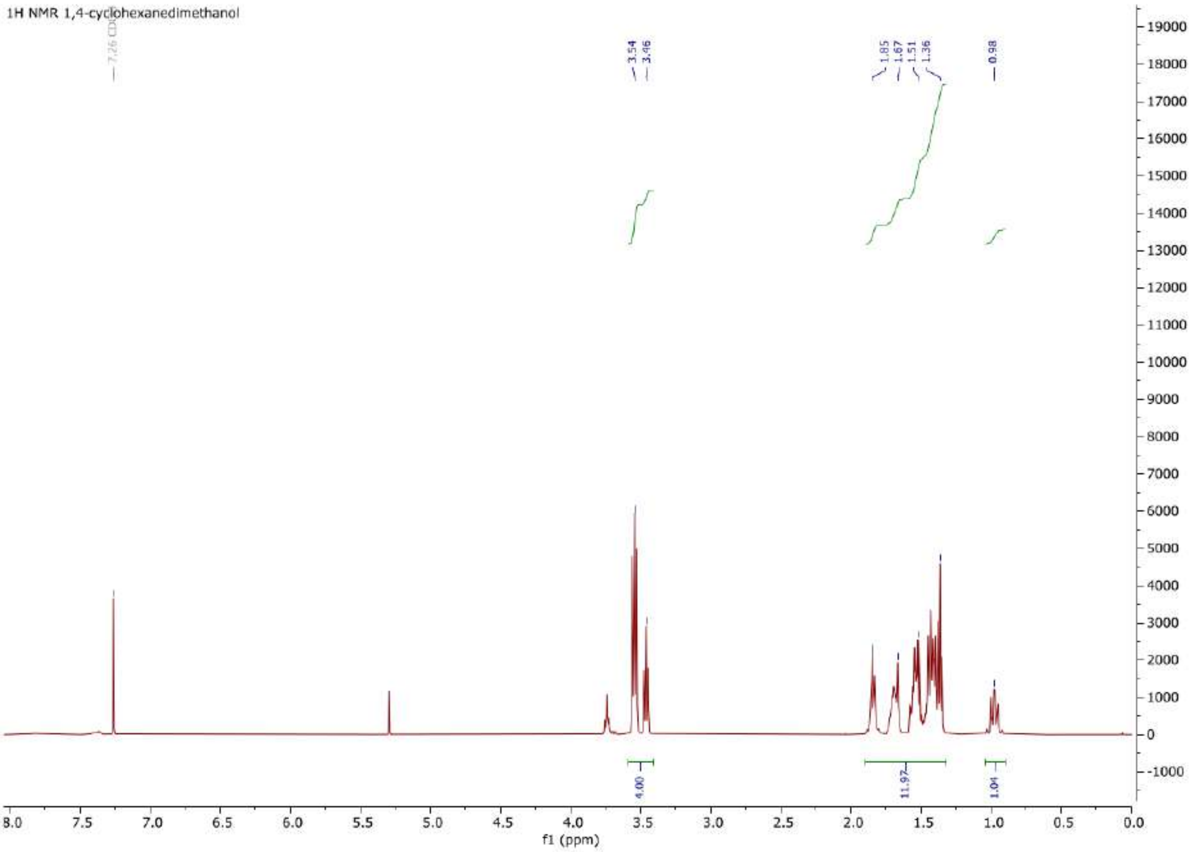
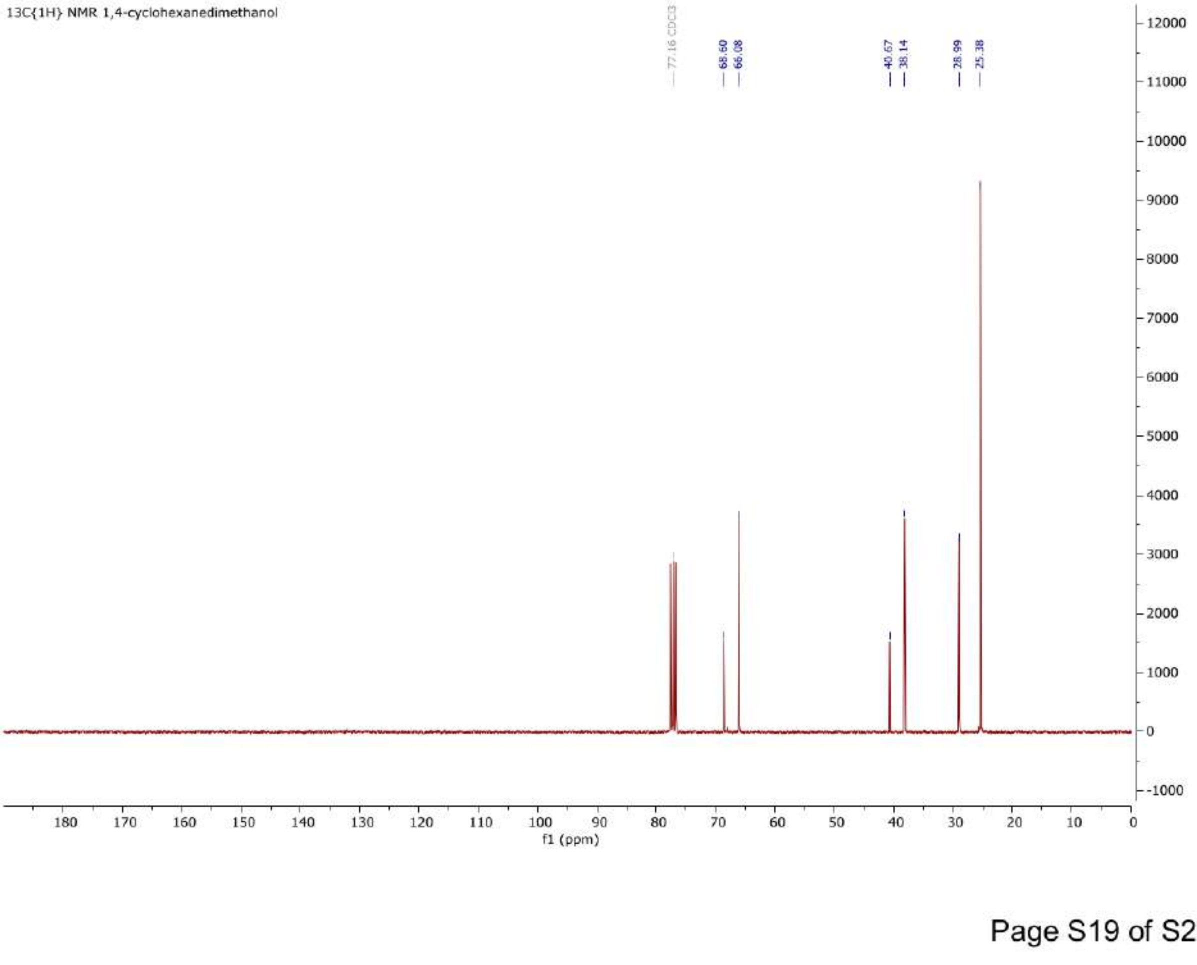


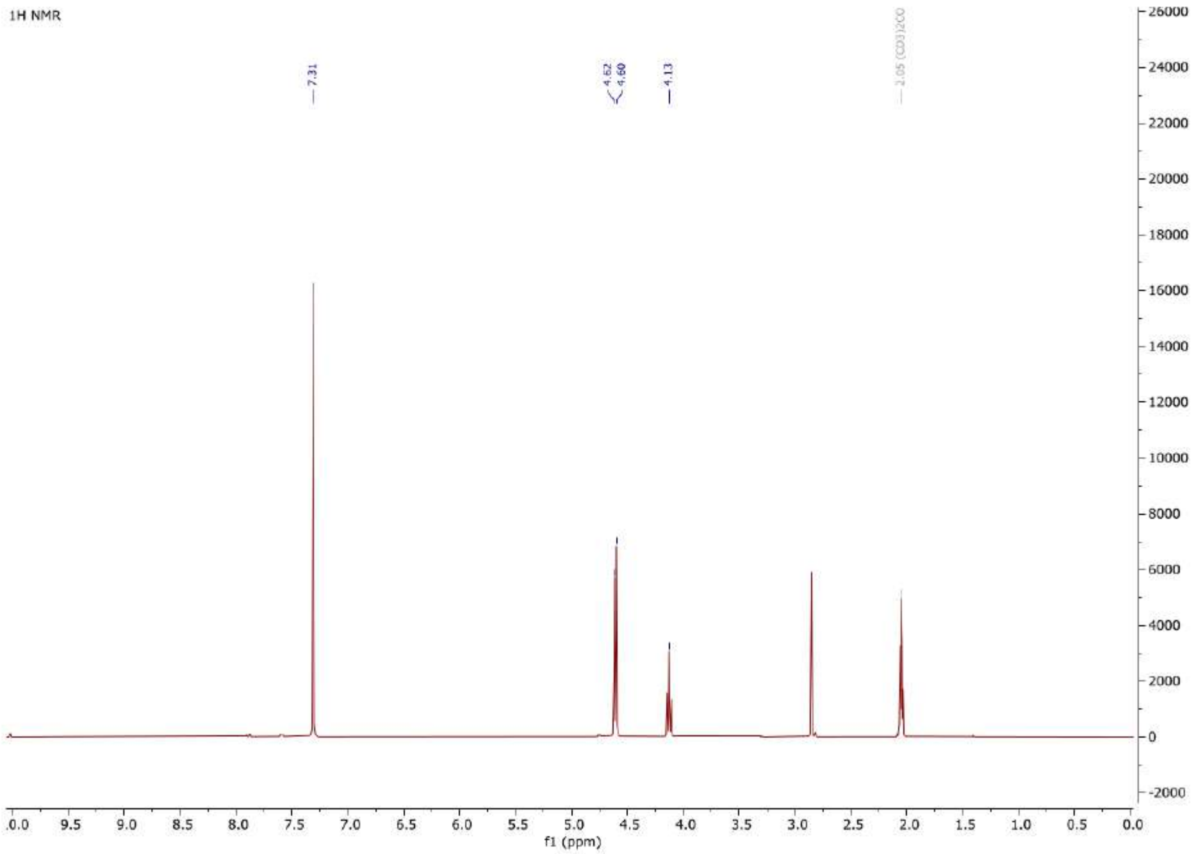
Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of **5** ($^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, 25 °C)).



Procedure for hydrogenation of the aromatic unit of 1,4-benzenedimethanol (4): A mixture of 1,4-benzenedimethanol (**4**) (186.4 mg, 1.35 mmol) and Ruthenium (5 wt%)/C (6.8 mg, 5 mol%, 0.0067 mmol based on the metal) was placed with a stir bar in a vial. THF (2.0 mL) was added. The vial was placed in an autoclave, which was sealed and purged with hydrogen (5 times). Afterwards the desired hydrogen pressure was adjusted (45 bar) the autoclave was heated to the desired temperature (120 °C). The temperature was hold for 24 hours, while stirring the reaction mixture. Afterwards the autoclave was cooled to room temperature and the hydrogen pressure was carefully released. An aliquot of the solution was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.6 mL). The sample was subjected to ^{1}H NMR to determine the conversion of **4**. No product formation was observed.

Procedure for hydrogenation of the aromatic unit and the ester functionalities of dimethyl terephthalate (2): A mixture of dimethyl terephthalate (**2**) (260.1 mg, 1.35 mmol), Ruthenium (5 wt%)/C (6.8 mg, 5 mol%, 0.0067 mmol based on the metal) and Ruthenium-MACHO-BH (7.9 mg, 1.0 mol%, 0.0135 mmol) were placed with a stir bar in a vial. THF (2.0 mL) was added. The vial was placed in an autoclave, which was sealed and purged with hydrogen (5 times). Afterwards, the desired hydrogen pressure was adjusted (45 bar) the autoclave was heated to the desired temperature (120 °C). The temperature was hold for 24 hours, while stirring the reaction mixture. Afterwards, the autoclave was cooled to room temperature and the hydrogen pressure was carefully released. An aliquot of the solution was transferred to an NMR tube and was dissolved in $CDCl_3$ (0.6 mL). The sample was subjected to ^{1}H NMR to determine the conversion of **2**. As product compound **4** was detected and isolated in 98% yield (m = 184 mg).

Figure S20. Spectrum of **4** (^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)).



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[2] Compared with an authentic sample.

[3] Compared with an authentic sample.

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[9] Compared with an authentic sample.

ChemistrySelect

Supporting Information

Zinc-Catalyzed Depolymerization of the End-of-Life Poly (ethylene 2,5-furandicarboxylate)

Christoph Alberti, Konstantin Matthiesen, Moritz Wehrmeister, Sergej Bycinskij, and Stephan Enthaler*

General: All chemicals were used as received without further manipulations. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a *Fourier 300 MHz* (^{1}H: 300 MHz, ^{13}C: 75 MHz), *Avance I-400* (^{1}H: 400 MHz, ^{13}C: 101 MHz) or *Avance I 500* (^{1}H: 500 MHz, ^{13}C: 126 MHz) by Bruker, using the signals of the deuterated solvents as reference or external standards. Mass spectrometry was performed using a *Thermo ISQ LT EI* by Thermo Fisher Scientific. For microwave heating experiments a Microwave Synthesis Reactor Monowave 400 (Anton Paar GmbH) was used. The scale-up was performed in a Parr autoclave (model: 4774) (Parr Instrument Company).

Synthesis of Poly(ethylene-2,5-furandicarboxylate) (1, PEF)

The synthesis of poly(ethylene-2,5-furandicarboxylate) (PEF) was carried out according to Kucherov *et al.* with slight modifications.[11]

Dimethyl furan-2,5-dicarboxylate (15.8 g, 85.9 mmol, 1.00 equiv.) and ethylene glycol (10.7 g, 172 mmol, 2.00 equiv.) were heated under nitrogen to 115 °C until dimethyl furan-2,5-dicarboxylate is dissolved/melted. To the homogeneous solution was added Ti(O*i*Pr)$_4$ (1.25 mol%, 0.306 g, 1.08 mmol) dissolved in toluene (5.3 mL). Afterwards the temperature was increased to 170 °C and the mixture was stirred for 17 h. After that the temperature was raised to 215 °C and hold for 2 h. Afterwards the temperature was increased to 235 °C and hold for 4 hours under a vacuum of 8 mbar. For purification, the polymer was dissolved in a mixture of trifluoracetic acid (TFA)-chloroform (230 mL, 1:2.5), precipitated in methanol (600 mL), then filtered and dried in vacuum. The polymer (15.0 g, 82.2 mmol, 96%) was obtained as colourless powder.

^{1}H NMR (300 MHz, $CDCl_3$ + CF_3COOH): δ [ppm] = 7.34 (s, 2H, furan-C*H*), 4.74 (s, 4H, C*H*$_2$), 4.01 (s, 0.19, C*H*$_2$OH).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ + CF_3COOH): δ [ppm] = 160.1 (*C*=O), 146.5 (furan-*C*$_q$), 120.7 (furan-*C*H), 64.2 (O*C*H$_2$).

Calculation of the number average molar mass of **1** from ^{1}H NMR data using the end-groups of **1**: M_n ~3947 g/mol

Figure S1: ^{1}H NMR spectrum of PEF ($CDCl_3$/TFA, 300 MHz, 25 °C).

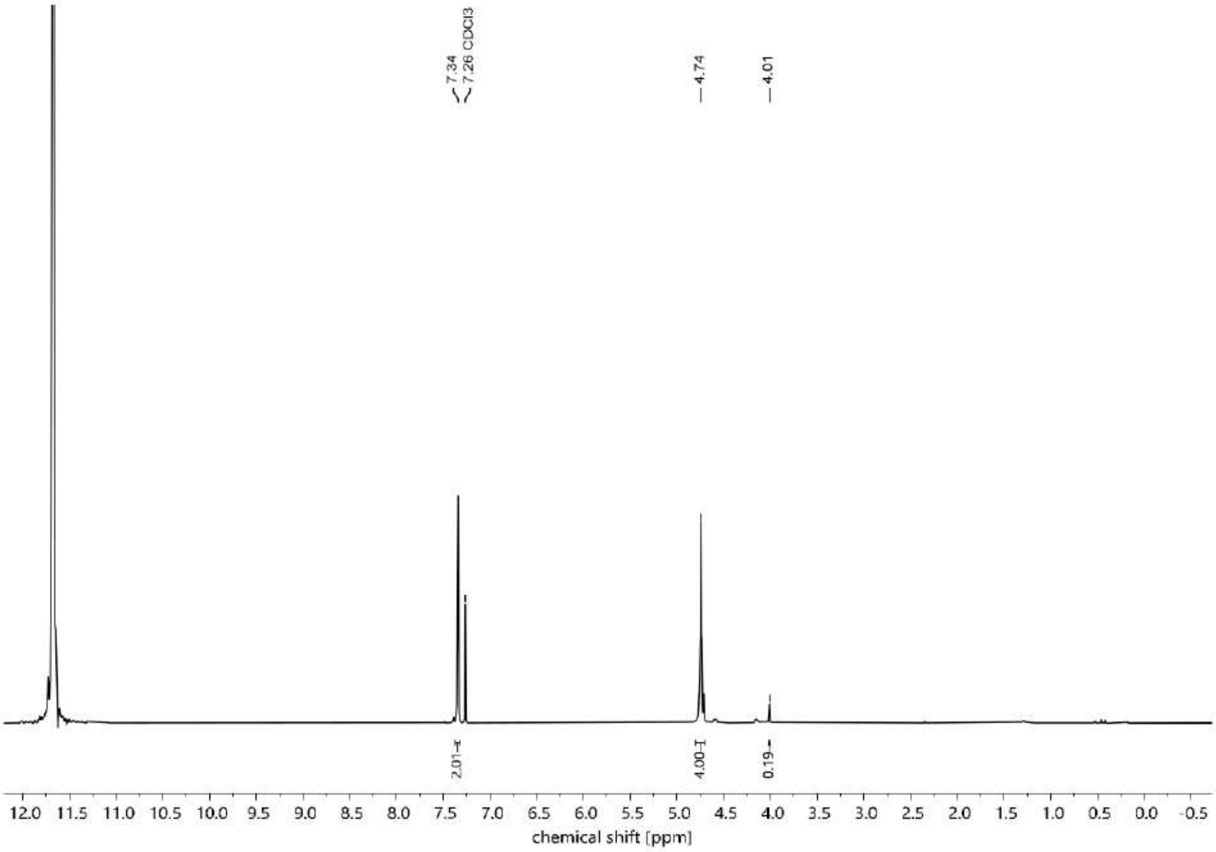
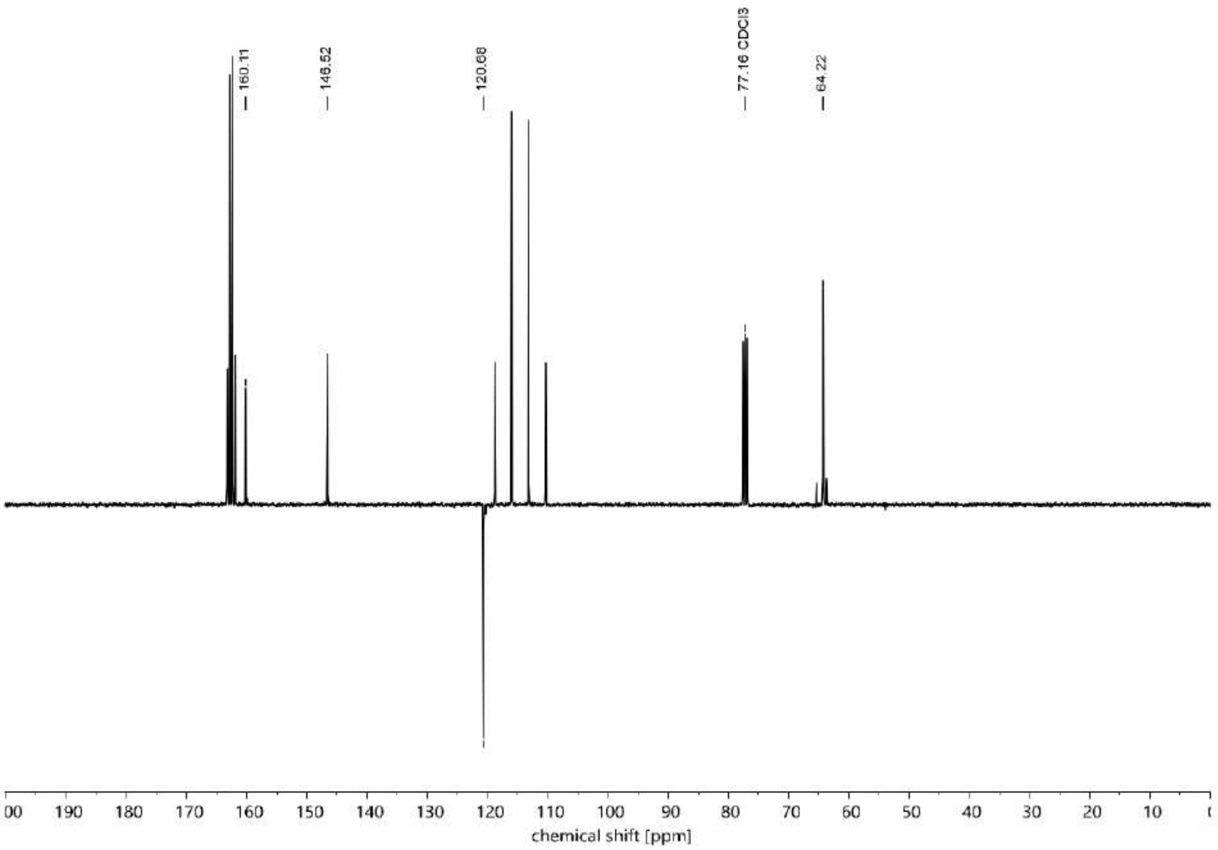


Figure S2: $^{13}C\{^1H\}$ NMR spectrum of PEF ($CDCl_3$/TFA, 101 MHz, 25 °C).

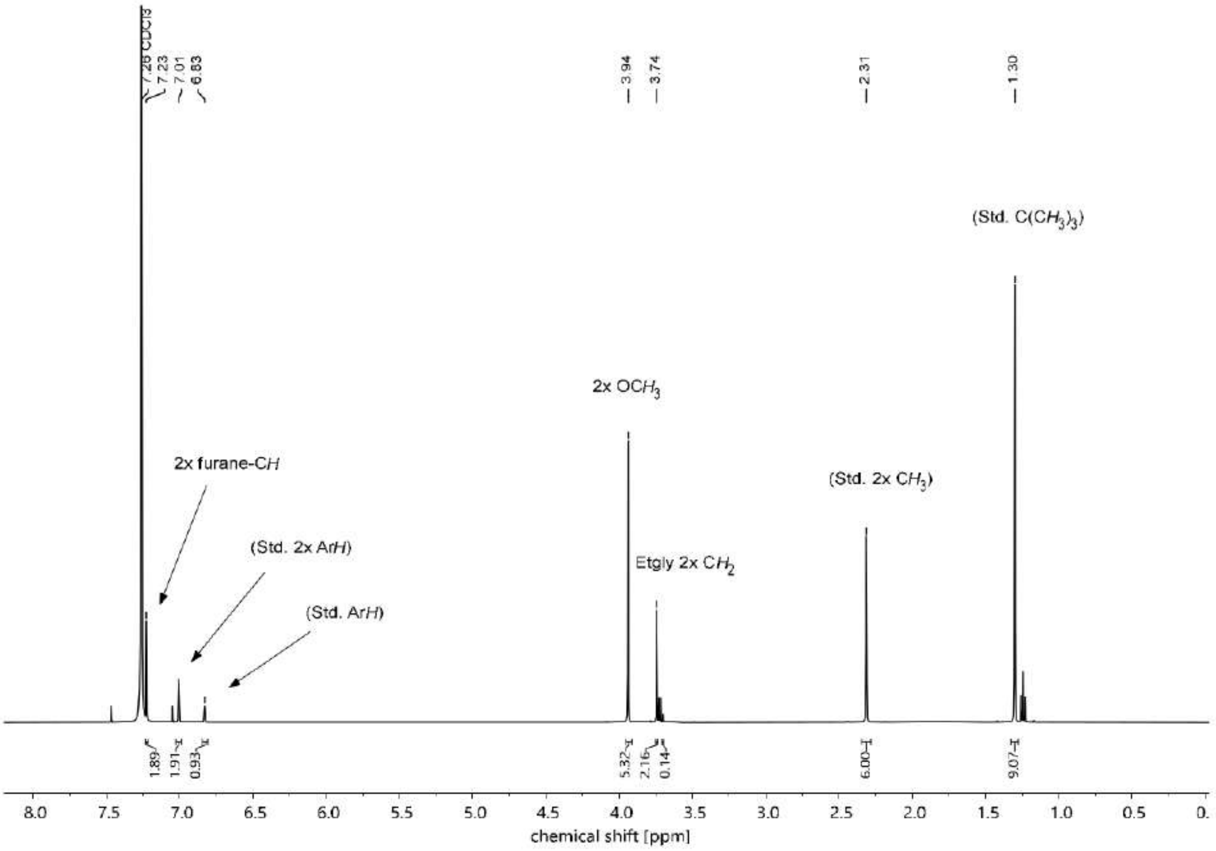


General procedure for the depolymerization of Poly(ethylene-2,5-furandicarboxylate) (1) (optimization of the reaction conditions): A mixture of PEF (**1**) (200 mg, 1.1 mmol based on the repeating unit), methanol (1.58-3.17 g, 44.0-90.0 equiv., 49.4-98.8 mmol based on the repeating unit of **1**) and catalytic amounts of zinc salts (0-5.0 mol%, 0-0.059 mmol based on the repeating unit of **1**) was placed with a stir bar in a vial. The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 10-60 minutes (hold time) at 120-160 °C and with a stirring rate of 400 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature. The excess of methanol was carefully removed in vacuum. The residue was dissolved in chloroform and 1-*tert*-butyl-3,5-dimethylbenzene was added as standard. An aliquot of the clear solution was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^1H NMR to determine the yield of dimethyl furan-2,5-dicarboxylate (**2**) [The yield of **2** was calculated on the basis of the C*H*-functions and CH_3-functions of **2** and the signals of the standard].

2: ^1H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.22 (s, 2H, furan-C*H*), 3.93 (s, 6H, OCH_3).

3: ^1H NMR (300 MHz, $CDCl_3$): δ [ppm] = 3.74 (s, 4H, OCH_2).

Figure S3: ^{1}H NMR spectrum of the reaction mixture of the depolymerization of PEF ($CDCl_3$, 300 MHz, 25 °C).



Procedure for the depolymerization of Poly(ethylene-2,5-furandicarboxylate) (1) (scale-up, microwave synthesis reactor): A mixture of PEF (**1**) (1.00 g, 5.5 mmol based on the repeating unit), methanol (11.88 g, 67.5 equiv., 370.7 mmol based on the repeating unit of **1**) and catalytic amounts zinc(II) acetate (5.0 mol%, 0.28 mmol based on the repeating unit of **1**) was placed with a stir bar in a vial. The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 60 minutes (hold time) at 120 °C and with a stirring rate of 400 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature. The dimethyl furan-2,5-dicarboxylate (**2**) was filtered off and was recrystallized from methanol. The resulting crystals were washed with methanol and dried in vacuum. The dimethyl furan-2,5-dicarboxylate (**2**) (0.96 g, 5.2 mmol, 95%) was obtained as colourless crystals.

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.22 (s, 2H, furan-C*H*), 3.93 (s, 6H, OCH_3).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ [ppm] = 158.6 (*C*=O), 146.8 (furan-C_q), 118.6 (furan-*C*H), 52.6 (OCH_3).

Figure S4: ^{1}H NMR spectrum of dimethyl furan-2,5-dicarboxylate ($CDCl_3$, 300 MHz, 25 °C).

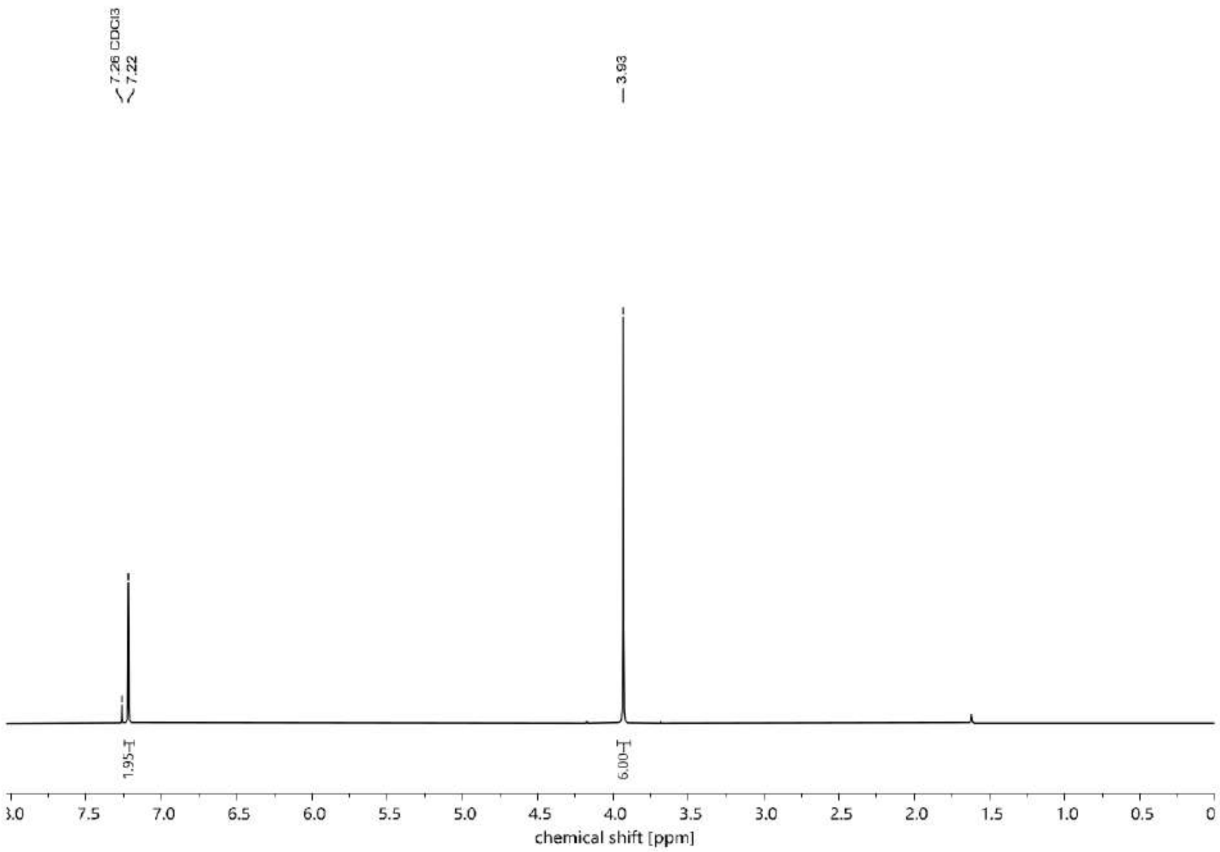
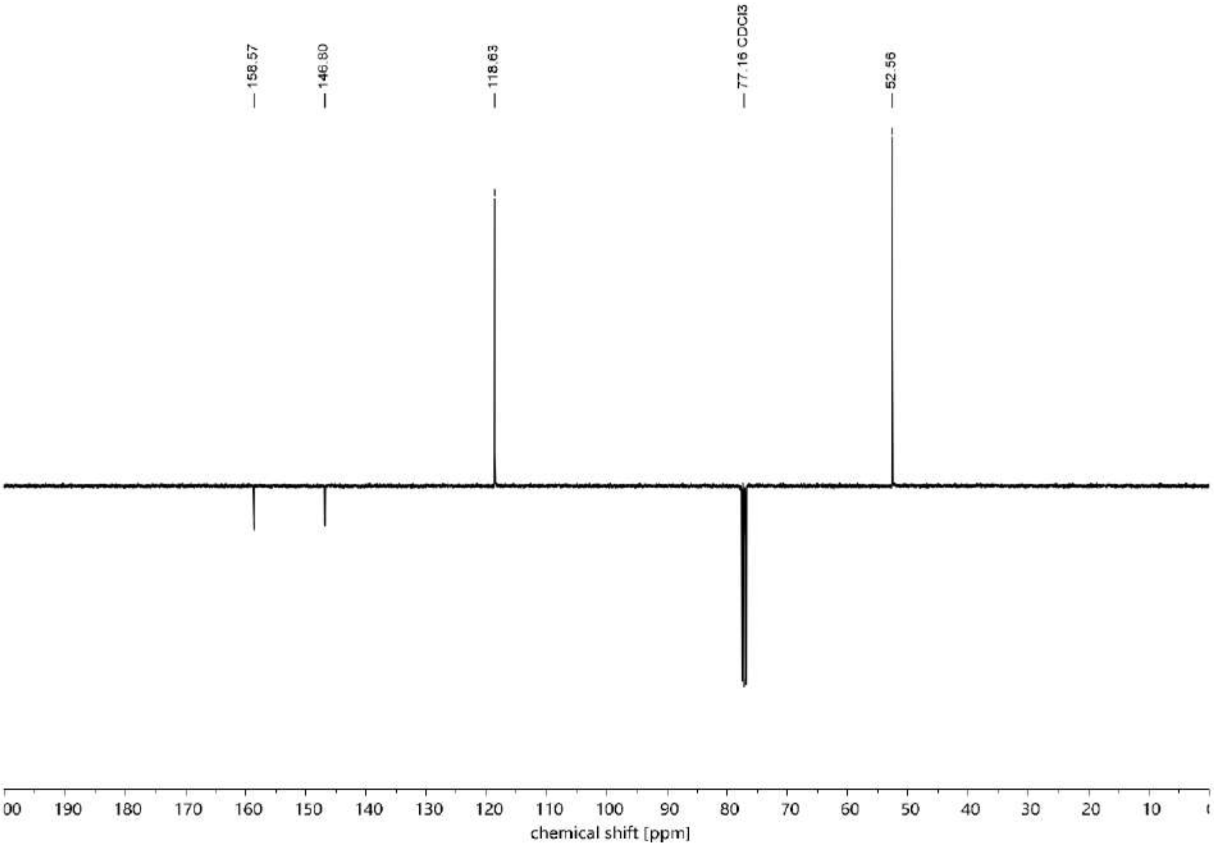


Figure S5: $^{13}C\{^{1}H\}$ NMR spectrum of dimethyl furan-2,5-dicarboxylate ($CDCl_3$, 101 MHz, 25 °C).



Procedure for the depolymerization of Poly(ethylene-2,5-furandicarboxylate) (1) (scale-up, autoclave): A mixture of PEF (**1**) (5.00 g, 27.5 mmol based on the repeating unit), methanol (59.4 g, 67.5 equiv., 1.85 mol based on the repeating unit of **1**) and catalytic amounts zinc(II) acetate (5.0 mol%, 1.37 mmol based on the repeating unit of **1**) was placed with a stir bar a Parr autoclave (model: 4774) (Parr Instrument Company). The reaction was performed for 120 minutes (hold time) at 120 °C and with a stirring. Afterwards the autoclave was cooled to room temperature. The dimethyl furan-2,5-dicarboxylate (**2**) was filtered off and was recrystallized from methanol. The resulting crystals were washed with methanol and dried in vacuum. The dimethyl furan-2,5-dicarboxylate (**2**) (4.63 g, 25.1 mmol, 92%) was obtained as colourless crystals. The NMR data are in accordance to the microwave scale-up experiment.

General procedure for the depolymerization of Poly(ethylene-2,5-furandicarboxylate) (1) with additional polymer B: A mixture of PEF (**1**) (200 mg, 1.1 mmol based on the repeating unit), methanol (2.37 g, 67.5 equiv., 74.1 mmol based on the repeating unit of **1**), a second polymer (30.8-210.8 mg, 1.0 equiv., 1.1 mmol based on the repeating unit of **1**) and catalytic amounts of zinc salts (5.0 mol%, 0.059 mmol based on the repeating unit of **1**) was placed with a stir bar in a vial. The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 30 minutes (hold time) at 120 °C and with a stirring of 400 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature. The excess of methanol was carefully removed in vacuum. The residue was dissolved in chloroform and 1-*tert*-butyl-3,5-dimethylbenzene was added as standard. An aliquot of the clear solution was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^1H NMR to determine the yield of dimethyl furan-2,5-dicarboxylate (**2**) [The yield of **2** and the depolymerization products of polymer B were calculated on the basis of the C*H*-functions and CH_3-functions of **2**, characteristic signals of polymer B and the signals of the standard].

Zinc-catalyzed Synthesis of Poly(ethylene-2,5-furandicarboxylate) (1, PEF)

Dimethyl furan-2,5-dicarboxylate (5,48 g, 29.8 mmol, 1.00 equiv.), ethylene glycol (5.66 g, 91.2 mmol, 3.64 equiv.) and zinc(II) acetate (1.25 mol%, 69.9 mg, 0.38 mmol) were heated under nitrogen to 170 °C and the mixture was stirred for 16 h. Afterwards, the temperature was raised to 215 °C for 2 h. To achieve high molar weights in the second step, a vacuum of 8 mbar was applied, and the reaction solution was heated under stirring to 235 °C. After 4 h at 235 °C the solution was cooled down to room temperature. For purification, the polymer was dissolved in a TFA-chloroform mixture (70 mL, 1:2.5), precipitated in methanol (250 mL), then filtered and dried in vacuum. The polymer (4.39 g, 24.2 mmol, 81%) was obtained as colourless powder.

^1H NMR (300 MHz, $CDCl_3$ + CF_3COOH): δ [ppm] = 7.34 (s, 2H, furan-C*H*), 4.74 (s, 4H, CH_2), 4.01 (s, 0.09, CH_2OH).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$ + CF_3COOH): δ [ppm] = 160.1 (*C*=O), 146.6 (furan-C_q), 120.7 (furan-*C*H), 64.2 (O*C*H_2).

Calculation of the number average molar mass of **1** from ^1H NMR data using the end-groups of **1**: M_n ~8295 g/mol

Figure S6: ^{1}H NMR spectrum of PEF ($CDCl_3$/TFA, 300 MHz, 25 °C).

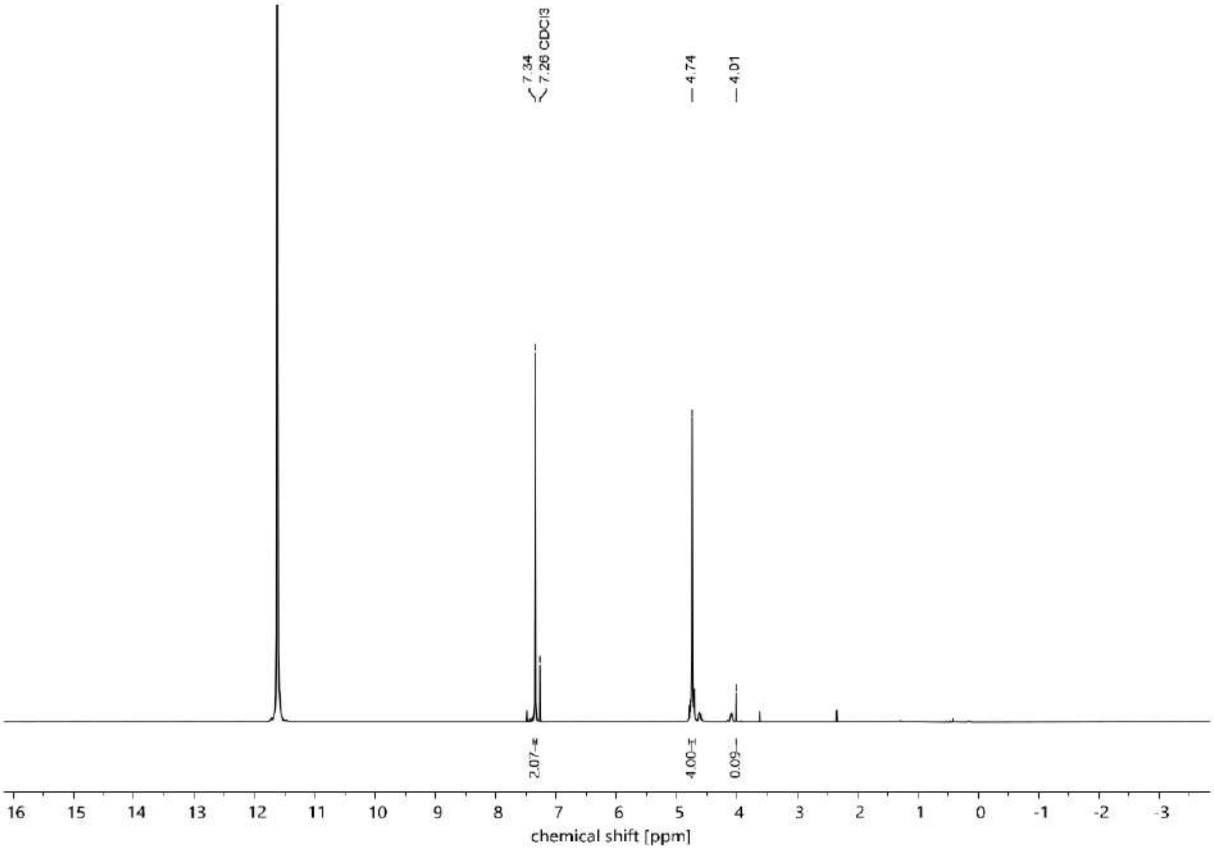
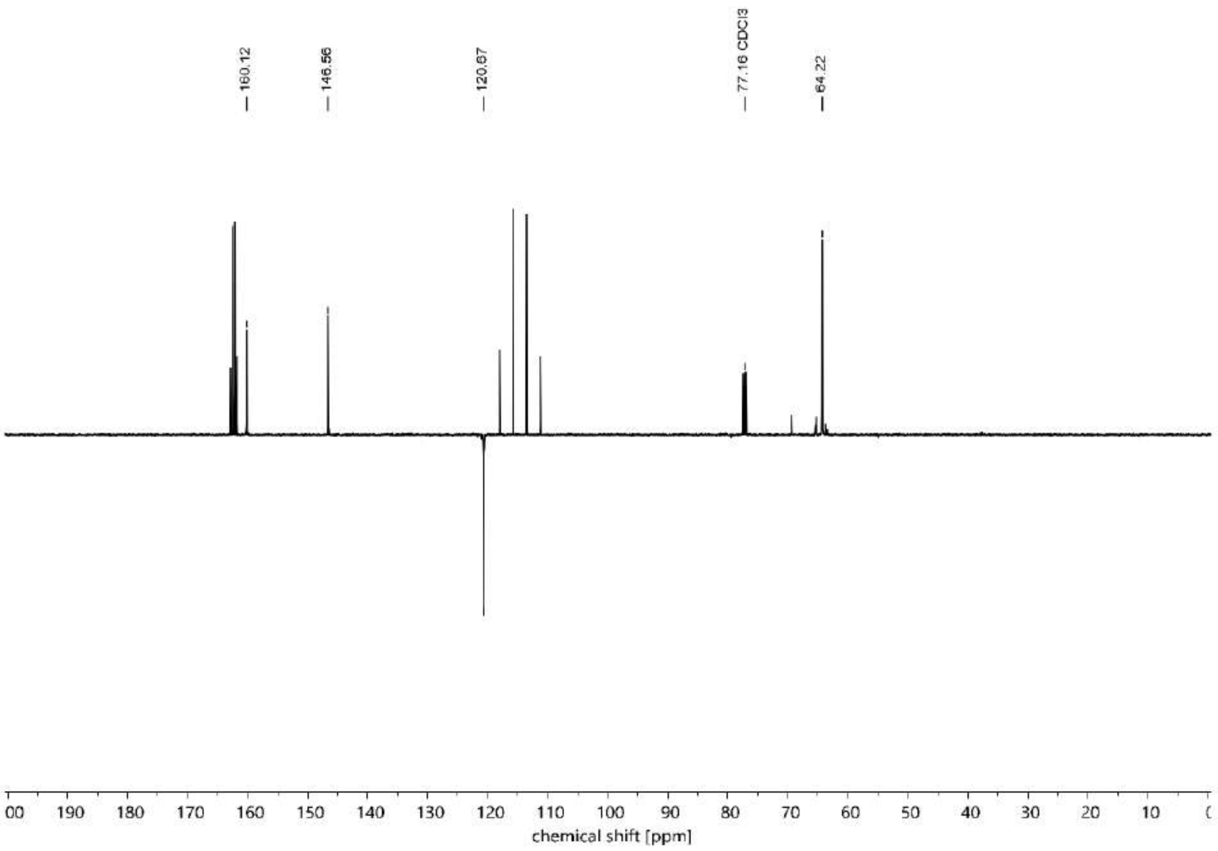


Figure S7: $^{13}C\{^1H\}$ NMR spectrum of PEF ($CDCl_3$/TFA, 101 MHz, 25 °C).



Determination of rate constants k, activation energy E_a and frequency factor A_0

For the transesterification reaction of ethylene glycol esters (COOEg) to methyl ester groups (COOMe) the following rate law was constructed, based on the assumption, that [MeOH] is constant during the reaction (pseudo first order kinetics)

$\frac{d[COOEg]}{dt} = -\frac{d[COOMe]}{dt} = k' \cdot [COOEg] \cdot [MeOH] = k \cdot [COOEg]$ (eq. 1)

Accordingly, the concentration of Eg-Esters is: $[COOEg]_t = [COOEg]_0 \cdot e^{-k\cdot t}$ (eq. 2)

$\Rightarrow \frac{[COOEg]_t}{[COOEg]_0} = e^{-k\cdot t} = 1-\eta_{COOMe}$ (eq. 3)

η_{COOMe} was determined from the ^1H NMR data. k was determined by a linearized plot of eq. 3 (Figure S8-S11):

$\ln([1-\eta_{COOMe}] = -k \cdot t$ (eq. 4)

$k = A_0 \cdot e^{-\frac{E_a}{RT}}$ (eq. 5)

$\ln(k) = \ln(A_0) - \frac{E_a}{R} \cdot \frac{1}{T}$ (eq. 6)

The activation energy was calculated form the slope ($-E_a/R$) of the linearized Arrhenius equation (eq. 6) and the frequency factor A_0 from the y-intercept (Figure S13).

E_a= 105.1 kJ/mol; $A_0 = 1.53 \cdot 10^{11} \frac{1}{s}$

Figure S8: Plot of ln $(1-\eta_{COOMe})$ vs. time [s] for 100°C.

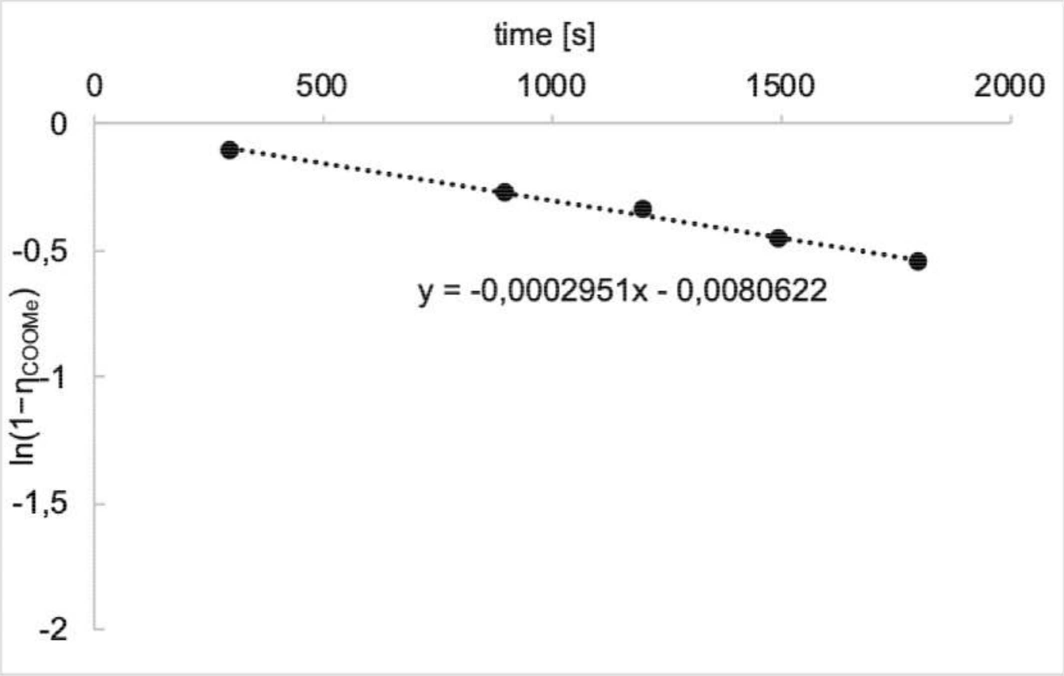


Figure S9: Plot of ln (1−η_{COOMe}) vs. time [s] for 110°C.

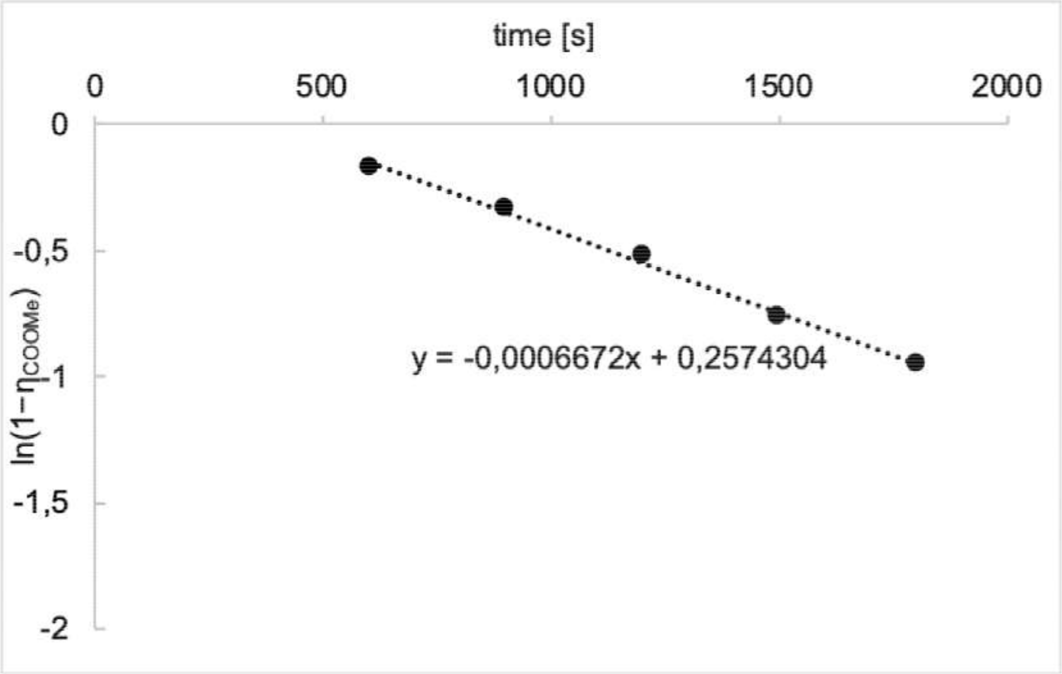


Figure S10: Plot of ln (1−η_{COOMe}) vs. time [s] for 120°C.

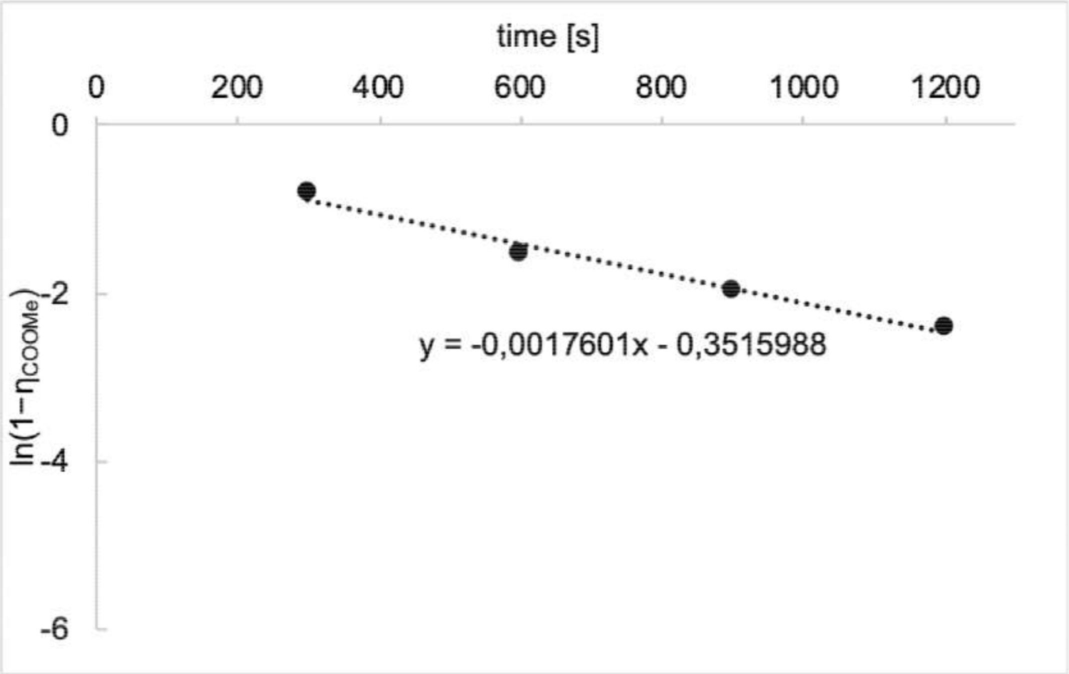


Figure S11: Plot of ln (1−η_{COOMe}) vs. time [s] for 130°C.

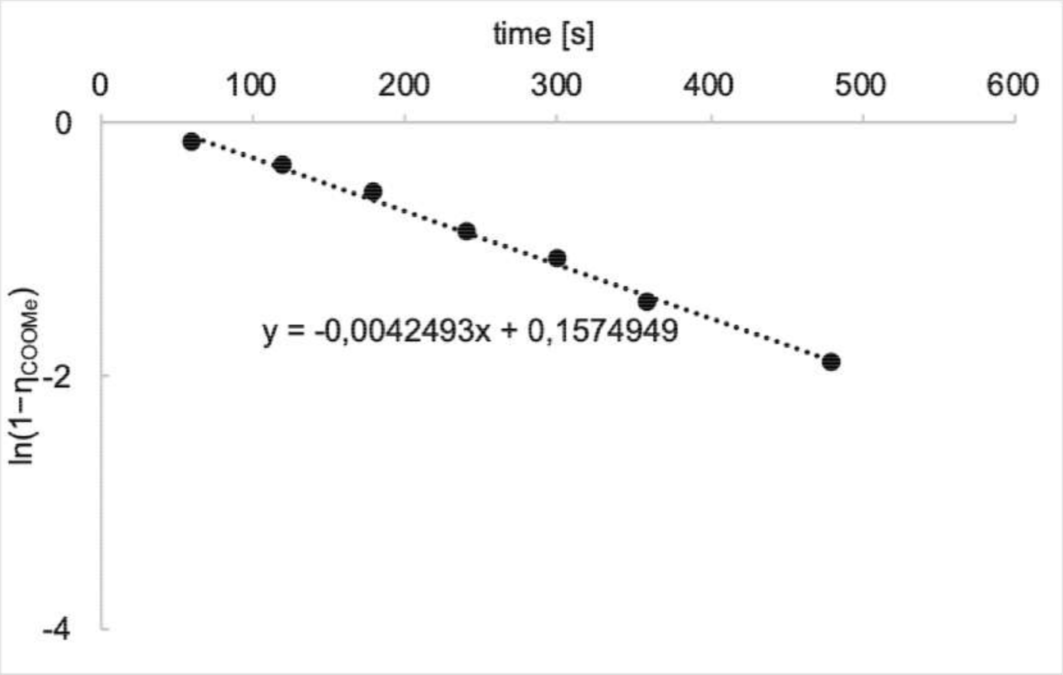


Figure S12: Plot of ln (1−η_{COOMe}) vs. time [s] for 140°C.

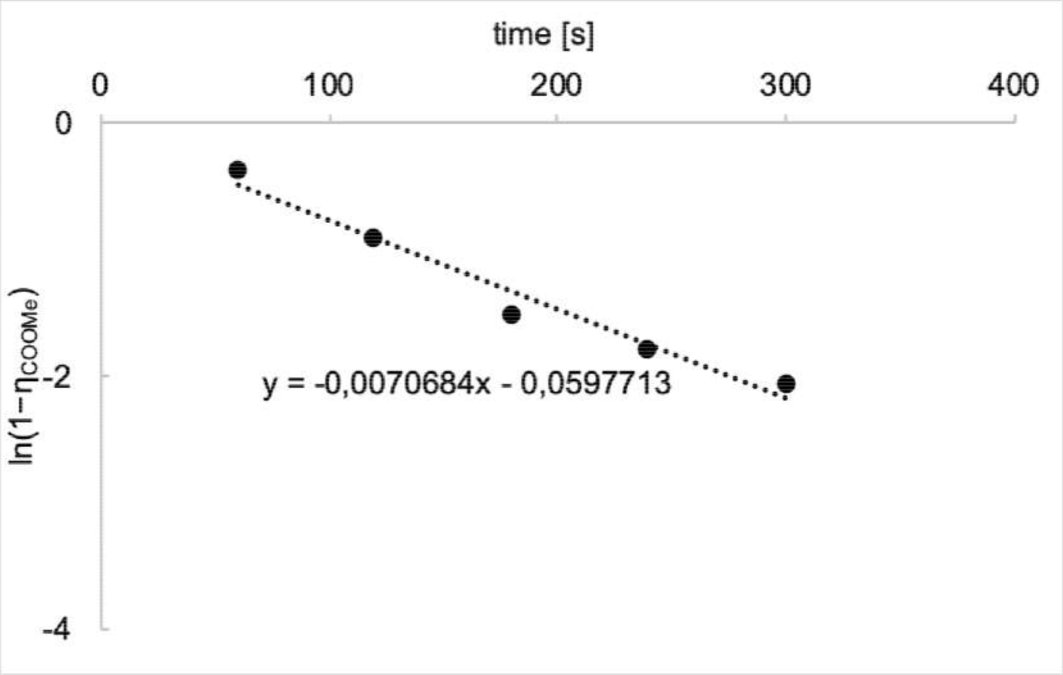
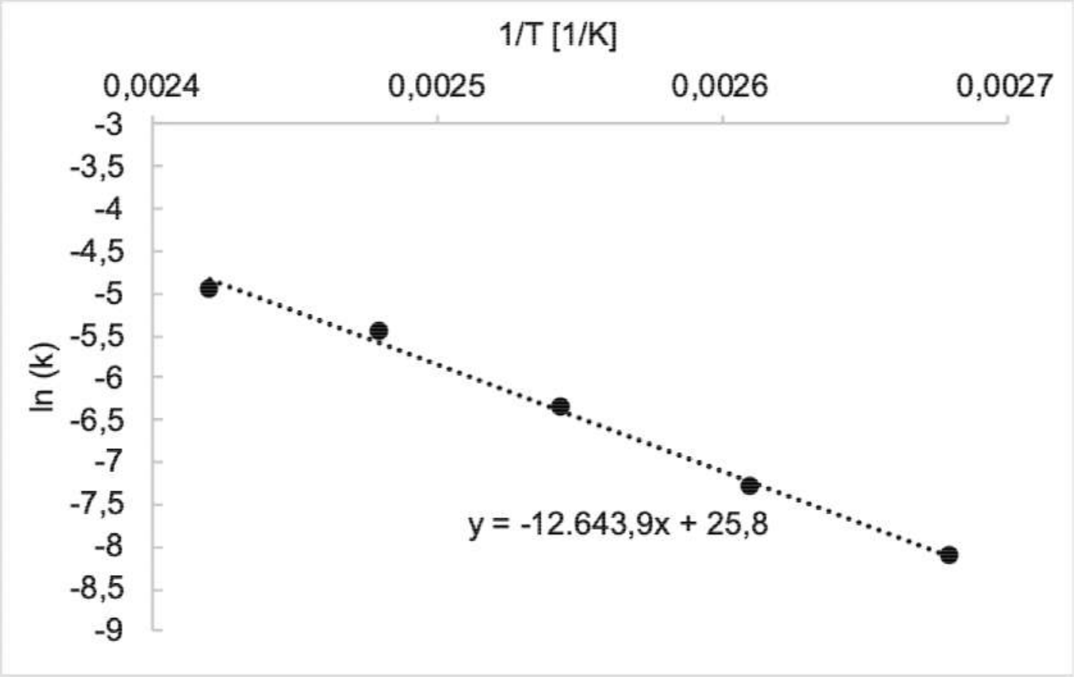


Figure S13: Arrhenius Plot with ln (k)-values for 100-140°C.



References

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[1] F. A. Kucherov, E. G. Gordeev, A. S. Kashin, V. P. Ananikov, *Angew. Chem. Int. Ed.* **2017**, *56*, 15931-15935.

ChemistrySelect

Supporting Information

Zinc-Catalyzed Chemical Recycling of Poly(ε-caprolactone) Applying Transesterification Reactions

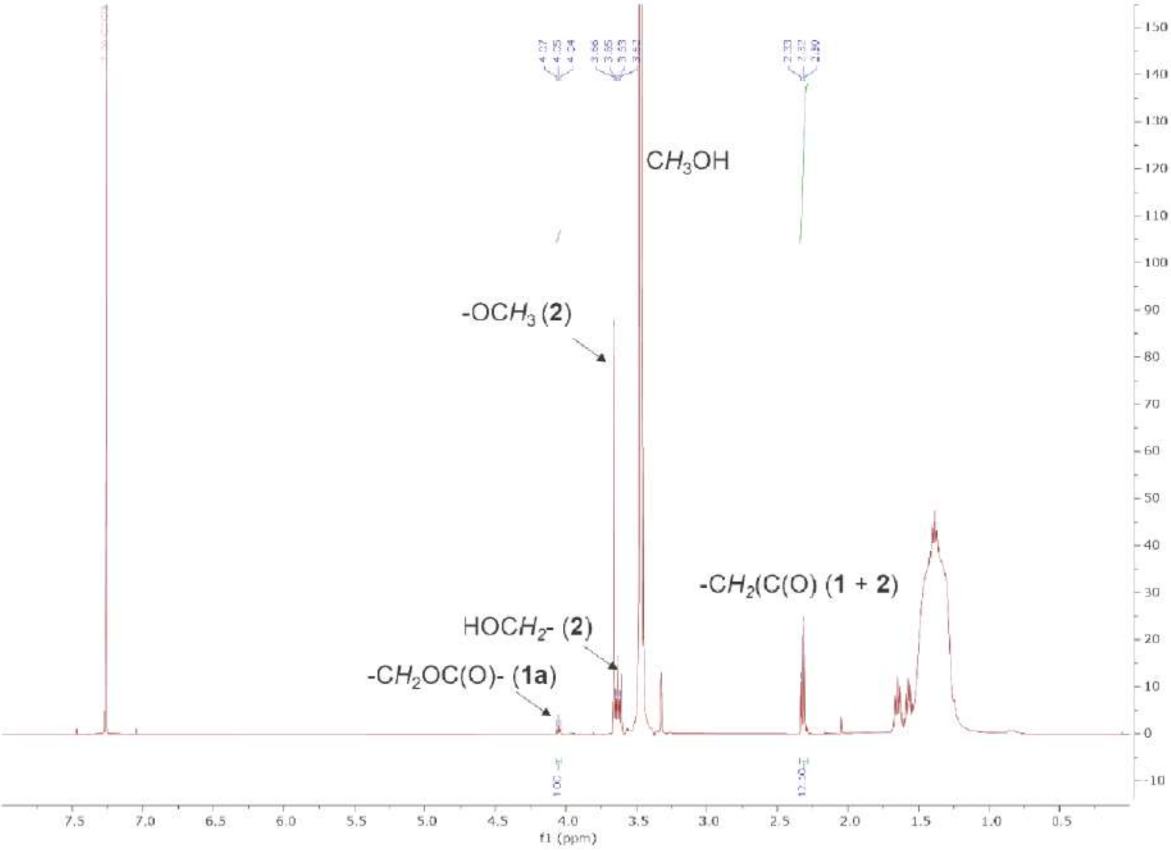
Even Cheung, Christoph Alberti, Sergej Bycinskij, and Stephan Enthaler*

General: All chemicals were used as received without further manipulations. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a *Fourier 300 MHz* (^{1}H: 300 MHz, ^{13}C: 75 MHz), *Avance I-400* (^{1}H: 400 MHz, ^{13}C: 101 MHz) or *Avance I 500* (^{1}H: 500 MHz, ^{13}C: 126 MHz) by Bruker, using the signals of the deuterated solvents as reference or external standards. Mass spectrometry was performed using a *Thermo ISQ LT EI* by Thermo Fisher Scientific. For microwave heating experiments a Microwave Synthesis Reactor Monowave 400 (Anton Paar GmbH) was used. SEC analysis was performed using a "mixed bed" linear SEC-column (5 µm porous styrene-divinylbenzene particles, separation range 200-1000k g/mol) at a flow rate of 1 mL/min in tetrahydrofuran as eluent. Molecular weights refer to a so-called relative calibration based on narrow polystyrene samples supplied by Agilent Technologies. The SEC system was equipped with a Shimadzu LC-10ATvP pump, an AS1000 autosampler from Thermo Separation Products and a RI2012 refractive index detector from Schambeck SFD GmbH.

General procedure for the depolymerization of poly(ε-caprolactone) (1a) (optimization of the reaction conditions: A mixture of poly(ε-caprolactone) (**1a**, Sigma Aldrich/Merck M_n ~80,000 g/mol) (100 mg, 0.876 mmol based on the repeating unit), methanol (2.0-3.0 g, 62.4-93.6 mmol, 71.3-107 equiv. based on the repeating unit of **1a**) and a catalyst (0-2.0 mol%, 0-0.0175 mmol based on the repeating unit of **1a**) was placed with a stir bar in a vial. The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 5-60 minutes (hold time) at 120-180 °C and with a stirring of 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature. An aliquot of the clear solution was transferred to an NMR tube and was dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^{1}H NMR to determine the yield of methyl 6-hydroxyhexanoate (**2**) [The yield of **2** was calculated on the basis of the CH_2-function of **2** and the leftover signals of the CH_2 function of the polymer/oligomers. The signals at ~2.33 ppm is a combination of the -$CH_2C(=O)$) of the polymer **1a** and the -$CH_2C(=O)$) of the product **2**. The yield was calculated: yield (**2**) = (area(**1a**+**2**)-area(**1a** at 4.05 ppm))/area(**1a**+**2**)*100.].

Methyl 6-hydroxyhexanoate[1] (**2**): ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 3.67 (s, 3H, CH_3O-), 3.65 (t, J = 6.51 Hz, 2H, -CH_2OH, signal overlap with 3.67 ppm), 2.33 (t, J = 7.43 Hz, 2H, -$CH_2C(=O)$) ppm.

Figure S1. Spectrum of a reaction mixture (^1H NMR (500 MHz, $CDCl_3$, 25 °C)).



Procedure for the depolymerization of poly(ε-caprolactone) (1): A mixture of poly(ε-caprolactone) (**1a** (M_n ~80,000 g/mol) or **1b** (M_n ~14,000 g/mol) or **1c** (M_n ~2,000 g/mol)) (100 mg, 0.876 mmol based on the repeating unit), methanol (2.0 g, 62.4 mmol, 71.3 equiv. based on the repeating unit of **1**) and $Zn(OAc)_2$ (2.0 mol%, 3.2 mg, 0.0175 mmol based on the repeating unit of **1**) was placed with a stir bar in a vial. The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 60 minutes (hold time) at 160 °C and with a stirring of 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature. An aliquot of the clear solution was transferred to an NMR tube and was dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^1H NMR to determine the yield of methyl 6-hydroxyhexanoate (**2**) [The yield of **2** was calculated on the basis of the CH_2-function of **2** and the leftover signals of the CH_2 function of the polymer/oligomers. The signals at ~2.33 ppm is a combination of the -$CH_2C(=O)$) of the polymer **1** and the -$CH_2C(=O)$) of the product **2**. The yield was calculated: yield (**2**) = (area(**1**+**2**)-area(**1** at 4.05 ppm))/area(**1**+**2**)*100.].

Procedure for the depolymerization of poly(ε-caprolactone) (1) (yield-time-dependency): A mixture of poly(ε-caprolactone) (**1a** (M_n ~80,000 g/mol) or **1b** (M_n ~14,000 g/mol)) (300 mg, 2.63 mmol based on the repeating unit), methanol (6.0 g, 187.3 mmol, 71.2 equiv. based on the repeating unit of **1**) and $Zn(OAc)_2$ (2.0 mol%, 9.7 mg, 0.0526 mmol based on the repeating unit of **1**) or $Zn(MA)_2$ (2.0 mol%, 12.4 mg, 0.0526 mmol based on the repeating unit of **1a**)was placed with a stir bar in a vial. The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 100 minutes (hold time) at 160 °C and with a stirring of 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). After specific times samples were taken. The vial was cooled to room temperature. An aliquot of the clear solution was transferred to an NMR tube and was dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^1H NMR to determine the yield of methyl 6-hydroxyhexanoate (**2**) [The yield of **2** was calculated on the basis of the CH_2-function of **2** and the leftover signals of the CH_2 function of the polymer/oligomers. The signals at ~2.33 ppm is a combination of the -$CH_2C(=O)$) of the polymer **1** and the -$CH_2C(=O)$) of the product **2**. The yield was calculated: yield (**2**) = (area(**1**+**2**)-area(**1** at 4.05 ppm))/area(**1**+**2**)*100.]. After taking a sample the vial was resubmitted to microwave heating.

General procedure for the depolymerization of poly(ε-caprolactone) in the presence of other polymers: A mixture of poly(ε-caprolactone) (**1a** (M_n ~80,000 g/mol)) (100 mg, 0.876 mmol based on the repeating unit), polymer B (0.876 mmol based on the repeating unit), methanol (2.0 g, 62.4 mmol, 71.3 equiv. based on the repeating unit of **1a**) and $Zn(OAc)_2$ (2.0 mol%, 3.2 mg, 0.0175 mmol based on the repeating unit of **1a**) or $Zn(MA)_2$ (1.0 mol%, 2.1 mg, 0.00875 mmol based on the repeating unit of **1a**) was placed with a stir bar in a vial. The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 30 minutes (hold time) at 160 °C and with a stirring of 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature. An aliquot of the clear solution was transferred to an NMR tube and was dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^1H NMR to determine the yield of methyl 6-hydroxyhexanoate (**2**) [The yield of **2** was calculated on the basis of the CH_2-function of **2** and the leftover signals of the CH_2 function of the polymer/oligomers. The signals at ~2.33 ppm is a combination of the -$CH_2C(=O)$) of the polymer **1a** and the -$CH_2C(=O)$) of the product **2**. The yield was calculated: yield (**2**) = (area(**1a**+**2**)-area(**1a** at 4.05 ppm))/area(**1a**+**2**)*100. The conversion of the additional polymer was studied by NMR].

Procedure for the depolymerization of poly(ε-caprolactone) (1b) – scale-up: A mixture of poly(ε-caprolactone) (**1b** (M_n ~14,000 g/mol)) (2.0 g, 17.5 mmol based on the repeating unit), methanol (24 g, 749 mmol, 42.8 equiv. based on the repeating unit of **1b**) and $Zn(OAc)_2$ (2.0 mol%, 64.2 mg, 0.35 mmol based on the repeating unit of **1b**) was placed with stir bars in four vials. The vials were sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 60 minutes (hold time) at 160 °C and with a stirring of 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature. An aliquot of the clear solution was transferred to an NMR tube and was dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^1H NMR to determine the yield of methyl 6-hydroxyhexanoate (**2**) [The yield of **2** was calculated on the basis of the CH_2-function of **2** and the leftover signals of the CH_2 function of the polymer/oligomers. The signals at ~2.33 ppm is a combination of the -$CH_2C(=O)$) of the polymer **1b** and the -$CH_2C(=O)$) of the product **2**. The yield was calculated: yield (**2**) = (area(**1b**+**2**)-area(**1b** at 4.05 ppm))/area(**1b**+**2**)*100.]. An NMR yield of 92% was monitored. The reaction mixture was transferred to a flask, which was connected to distillation equipment. The methanol and the product were distilled off from the reaction mixture. Methyl 6-hydroxyhexanoate (**2**) was obtained as colorless liquid in 50% isolated yield (m = 1.29 g, n = 8.82 mmol).

Methyl 6-hydroxyhexanoate (**2**): ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 3.65 (s, 3H, CH_3O-), 3.63 (t, J = 6.51 Hz, 2H, -CH_2OH, signal overlap with 3.65 ppm), 2.33 (t, J = 7.43 Hz, 2H, -$CH_2C(=O)$), 1.37-1.71 (m, 6H, CH_2), ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25 °C): δ = 174.3, 62.8, 51.7, 33.4, 32.5, 26.6, 24.7 ppm.

Figure S2. Spectrum of **2** (^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)).

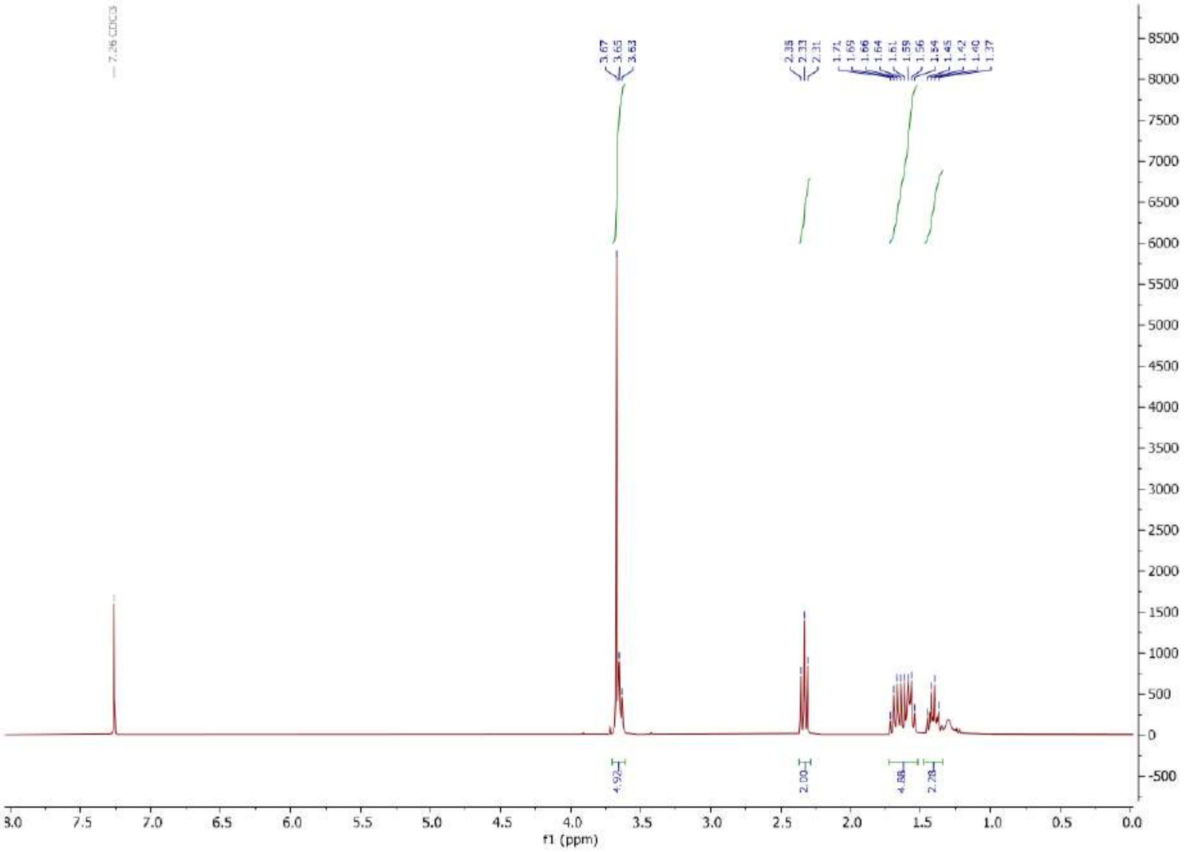
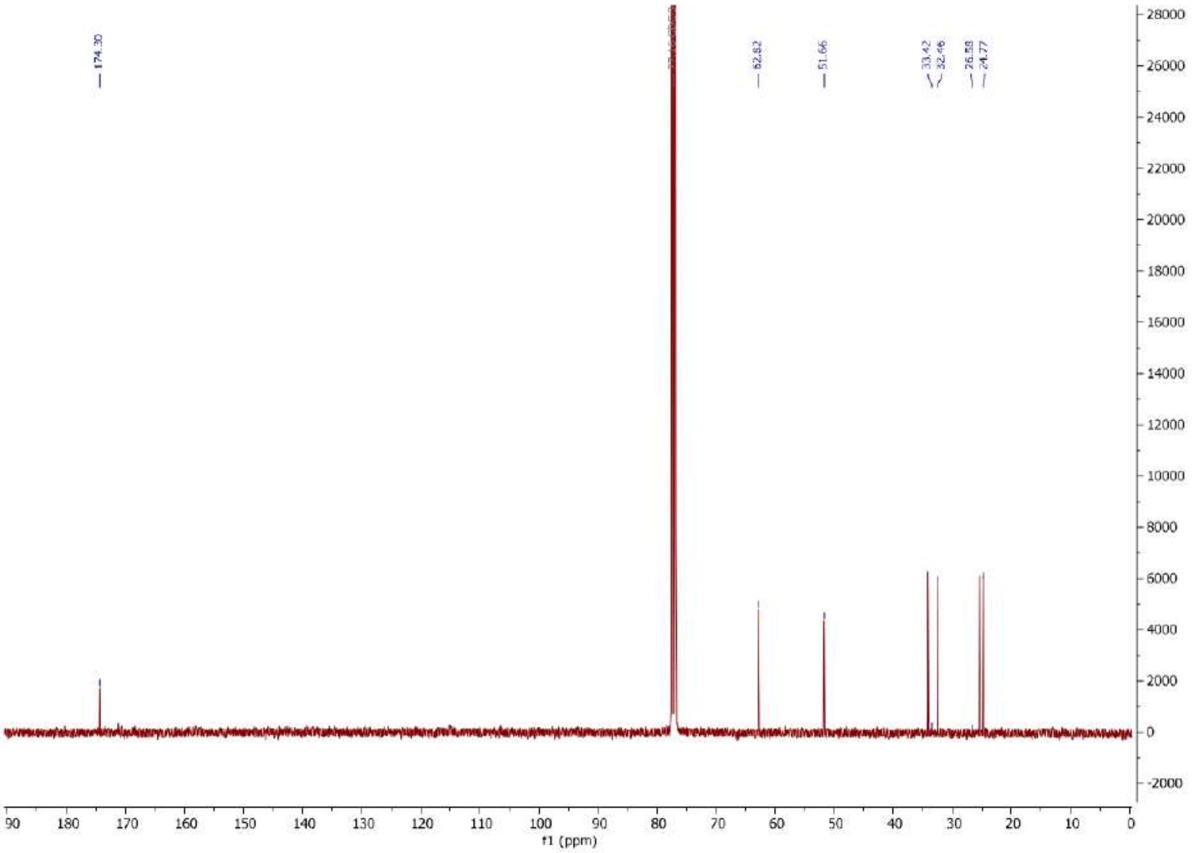


Figure S3. Spectrum of **2** ($^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25 °C)).



Procedure for the polymerization of methyl 6-hydroxyhexanoate (2): A mixture of methyl 6-hydroxyhexanoate (**2**, 139 mg, 0.951 mmol) and catalytic amounts of $Zn(OAc)_2$ (1.8 mg, 0.0098 mmol, 1.0 mol%) was placed with a stir bar in a flask. The reaction was performed for 48 hours at 130 °C with a stirring. Afterwards the mixture was cooled to room temperature. An aliquot was transferred to an NMR tube and was dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^1H NMR to determine the conversion of methyl 6-hydroxyhexanoate (**2**) [The yield of **1d** was calculated on the basis of the CH_2-function of **2** and the signals of the CH_2 function of the polymer **1d**. The signals at ~2.33 ppm is a combination of the -$CH_2C(=O)$) of the polymer **1d** and the -$CH_2C(=O)$) of the product **2**. The yield was calculated: yield (**1d**) = (area(**1d** at 4.05 ppm))/area(**1d**+**2**)*100.]. To the reaction mixture water was added and the polymer was filtered off and dried in vacuum (40 °C, 1 mbar).

Poly(ε-caprolactone) (**1d**): ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.03-4.06 (m, 2H, CH_2O-), 2.27-2.33 (m, 2H, CH_2O-), 1.59-1.67 (m, 4H, CH_2), 1.33-1.40 (m, 2H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25 °C): δ = 173.6, 64.3, 34.2, 28.5, 25.6, 24.7 ppm. The polymer contains traces of the monomer (~3%).

Figure S4. Spectrum of **1d** (^{1}H NMR (500 MHz, $CDCl_3$, 25 °C)).

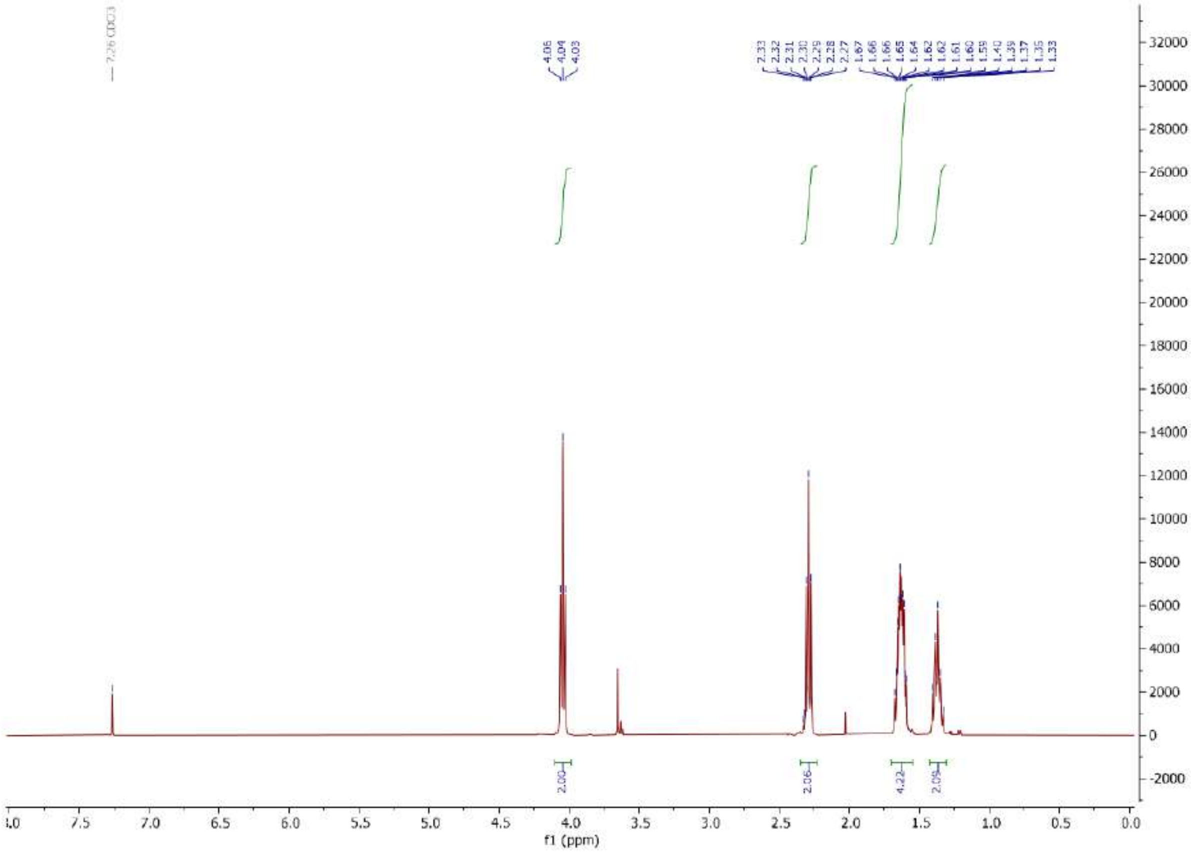
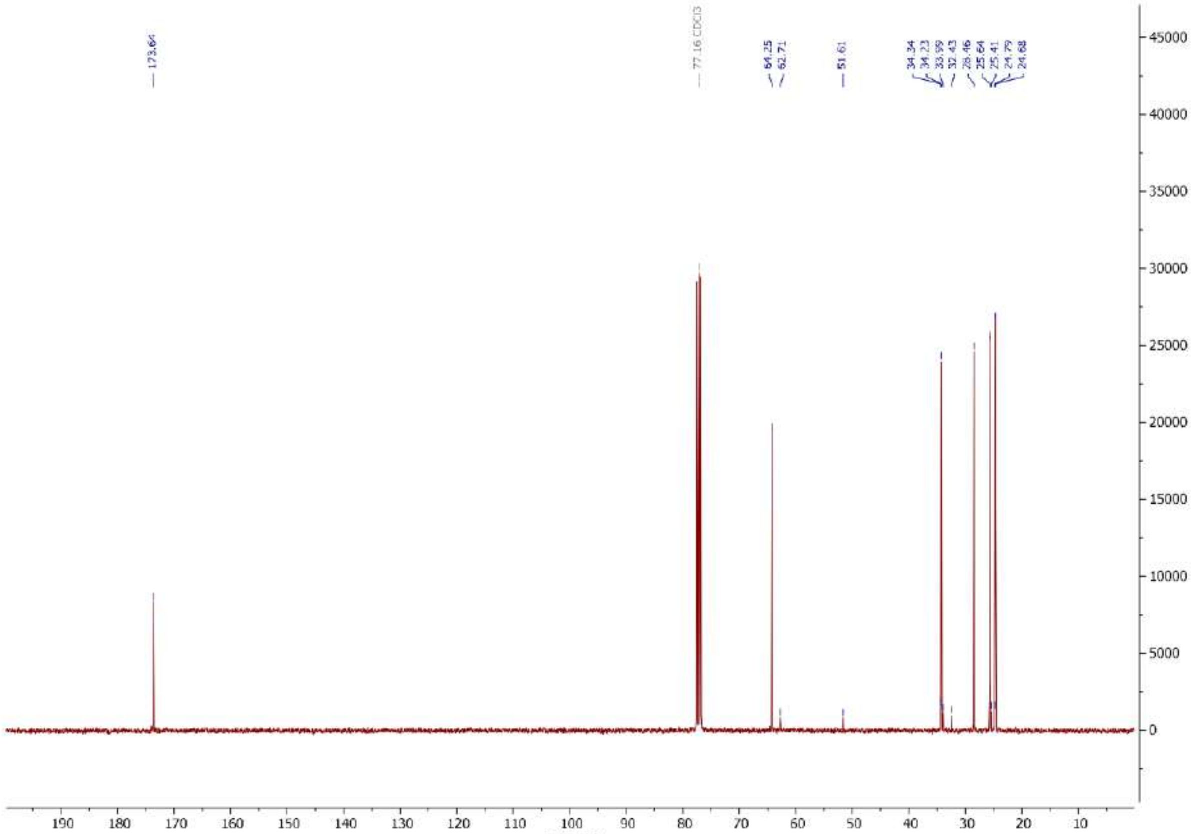


Figure S5. Spectrum of **1d** ($^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25 °C)).



Determination of rate constants k, activation energy E_a and frequency factor A_0

For the transesterification reaction of PCL-esters (PCL) to methyl ester groups (COOMe) the following rate law was constructed, based on the assumption, that [MeOH] is constant during the reaction (pseudo first order kinetics)

$\frac{d[PCL]}{dt} = -\frac{d[COOMe]}{dt} = k' \cdot [PCL] \cdot [MeOH] = k \cdot [PCL]$ (eq. 1)

Accordingly, the concentration of Eg-Esters is: $[PCL]_t = [PCL]_0 \cdot e^{-k \cdot t}$ (eq. 2)

$\Rightarrow \frac{[PCL]_t}{[PCL]_0} = e^{-k \cdot t} = 1 - \eta_{COOMe}$ (eq. 3)

η_{COOMe} was determined form the ^1H NMR data. Now, k was determined by a linearized plot of eq. 3 (Figure S#-S#):

$\ln([1-\eta_{COOMe}]) = -k \cdot t$ (eq. 4)

$k = A_0 \cdot e^{-\frac{E_a}{RT}}$ (eq. 5)

$\ln(k) = \ln(A_0) - \frac{E_a}{R} \cdot \frac{1}{T}$ (eq. 6)

The activation energy was calculated from the slope ($-E_a/R$) of the linearized Arrhenius equation (eq. 6) and the frequency factor A_0 from the y-intercept (Figure S13).

E_a= 90.9 kJ/mol; $A_0 = 1.58 \cdot 10^8 \frac{1}{s}$

Figure S6. Plot of ln (1−η_{COOMe}) vs. time [s] for 150 °C.

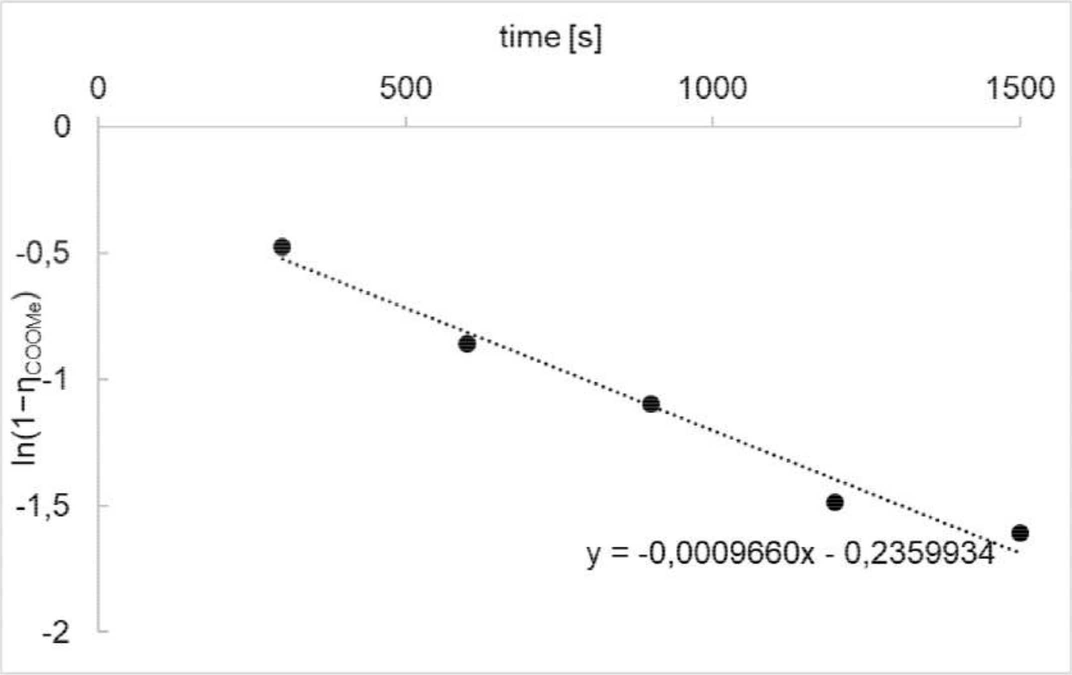


Figure S7. Plot of ln (1−η_{COOMe}) vs. time [s] for 160 °C.

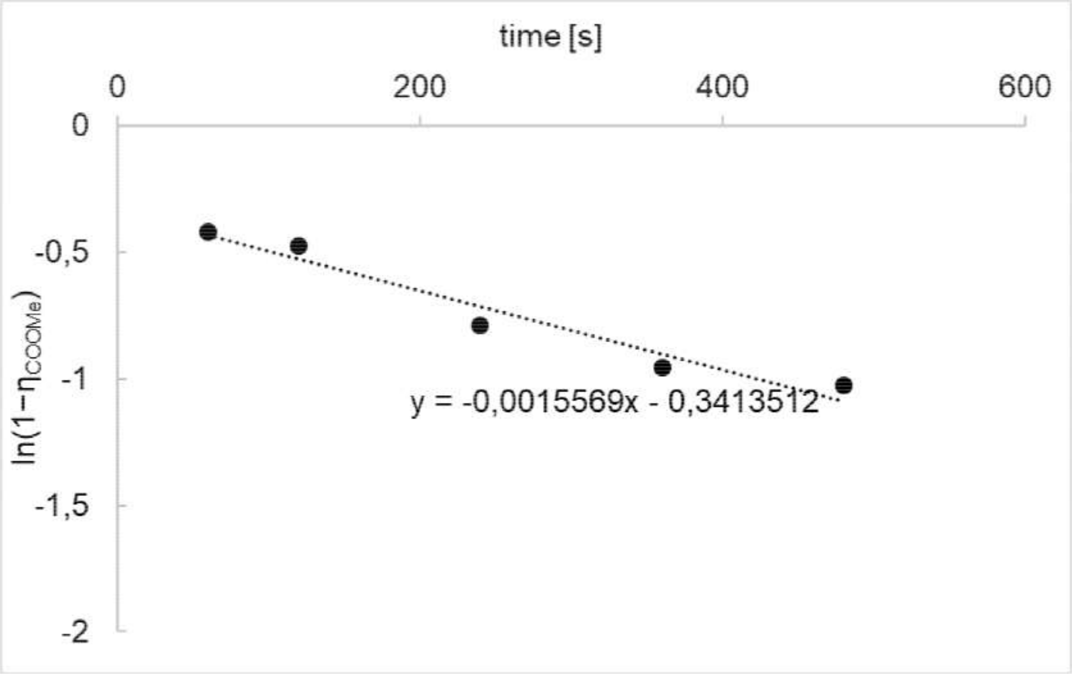


Figure S8. Plot of ln (1−η_{COOMe}) vs. time [s] for 170 °C.

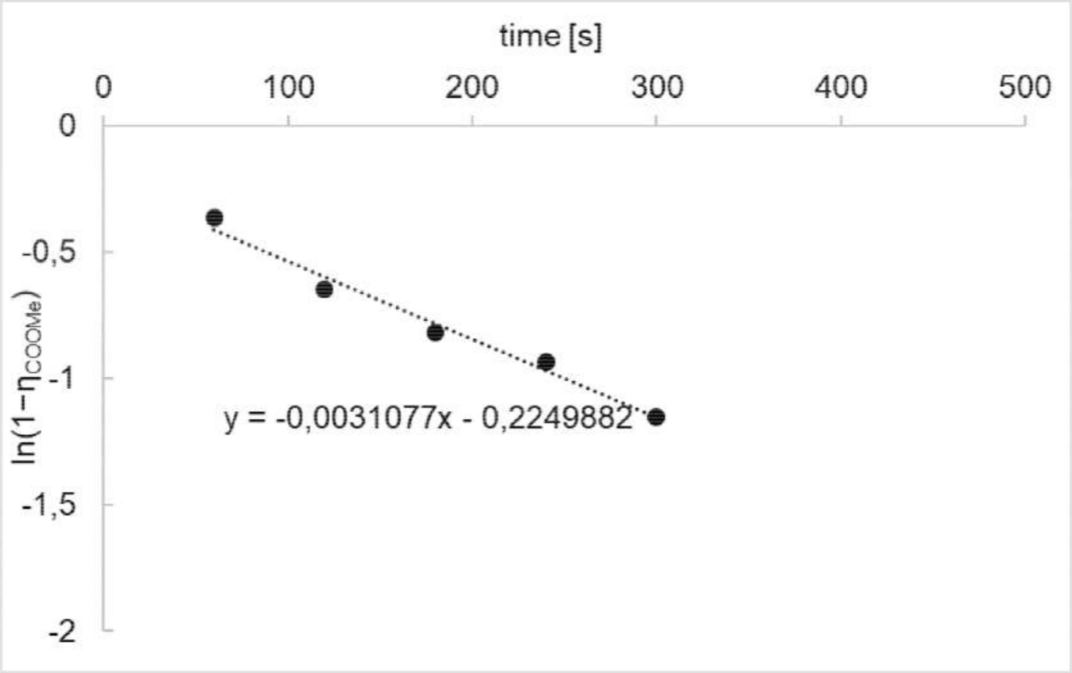
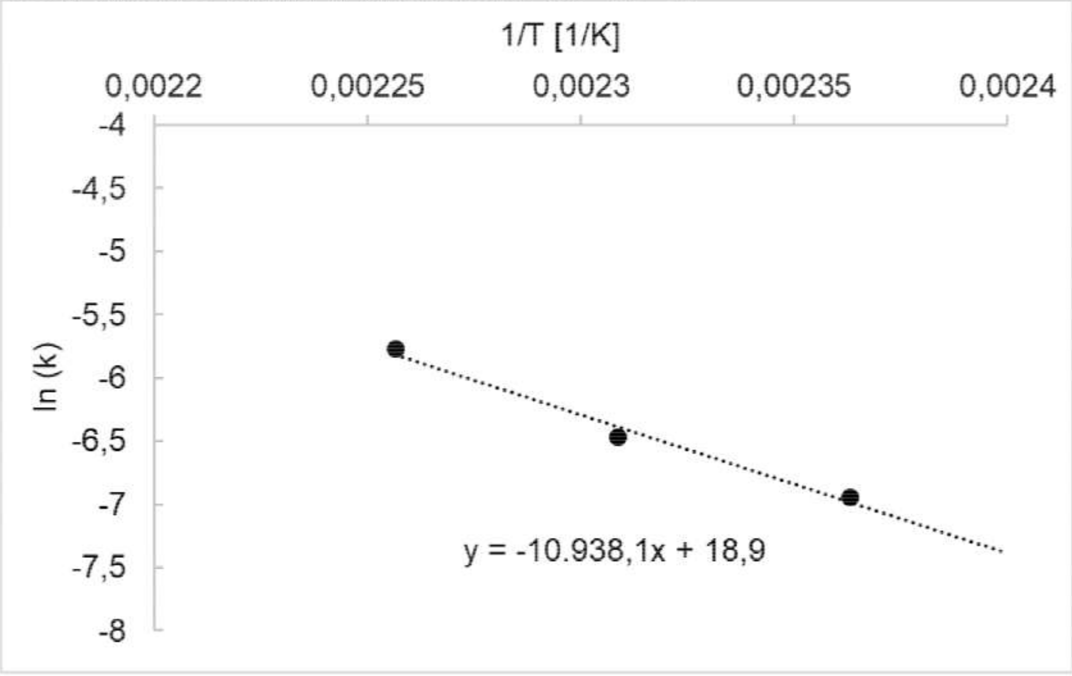


Figure S9. Arrhenius Plot with ln (k)-values for 150-170 °C.



References

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[1] A. Kamimura, K. Kaiso, S. Suzuki, Y. Oishi, Y. Ohara, T. Sugimoto, K. Kashiwagi, M. Yoshimoto, *Green Chem.* **2011**, *13*, 2055-2061.

Chemistry SELECT

Supporting Information

Chemical Recycling of End-of-Life Polyamide 6 via Ring Closing Depolymerization

Christoph Alberti, Ruben Figueira, Melanie Hofmann, Svetlana Koschke, and
Stephan Enthaler*

General: All chemicals were used as received without further manipulations. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a *Fourier 300 MHz* (^{1}H: 300 MHz, ^{13}C: 75 MHz) or *Avance I-400* (^{1}H: 400 MHz, ^{13}C: 101 MHz) by Bruker, using the proton signals of the deuterated solvents as reference or external standards. Mass spectrometry was performed using a *Thermo ISQ LT EI* by Thermo Fisher Scientific. TLC was performed on *ALUGRAM XTRA SIL G/UV$_{254}$* cards from *Macherey-Nagel* GmbH & Co. KG with a thickness of 0.20 mm. Detection succeeded with UV-light (254 nm) and $KMnO_4$-stain solution. For microwave screening experiments a Microwave Synthesis Reactor Monowave 400 (Anton Paar GmbH) and for preparative scale an Initiator+ by Biotage® were used. The large scale depolymerization was performed with CEM Mars 6. For Kugelrohr distillation the glass oven B-585 by BÜCHI Labortechnik AG was used.

Optimization of the reaction conditions of the depolymerization of Nylon 6 (1a) to *N*-acetylcaprolactam (2): Commercially available Nylon 6 (Sigma Aldrich, pellets dimension: ~2 mm, **1a**) (113 mg-1.58 g, 1.00-14.0 mmol based on the repeating unit, 1.00 equiv.), acetic anhydride (2.15-2.85 g, 21.0-28.0 mmol, 1.50-30 equiv., based on the repeating unit of **1a**) and a catalyst (10.0-150 µmol, 1.0-10 mol%, based on the repeating unit of **1a**) were placed in a vial with a stir bar. The mixture was heated up (as fast as possible) and the temperature (160-280 °C) was hold for 15-30 min. After cooling to room temperature an aliquot was dissolved in $CDCl_3$ (0.5 mL) and was analyzed by ^{1}H NMR. The yield of **2** was determined by integration of the NCH_2 signals of the three main products resulting from depolymerization.

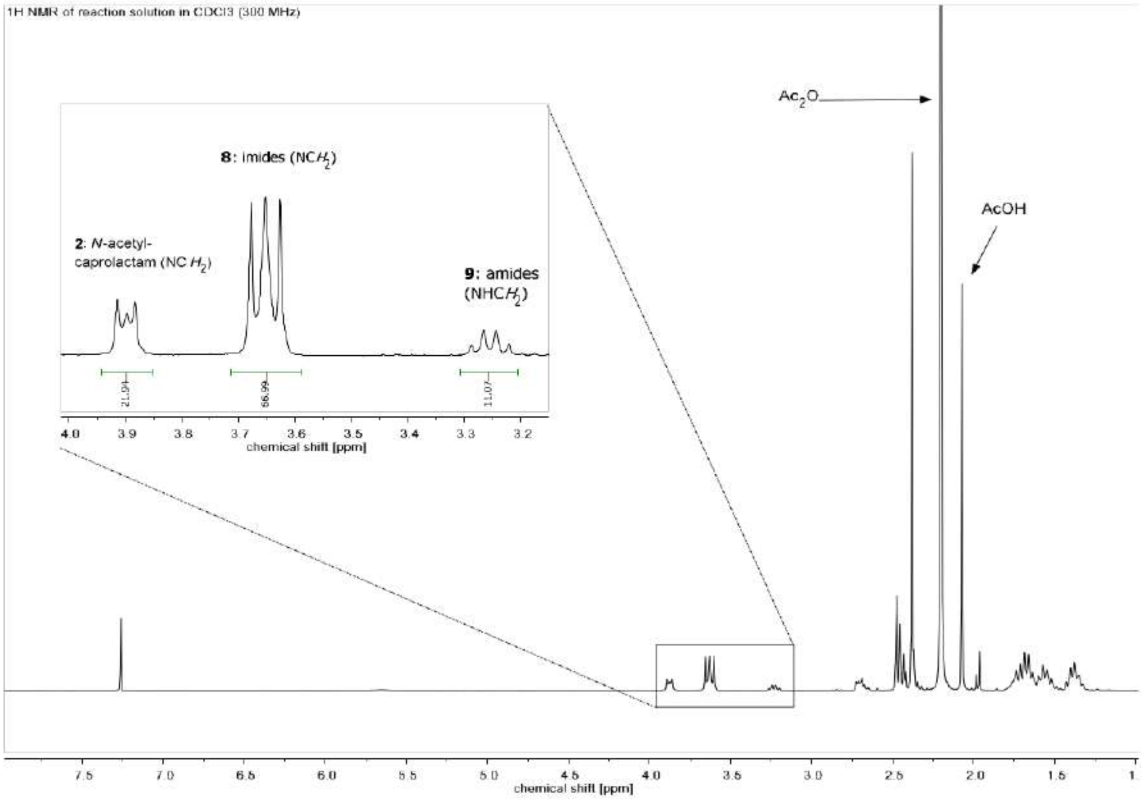


Figure S1: Typical ^{1}H NMR spectrum of the crude reaction mixture, conditions: Nylon 6 (**1a**, 1 mmol), Ac_2O (5 equiv.), microwave heating to 220 °C for 15 min (Table 1, entry 12).

Depolymerization of Nylon 6 to *N*-acetylcaprolactam (2): Commercially available Nylon 6 (**1**) commodities (1.21 g-2.27 g, 10.7 mmol based on repeating unit, 1.00 equiv., it was assumed that the commodities contain 100% Nylon 6), acetic anhydride (6.80 g-10.3 g, 66.6-100 mmol, 5.01-11.0 equiv.) and DMAP (81.0 mg, 66.3 µmol, 4.99 mol%) were placed in a microwave vial with a stir bar. The mixture was heated up to 250 °C (as fast as possible) and the temperature was hold for 15 min. After cooling to room temperature the reaction mixture was transferred to a distillation apparatus and Ac_2O and AcOH were carefully removed by vacuum distillation at 50 °C over a Vigreux column. The dark residue was transferred to a Kugelrohr distillation apparatus with the aid of small amounts of Ac_2O and subsequently *N*-acetylcaprolactam (**2**) was distilled off by Kugelrohr distillation to obtain *N*-acetylcaprolactam (**2**) as a yellow viscous liquid (424 mg-2.02 g, 2.73-13.0 mmol, 27-107wt%, 20-78%). Analytical data for *N*-acetylcaprolactam[1] (**2**) is in accordance with the data reported in the literature.

Table 1: Depolymerization of household goods and commodities with yields given for the assumption that the material contains 100% Nylon 6 (**1a-f**).

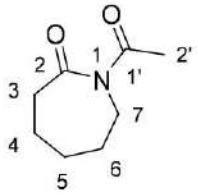
Commodity (mass)	Ac_2O [equiv.]	Picture of commodity	Microwave vial before (after) reaction	Yield
pellets (**1a**) (1.51 g) (1.52 g)	5 5 (recycled Ac_2O was used)			78% (1.62 g, 107wt%) 70% (1.46 g, 96wt% for recycled Ac_2O)
test stripes (**1b**) (2.21 g)	5			67% (2.02 g, 91wt%)
thread (**1c**) (1.21 g)	11			66% (1.09 g, 90wt%)
hammock (**1d**) (1.50 g)	5			52% (1.08 g, 72wt%)
screw anchors (**1e**) (2.27 g)	5			52% (1.62 g, 71wt%)
patch (**1f**) (1.55 g)	5			20% (424 mg, 27wt%)

Large scale depolymerization of Nylon 6 (1e)

a) microwave set-up

b) screw anchors

Commercially available screw anchors (**1e**) (70.5 g, 623 mmol based on the repeating unit, 1.00 equiv., it was assumed that the screw anchors contain 100% Nylon 6), acetic anhydride (294 mL, 318 g, 3.11 mol, 5.00 equiv.) and DMAP (3.47 g, 28.4 mmol, 4.89 mol%) were allocated to seven microwave vials with a stir bar. The mixtures were heated up under irradiation within 10 min to 230 °C and the temperature was hold for 5 min. After cooling to ambient temperature, elastic colorless solids were removed from the reaction mixtures by filtration and the dark liquids were combined and transferred to a distillation apparatus and Ac_2O was carefully removed by vacuum distillation at 70 °C. The dark residue was further purified by distillation (2.0 mbar, 130 °C oil bath temperature) to obtain *N*-acetylcaprolactam (**2**) (45.4 g, 293 mmol, 64wt%, 47%) as a yellow viscous liquid.



^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ [ppm] = 1.56 – 1.74 (m, 6 H, 4-H_2, 5-H_2, 6-H_2), 2.41 (s, 3 H, 2'-H_3), 2.62 – 2.68 (m, 2 H, 3-H_2), 3.79 – 3.85 (m, 2 H, 7-H_2).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ [ppm] = 23.7 (C-4), 27.4 (C-2'), 28.5 (C-6), 29.2 (C-5), 39.7 (C-3), 43.0 (C-7), 173.0 (C-1'), 177.7 (C-2).

MS-EI: *m/z* (%): 155.08 (6) $[M^+]$, 127 (16) $[M^+ - CO]$, 114.10 (17) $[- CO - CH]$, 113.10 (100) $[M^+ - CO - CH_2]$, 85.08 (98) $[M^+ - CO - CH_2 - C_2H_4]$, 84.09 (60) $[M^+ - CO - CH_2 - C_2H_5]$.

IR: $\tilde{\upsilon}$ [cm^{-1}] = 2931, 2858, 1685, 1461, 1435, 1416, 1367, 1332, 1316, 1253, 1210, 1080, 960, 557.

R_f (silica gel, petrol ether:EtOAc, 4:1) = 0.24.

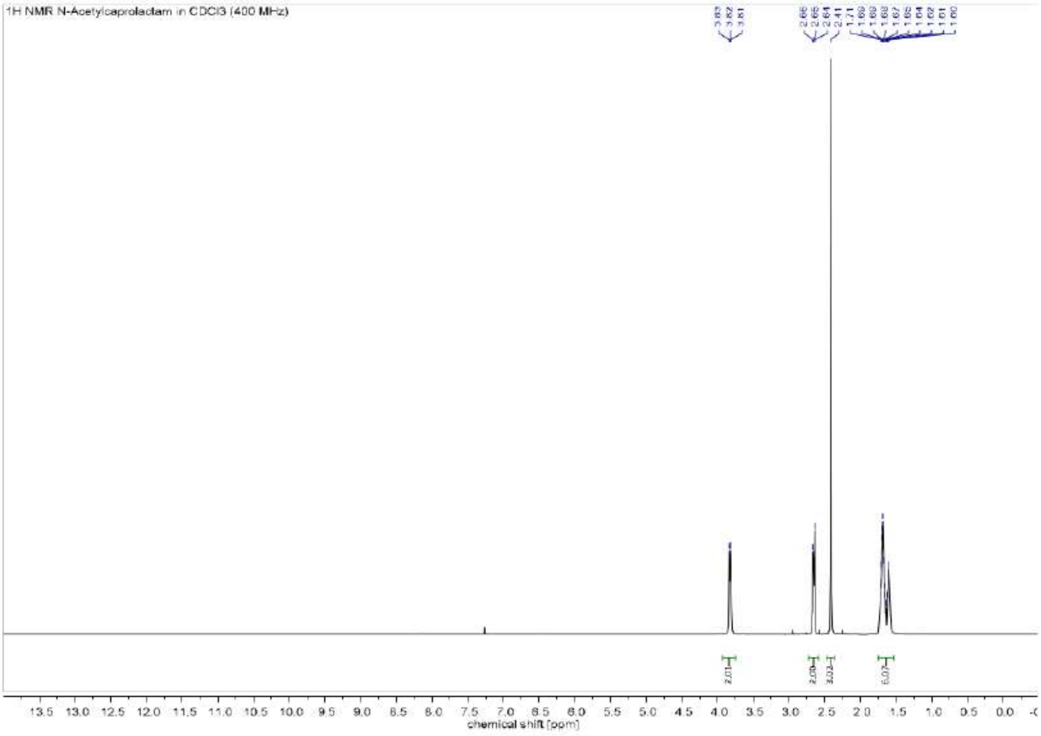


Figure S2: ^{1}H NMR spectrum of *N*-acetylcaprolactam (**2**).

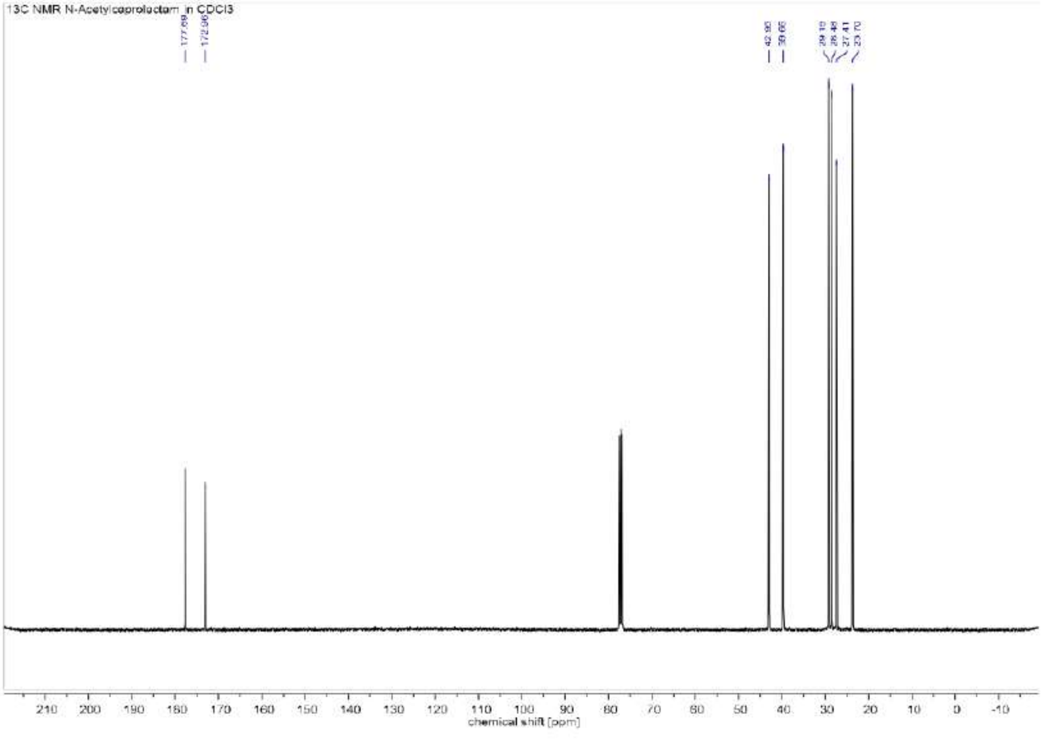


Figure S3: $^{13}C\{^{1}H\}$ NMR spectrum of *N*-acetylcaprolactam (**2**).

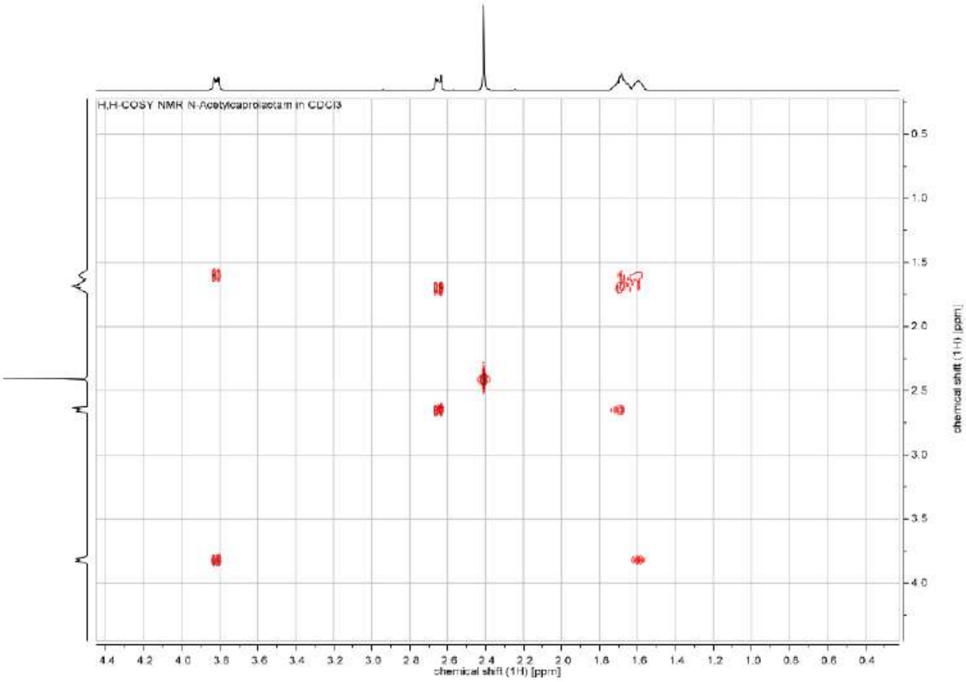


Figure S4: H,H-COSY spectrum of *N*-acetylcaprolactam (**2**).

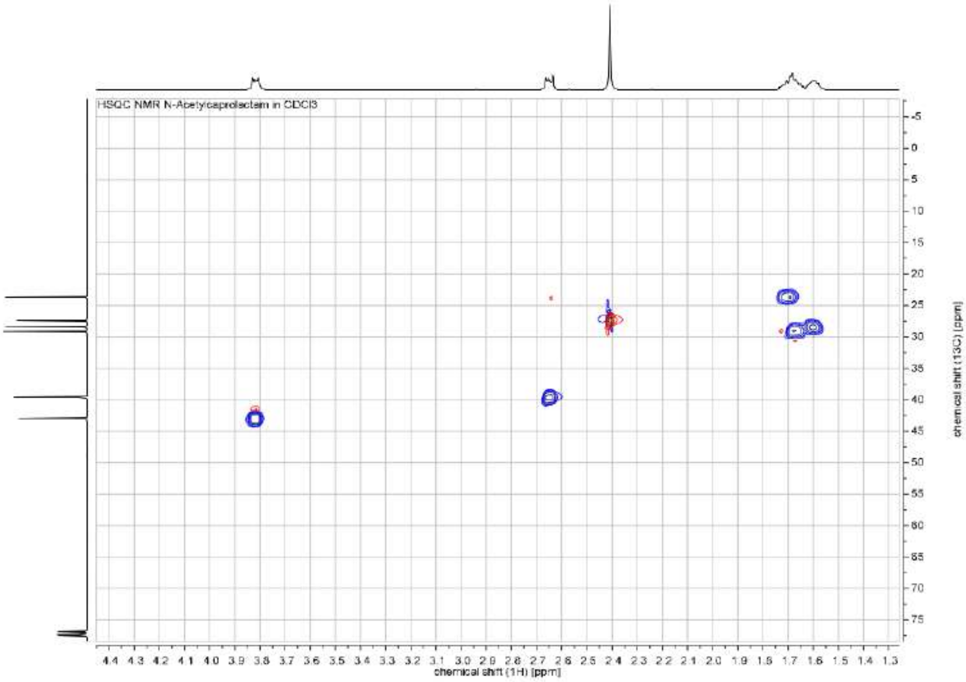


Figure S5: HSQC NMR of *N*-acetylcaprolactam (**2**).

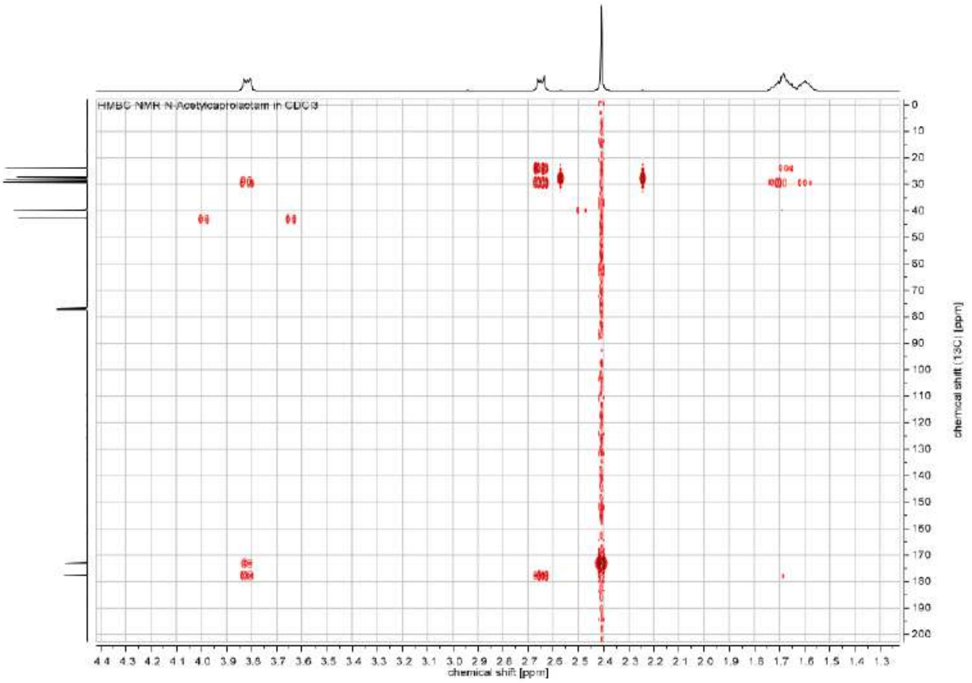
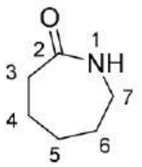


Figure S6: HMBC NMR of *N*-acetylcaprolactam (**2**).

Synthesis of ε-caprolactam (3)

A mixture of *N*-acetylcaprolactam (**2**) (776 mg, 5.00 mmol, 1.00 equiv.) and 2-aminoethanol (**4**) (309 mg, 5.06 mmol, 1.01 equiv.) was stirred and heated to 80 °C for 2.5 h in a flask equipped with a reflux condenser. After cooling to room temperature the mixture was purified by column chromatography (silica gel, CH_2Cl_2:MeOH, 19:1 -> 9:1). ε-Caprolactam (**3**) (518 mg, 4.58 mmol, 92%) was obtained as colorless crystalline solid and *N*-(2-hydroxyethyl)acetamide (**5**) (446 mg, 4.33 mmol, 87%) as colorless oil. Analytical data for ε-caprolactam[2] (**3**) and *N*-(2-hydroxyethyl)acetamide[3] (**5**) are in accordance with the data reported in literature.



m. p.: 67 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): *δ* [ppm] = 1.58 – 1.78 (m, 6 H, 4-H_2, 5-H_2, 6-H_2), 2.41 – 2.47 (m, 2 H, 3-H_2), 3.15 – 3.22 (m, 2 H, 7-H_2), 6.36 (br s, 1 H, 1-H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ [ppm] = 23.4 (C-4), 29.9 (C-5), 30.7 (C-6), 36.8 (C-2), 43.0 (C-7), 179.3 (C-2).

MS-EI: 113.09 (93%) [M^+].

IR: $\tilde{\upsilon}$ [cm^{-1}] = 3292, 3201, 3072, 1651, 1466, 1415, 1364, 1352, 1290, 1237, 1196, 1087, 962, 582, 503.

R_f (silica gel, CH_2Cl_2:MeOH, 19:1) = 0.25.

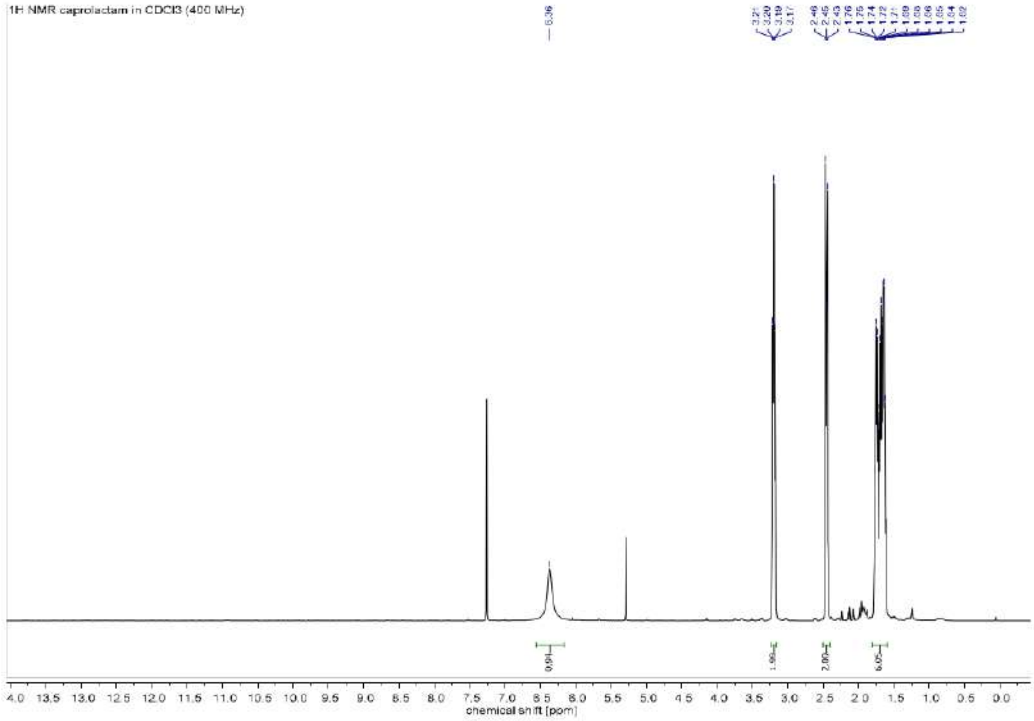


Figure S7: ^{1}H NMR spectrum of ε-caprolactam (**3**).

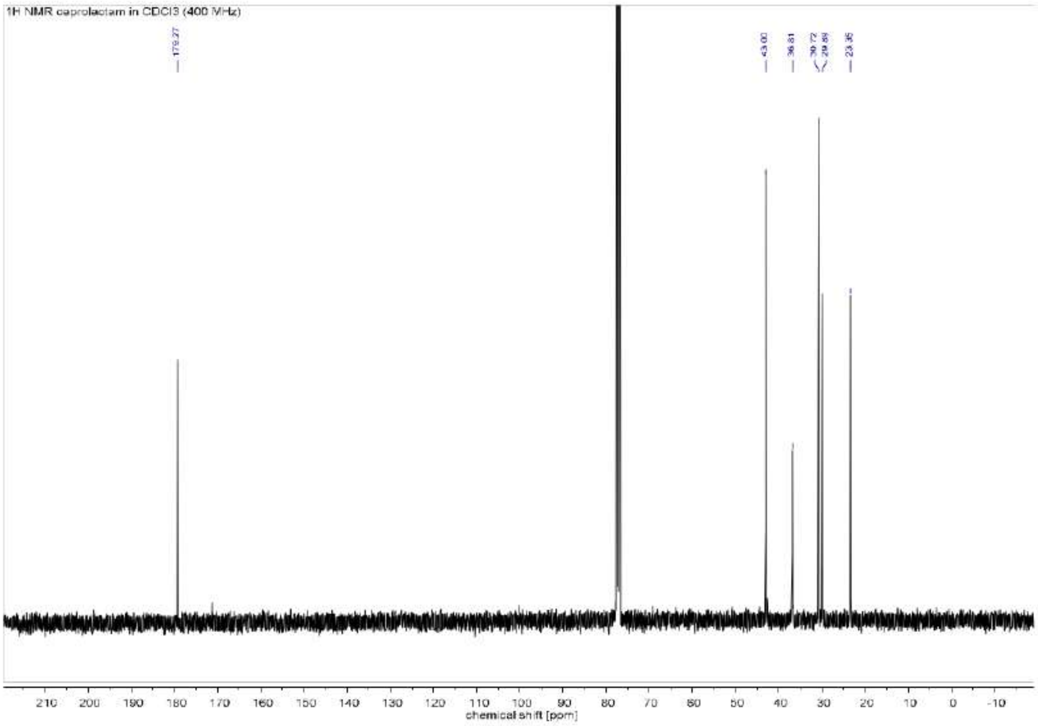
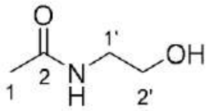


Figure S8: $^{13}C\{^1H\}$ NMR spectrum of ε-caprolactam (**3**).

Analytical data of *N*-(2-hydroxyethyl)acetamide (5).



^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): *δ* [ppm] = 1.99 (s, 3 H, 1-H_3), 3.36 – 3.41 (m, 2 H, 1'-H_2), 3.68 – 3.72 (m, 2 H, 2'-H_2), 6.36 (br s, NH, 1-H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25 °C): *δ* [ppm] = 23.3 (C-1), 42.6 (C-1'), 62.3 (C-2'), 171.5 (C-2).

MS-EI: 85.05 (85%) [M^+-H_2O].

IR: ṽ [cm^{-1}] = 3286, 3095, 2934, 2876, 1628, 1549, 1429, 1373, 1292, 1220, 1113, 1059, 1002, 597, 505.

R_f (silica gel, CH_2Cl_2:MeOH, 19:1) = 0.11.

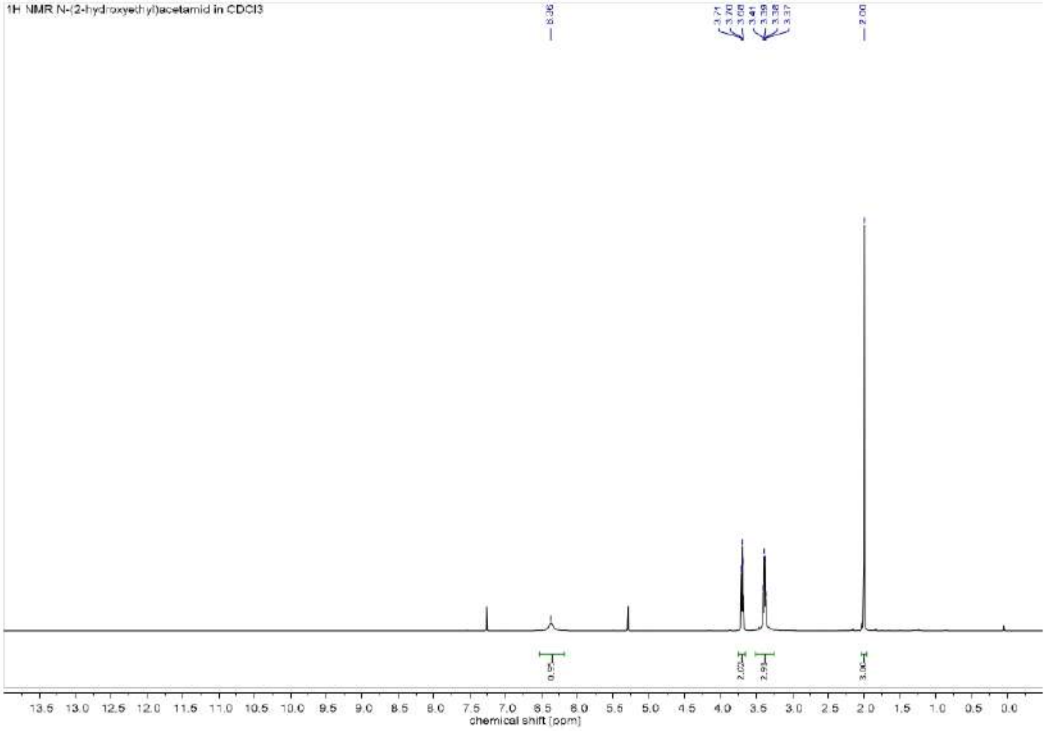


Figure S9: ^{1}H NMR spectrum of *N*-(2-hydroxyethyl)acetamide (**5**).

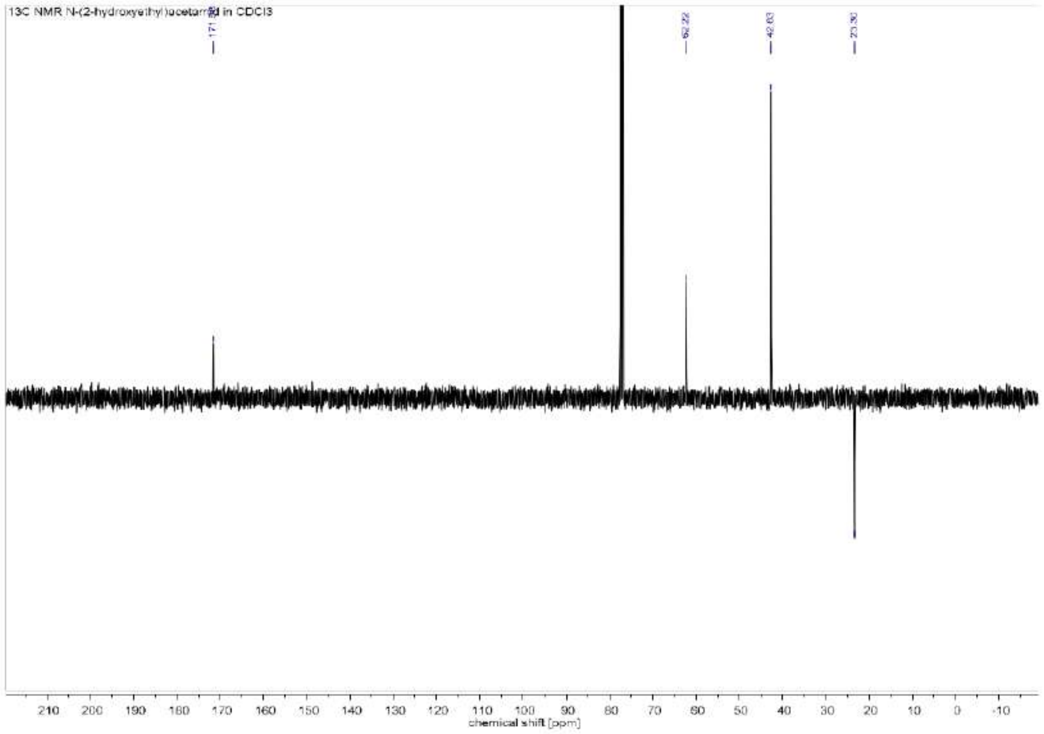
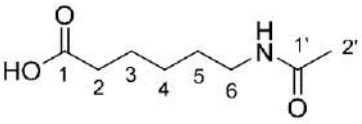


Figure S10: ^{13}C{^{1}H} NMR spectrum of *N*-(2-hydroxyethyl)acetamide (**5**).

Analytical data of 6-acetamidohexanoic acid (9a)

A sample of 6-acetamidohexanoic acid (**9a)** was prepared by a procedure reported in literature.[4]



m. p.: 109 °C.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): *δ* [ppm] = 1.35 – 1.42 (m, 2 H, 4-H_2), 1.49 – 1.56 (m, 2 H, 5-H_2), 1.63 – 1.70 (m, 2 H, 3-H_2), 1.98 (s, 3 H, 2'-H_3), 2.37 (t, J = 7.3 Hz, 2 H, 2-H_2), 3.23 – 3.28 (m, 2 H, 6-H_2), 5.49 (br s, 1 H, NH).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): *δ* [ppm] = 39.5 (C-6), 33.5 (C-2), 29.4 (C-5), 26.4 (C-4), 24.4 (C-3), 23.5 (C-2').

MS-ESI (*m/z*) = 172.1 [M-H]$^-$.

IR: ṽ [cm^{-1}] = 3348, 2945, 2904, 2864, 1703, 1602, 1556, 1371, 1350, 1279, 1244, 1112, 1026, 957, 598.

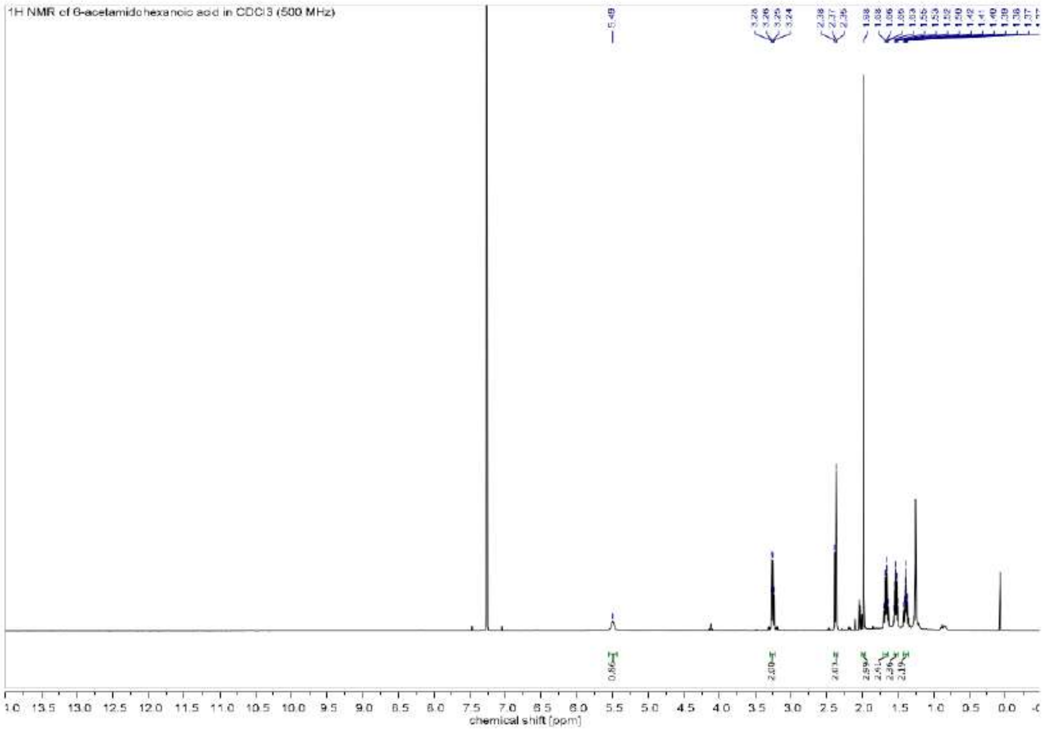


Figure S11: ^{1}H NMR spectrum of 6-acetamidohexanoic acid (**9a**).

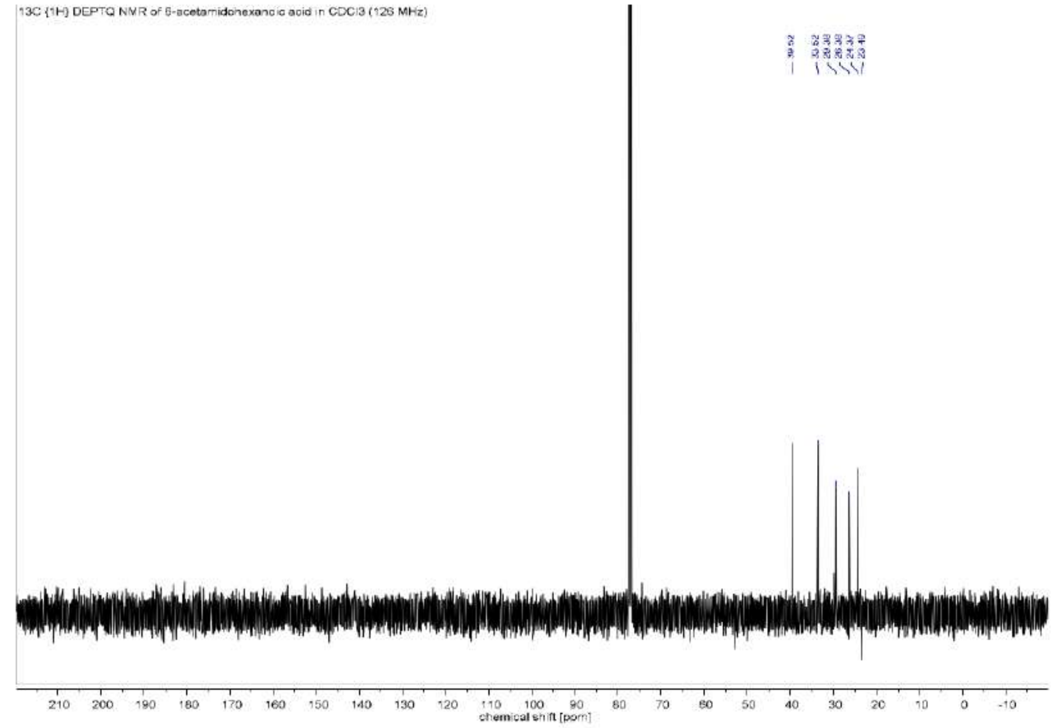


Figure S12: $^{13}C\{^1H\}$ NMR spectrum of 6-acetamidohexanoic acid (**9a**).

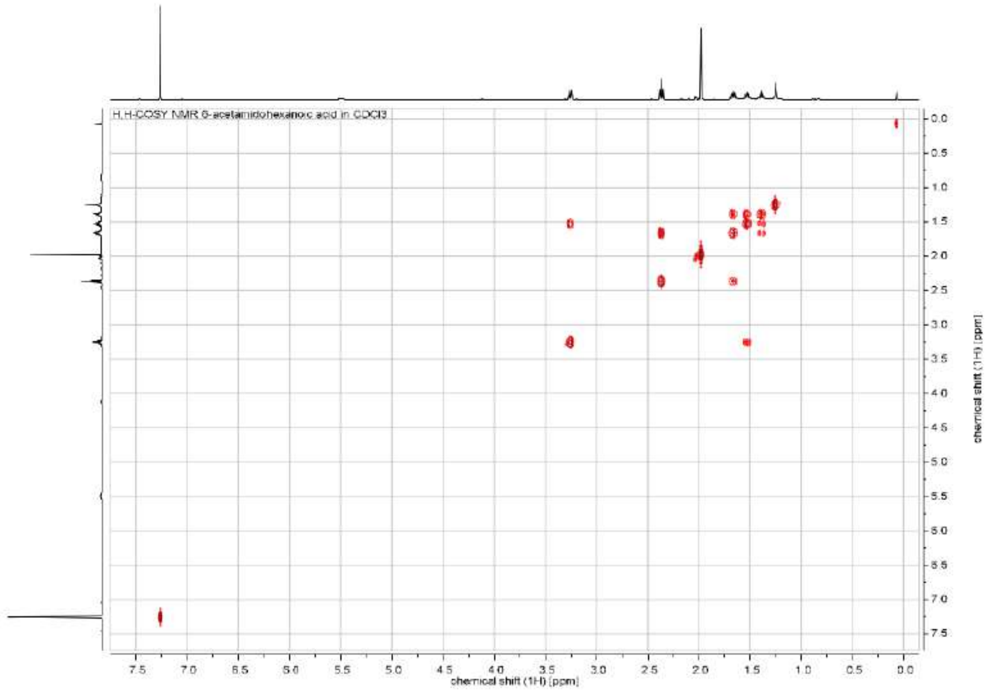


Figure S13: H,H-COSY spectrum of 6-acetamidohexanoic acid (**9a**).

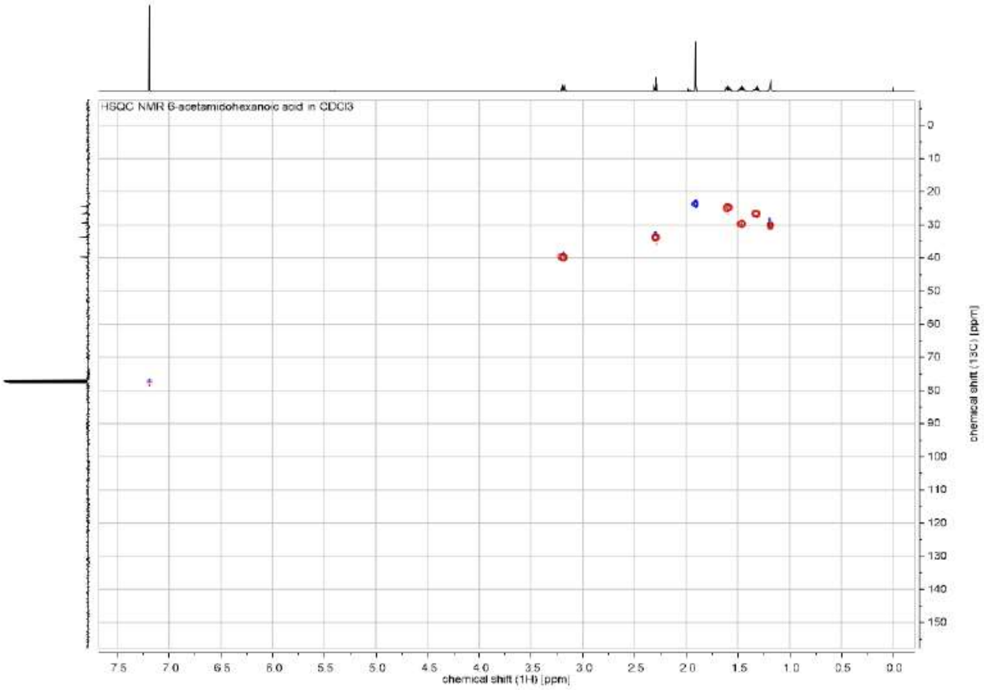


Figure S14: HSQC NMR of 6-acetamidohexanoic acid (**9a**).

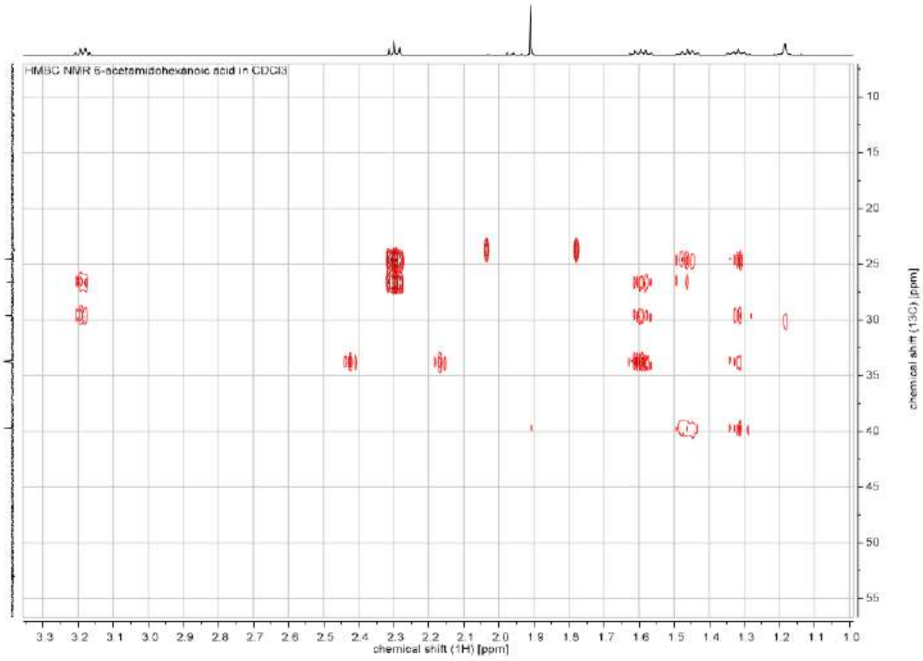
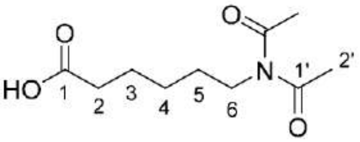


Figure S15: HMBC NMR of 6-acetamidohexanoic acid (**9a**).

Synthesis of 6-(*N*-acetylacetamido)hexanoic acid (8a).

A mixture of 6-aminohexanoic acid **10** (2.30 g, 17.5 mmol, 1.00 equiv.) and Ac_2O (16.6 mL, 175 mmol, 10.0 equiv.) was stirred at 120 °C for 24 h. After cooling Ac_2O and AcOH were removed vacuum. Then, the brown residue was stirred for 15 h in THF (10 mL) and sat. aqueous $NaHCO_3$-solution (10 mL) at room temperature. The solution was acidified to a pH-value of 3 by addition of aqueous HCl-solution (20%). The mixture was extracted with EtOAc (3×50 mL). The organic layer was dried over $MgSO_4$, filtered and the solvent was removed in vacuum. Now, the side product 6-acetamidohexanoic acid **9a** was removed by recrystallization from PE:EtOAc. The filtrate was evaporated and 6-(*N*-acetylacetamido)hexanoic acid **8a** (2.81 g, 13.1 mmol, 74%) was obtained as a yellow viscous oil.



^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ [ppm] = 1.35 – 1.41 (m, 2 H, 4-H_2), 1.54 – 1.62 (m, 2 H, 5-H_2), 1.63 – 1.70 (m, 2 H, 3-H_2), 2.37 (t, J = 7.3 Hz, 2 H, 2-H_2), 2.40 (s, 6 H, 2'-H_3), 3.61 – 3.66 (m, 2 H, 6-H_2).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 25 °C): δ [ppm] = 179.0 (C-1), 173.3 (C-1'), 45.0 (C-6), 33.8 (C-2), 29.0 (C-5), 26.5 (C-2'), 26.5 (C-4), 24.4 (C-3).

MS-ESI (*m/z*) = 214.1 $[M-H]^-$.

IR: ṽ [cm^{-1}] = 2939, 2865, 1693, 1464, 1418, 1369, 1343, 1239, 1188, 1156, 1019, 972, 731, 640, 612.

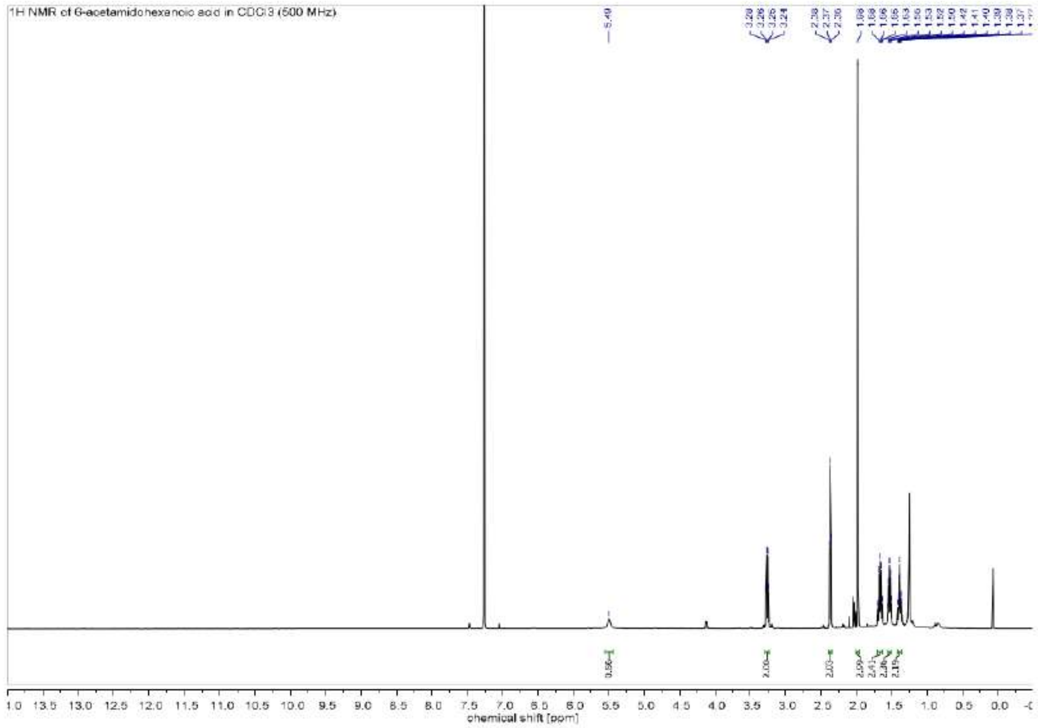


Figure S16: ^{1}H NMR of 6-(*N*-acetylacetamido)hexanoic acid (**8a**).

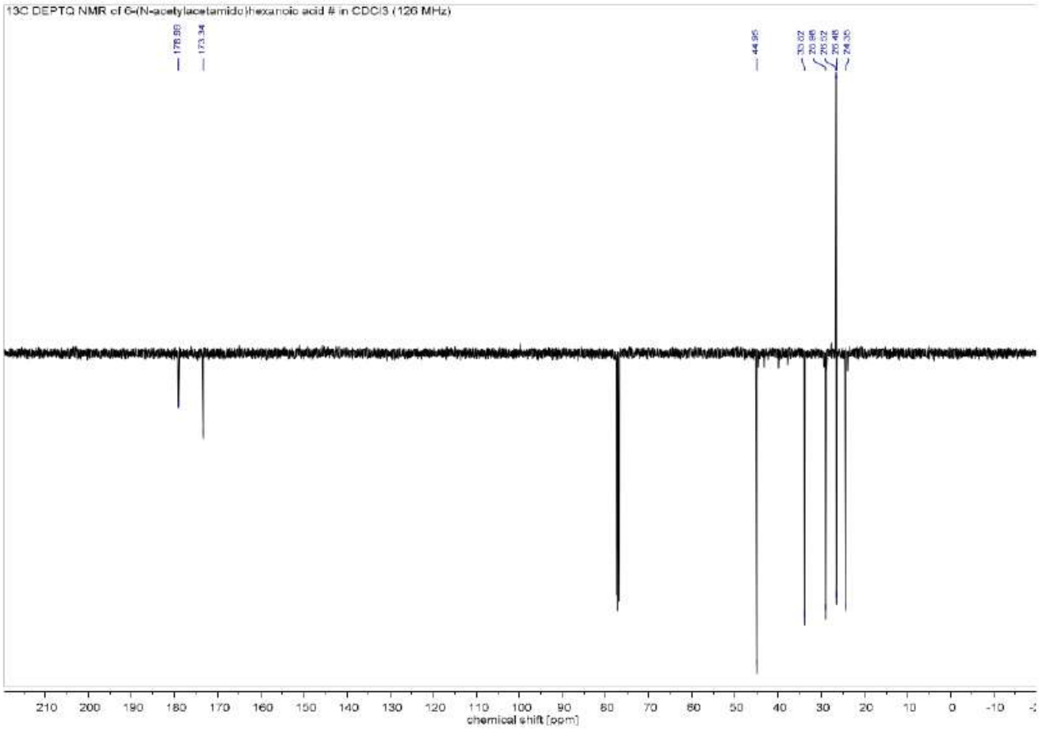


Figure S17: ^{13}C{^{1}H} NMR of 6-(*N*-acetylacetamido)hexanoic acid (**8a**).

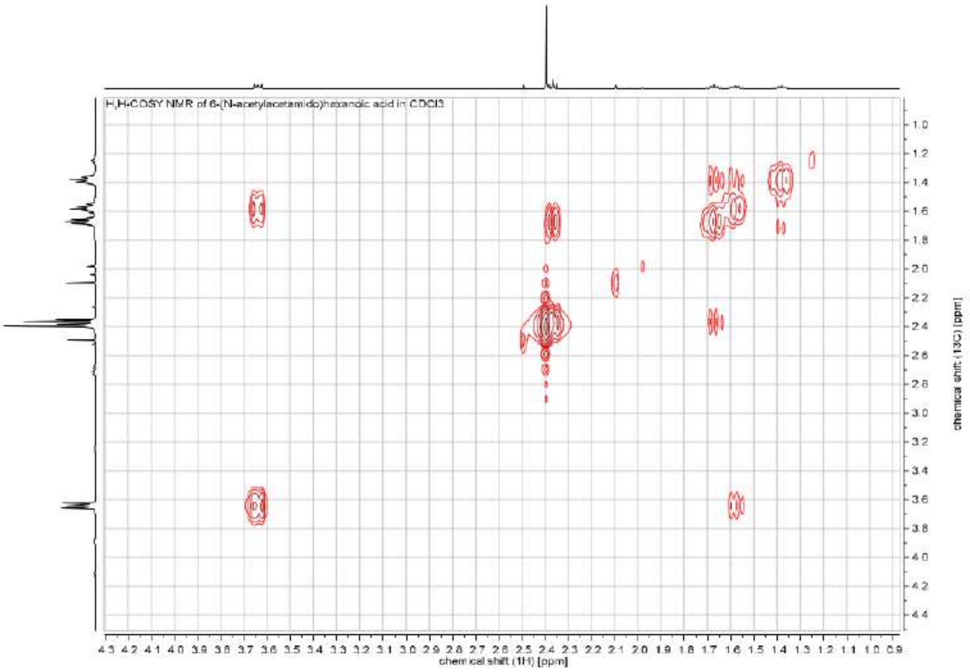


Figure 18: H,H-COSY spectrum of 6-(*N*-acetylacetamido)hexanoic acid (**8a**).

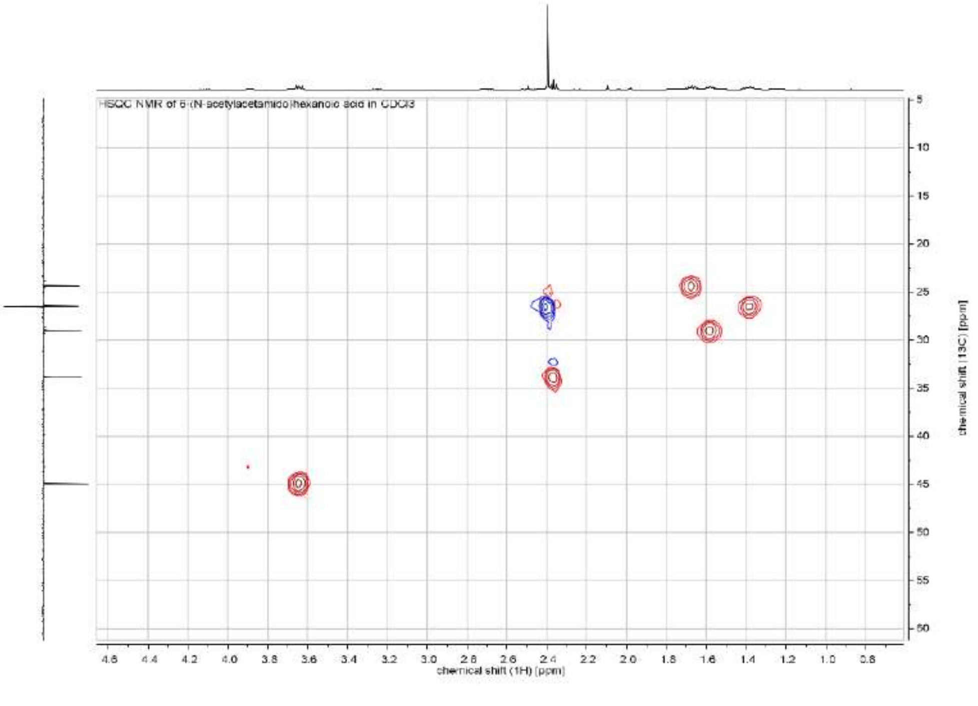


Figure 19: HSQC NMR of 6-(*N*-acetylacetamido)hexanoic acid (**8a**).

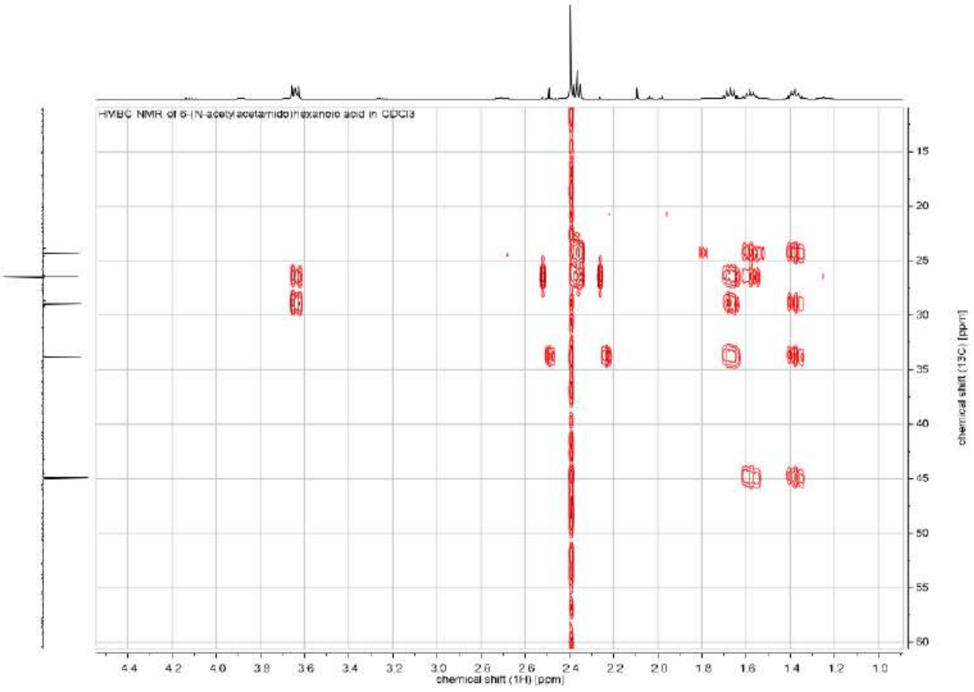


Figure 20: HMBC NMR of 6-(*N*-acetylacetamido)hexanoic acid (**8a**).

References

[1] D. Sun, J. Li, Q. Pan, C. Hao, G. Lai, *J. Spectroscopy* **2013**, 16275.

[2] J. H. Dam, G. Osztrovszky, L. U. Nordstrøm, R. Madsen, *Chem Eur. J.* **2010**, *16*, 6820–6827.

[3] M. Movassaghi, M. A. Schmidt, *Org. Lett.* **2005**, *7*, 2453–2456.

[4] D. Plażuk, J. Zakrzewski, M. Salmain, A. Błauż, B. Rychlik, P. Strzelczyk, A. Bujacz, G. Bujacz, *Organometallics* **2013**, *32*, 5774–5783.

Chemistry SELECT

Supporting Information

Ruthenium-Catalyzed Hydrogenative Depolymerization of End-of-Life Poly(bisphenol A carbonate)

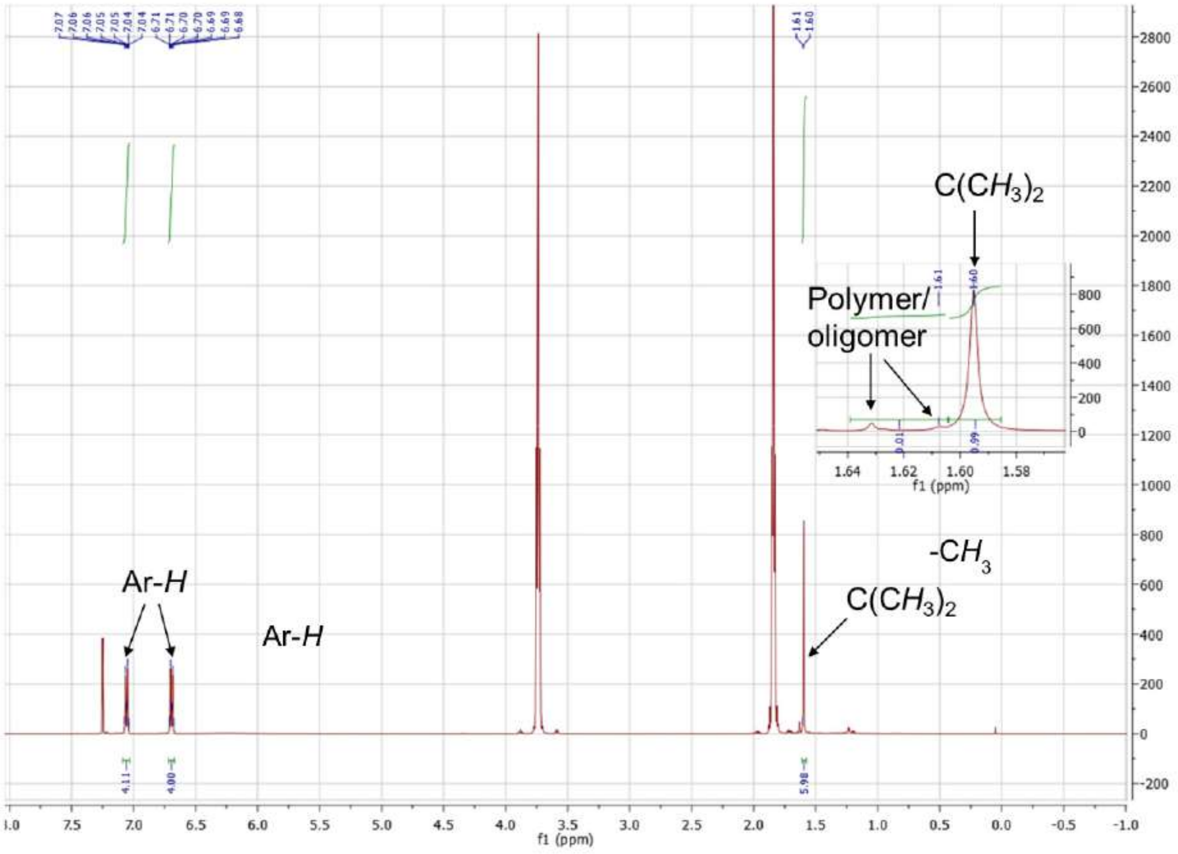
Christoph Alberti, Sarah Eckelt, and Stephan Enthaler*

General: All chemicals were used as received without further manipulations. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a *Fourier 300 MHz* (^{1}H: 300 MHz, ^{13}C: 75 MHz) or *Avance I-400* (^{1}H: 400 MHz, ^{13}C: 101 MHz) by Bruker, using the proton signals of the deuterated solvents as reference or external standards. Mass spectrometry was performed using a *Thermo ISQ LT EI* by Thermo Fisher Scientific. TLC was performed on *ALUGRAM XTRA SIL G/UV$_{254}$* cards from *Macherey-Nagel* GmbH & Co. KG with a thickness of 0.20 mm. Detection succeeded with UV-light (254 nm). For preparative column chromatography silica gel 60 (particle size 40 – 63 µm) from *Fluka* was used. All catalytic set-ups were prepared in a glovebox under argon. Milstein Catalyst: carbonylhydrido[6-(di-*t*-butylphosphinomethylene)-2-(*N*,*N*-diethylaminomethyl)-1,6-dihydropyridine]ruthenium(II) (CAS Number: 863971-63-5) was received from Strem Chemicals. THF was dried over sodium-benzophenone, was distilled off and stored over molecular sieves 4 Å under a nitrogen atmosphere. Anisole was degassed in a freeze-pump-thaw cycle and stored over molecular sieves 4 Å under a nitrogen atmosphere. The screening of reaction conditions were performed in a Parr autoclave (model: 4774).

General procedure for the hydrogenation of poly(bisphenol A carbonate) 1a (optimization of reaction conditions): A mixture of commercially available poly(bisphenol A carbonate) (**1a**) (344 mg, 1.35 mmol based on the repeating unit, obtained from Sigma Aldrich), potassium *tert*-butoxide (0-38.3 mg, 0-0.341 mmol, 0-25 mol% based on the repeating unit of **1a**) and catalytic amounts of complex **4** (0-30.4 mg, 0-0.0673 mmol, 0-5 mol%, based on the repeating unit of **1a**) were placed with a stir bar in a vial. THF (2.0 mL) was added. The vial was placed in an autoclave (Parr Instrument Company), which was sealed and purged with hydrogen (5 times). Afterwards the desired hydrogen pressure was adjusted (10-45 bar) and the autoclave was heated to the desired temperature. The temperature was hold for 6-24 hours, while stirring the reaction mixture. Afterwards the autoclave was cooled to room temperature and the hydrogen pressure was carefully released. An aliquot of the solution was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^{1}H NMR to determine the yield of bisphenol A (**2**). The yield of **2** was calculated on the basis of the Ar-H or $C(CH_3)_2$ and the Ar-H or $C(CH_3)_2$ leftover signals of the polymer/oligomer. *Note:* Methanol was not detected. The screening of reaction conditions were performed in a Parr autoclave (model: 4774) containing sites for six glass-vials (~4 mL). Importantly, the vials were not sealed; hence during reaction the methanol may evaporate from the vials.

Bisphenol A (**2**):[1] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.06-7.07 (d, *J* = 8.61 Hz, 4H, Ar-*H*), 6.70-6.71 (d, *J* = 8.61 Hz, 4H, Ar-*H*), 1.61 (s, 6H, $(CH_3)_2C$-) ppm. (The signal for 2xOH was not observed).

Figure S1. Spectrum of a reaction mixture (5 mol% **4**, 5 mol% KO^{t}Bu, THF, 140 °C, 45 bar H_2, 24 h) (^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)).



Procedure for the hydrogenation of poly(bisphenol A carbonate) 1a: A mixture of commercially available poly(bisphenol A carbonate) (**1a**) (344 mg, 1.35 mmol based on the repeating unit, obtained from Sigma Aldrich), potassium *tert*-butoxide (0.0074 g, 0.0651 mmol, 5 mol% based on the repeating unit of **1a**) and catalytic amounts of complex **4** (0.0294 mg, 0.0651 mmol, 5 mol%, based on the repeating unit of **1a**) were placed with a stir bar in a vial. THF (2.0 mL) was added. The vial was placed in an autoclave (Parr Instrument Company), which was sealed and purged with hydrogen (5 times). Afterwards the desired hydrogen pressure was adjusted and the autoclave was heated to the desired temperature. The temperature was hold for 24 hours, while stirring the reaction mixture. Afterwards the autoclave was cooled to room temperature and the hydrogen pressure was carefully released. Purification was performed by silica gel column chromatography (petroleum ether: acetone, 8:2, R_f = 0.18). Bisphenol A was obtained as colorless crystals in 91 % yield (280 mg, 1.23 mmol).

Bisphenol A (**2**): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.10 (d, *J* = 8.67 Hz, 4H, Ar-*H, 4*), 6.74 (d, *J* = 8.67 Hz, 4H, Ar-*H, 3*), 4.69 (s, 2H, -O*H, 1*), 1.62 (s, 6H, $(CH_3)_2C$, *7*) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C): δ = 153.4 (C_q-OH, *2*), 143.5 ($C_q(C\text{-}CH_3)_2$, *5*), 128.1 (C_{Ar}, *4*), 114.8 (C_{Ar}, *3*), 41.8 ($C_q(CH_3)_2$, *6*), 31.2 (CH_3, *7*) ppm.

EI-MS m/z: 228 [M^+], 213 [M^+ -(CH_3)].

IR (ATR): $\tilde{\nu}$ [cm^{-1}]: 3323 (w), 2969 (m), 1738 (s), 1508 (s), 1217 (vs), 824 (vs), 562 (vs).

Melting point: 156 °C

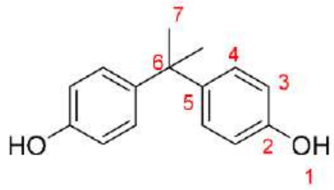


Figure S2. ^{1}H NMR spectrum of **2** obtained from depolymerization of **1a** (^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)).

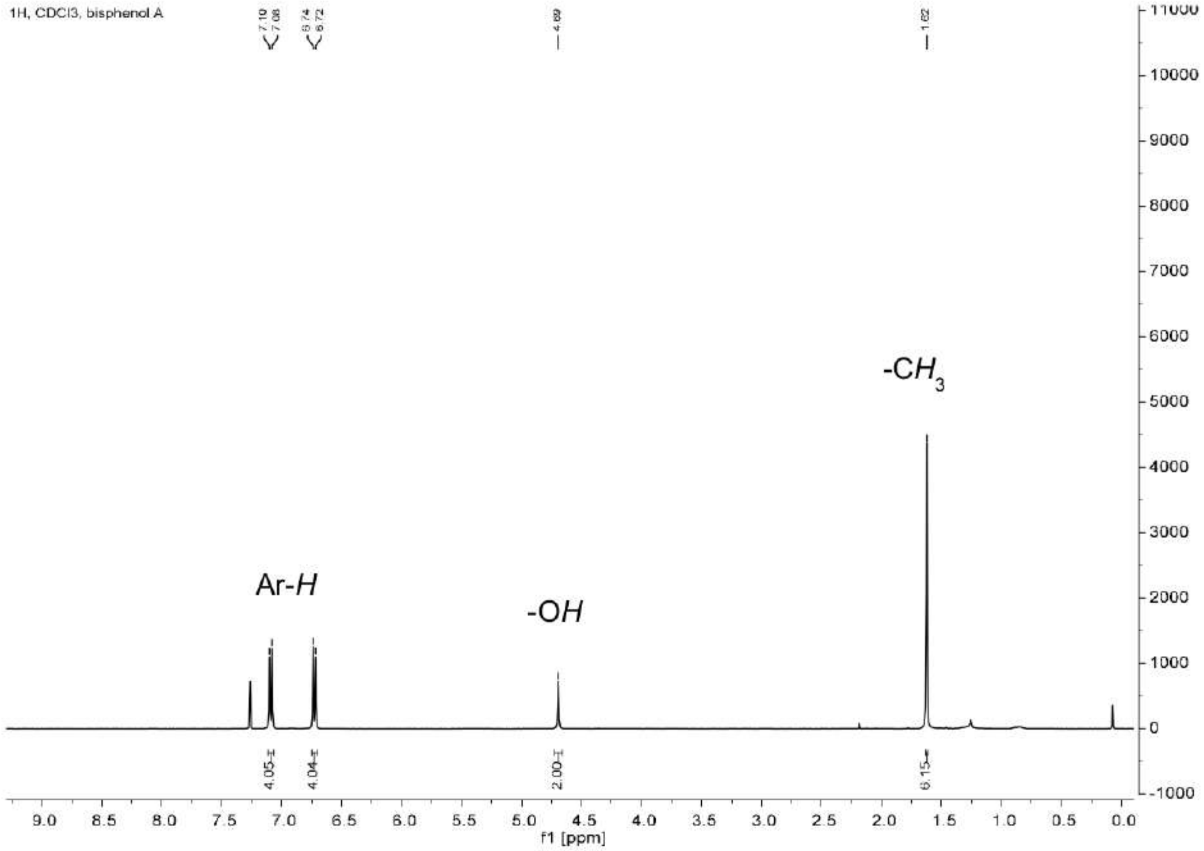


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of **2** obtained from depolymerization of **1a** ($^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, 25 °C)).

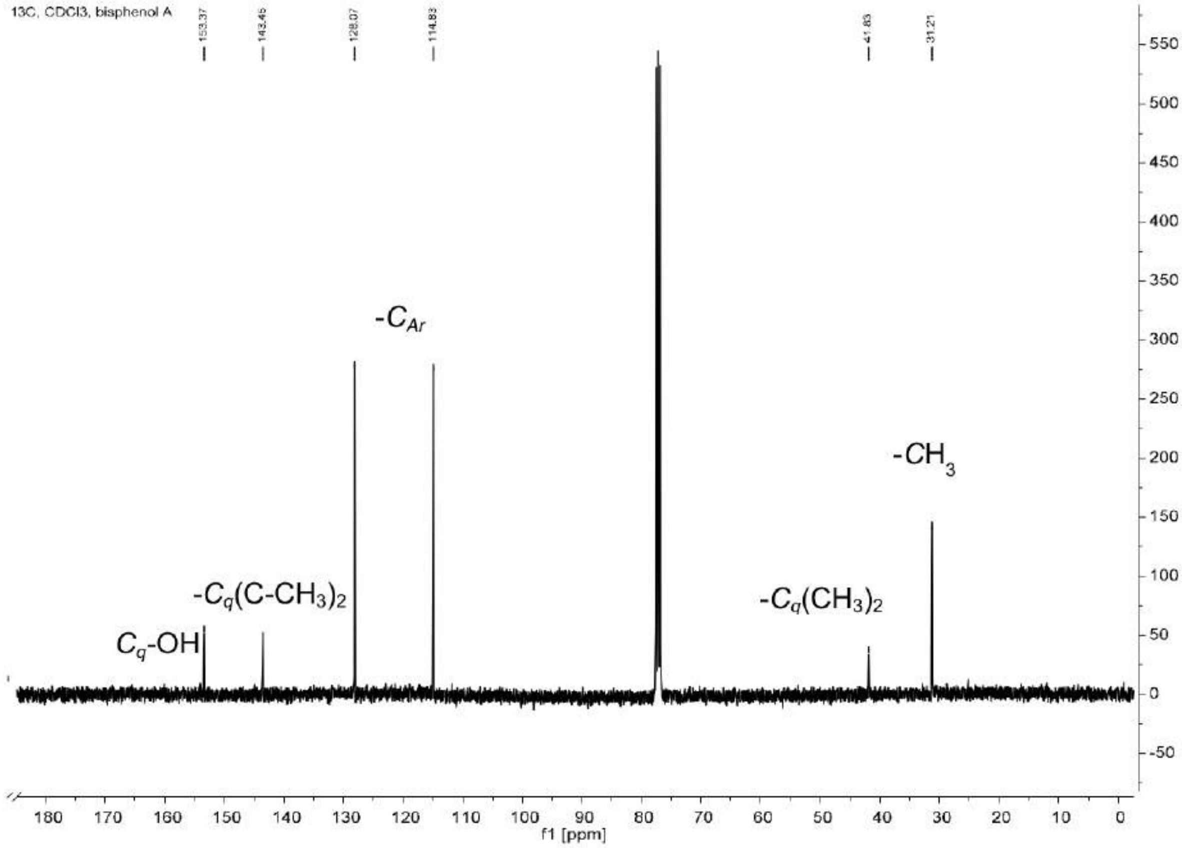


Figure S4. H,H COSY spectrum of **2** obtained from depolymerization of **1a**.

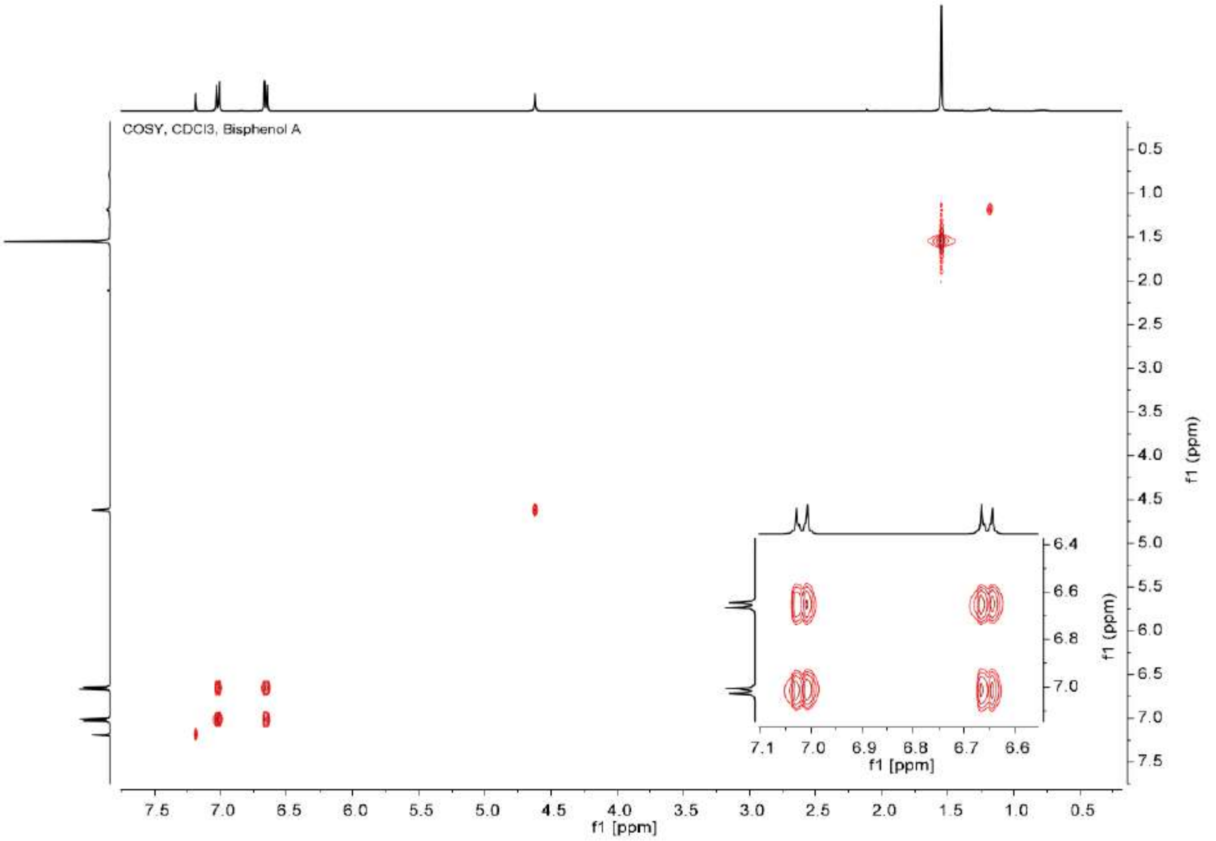


Figure S5. $^1H,^{13}C\{^1H\}$ HSQC spectrum of **2** obtained from depolymerization of **1a**.

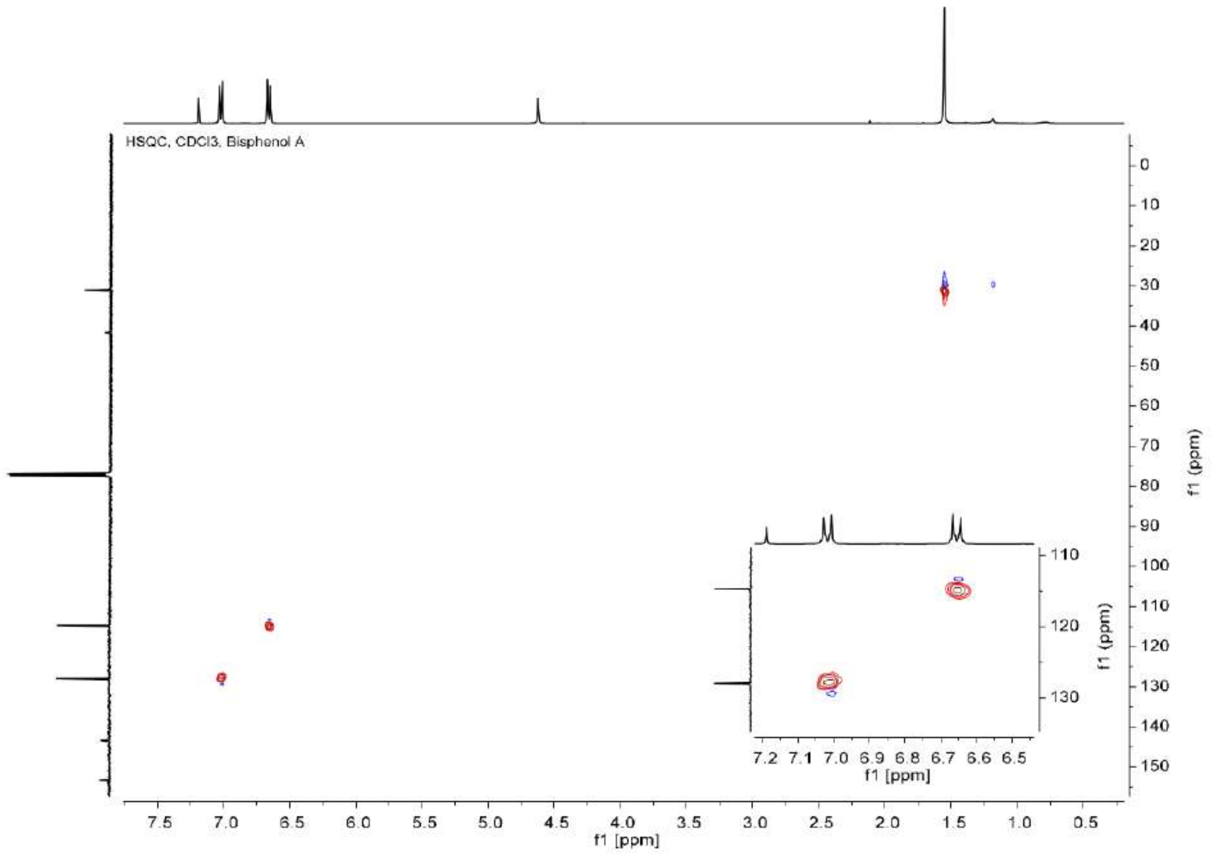
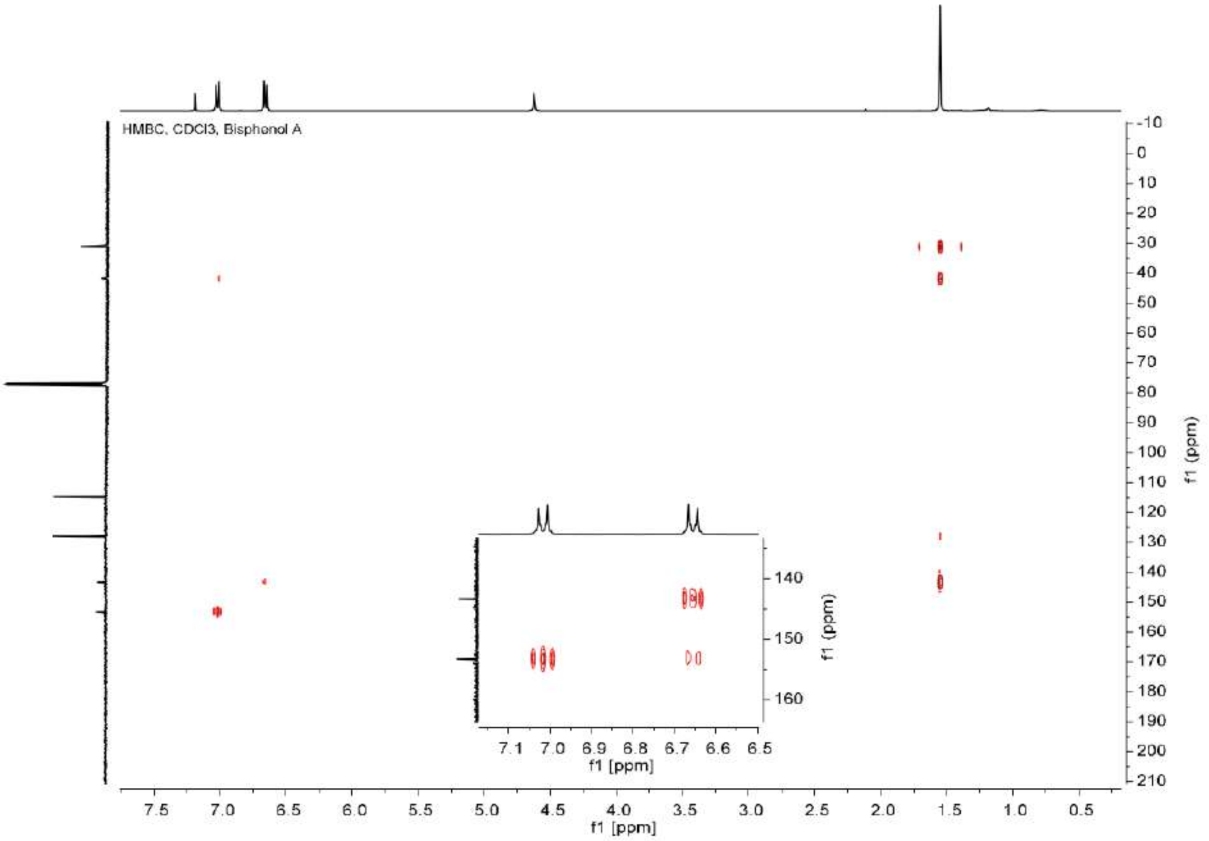


Figure S6. ^{1}H,^{13}C{^{1}H} HMBC spectrum of **2** obtained from depolymerization of **1a**.



Procedure for the depolymerization of poly(bisphenol A carbonate) starting from DVD:

a) Depolymerization of poly(bisphenol A carbonate) **1b** (DVD)

A mixture of the DVD powder **1c** (obtained by ball milling of DVD pieces) (343 mg, 1.35 mmol based on the repeating unit), potassium *tert*-butoxide (0.0073 g, 0.0651 mmol, 5 mol% based on the repeating unit of **1c**) and catalytic amounts of complex **4** (0.0294 mg, 0.0651 mmol, 5 mol%, based on the repeating unit of **1c**) were placed with a stir bar in a vial. THF (2.0 mL) was added. The vial was placed in an autoclave (Parr Instrument Company), which was sealed and purged with hydrogen (5 times). Afterwards the desired hydrogen pressure was adjusted and the autoclave was heated to the desired temperature. The temperature was hold for 24 hours, while stirring the reaction mixture. Afterwards the autoclave was cooled to room temperature and the hydrogen pressure was carefully released. The mixture was filtered and the solvent was removed in vacuum. Purification of the residue was performed by silica gel column chromatography (petroleum ether: acetone, 8:2, R_f = 0.18). Bisphenol A was obtained as colorless crystals in 86 % yield (264 mg, 1.16 mmol). The NMR spectra are in accordance to the spectra presented for depolymerization of commercially available poly(bisphenol A carbonate) **1a** (*vide supra*).

b) Poly(bisphenol A carbonate) **1c** isolation from DVDs

To pieces of a DVD (16.67 g, cut in small pieces) and a stir bar in a 250 mL-flask was added THF (100 mL). A reflux condenser was added and the flask was placed in an oil bath. The mixture was heated under reflux for 30 min. The polycarbonate part of the DVD dissolved, while the aluminum foil and another plastic foil didn´t dissolve. The hot mixture was filtered through a filter paper into a 250 mL flask. The solvent was removed on a rotary evaporator (Note: the collected solvent can be reused for further poly(bisphenol A carbonate) dissolving). The solid residue was added to a frit and was washed with acetone. Afterwards the solid was dried in an oven at 80 °C for 6 hours yielding poly(bisphenol A carbonate) **1b** (13.74 g, 82 wt% based on the starting DVD) (Note: the color of the poly(bisphenol A carbonate) varies depending on the applied starting DVD).

A mixture of the isolated poly(bisphenol A carbonate) (**1c**) (344 mg, 1.35 mmol based on the repeating unit), potassium *tert*-butoxide (0.0074 g, 0.0659 mmol, 5 mol% based on the repeating unit of **1c**) and catalytic amounts of complex **4** (0.0293 g, 0.0648 mmol, 5 mol%, 0-0.135 mmol based on the repeating unit of **1c**) were placed with a stir bar in a vial. THF (2.0 mL) was added. The vial was placed in an autoclave (Parr Instrument Company), which was sealed and purged with hydrogen (5 times). Afterwards the desired hydrogen pressure was adjusted and the autoclave was heated to the desired temperature. The temperature was hold for 24 hours, while stirring the reaction mixture. Afterwards the autoclave was cooled to room temperature and the hydrogen pressure was carefully released. The mixture was transferred to a flask, which was connected to distillation equipment. The THF and methanol were collected and the identity was check by ^{1}H NMR. Purification of the residue was performed by silica gel column chromatography (petroleum ether: acetone, 8:2, $R_f = 0.18$). Bisphenol A was obtained as colorless crystals in 73 % yield (226 mg, 0.99 mmol). The content of **1** in the DVD is ~87%; therefore the yield of **2** can be corrected to approximately 84%. The NMR spectra are in accordance to the spectra presented for depolymerization of commercially available poly(bisphenol A carbonate) **1a** (*vide supra*).

Figure S7. ^{1}H NMR spectrum of the reaction mixture of the depolymerization of **1c** (^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)).

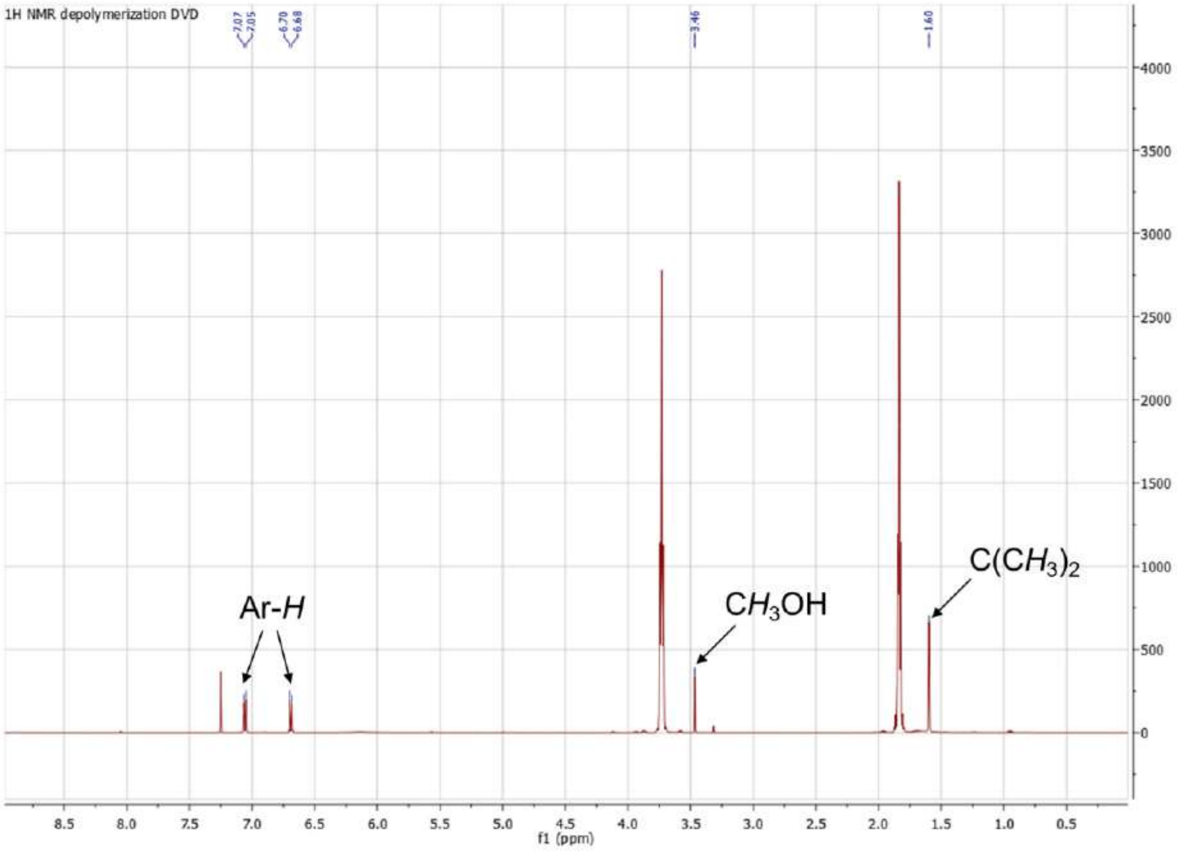
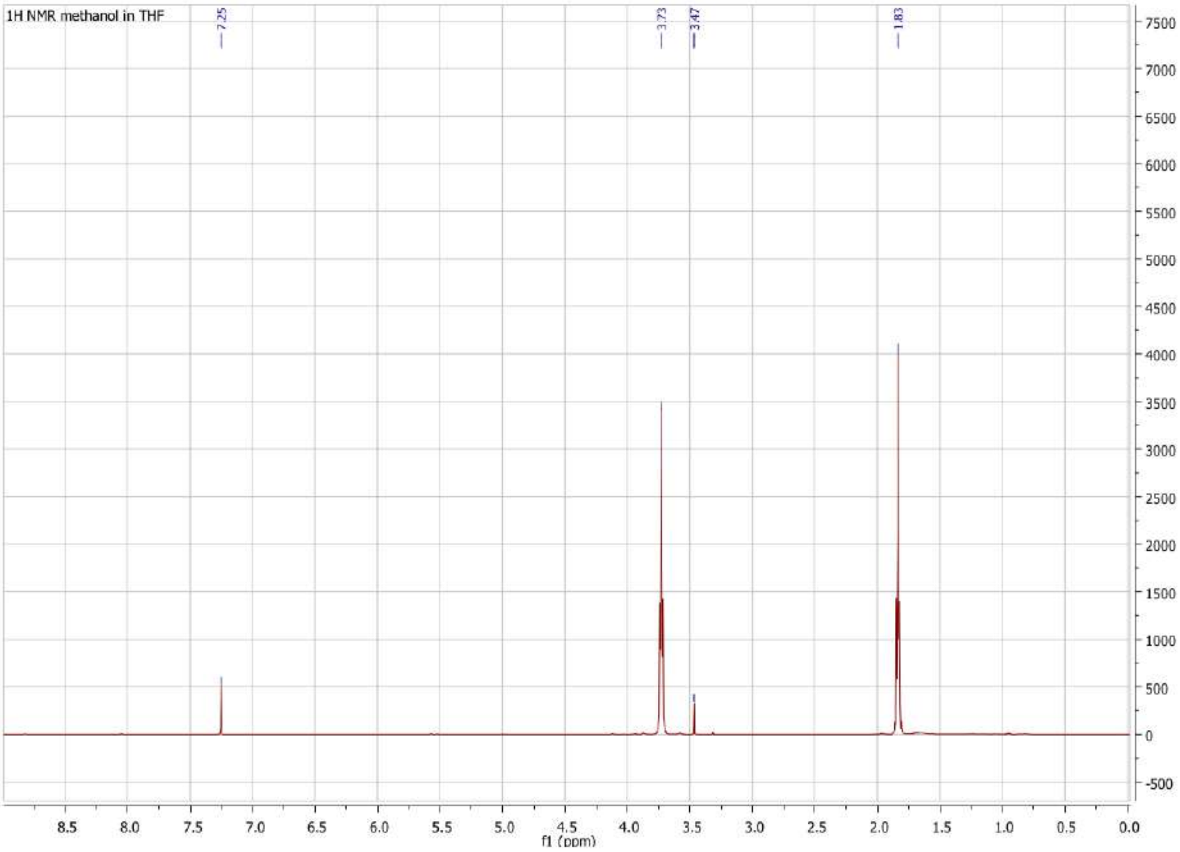


Figure S8. ^{1}H NMR spectrum of collected methanol in THF (^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)).



References

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[1] a) S. Kiran, N. R. James, R. Joseph, A. Jayakrishnan, *Biomaterials* **2009**, *30*, 5552-5559; b) C. Alberti, F. Scheliga, S. Enthaler, *ChemistrySelect* **2019**, *4*, 2639–2643; c) C. Alberti, S. Enthaler, *Asian J. Org. Chem.* **2019**, *DOI: 10.1002/ajoc.201900242R1*; d) C. Alberti, F. Scheliga, S. Enthaler, *ChemistryOpen* **2019**, *8,* 822-827.

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Supporting Information

Hydrogenative Depolymerization of End-of-Life Poly-(Bisphenol A Carbonate) Catalyzed by a Ruthenium-MACHO-Complex

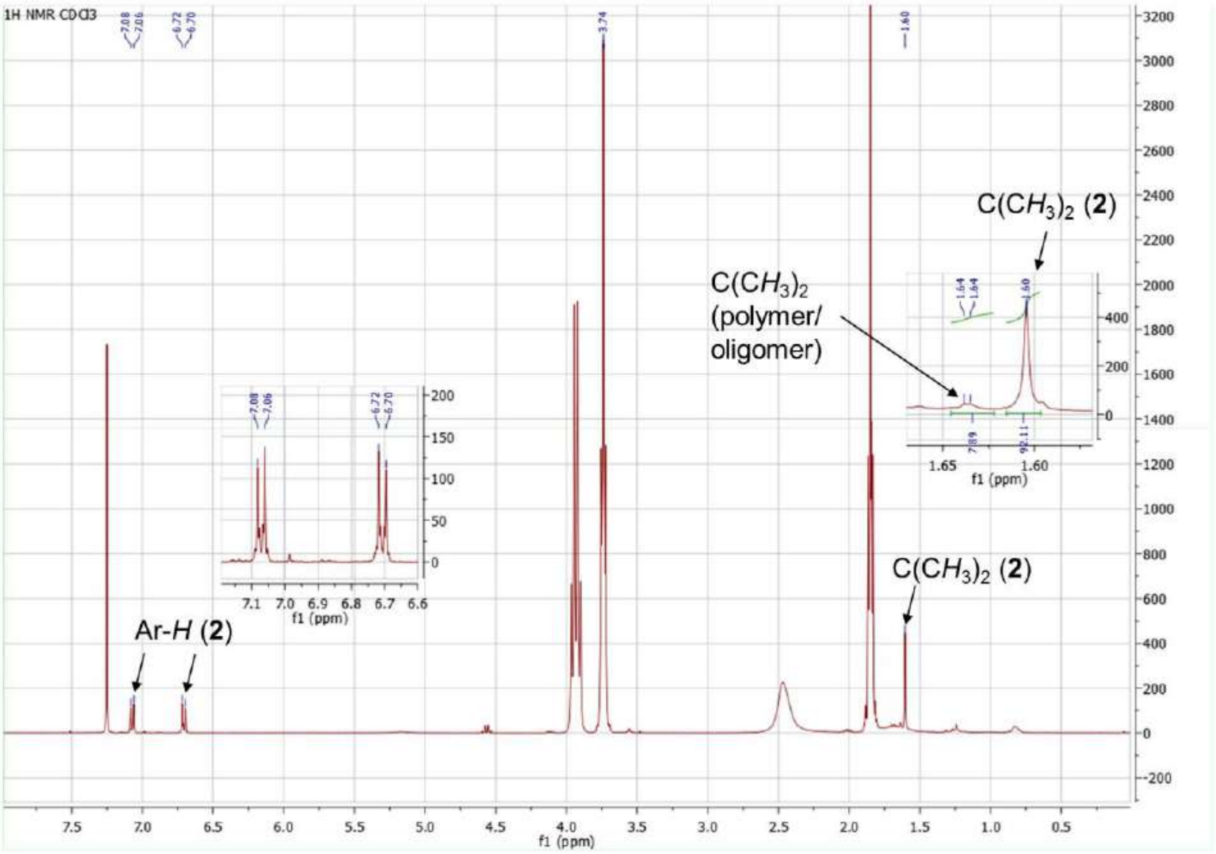
Tim-Oliver Kindler, Christoph Alberti, Jannis Sundermeier, and Stephan Enthaler*

General: All chemicals were used as received without further manipulations. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a *Fourier 300 MHz* (^{1}H: 300 MHz, ^{13}C: 75 MHz) or *Avance I-400* (^{1}H: 400 MHz, ^{13}C: 101 MHz) by Bruker, using the proton signals of the deuterated solvents as reference or external standards. Mass spectrometry was performed using a *Thermo ISQ LT EI* by Thermo Fisher Scientific. TLC was performed on *ALUGRAM XTRA SIL G/UV$_{254}$* cards from *Macherey-Nagel* GmbH & Co. KG with a thickness of 0.20 mm. Detection succeeded with UV-light (254 nm). For preparative column chromatography silica gel 60 (particle size 40 – 63 µm) from *Fluka* was used. All catalytic set-ups were prepared in a glovebox under argon. Ru-MACHO®-BH: Carbonylhydrido(tetrahydroborato)[bis(2-diphenylphosphinoethyl)amino]ruthenium(II) (CAS Number: 1295649-41-0) was received from TCI Deutschland GmbH. THF was dried over sodium-benzophenone, was distilled off and stored over molecular sieves 4 Å under a nitrogen atmosphere. The hydrogenations were performed in a Parr autoclave (model: 4774) (Parr Instrument Company).

General procedure for the hydrogenation of poly(bisphenol A carbonate) 1a (optimization of reaction conditions): A mixture of commercially available poly(bisphenol A carbonate) (**1a**) (17.3 mg, 0.0682 mmol based on the repeating unit, obtained from Sigma Aldrich), potassium *tert*-butoxide (0-0.38 mg, 0-0.0034 mmol, 0-5 mol% based on the repeating unit of **1a**) and catalytic amounts of complex **5** (0-2.0 mg, 0-0.034 mmol, 0-5 mol%, based on the repeating unit of **1a**) were placed with a stir bar in a vial. THF (1.0 mL) was added. The vial was placed in an autoclave, which was sealed and purged with hydrogen (5 times). Afterwards the desired hydrogen pressure was adjusted (10-45 bar) and the autoclave was heated to the desired temperature. The temperature was hold for 6-24 hours, while stirring the reaction mixture. Afterwards the autoclave was cooled to room temperature and the hydrogen pressure was carefully released. An aliquot of the solution was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.6 mL). The sample was subjected to ^{1}H NMR to determine the yield of bisphenol A (**2**). The yield of **2** was calculated on the basis of the Ar-H or $C(CH_3)_2$ and the Ar-H or $C(CH_3)_2$ leftover signals of the polymer/oligomer. *Note:* Methanol was not detected. The screening of reaction conditions were performed in a Parr autoclave (model: 4774) containing sites for six glass-vials (~4 mL). Importantly, the vials were not sealed; hence during reaction the methanol may evaporate from the vials.

Bisphenol A (**2**):[1] ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.05-7.10 (m, 4H, Ar-*H*), 6.69-6.75 (m, 4H, Ar-*H*), 1.60 (s, 6H, $(CH_3)_2$, (The signal for 2xOH was not observed).

Figure S1. ^{1}H NMR spectrum of a reaction mixture (0.5 mol% Ru-MACHO-BH, THF, 140 °C, 45 bar H_2, 6 h) (300 MHz, $CDCl_3$, 25 °C).



Bisphenol A (**2**): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.04–7.07 (m, 4H, Ar-*H*, *4*), 6.71–6.74 (m, 4H, Ar-*H*, *3*) 1.59 (s, 6H, -C*H*$_3$, *7*) ppm.

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C): δ = 156.0 (*C$_q$*-OH, *2*), 142.9 (*C$_q$*(C-CH$_3$)$_2$, *5*), 128.5 (*C$_{Ar}$ 4*), 115.5 (*C$_{Ar}$*, *3*), 42.1 (*C$_q$*(CH$_3$)$_2$, *6*), 31.6 (CH$_3$, *7*) ppm.

EI-MS m/z: 228 [M^+], 213 [M^+ -(CH_3)].

IR (ATR): $\tilde{\nu}$ [cm^{-1}]: 3307 (w), 2969 (m), 1508 (s), 1216 (s), 824 (vs), 562 (vs).

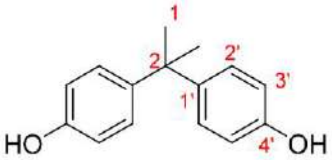


Figure S2. ^{1}H NMR spectrum of **2** obtained from depolymerization of DVD powder (400 MHz, acetone-*D*6, 25 °C)).

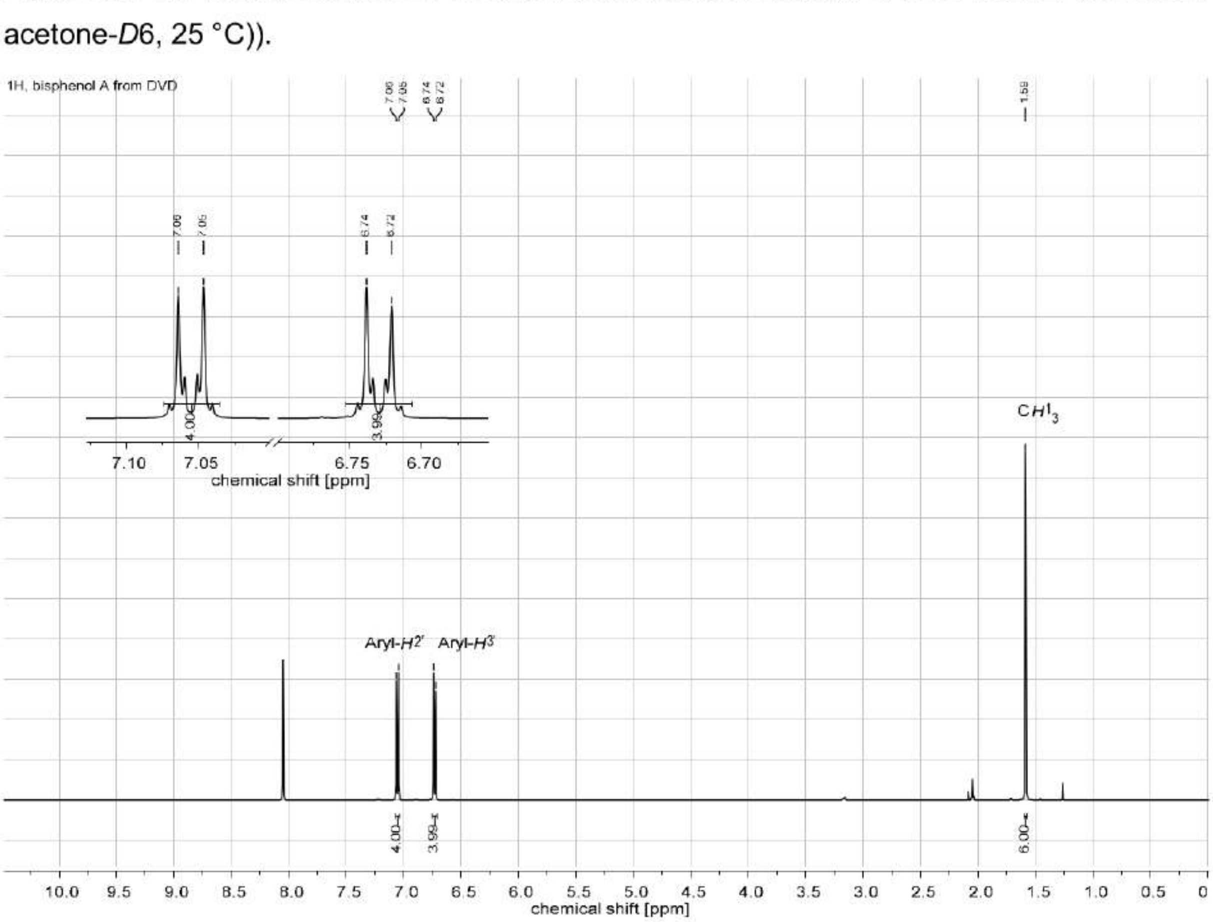


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of **2** obtained from depolymerization of DVD powder (125 MHz, acetone-*D*6, 25 °C)).

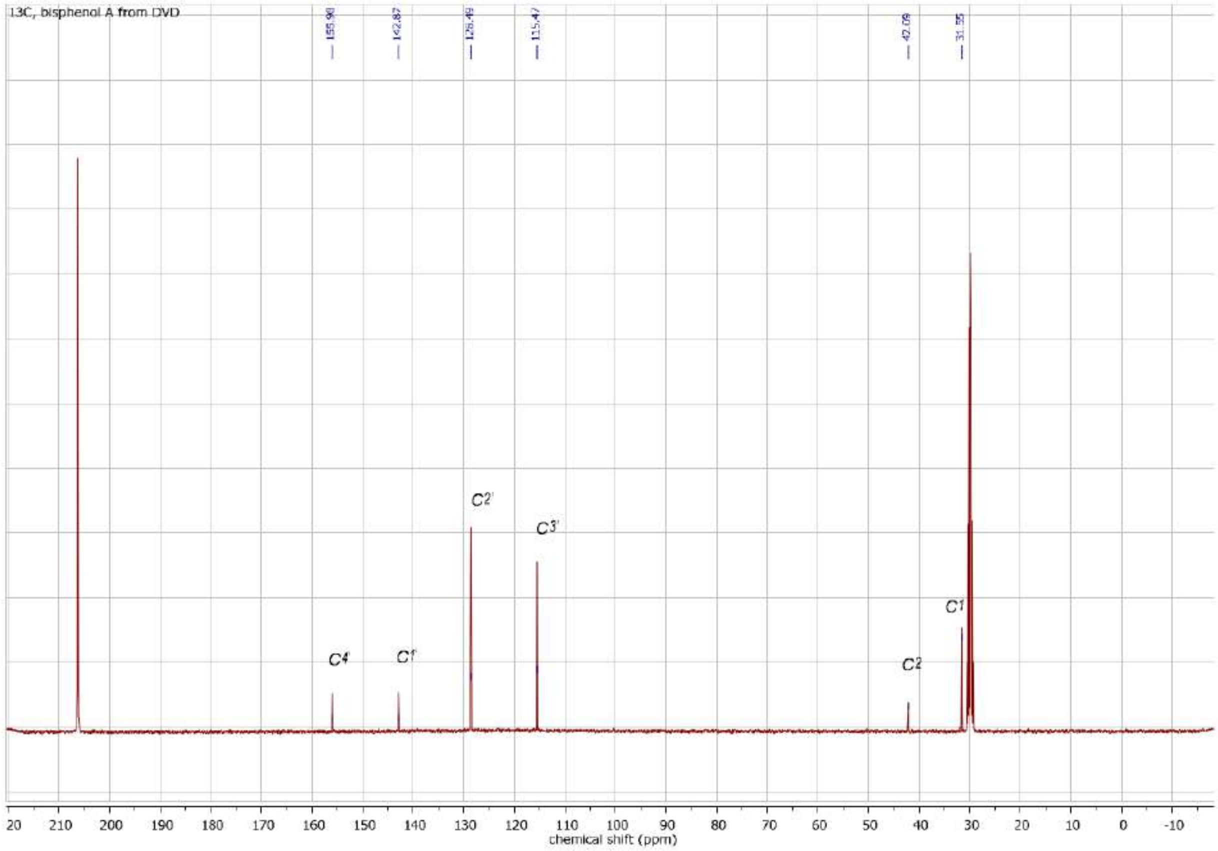


Figure S4. H,H COSY spectrum of **2** obtained from depolymerization of DVD powder.

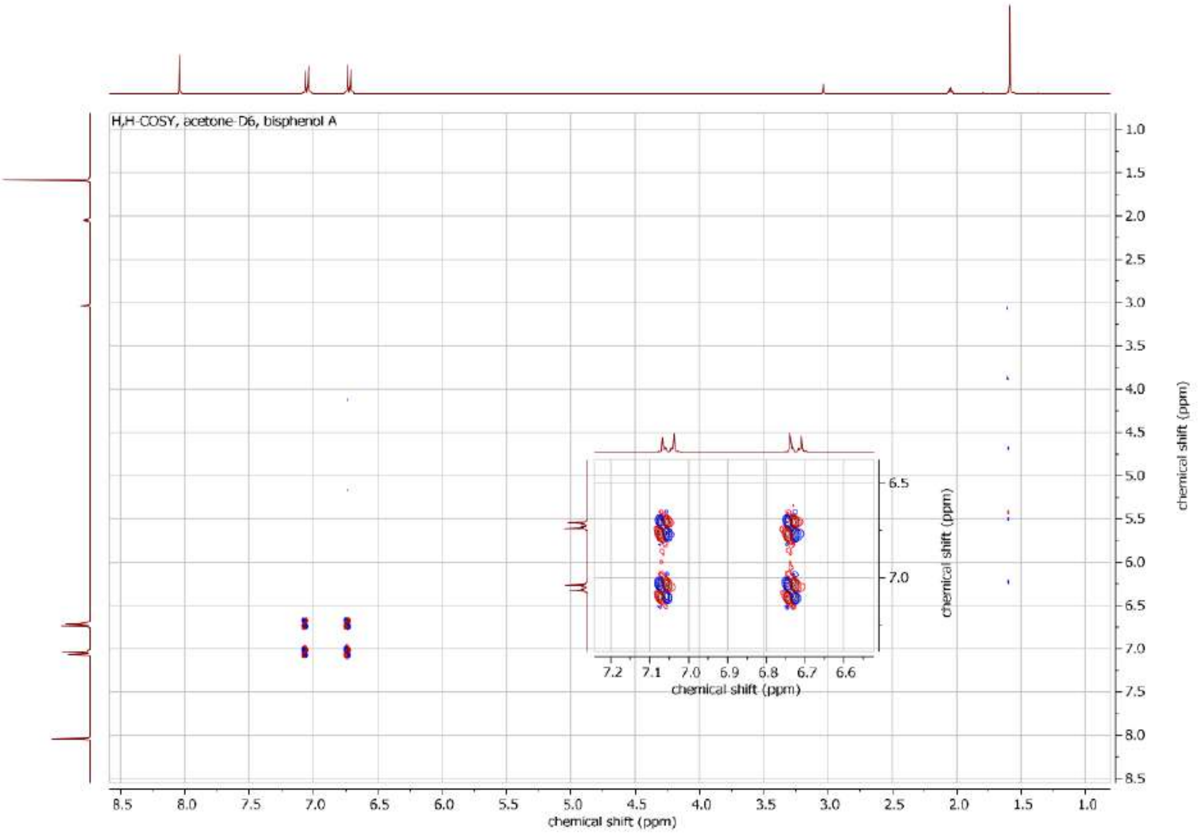


Figure S5. ^{1}H,^{13}C{^{1}H} HSQC spectrum of **2** obtained from depolymerization of DVD powder.

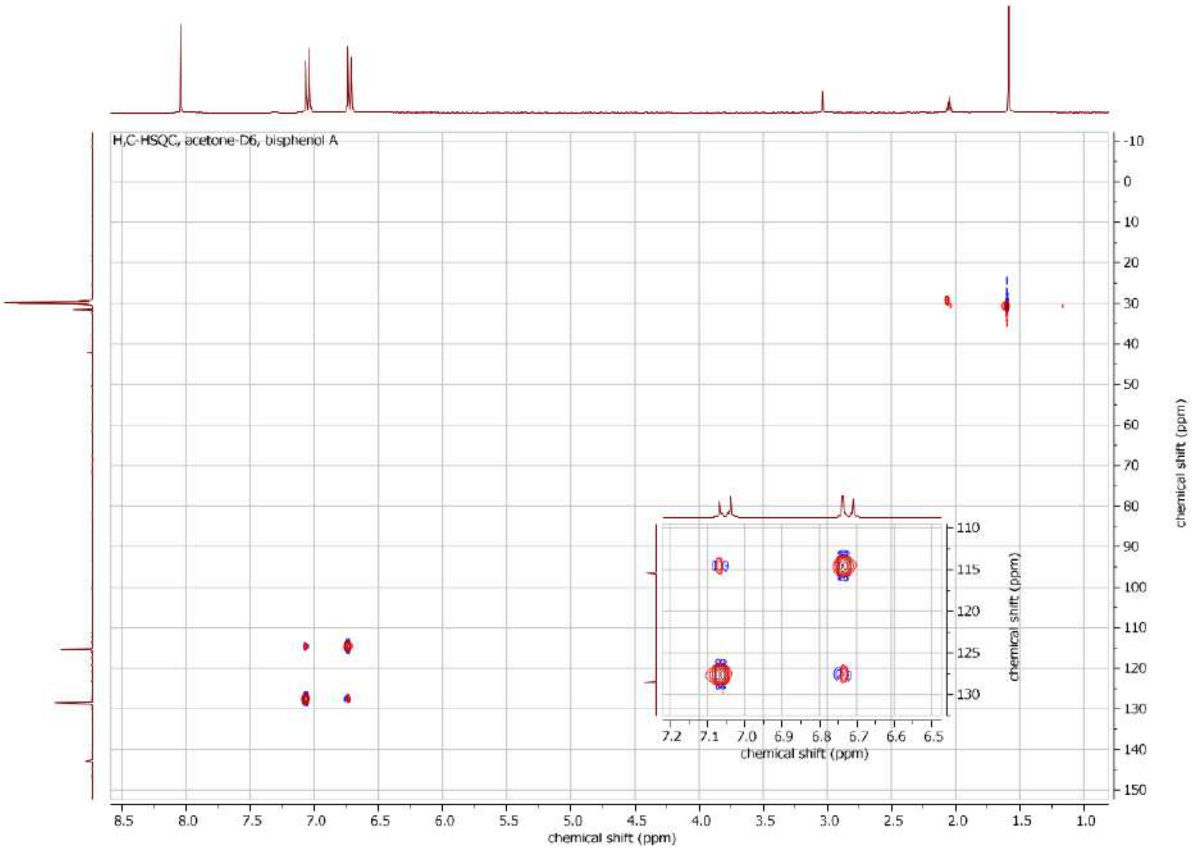


Figure S6. $^{1}H,^{13}C\{^{1}H\}$ HMBC spectrum of **2** obtained from depolymerization of DVD powder.

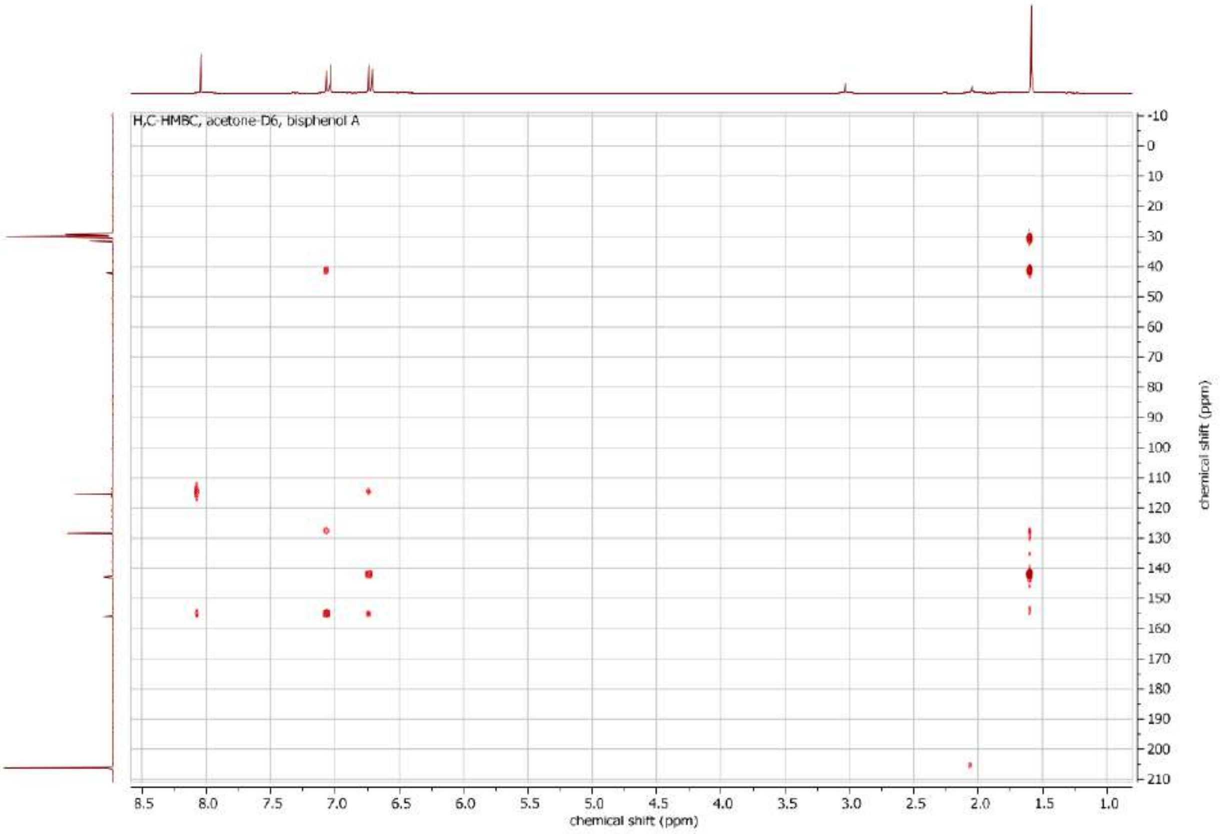


Figure S7. GC-MS-EI spectrum of **2** obtained from depolymerization of DVD powder.

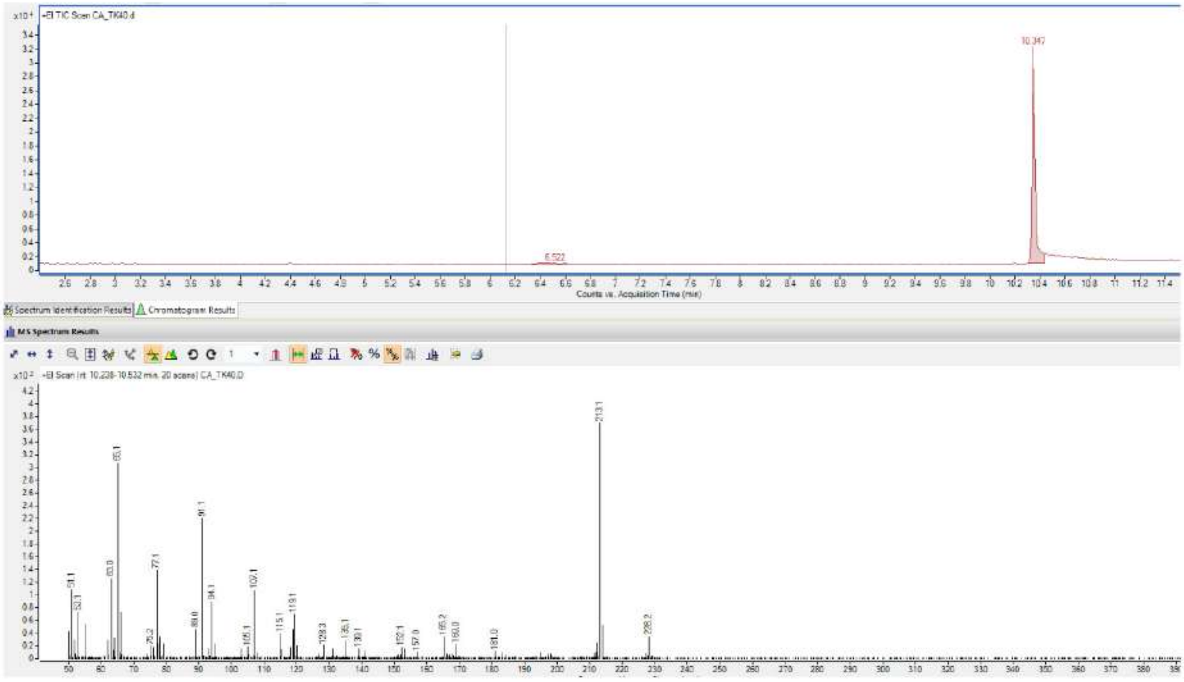
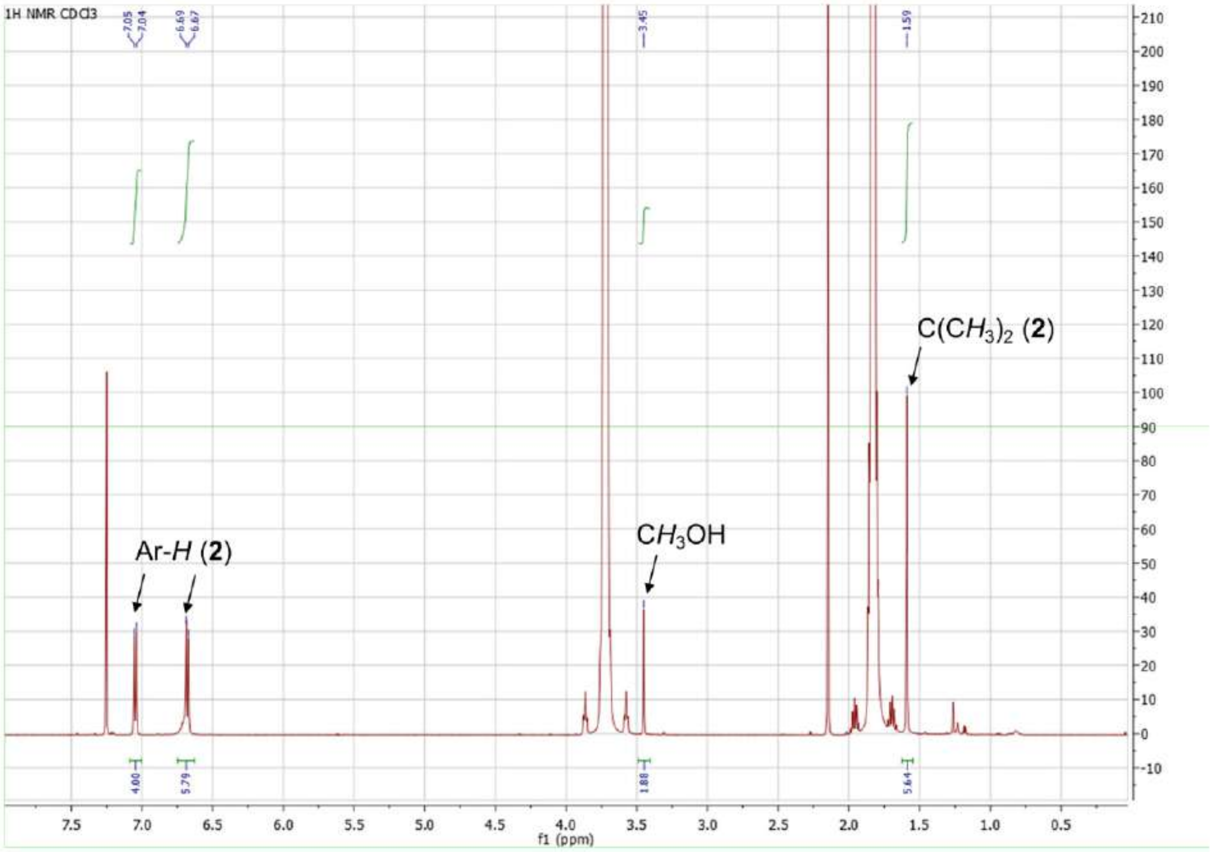


Figure S8. ^{1}H NMR spectrum of the reaction mixture obtained from depolymerization of DVD powder with detection of methanol.



Procedure for the depolymerization of poly(bisphenol A carbonate) starting from DVD:

a) Depolymerization of poly(bisphenol A carbonate) **1b** (DVD)

A mixture of the DVD powder **1c** (obtained by ball milling of DVD pieces) (1.74 g, 6.85 mmol based on the repeating unit, catalytic amounts of complex **5** (19.9 mg, 0.0341 mmol, 0.5 mol%, based on the repeating unit of **1c**) and THF (2.0 mL) was added with a stir bar in an autoclave (Parr Instrument Company), which was sealed and purged with hydrogen (5 times). Afterwards the desired hydrogen pressure was adjusted and the autoclave was heated to the desired temperature. The temperature was hold for 16 hours, while stirring the reaction mixture. Afterwards the autoclave was cooled to room temperature and the hydrogen pressure was carefully released. Purification was performed by silica gel column chromatography (petroleum ether: acetone, 4:1, R_f = 0.18). Bisphenol A was obtained as colorless crystals in 81 % yield (1.2 g, 5.54 mmol). The content of **1** in the DVD is ~87 %; therefore the yield of **2** can be corrected to approximately 92 %. The NMR spectra are in accordance to the spectra presented for depolymerization of commercially available poly(bisphenol A carbonate) **1a** (*vide supra*).

b) Poly(bisphenol A carbonate) **1c** isolation from DVDs

To pieces of a DVD (16.7 g, cut in small pieces) and a stir bar in a 250 mL-flask was added THF (100 mL). A reflux condenser was added and the flask was placed in an oil bath. The mixture was heated under reflux for 30 min. The polycarbonate part of the DVD dissolved, while the aluminum foil and another plastic foil didn´t dissolve. The hot mixture was filtered through a filter paper into a 250 mL flask. The solvent was removed on a rotary evaporator (Note: the collected solvent can be reused for further poly(bisphenol A carbonate) dissolving). The solid residue was added to a frit and was washed with acetone. Afterwards the solid was dried in an oven at 80 °C for 6 hours yielding poly(bisphenol A carbonate) **1b** (13.7 g, 82 wt% based on the starting DVD) (Note: the color of the poly(bisphenol A carbonate) varies depending on the applied starting DVD).

A mixture of the isolated poly(bisphenol A carbonate) (**1c**) (1.74 g, 6.85 mmol based on the repeating unit, catalytic amounts of complex **5** (20.2 mg, 34.4 µmol, 0.5 mol%, based on the repeating unit of **1c**) and THF (2.0 mL) was added with a stir bar in an autoclave (Parr Instrument Company), which was sealed and purged with hydrogen (5 times). Afterwards the desired hydrogen pressure was adjusted and the autoclave was heated to the desired temperature. The temperature was hold for 16 hours, while stirring the reaction mixture. Afterwards the autoclave was cooled to room temperature and the hydrogen pressure was carefully released. Purification was performed by silica gel column chromatography (petroleum ether: acetone, 8:2, R_f = 0.18). Bisphenol A was obtained as colorless crystals in 97 % yield (1.516 g, 6.641 mmol). The NMR spectra are in accordance to the spectra presented for depolymerization of commercially available poly(bisphenol A carbonate) **1a** (*vide supra*).

References

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[1] a) S. Kiran, N. R. James, R. Joseph, A. Jayakrishnan, *Biomaterials* **2009**, *30*, 5552-5559; b) C. Alberti, F. Scheliga, S. Enthaler, *ChemistrySelect* **2019**, *4*, 2639–2643; c) C. Alberti, S. Enthaler, *Asian J. Org. Chem.* **2019**, *DOI: 10.1002/ajoc.201900242R1*; d) C. Alberti, F. Scheliga, S. Enthaler, *ChemistryOpen* **2019**, *8*, 822-827.

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Supporting Information

Hydrogenative Depolymerization of End-of-Life Poly (bisphenol A carbonate) with *in situ* Generated Ruthenium Catalysts

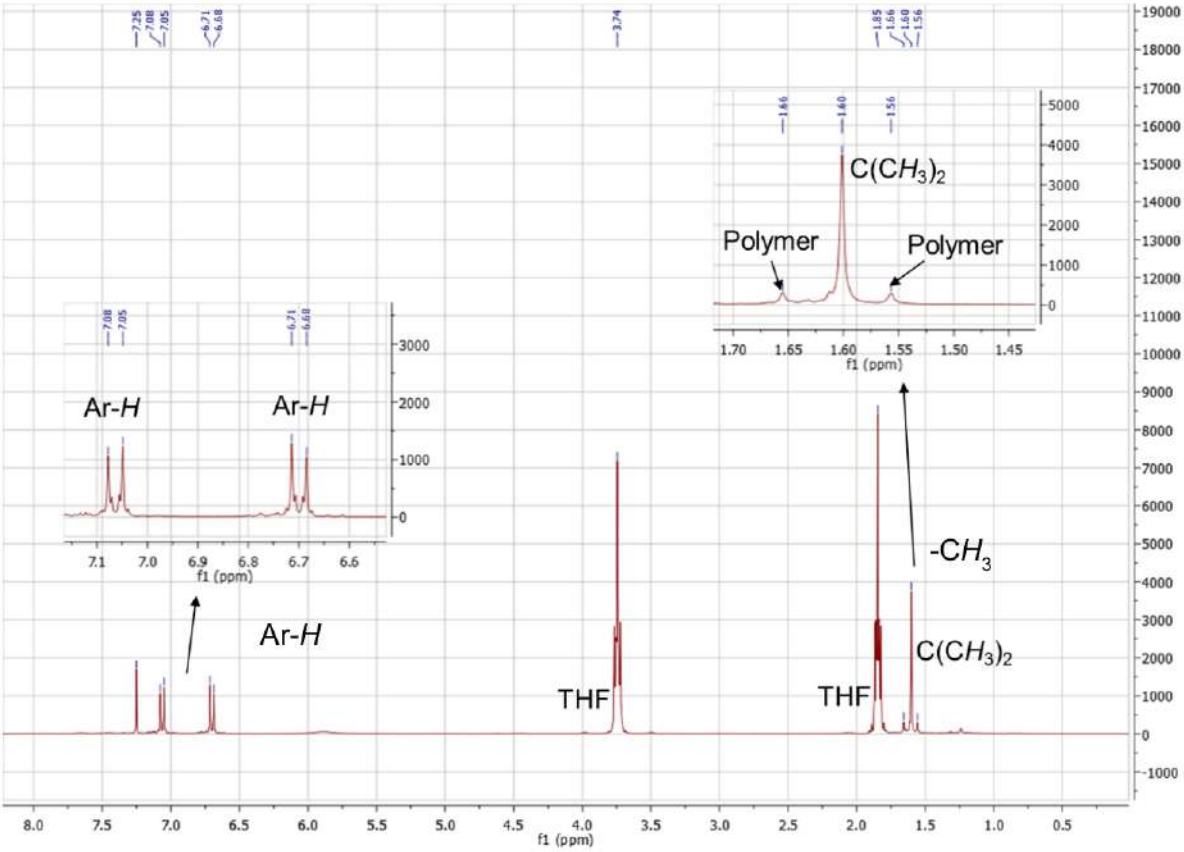
Christoph Alberti, Jannik Kessler, Sarah Eckelt, Melanie Hofmann, Tim-Oliver Kindler, Nicolo Santangelo, Elena Fedorenko, and Stephan Enthaler*

General: All chemicals were used as received without further manipulations. ^{1}H and ^{13}C{^{1}H}NMR spectra were recorded on a *Fourier 300 MHz* (^{1}H: 300 MHz, ^{13}C: 75 MHz, ^{31}P: 162 MHz) or *Avance I-400* (^{1}H: 400 MHz, ^{13}C: 101 MHz) by Bruker, using the proton signals of the deuterated solvents as reference or external standards. Mass spectrometry was performed using a *Thermo ISQ LT EI* by Thermo Fisher Scientific. TLC was performed on *ALUGRAM XTRA SIL G/UV$_{254}$* cards from *Macherey-Nagel* GmbH & Co. KG with a thickness of 0.20 mm. Detection succeeded with UV-light (254 nm). For preparative column chromatography silica gel 60 (particle size 40–63 µm) from *Fluka* was used. All catalytic set-ups were prepared in a glovebox under argon. Carbonylchloridohydridotris(triphenylphosphane)ruthenium(II) (CAS Number: 16971-33-8) and 2-(di-*iso*-propylphosphino)ethylamine solution (10 wt% in THF, CAS Number: 1053657-14-9) were received from Strem Chemicals. THF was dried over sodium-benzophenone, was distilled off and stored over molecular sieves under a nitrogen atmosphere. For experiments for the optimization of the reaction conditions stock solutions (THF) of the required compounds were used. The hydrogenations were performed in a Parr autoclave (model: 4774) (Parr Instrument Company).

General procedure for the hydrogenation of poly(bisphenol A carbonate) 1a (optimization of reaction conditions): A mixture of commercially available poly(bisphenol A carbonate) (**1a**) (17.2 mg, 0.0675 mmol based on the repeating unit, obtained from Sigma Aldrich), potassium *tert*-butoxide (0-0.76 mg, 0-0.00675 mmol, 0-10 mol% based on the repeating unit of **1a**), catalytic amounts of the complex [RuClH(CO)(PPh$_3$)$_3$] **8** (0-1.3 mg, 0-0.00135 mmol, 0-2 mol%, based on the repeating unit of **1a**) and 2-(di-*iso*-propylphosphino)ethylamine **9** (0-0.43 mg, 0-0.0027 mmol, 0-4 mol%, 10 wt% in THF) were placed with a stir bar in a vial. THF (2.0 mL) was added. The vial was placed in an autoclave (Parr Instrument Company), which was sealed and purged with hydrogen (5 times). Afterwards the desired hydrogen pressure (10-45 bar) was adjusted and the autoclave was heated to the desired temperature. The temperature was hold for 3-72 hours, while stirring the reaction mixture. Afterwards the autoclave was cooled to room temperature and the hydrogen pressure was carefully released. An aliquot of the solution was transferred to a NMR tube and was dissolved in CDCl$_3$ (0.5 mL). The sample was subjected to ^{1}H NMR to determine the yield of bisphenol A (**2**). The yield of **2** was calculated on the basis of the Ar-H or C(C*H*$_3$)$_2$ and the Ar-H or C(C*H*$_3$)$_2$ leftover signals of the polymer/oligomer. *Note:* Methanol was not detected. The screening of the reaction conditions was performed in a Parr autoclave (model: 4774) containing sites for six glass-vials (~4 mL). Importantly, the vials were not sealed; hence during reaction the methanol may evaporate from the vials.

Bisphenol A (**2**):[1] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.06-7.07 (d, *J* = 8.61 Hz, 4H, Ar-*H*), 6.70-6.71 (d, *J* = 8.61 Hz, 4H, Ar-*H*), 1.61 (s, 6H, $(CH_3)_2C$-) ppm. (The signal for 2xOH was not observed in $CDCl_3$).

Figure S1. Spectrum of a reaction mixture (^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)).



General procedure for the hydrogenation of poly(bisphenol A carbonate) 1a (optimization of reaction conditions): A mixture of commercially available poly(bisphenol A carbonate) (**1a**) (17.2 mg, 0.0675 mmol based on the repeating unit), potassium *tert*-butoxide (0.38 mg, 0.03375 mmol, 5 mol% based on the repeating unit of **1a**, stock solution in THF), catalytic amounts of the complex $[RuClH(CO)(PPh_3)_3]$ **8** (0.64 mg, 0.000675 mmol, 1 mol%, based on the repeating unit of **1a**, stock solution in THF), 2-(di-*iso*-propylphosphino)ethylamine **9** (0.11 mg, 0.000675 mmol, 1 mol%, 10 wt% in THF) and an additional ligand (in case of a monodentate ligand 0.000675-0.003375 mmol, 1-5 mol% in case of a bidentate ligand 0.0003375 mmol, 0.5 mol%) were placed with a stir bar in a vial.

THF (2.0 mL) was added. The vial was placed in an autoclave (Parr Instrument Company), which was sealed and purged with hydrogen (5 times). Afterwards the desired hydrogen pressure (45 bar) was adjusted and the autoclave was heated to the desired temperature (140 °C). The temperature was hold for 3 hours, while stirring the reaction mixture. Afterwards the autoclave was cooled to room temperature and the hydrogen pressure was carefully released. An aliquot of the solution was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^1H NMR to determine the yield of bisphenol A (**2**). The yield of **2** was calculated on the basis of the Ar-H or $C(CH_3)_2$ and the Ar-H or $C(CH_3)_2$ leftover signals of the polymer/oligomer. *Note:* Methanol was not detected. The screening of ligand effects was performed in a Parr autoclave (model: 4774) containing sites for six glass-vials (~4 mL). Importantly, the vials were not sealed; hence during reaction the methanol may evaporate from the vials.

Procedure for the depolymerization of poly(bisphenol A carbonate) starting from DVD:

a) Reaction without DBU

A mixture of the DVD powder **1b** (obtained by ball milling of DVD pieces) (3.49 g, 13.7 mmol based on the repeating unit), catalytic amounts of complex **8** (129.1 mg, 0.137 mmol, 1.0 mol%, based on the repeating unit of **1b**), 2-(di-*iso*-propylphosphino)ethylamine **9** (214 mg, 0.137 mmol, 1 mol%, 10 wt% in THF), potassium *tert*-butoxide (153.5 mg, 1.37 mmol based on the repeating unit of **1b**) and THF (20 mL) was added with a stir bar in an autoclave (Parr Instrument Company), which was sealed and purged with hydrogen (5 times). Afterwards the desired hydrogen pressure (20 bar) was adjusted and the autoclave was heated to the desired temperature (120 °C). The temperature was hold for 24 hours, while stirring the reaction mixture. Afterwards the autoclave was cooled to room temperature and the hydrogen pressure was carefully released. An aliquot of the solution was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^1H NMR to determine the yield of bisphenol A (**2**). The yield of **2** was calculated on the basis of the Ar-H or $C(CH_3)_2$ and the Ar-H or $C(CH_3)_2$ leftover signals of the polymer/oligomer. Yield (**2**) = 29%.

b) Reaction with DBU

DBU (20.6 mg, 0.137 mmol, 1.0 mol%) was added as additional ligand to the reaction mixture. Yield (**2**) = 40%.

Procedure for the depolymerization of poly(bisphenol A carbonate) isolated from a DVD:

a) Poly(bisphenol A carbonate) isolation from DVDs[2]

To pieces of a DVD **1b** (16.7 g, cut in small pieces) and a stir bar in a 250 mL-flask was added THF (100 mL). A reflux condenser was added and the flask was placed in an oil bath. The mixture was heated under reflux for 30 min. The polycarbonate part of the DVD dissolved, while the aluminum foil and another plastic foil didn´t dissolve. The hot mixture was filtered through a filter paper into a 250 mL flask. The solvent was removed on a rotary evaporator The solid residue was added to a frit and was washed with acetone. Afterwards the solid was dried in an oven at 80 °C for 6 hours yielding 13.7 g of poly(bisphenol A carbonate) **1c** (82 wt% based on the starting DVD) (Note: the color of the poly(bisphenol A carbonate) varies depending on the applied starting DVD).

b) Poly(bisphenol A carbonate) **1c** hydrogenative depolymerization - 140 °C, 45 bar

A mixture of **1c** (3.49 g, 13.7 mmol based on the repeating unit), catalytic amounts of complex **8** (129.1 mg, 0.137 mmol, 1.0 mol%, based on the repeating unit of **1b**), 2-(di-*iso*-propylphosphino)ethylamine **9** (214 mg, 0.137 mmol, 1 mol%, 10 wt% in THF), DBU (20.6 mg, 0.137 mmol, 1.0 mol%), potassium *tert*-butoxide (153.5 mg, 1.37 mmol based on the repeating unit of **1c**) potassium *tert*-butoxide (153.5 mg, 1.37 mmol based on the repeating unit of **1c**) and THF (20 mL) was added with a stir bar in an autoclave (Parr Instrument Company), which was sealed and purged with hydrogen (5 times). Afterwards the desired hydrogen pressure (20 bar) was adjusted and the autoclave was heated to the desired temperature (120 °C). The temperature was hold for 24 hours, while stirring the reaction mixture. Afterwards the autoclave was cooled to room temperature and the hydrogen pressure was carefully released. An aliquot of the solution was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^{1}H NMR to determine the yield of bisphenol A (**2**). The yield of **2** was calculated on the basis of the Ar-H or $C(CH_3)_2$ and the Ar-H or $C(CH_3)_2$ leftover signals of the polymer/oligomer. Yield (**2**) = 35%.

c) Poly(bisphenol A carbonate) **1c** hydrogenative depolymerization – 140 °C, 45 bar

Carried out in accordance to b) with 909 mg **1c** (909 mg, 3.58 mmol), **8** (35.8 mg, 0.0358 mmol, 1.0 mol%, based on the repeating unit of **1c**), 2-(di-*iso*-propylphosphino)ethylamine **9** (56.0 mg, 0.0358 mmol, 1 mol%, 10 wt% in THF), DBU (5.4 mg, 0.0358 mmol, 1.0 mol%), potassium *tert*-butoxide (40.1 mg, 0.3528 mmol based on the repeating unit of **1c**) and THF (15 mL). Afterwards the desired hydrogen pressure (45 bar) was adjusted and the autoclave was heated to the desired temperature (140 °C). The temperature was hold for 24 hours, while stirring the reaction mixture. Afterwards the autoclave was cooled to room temperature and the hydrogen pressure was carefully released. An aliquot of the solution was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^1H NMR to determine the yield of bisphenol A (**2**). The yield of **2** was calculated on the basis of the Ar-H or $C(CH_3)_2$ and the Ar-H or $C(CH_3)_2$ leftover signals of the polymer/oligomer. Yield (**2**) = 85%. Purification was performed by silica gel column chromatography (petroleum ether: acetone, 4:1, R_f = 0.18). Bisphenol A was obtained as colorless crystals in 64 % yield (523 mg, 2.29 mmol).

Procedure for the depolymerization of poly(bisphenol A carbonate) starting from safety goggles:

A mixture of the **1d** (obtained from safety goggles) (3.49 g, 13.7 mmol based on the repeating unit), catalytic amounts of complex **8** (129.1 mg, 0.137 mmol, 1.0 mol%, based on the repeating unit of **1d**), 2-(di-*iso*-propylphosphino)ethylamine **9** (214 mg, 0.137 mmol, 1 mol%, 10 wt% in THF), DBU (20.6 mg, 0.137 mmol, 1.0 mol%), potassium *tert*-butoxide (153.5 mg, 1.37 mmol based on the repeating unit of **1c**) and THF (20 mL) was added with a stir bar in an autoclave (Parr Instrument Company), which was sealed and purged with hydrogen (5 times). Afterwards the desired hydrogen pressure (20 bar) was adjusted and the autoclave was heated to the desired temperature (120 °C). The temperature was hold for 24 hours, while stirring the reaction mixture. Afterwards the autoclave was cooled to room temperature and the hydrogen pressure was carefully released. An aliquot of the solution was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^1H NMR to determine the yield of bisphenol A (**2**). The yield of **2** was calculated on the basis of the Ar-H or $C(CH_3)_2$ and the Ar-H or $C(CH_3)_2$ leftover signals of the polymer/oligomer. Yield (**2**) = 33%.

Bisphenol A (**2**): ^1H NMR (400 MHz, acetone-d_6, 25 °C): δ = 7.10 (d, *J* = 8.67 Hz, 4H, Ar-*H*, *4*), 6.74 (d, *J* = 8.67 Hz, 4H, Ar-*H*, *3*), 4.69 (s, 2H, -O*H*, *1*), 1.62 (s, 6H, $(CH_3)_2C$, 7) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, acetone-d_6, 25 °C): δ = 153.4 (C_q-OH, 2), 143.5 ($C_q(C-CH_3)_2$, *5*), 128.1 (C_{Ar}, *4*), 114.8 (C_{Ar}, *3*), 41.8 ($C_q(CH_3)_2$, *6*), 31.2 (CH_3, *7*) ppm.
EI-MS m/z: 228 [M^+], 213 [M^+ -(CH_3)].
IR (ATR): $\tilde{\nu}$ [cm^{-1}]: 3323 (w), 2969 (m), 1738 (s), 1508 (s), 1217 (vs), 824 (vs), 562 (vs).
Melting point: 156 °C

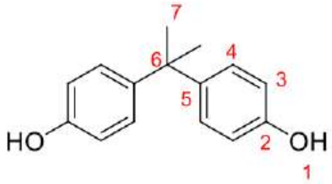


Figure S2. ^{1}H NMR spectrum of isolated **2** (^{1}H NMR (400 MHz, acetone-d_6, 25 °C)).

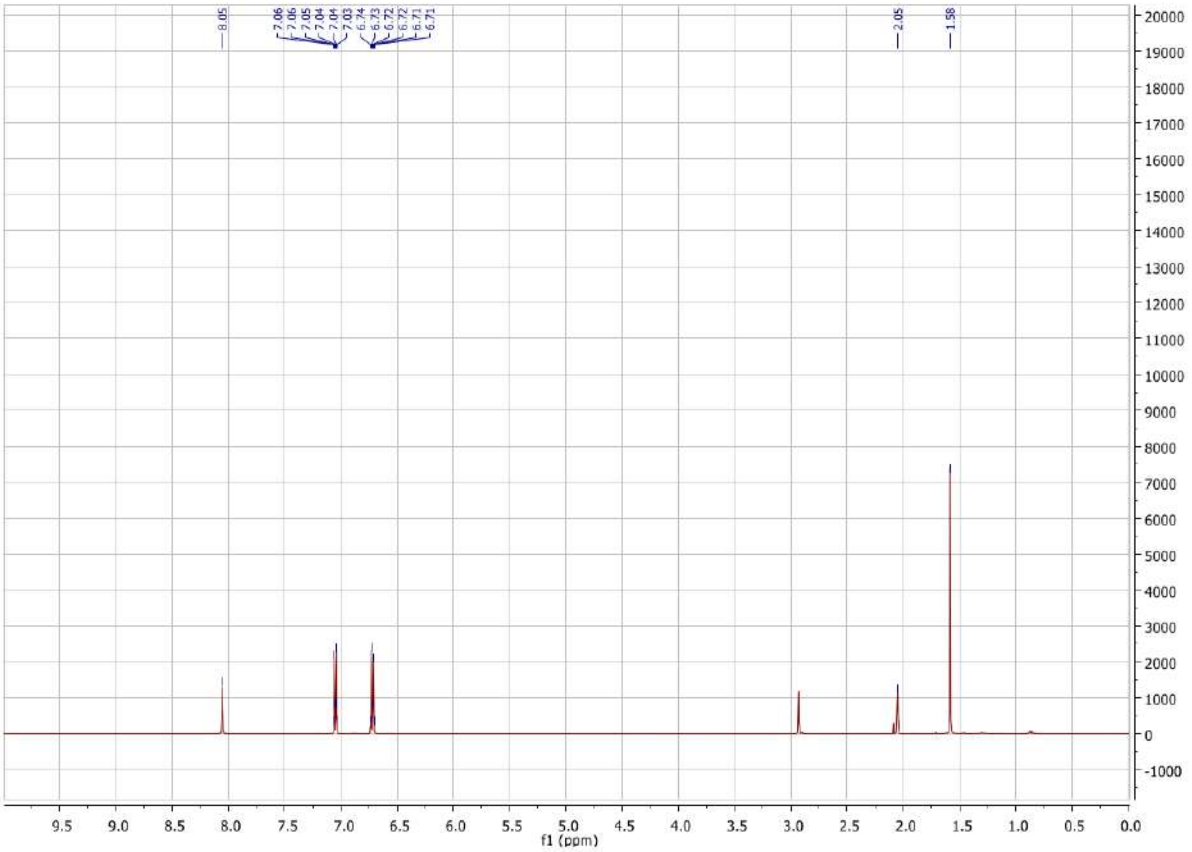
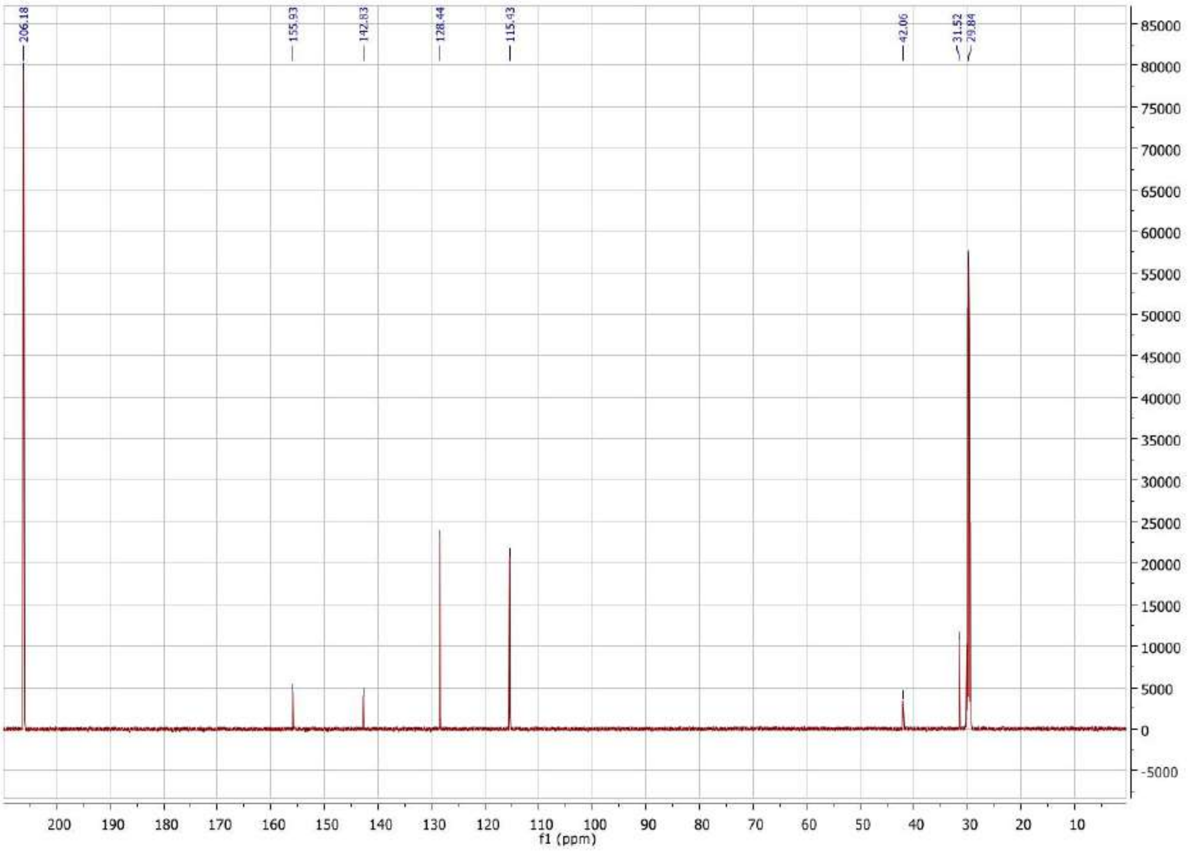
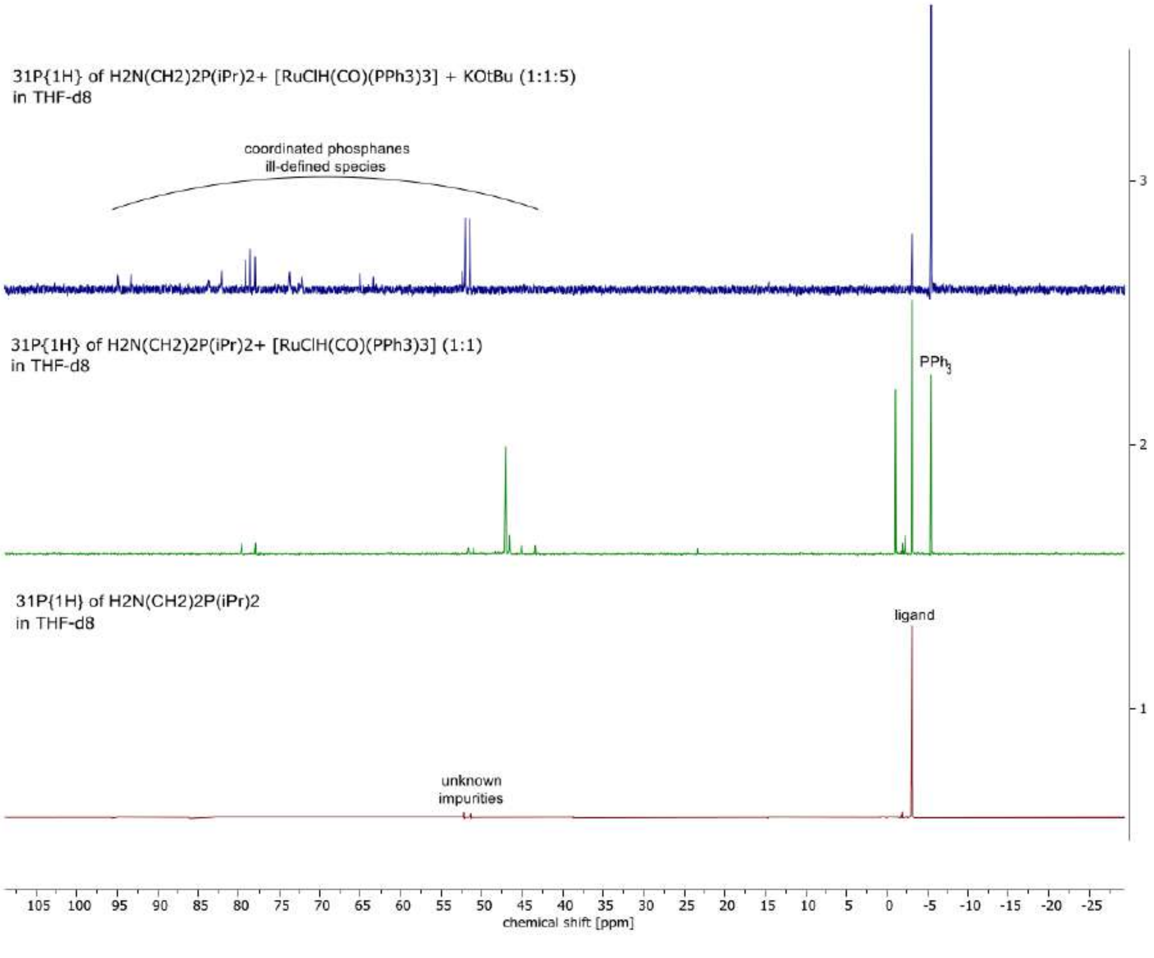


Figure S3. $^{13}C\{^1H\}$ NMR spectrum of isolated **2** ($^{13}C\{^1H\}$ NMR (125 MHz, acetone-d_6, 25 °C)).



$^{31}P\{^1H\}$ NMR spectroscopy of the catalytic system

Figure S4. $^{31}P\{^1H\}$ NMR (162 MHz, 25 °C, THF-d_8) of (1): free ligand **9**; (2): Ru-precatalyst **8** (0.031 mmol) and ligand **9** (0.031 mmol); (3): **8** (0.031 mmol) and **9** (0.031 mmol) + KO^{t}Bu (added after 16 h at r.t.) (0.155 mmol). The NMR-spectra were recorded 45 min after mixing the compounds. Spectrum (2) and (3) indicate the formation of free PPh$_3$ and complexation of the aminophosphane **9**.[3]



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[2] a) C. Alberti, F. Scheliga, S. Enthaler, *ChemistrySelect* **2019**, *4*, 2639–2643, *DOI: 10.1002/slct.201900556*; b) Methanolysis“ C. Alberti, S. Enthaler, *Asian J. Org. Chem.* **2019**, *DOI: 10.1002/ajoc.201900242R1*; c) C. Alberti, F. Scheliga, S. Enthaler, *ChemistryOpen* **2019**, *8*, 822-827, *DOI: 10.1002/open.201900149*; d) C. Alberti, S. Enthaler, *Waste Biomass Valori.* **2019**, *DOI: 10.1007/s12649-019-00794-8*.

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[3] a) C.-C. Lee, Y.-H. Liu, S.-M. Peng, P.-T. Chou, J.-T. Chen, S.-T. Liu, *Polyhedron* **2012**, *35*, 23-30; b) E. S. F. Ma, B. O. Patrick, B. R. James, *Inorg. Chim. Acta* **2013**, *408*, 126-130; c) E. S. F. Erin D. C. Mudalige, B. R. James, *Dalton Trans.* **2013**, *42*, 13628-13634; d) F. D. Fagundes, J. P. da Silva, C. L. Veber, A. Barison, C. B. Pinheiro, D. F. Back, J. R. de Sousa, M. P. de Araujo, *Polyhedron* **2012**, *42*, 207-215; e) W. Xu, R. Langer, *Dalton Trans.* **2015**, *44*, 16785-16790; f) I. D. Alshakova, I. Korobkov, L. G. Kuzmina, G. I. Nikonov, *J. Organomet. Chem.* **2017**, *853*, 68-73; g) J. T. Mague, J. L. Krinsky, *Inorg. Chem.* **2001**, *40*, 1962-1971; h) H. Yang, M. Alvarez-Gressier, N. Lugan, R. Mathieu, *Organometallics* **1997**, *16*, 1401-1409.

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Supporting Information

Hydrogenative Depolymerization of End-of-Life Polycarbonates by an Iron Pincer Complex

Christoph Alberti, Elena Fedorenko, and Stephan Enthaler*

General: All chemicals were used as received without further manipulations. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a *Fourier 300 MHz* (^{1}H: 300 MHz, ^{13}C: 75 MHz) or *Avance I-400* (^{1}H: 400 MHz, ^{13}C: 101 MHz, ^{31}P: 162 MHz) by Bruker, using the proton signals of the deuterated solvents as reference or external standards. Mass spectrometry was performed using a *Thermo ISQ LT EI* by Thermo Fisher Scientific. For preparative column chromatography silica gel 60 (particle size 40–63 µm) from *Fluka* was used. All catalytic set-ups were prepared in a glovebox under argon. THF, PhOMe and 1,4-dioxane were dried over sodium-benzophenone, were distilled off and stored over molecular sieves 4 Å under a nitrogen atmosphere. The hydrogenations were performed in a Parr autoclave (model: 4774) (Parr Instrument Company) containing sites for six glass-vials (~4 mL). Importantly, the vials were not sealed. The phosphines *i*Pr$_2$PCl[1] and bis(2-(diisopropylphosphanyl)ethyl)amine (PNP)[2] were prepared as reported in the literature.

Synthesis of *i*Pr$_2$PCl: The synthesis was performed by a modified protocol as reported in the literature.[1] A 500 mL three-necked flask equipped with a reflux condenser and a dropping funnel was charged with Mg turnings (12.2 g, 502 mmol, 1.00 eq.) and Et$_2$O (200 mL). Then, 2-chloropropane (45.8 mL, 39.4 g, 502 mmol, 1.00 eq.) was added carefully. Afterwards, the mixture was refluxed for 1 h and cooled to room temperature. The excess of Magnesium was filtered off and an aliquot of the pale grey Grignard-solution was titrated with I$_2$ in THF (90% yield of *i*PrMgCl). Then, in a 1 L three-necked flask equipped with a stir bar, a reflux condenser and a dropping funnel PCl$_3$ (19.0 mL, 29.8 g, 217 mmol) was dissolved in Et$_2$O (150 mL) and cooled to –50 °C. Now, the Grignard reagent (447 mmol, in 230 mL Et$_2$O) was added dropwise within 90 min. The reaction mixture was slowly warmed to room temperature and subsequently refluxed for 16 h. After cooling to room temperature, the mixture was filtered and the filter cake was rigorously washed with Et$_2$O (5 × 75 mL). Then, the solvent was removed in vacuum and the crude product was purified by fractional distillation to give *i*Pr$_2$PCl (16.5 mL, 113 mmol, 52%) as colorless liquid.

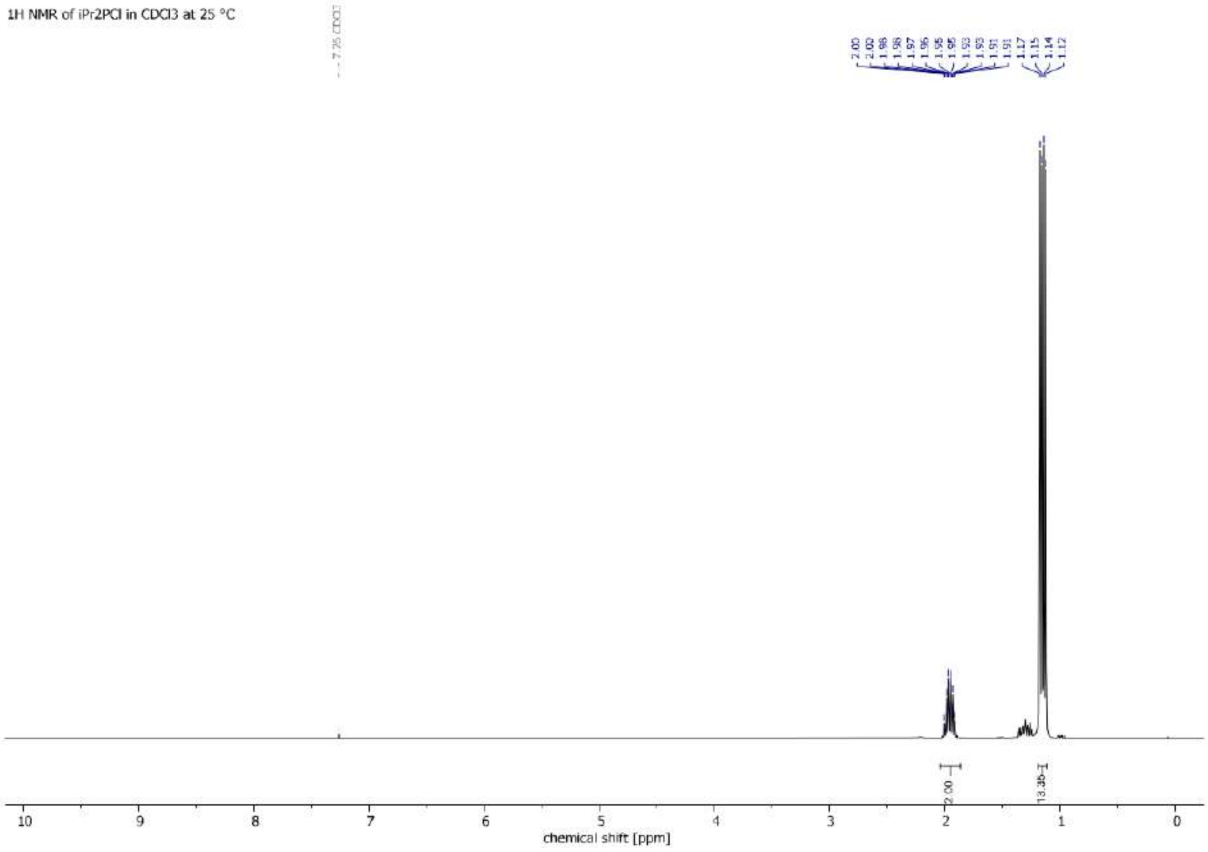
^{1}H NMR (500 MHz, CDCl$_3$, 25 °C) δ [ppm] = 2.01–1.90 (m, 2H, PC*H*(CH$_3$)$_2$), 1.16 (d, *J* = 7.0 Hz, 6H, PCH(C*H*$_3$)$_2$), 1.13 (d, *J* = 7.0 Hz, 6H, PCH(C*H*$_3$)$_2$).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ [ppm] = 29.99 (d, *J* = 30.0 Hz, P*C*H(CH$_3$)$_2$), 17.74 (s, P*C*H(CH$_3$)$_2$), 17.60 (s, P*C*H(CH$_3$)$_2$).

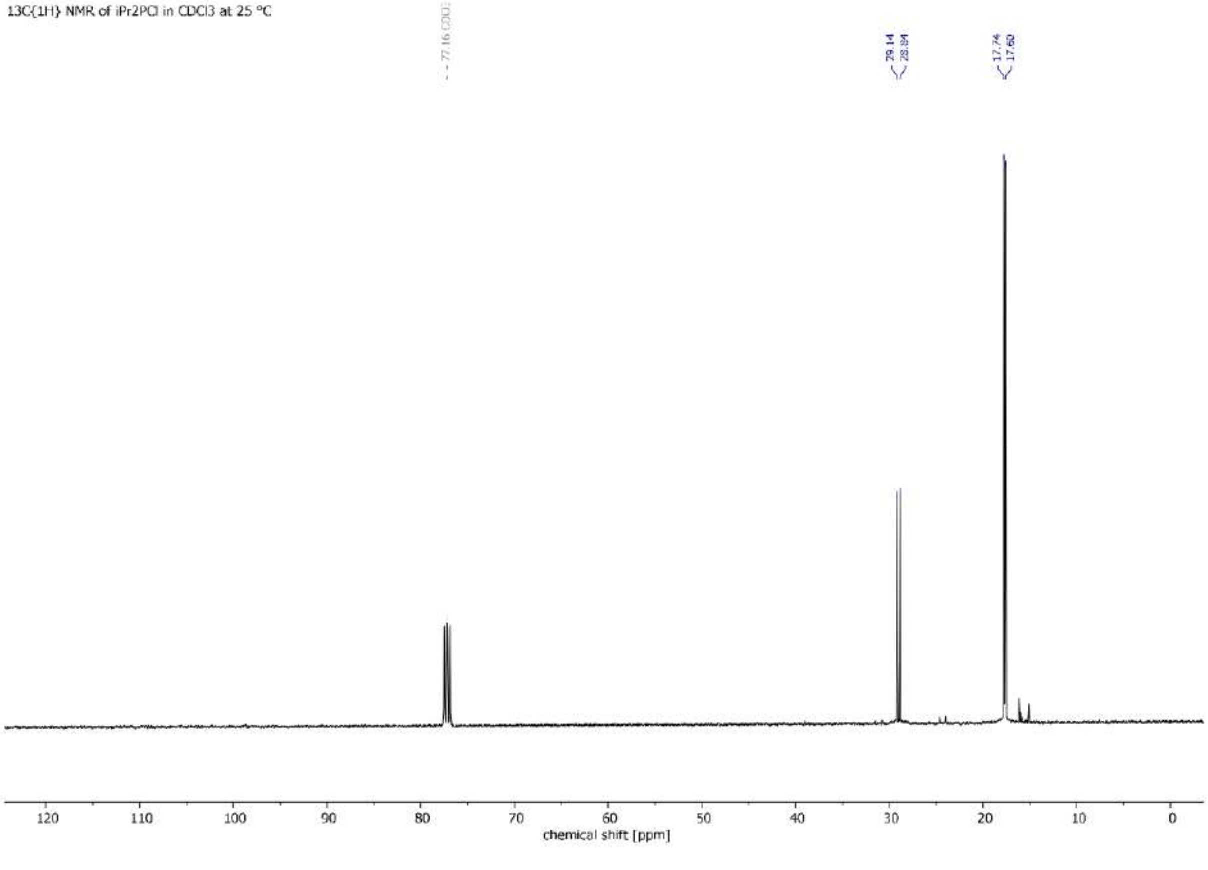
^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ [ppm] = 133.8 (s).

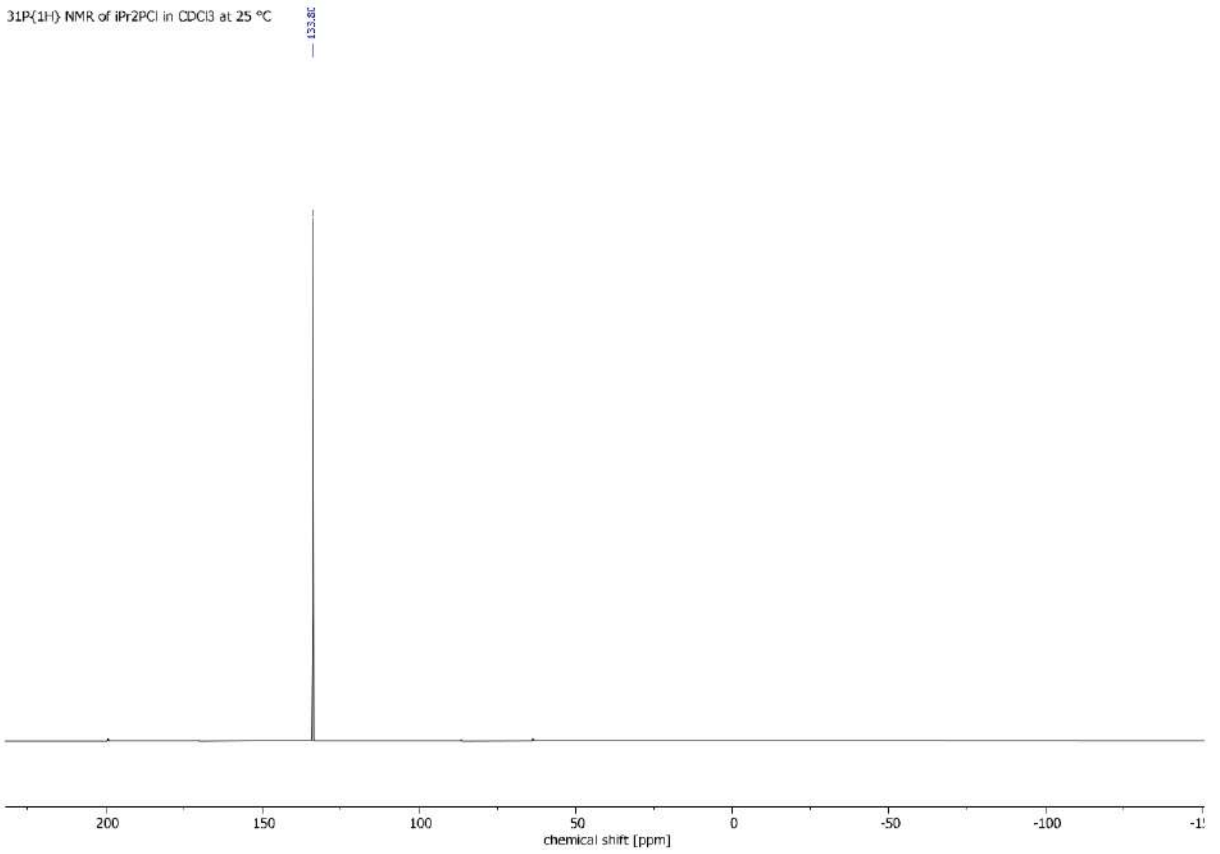
b. p.: 57 °C (30 mbar).

1H NMR of iPr2PCl in CDCl3 at 25 °C



13C{1H} NMR of iPr2PCl in CDCl3 at 25 °C





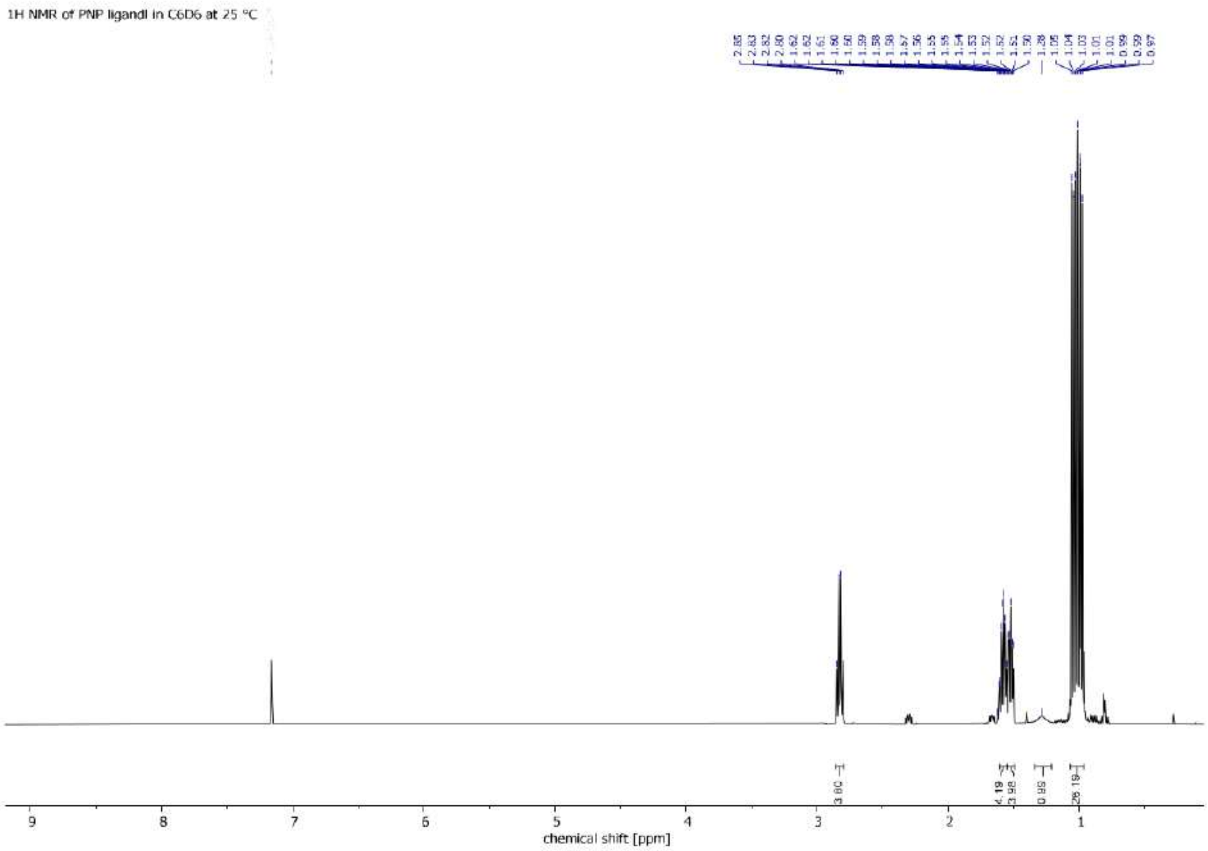
Synthesis of the PNP-Ligand: The synthesis was performed by a modified protocol as reported in the literature.[2] To a suspension of bis(2-chloroethyl)amine hydrochloride (7.10 g, 39.8 mmol, 1.00 eq.), NEt_3 (12.7 mL, 9.26 g, 91.5 mmol, 2.30 eq.) and DMSO (150 µL, 165 mg, 2.11 mmol, 5.3 mol%) in Et_2O (100 mL) was added freshly distilled trimethylsilylchloride (6.60 mL, 5.61 g, 51.7 mmol, 1.30 eq.) within half an hour. The solution was stirred at 0 °C for 1 h, and stirred for 3 days at room temperature. Afterwards, the mixture was filtered and the solids were washed with Et_2O (3 × 30 mL). The solvent was removed in vacuum and the yellow crude product was used for the next step without further purification. A 500 mL three-necked flask equipped with a reflux condenser was charged with Li granules (1.34 g, 193 mmol, 7.50 eq.) and THF (70 mL), then *i*Pr_2PCl (10.2 mL, 9.80 g, 64.2 mmol, 2.50 eq.) was added via syringe within 1 h. A gradual color change to dark yellow was observed. The mixture was stirred for 2 d and filtered to remove unreacted lithium. Now, a solution of the crude TMS-protected amine (5.45 g) in THF (20 mL) was added to the solution at –40 °C and stirred for 1 h. The mixture was slowly warmed to 50 °C and stirred for 1 h while a color change to black was observed. After cooling to room temperature, degassed water (25 mL) was added and the mixture stirred for 2 d. The aqueous layer was removed using a syringe and a second portion of degassed water (25 mL) was added and the mixture was stirred for 1 h, whereupon the aqueous layer was removed and the solvent of the organic phase was evaporated. The black crude product was distilled to obtain the PNP ligand (5.60 g, 18.3 mmol, 71%) as a colorless liquid.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ [ppm] = 2.85–2.78 (m, 4H, NCH_2CH_2), 1.58 (dsept, J = 7.1, 2.2 Hz, 4H, $PCH(CH_3)_2$), 1.52 (dt, 6H, J = 7.6, 3.0 Hz, PCH_2CH_2), 1.28 (br, 1H, NH), 1.06–0.97 (m, 24H, $PCH(CH_3)_2$).

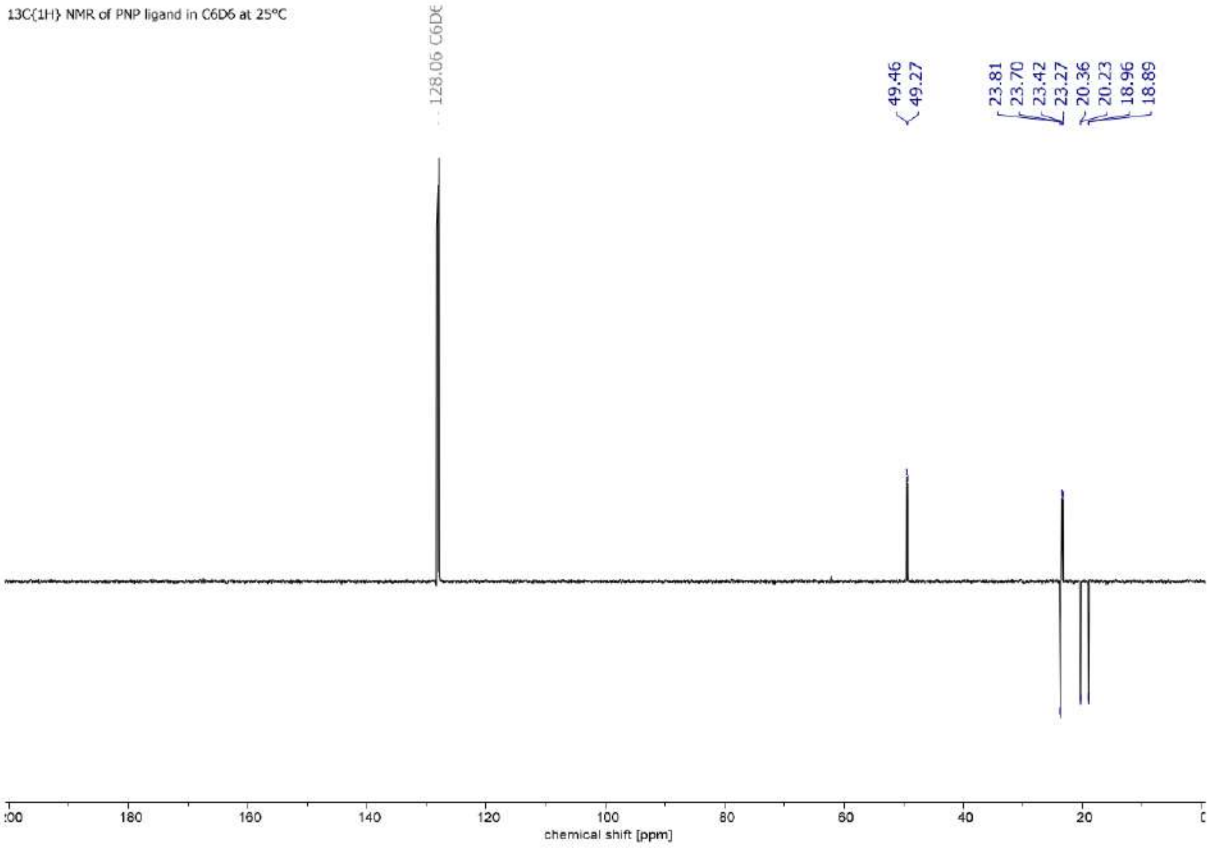
^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ [ppm] = 49.4 (d, J = 24.0 Hz, NCH_2CH_2), 23.8 (d, J = 23.8 Hz, $PCH(CH_3)_2$), 23.3 (d, J = 19.3 Hz, PCH_2CH_2), 20.3 (d, J = 16.7 Hz, $PCH(CH_3)_2$), 18.9 (d, J = 9.9 Hz, $PCH(CH_3)_2$).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ [ppm] = –0.90 (s).

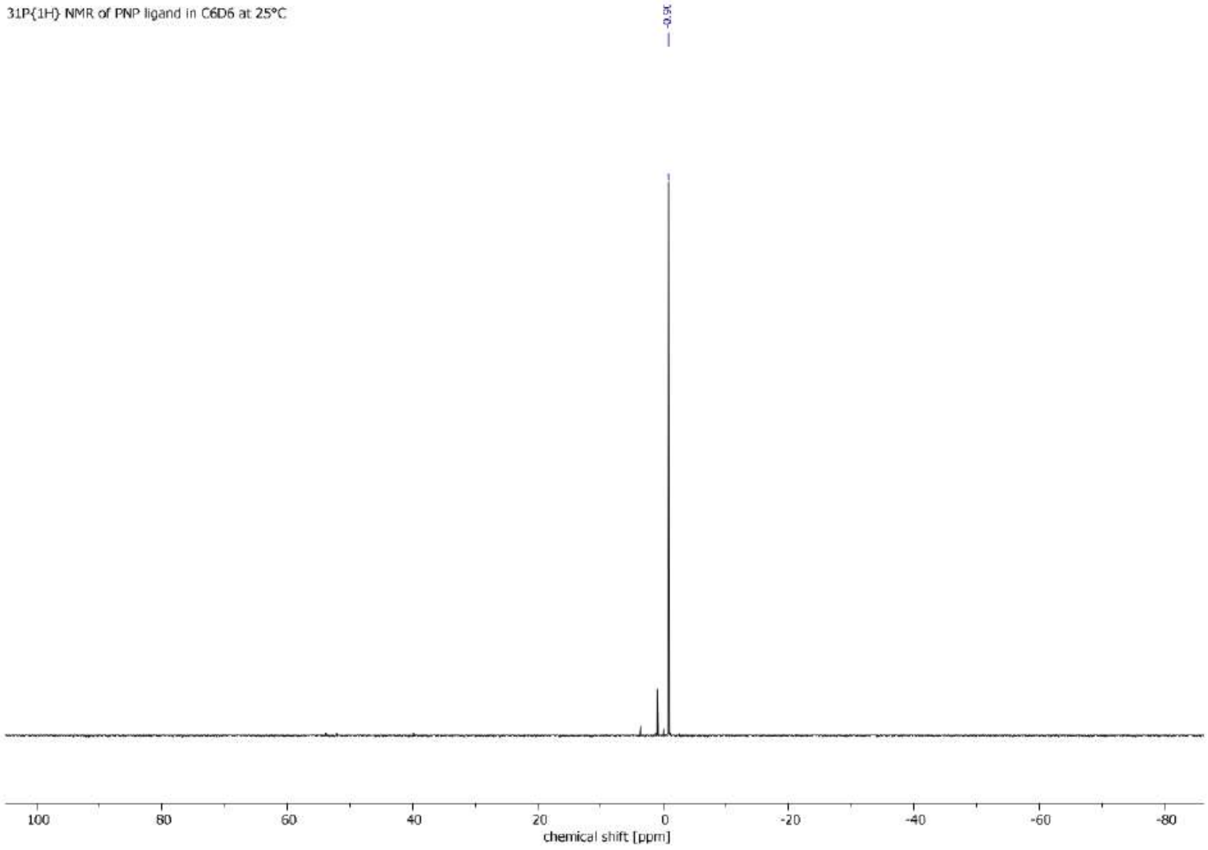
b. p.: 129 °C ($5 \cdot 10^{-2}$ mbar)



13C{1H} NMR of PNP ligand in C6D6 at 25°C



31P{1H} NMR of PNP ligand in C6D6 at 25°C



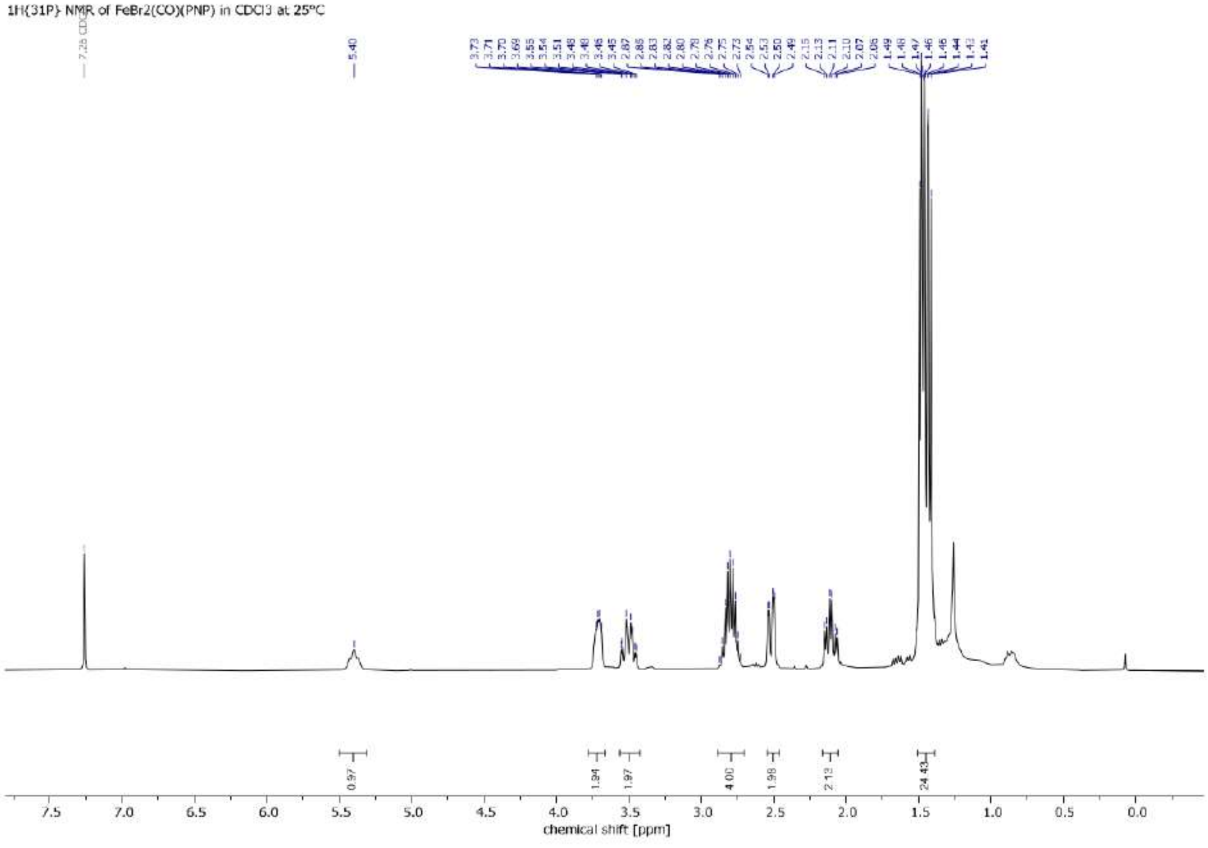
Synthesis of [$FeBr_2$(CO)(PNP)]: The synthesis was performed by a modified protocol as reported in the literature.[3] To a suspension of $FeBr_2$ (3.50 g, 16.2 mmol, 1.00 eq.) in THF (300 mL) was added a solution of bis(2-(diisopropylphosphanyl)ethyl)amine (5.45 g, 17.9 mmol, 1.10 eq.) in THF (10 mL) under rapid stirring. Within 30 min, a beige voluminous precipitate formed. Subsequently, the flask was cooled to -196 °C and evacuated followed by replacement of the atmosphere by 1 bar CO. Stirring under CO atmosphere at room temperature was continued for 6 h and a blue homogeneous solution was obtained. The solution was concentrated in vacuum and the residue extracted with $PhCH_3$ (3×25 mL). The solvent was evaporated in vacuum to yield the product as a blue solid (4.19 g, 7.63 mmol, 47%).

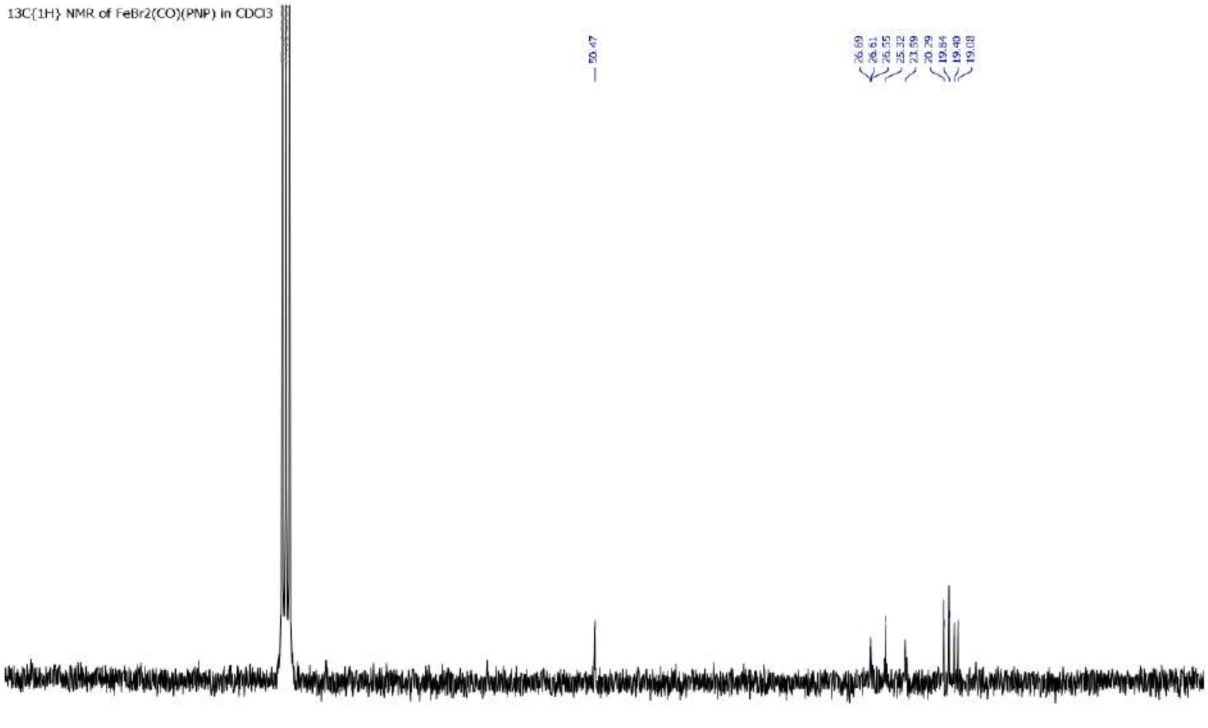
$^1H\{^{31}P\}$ NMR (500 MHz, $CDCl_3$, 25 °C) δ [ppm] = 5.40 (br, 1H, NH), 3.76–3.67 (m, 2H, NCH_2CH_2, 2H), 3.57–3.44 (m, 2H, NCH_2CH_2, 2H), 2.87–2.73 (m, 2H, $PCH(CH_3)_2$, 4H), 2.51 (m, 2H, J = 14.4 Hz, 3.1 Hz, PCH_2CH_2, 2H), 2.10 (dt, 2H, J = 14.4 Hz, 5.6 Hz, PCH_2CH_2), 1.51–1.39 (m, 24H, $PCH(CH_3)_2$).

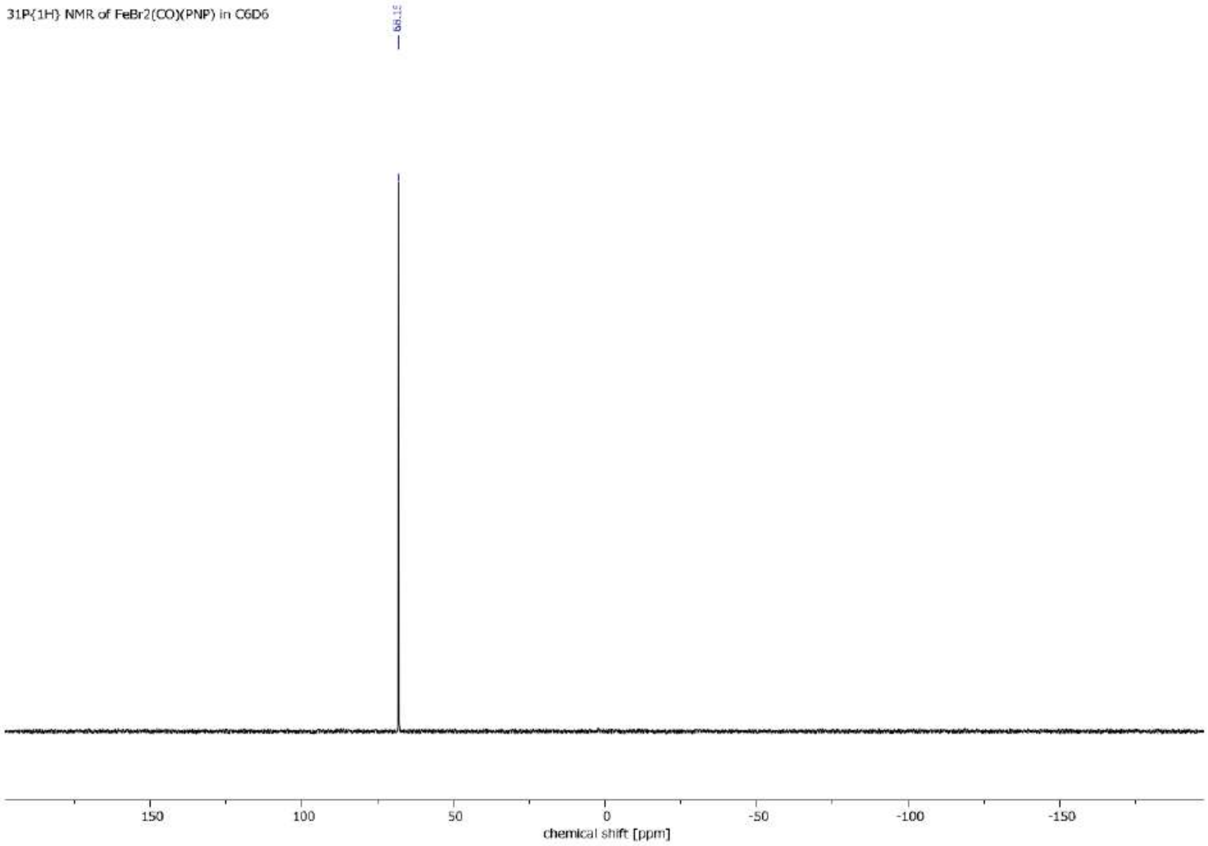
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ [ppm] = 50.5 (m, NCH_2CH_2, 2C), 26.5 (PCH_2CH_2), 25.3 (t, J = 10.6 Hz, $PCH(CH_3)_2$), 23.6 (t, J = 9.6 Hz, $PCH(CH_3)_2$), 20.3 (s, $PCH(CH_3)_2$), 19.8 (s, $PCH(CH_3)_2$), 19.4 (s, $PCH(CH_3)_2$), 19.1 (s, $PCH(CH_3)_2$). The signal for the CO ligand was not observed.

$^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6): δ [ppm] = 68.2 (s).

MS (ESI): (m/z) for $[M\text{-}Br\text{-}CO]^+$ = 440.09340 (calcd.), 440.09327 (found), Δ = 0.30 ppm.


1H{31P} NMR of FeBr2(CO)(PNP) in CDCl3 at 25°C
7.26 CDCl3
5.40
3.73 3.71 3.70 3.69 3.55 3.54 3.51 3.48 3.48 3.46 3.45 2.87 2.86 2.83 2.82 2.80 2.78 2.76 2.75 2.73 2.54 2.53 2.50 2.49 2.15 2.13 2.11 2.10 2.07 2.06 1.49 1.48 1.47 1.46 1.46 1.44 1.43 1.41
0.97
1.94
1.97
4.00
1.98
2.13
24.43
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
chemical shift [ppm]


13C{1H} NMR of FeBr2(CO)(PNP) in CDCl3
50.47
26.69 26.61 26.55 25.32 23.59 20.29 19.84 19.40 19.08
100 90 80 70 60 50 40 30 20 10 0
chemical shift [ppm]



Synthesis of [Fe(BH_4)H(CO)(PNP)] (12): The synthesis was performed by a modified protocol as reported in the literature.[3] To the blue solution of [$FeBr_2$(CO)(PNP)] (1.25 g, 2.28 mmol, 1.00 eq.) in EtOH (100 mL) was added $NaBH_4$ (431 mg, 11.4 mmol, 5.00 eq.) in one portion. The solution turned yellow and a gas evolution was observed. After 40 h, the solvent was removed in vacuum and the solid residue was mixed with PhMe (100 mL) and filtered over a plug of silica. The clear yellow filtrate was evaporated and the product **12** was obtained as yellow solid (523 mg, 1.29 mmol, 57%).

$^1H\{^{31}P\}$ NMR (500 MHz, THF-d_8) δ [ppm] = 3.96 (br, 1H, NH), 3.29–3.20 (m, 2H, NCH_2CH_2, 2H), 2.68–2.57 (m, $PCH(CH_3)_2$, 2H), 2.45–2.39 (m, $PCH(CH_3)_2$, 2H), 2.24–2.17 (m, PCH_2CH_2, 2H), 2.14–2.02 (m, NCH_2CH_2, 2H), 1.94–1.88 (m, PCH_2CH_2, 2H), 1.45 (d, J = 7.4 Hz, $PCH(CH_3)_2$, 6H), 1.30 (d, J = 7.4 Hz, $PCH(CH_3)_2$, 6H), 1.22 (d, J = 7.4 Hz, $PCH(CH_3)_2$, 6H), 1.15 (d, J = 6.9 Hz, $PCH(CH_3)_2$, 6H), –3.57 (br, 4H, BH_4), –22.6 (s, 1H, FeH).

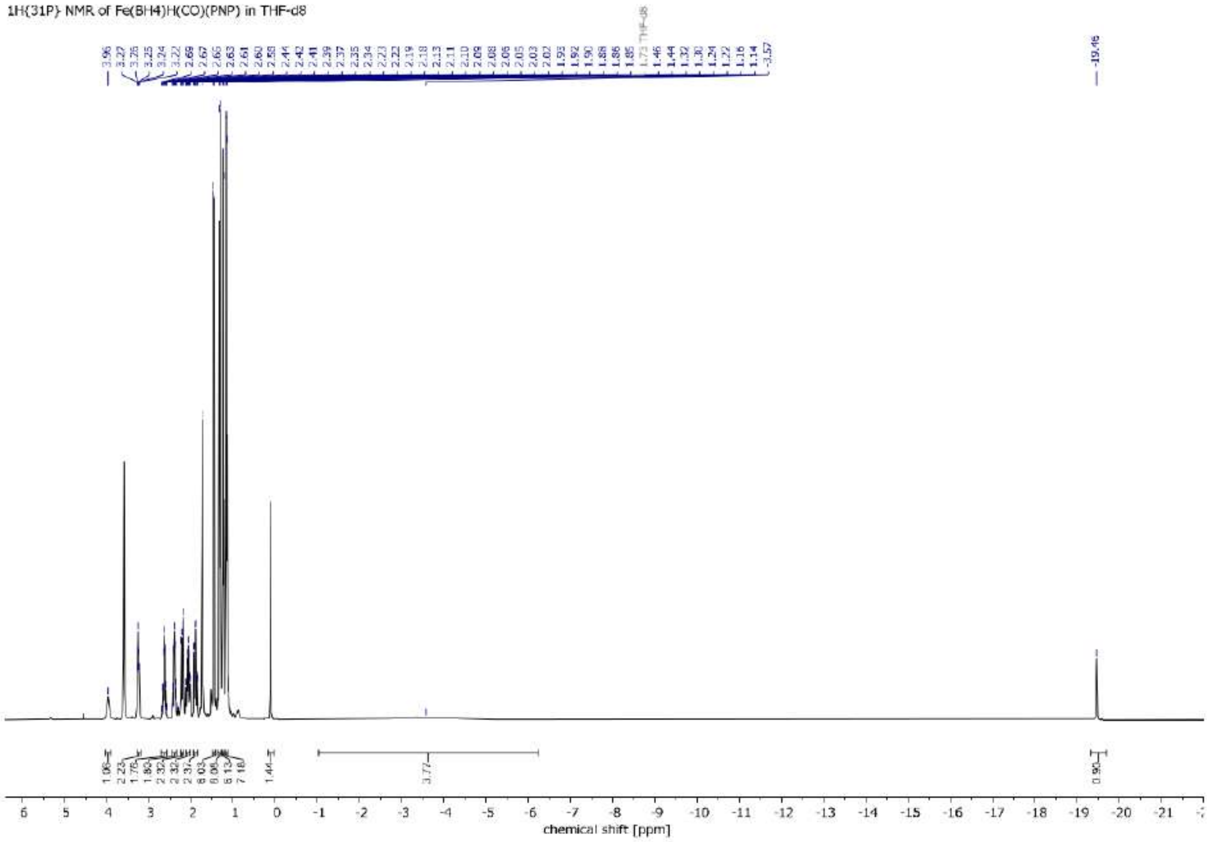
$^{13}C\{^1H\}$ NMR (126 MHz, THF-d_8) δ [ppm] = 54.9 (t, J = 5.5 Hz, NCH_2CH_2), 29.1 (t, J = 9.6 Hz, PCH_2CH_2), 28.7 (t, J = 7.6 Hz, PCH_2CH_2), 25.1 (t, J = 12.8 Hz, $PCH(CH_3)_2$), 19.9 (t, J = 2.1 Hz, $PCH(CH_3)_2$), 19.7 (t, J = 2.2 Hz, $PCH(CH_3)_2$), 18.3 (s, $PCH(CH_3)_2$), 17.5 (t, J = 2.3 Hz, $PCH(CH_3)_2$). The signal for the CO ligand was not observed.

^{11}B NMR (128.4 MHz, C_6D_6) δ [ppm] = 32.1 (quin, J = 75 Hz).

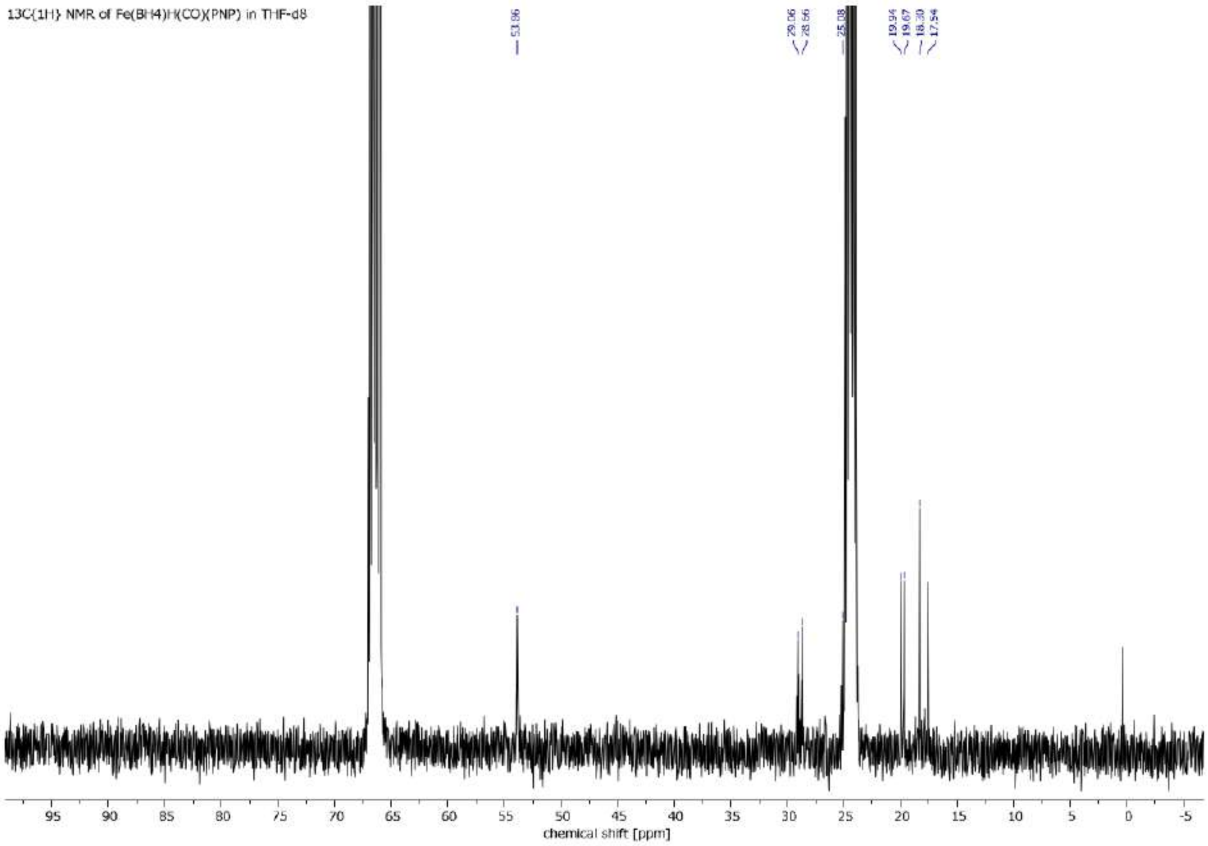
$^{31}P\{^1H\}$ NMR (162 MHz, THF-*d*$_8$): *δ* [ppm] = 99.1 (s).

MS (ESI): (*m*/*z*) for $[M\text{-}BH_4]^+$ = 390.17780 (calcd.), 390.17774 (found), Δ = 0.15 ppm.

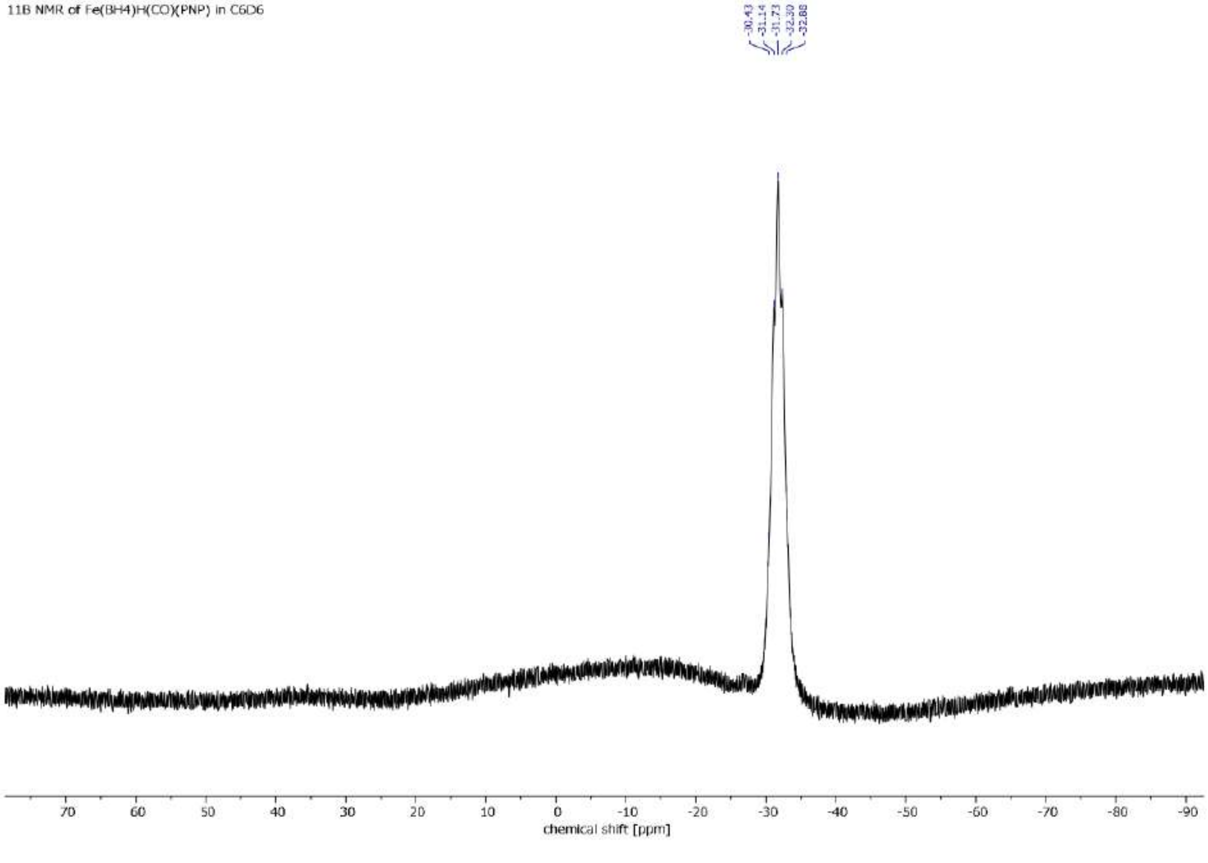
Elemental Analysis: Calcd for $C_{17}H_{42}BNOP_2Fe$: C, 50.40%; H, 10.45%; N, 3.46%; Found: C, 50.17%; H, 10.27%; N, 3.20%.

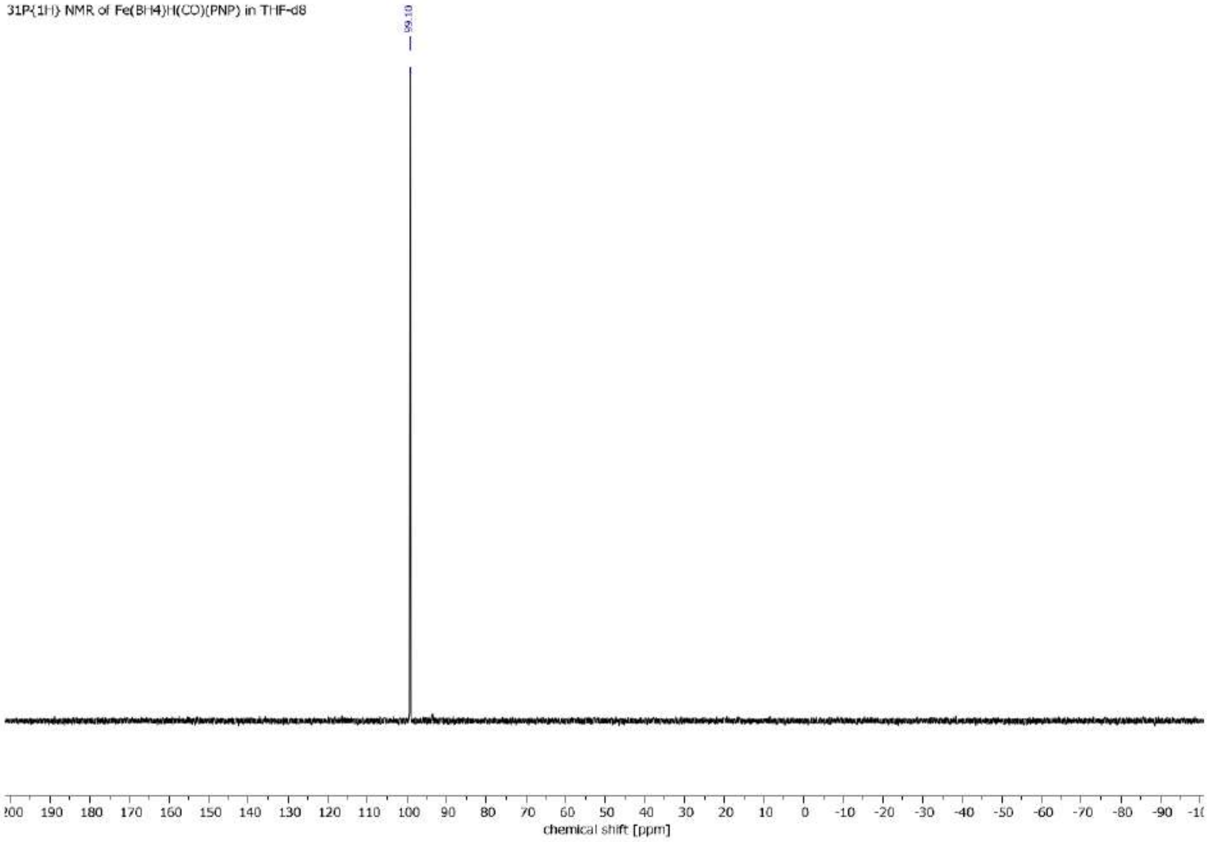


13C{1H} NMR of Fe(BH4)H(CO)(PNP) in THF-d8

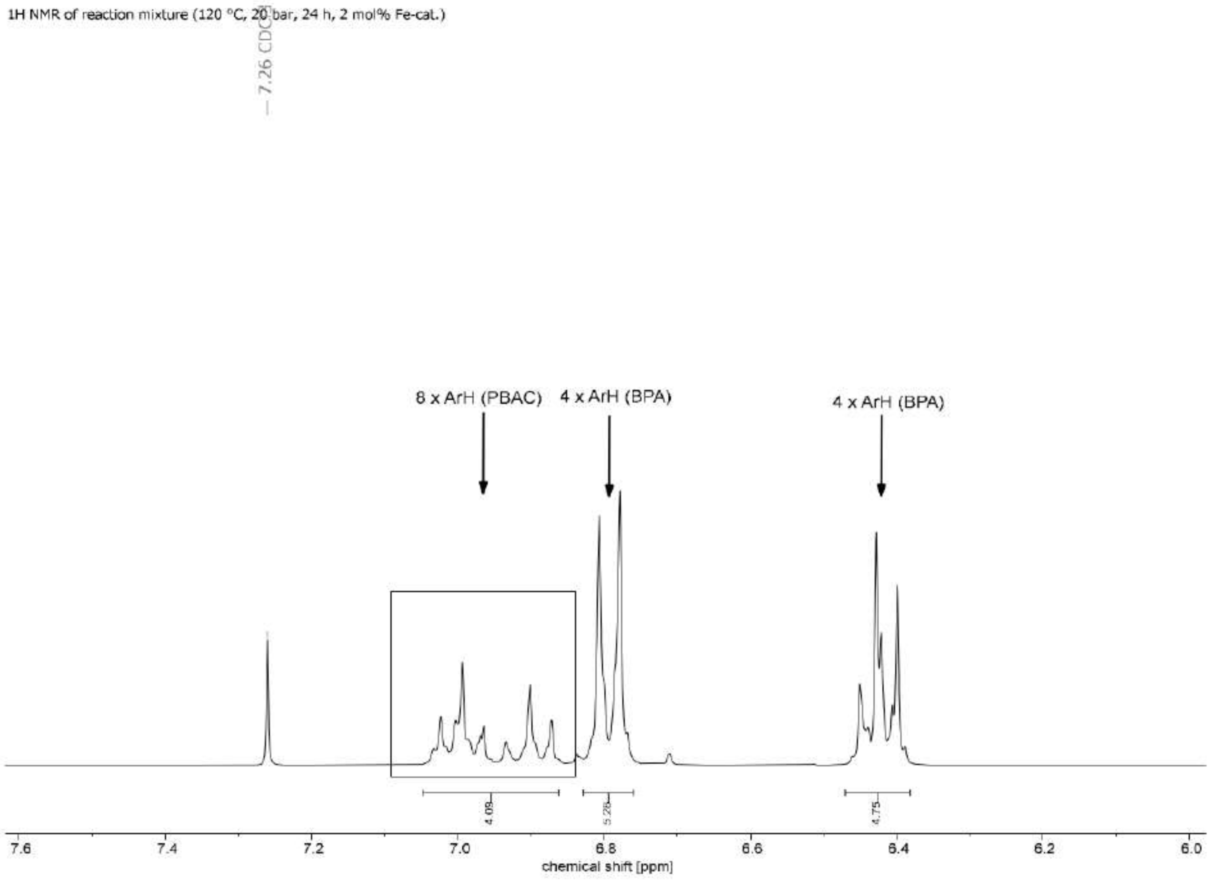


11B NMR of Fe(BH4)H(CO)(PNP) in C6D6





General procedure for the hydrogenation of poly(bisphenol A carbonate) 1a (optimization of reaction conditions): A mixture of commercially available poly(bisphenol A carbonate) (**1a**) (34.3 mg, 0.135 mmol, based on the repeating unit, obtained from Sigma Aldrich), and catalytic amounts of the complex **12** (0-1.09 mg, 0-2.7 µmol, 0-2 mol%, based on the repeating unit of **1a**, added as stock solution in THF) were placed with a stir bar in a vial. The solvent (1.0 mL) was added and vial was placed in an autoclave, which was sealed and purged with hydrogen (5 times). Afterwards the desired hydrogen pressure (5-45 bar) was adjusted and the autoclave was heated to the desired temperature (60-140 °C). The temperature was hold for 6-24 hours, while stirring the reaction mixture. Afterwards the autoclave was cooled to room temperature and the hydrogen pressure was carefully released. QuadraSil® MTU (2-4 mg) was added and the mixture was stirred for 3 h to remove paramagnetic compounds. Then, the mixture was filtered through a syringe filter and an aliquot of the solution was transferred to a NMR tube and dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^1H NMR to determine the yield of bisphenol A (**2**). The yield of **2** was determined by the integrals of the Ar-H or $C(CH_3)_2$ and the Ar-H or $C(CH_3)_2$ leftover signals of the polymer/oligomers.



General procedure for the hydrogenation of poly(bisphenol A carbonate) 1a in the presence of other polymers: A mixture of commercially available poly(bisphenol A carbonate) (**1a**) (34.3 mg, 0.135 mmol, based on the repeating unit, obtained from Sigma Aldrich), and catalytic amounts of the complex **12** (1.09 mg, 2.7 µmol, 2 mol%, based on the repeating unit of **1a**, added as stock solution in THF) were placed with a stir bar in a vial. The additional polymer (0.135 mmol, based on the repeating unit, obtained from Sigma Aldrich (PLA and PET were obtained from a bottle, for PU and epoxy resins, the same mass as for poly (bisphenol A carbonate) was added)). Dry THF (1.0 mL) was added. The vial was placed in an autoclave, which was sealed and purged with hydrogen (5 times). Afterwards the desired hydrogen pressure (45 bar) was adjusted and the autoclave was heated to the desired temperature 120 °C). The temperature was hold for 24 hours, while stirring the reaction mixture. Afterwards the autoclave was cooled to room temperature and the hydrogen pressure was carefully released. QuadraSil® MTU (2-4 mg) was added and the mixture was stirred for 3 h to remove paramagnetic compounds. Then the mixture was filtered through a syringe filter and an aliquot of the solution was transferred to a NMR tube and dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^{1}H NMR to determine the yield of bisphenol A (**2**). The yield of

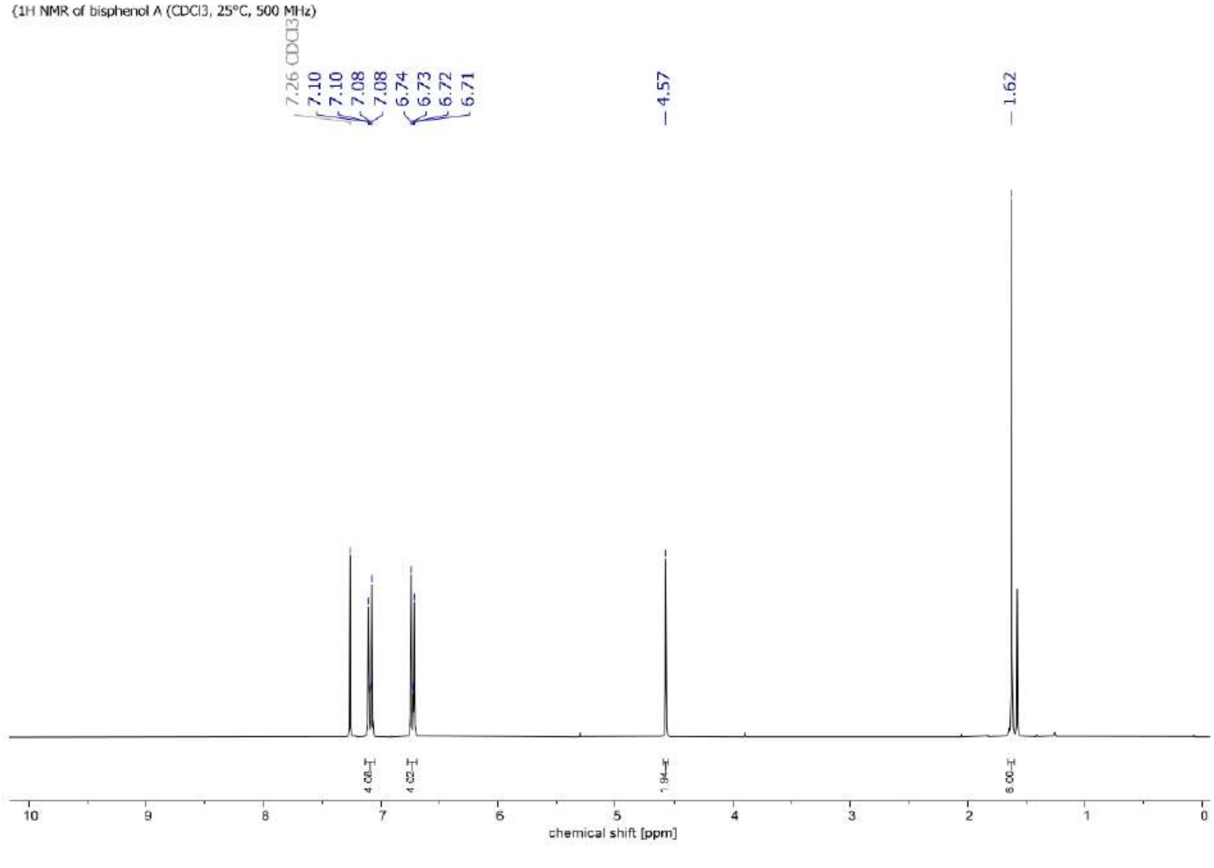
2 was determined by the integrals of the Ar-H or C(C*H*$_3$)$_2$ and the Ar-H or C(C*H*$_3$)$_2$ leftover signals of the polymer/oligomers.

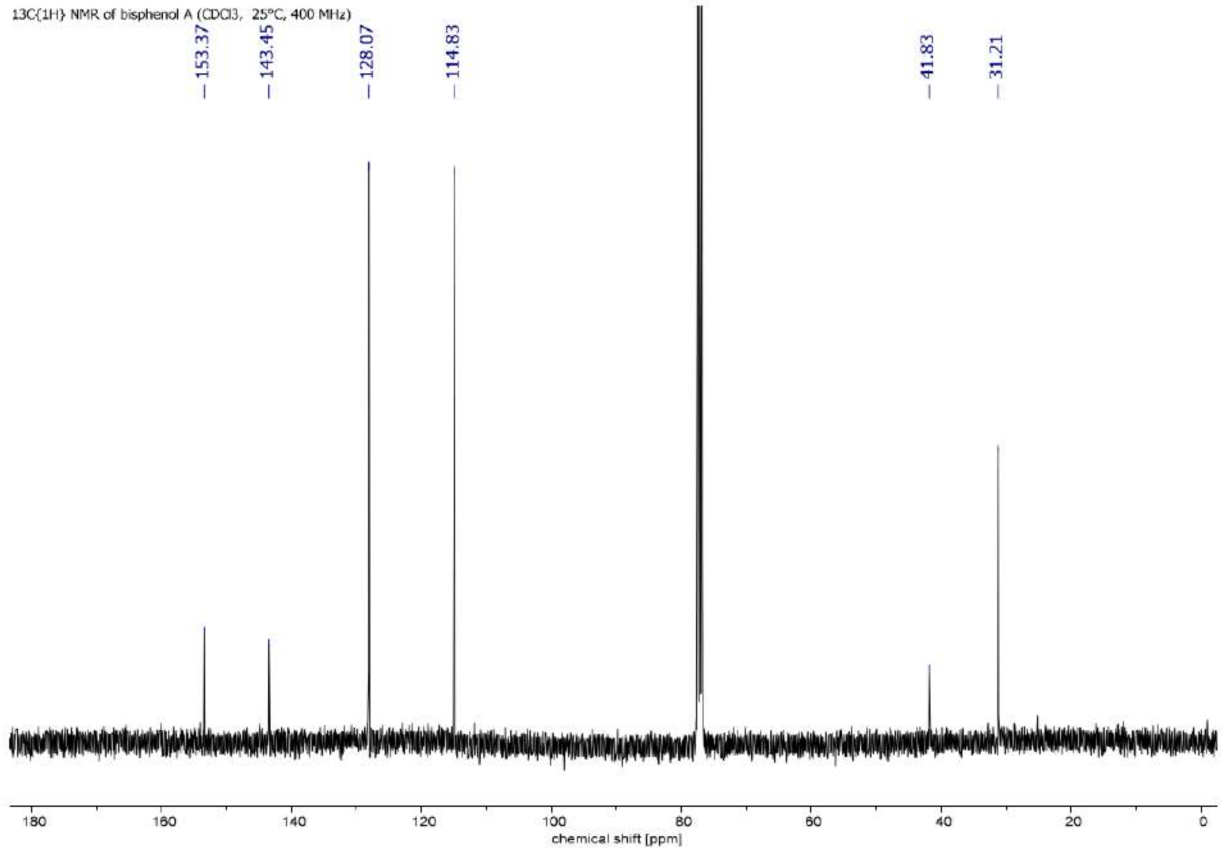
Procedure for the hydrogenation of poly(bisphenol A carbonate) 1aa/1ab derived from end-of-life DVD/laboratory safety goggles: A ball milled digital versatile disc (**1aa**) or safety goggles (**1ab**) (1.00 g, 3.95 mmol, based on the repeating unit, obtained from Sigma Aldrich), and catalytic amounts of the complex **12** (32.0 mg, 79. µmol, 2 mol%, based on the repeating unit of **1a**) were placed with a stir bar in a steal autoclave. Dry THF (20.0 mL) was added and the autoclave was sealed and purged with hydrogen (5 times). Afterwards the desired hydrogen pressure (45 bar) was adjusted and the autoclave was heated to the desired temperature (120 °C). The temperature was hold for 24 hours, while stirring the reaction mixture. Afterwards the autoclave was cooled to room temperature and the hydrogen pressure was carefully released. The reaction mixture was filtered over a plug of silica gel, washed with EtOAc and the solvent of the filtrate was evaporated. Then the residue was recrystallized from CH_2Cl_2/petroleum ether to obtain bisphenol A (**1aa**: 726 mg, 81%, **1ab**: 492 mg, 55%) as colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ [ppm] = 7.10-7.08 (m, Ar-*H*, 4H), 6.74-6.71 (m, Ar-*H*, 4H), 4.57 (s, O*H*, 2H), 1.62 (s, (C*H*$_3$)$_2$C, 6H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 °C): δ[ppm] = 153.4 (*C*-OH, 2C), 143.5 (*C*(C-CH$_3$)$_2$, 2C), 128.1 (C_{Ar}, 2C), 114.8 (C_{Ar}, 2C), 41.8 (*C*(CH$_3$)$_2$, 1C), 31.2 (*C*H$_3$, 2C).

(1H NMR of bisphenol A (CDCl3, 25°C, 500 MHz)



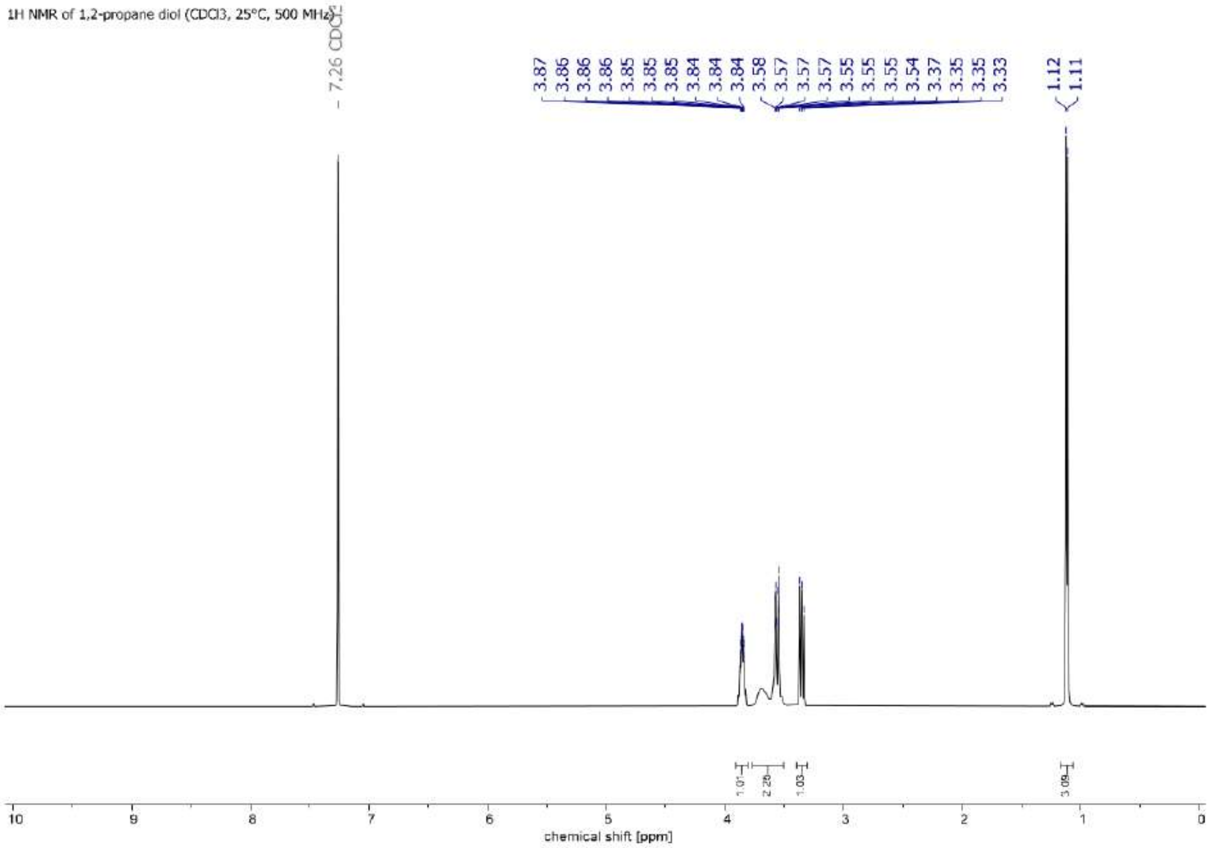


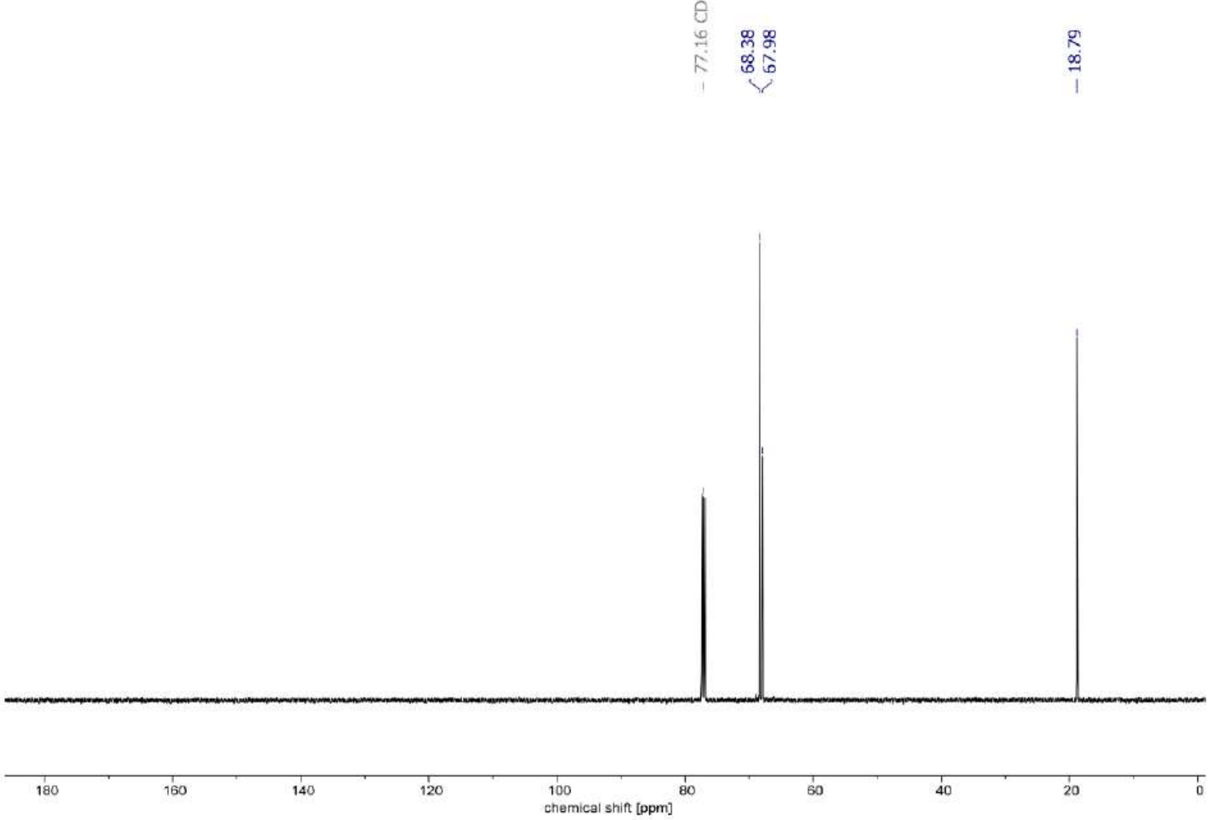
Procedure for the hydrogenation of poly(propylene carbonate) 1b derived from end-of-life DVD/laboratory safety goggles

Pellets of poly(propylene carbonate) (**1b**) (1.00 g, 9.84 mmol, based on the repeating unit, obtained from Sigma Aldrich), and catalytic amounts of the complex **12** (79.7 mg, 197 µmol, 2 mol%, based on the repeating unit of **1a**) were placed with a stir bar in an autoclave. Dry THF (40.0 mL) was added and the autoclave was sealed and purged with hydrogen (5 times). Afterwards the desired hydrogen pressure (45 bar) was adjusted and the autoclave was heated to the desired temperature (120 °C). The temperature was hold for 24 hours, while stirring the reaction mixture. Afterwards the autoclave was cooled to room temperature and the hydrogen pressure was carefully released. The solvent of the reaction mixture was carefully distilled of and the residue was purified by vacuum distillation, collecting all volatiles. 1,2-propane diol (573 mg, 77%) was obtained as colorless liquid.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ [ppm] = 3.89-3.81 (m, C*H*OH, 1H), 3.58-3.53 (m, CH_2OH, 1H), 3.37-3.33 (m, CH_2OH, 1H), 1.11 (d, *J* = 6.3 Hz, CH_3, 3H).

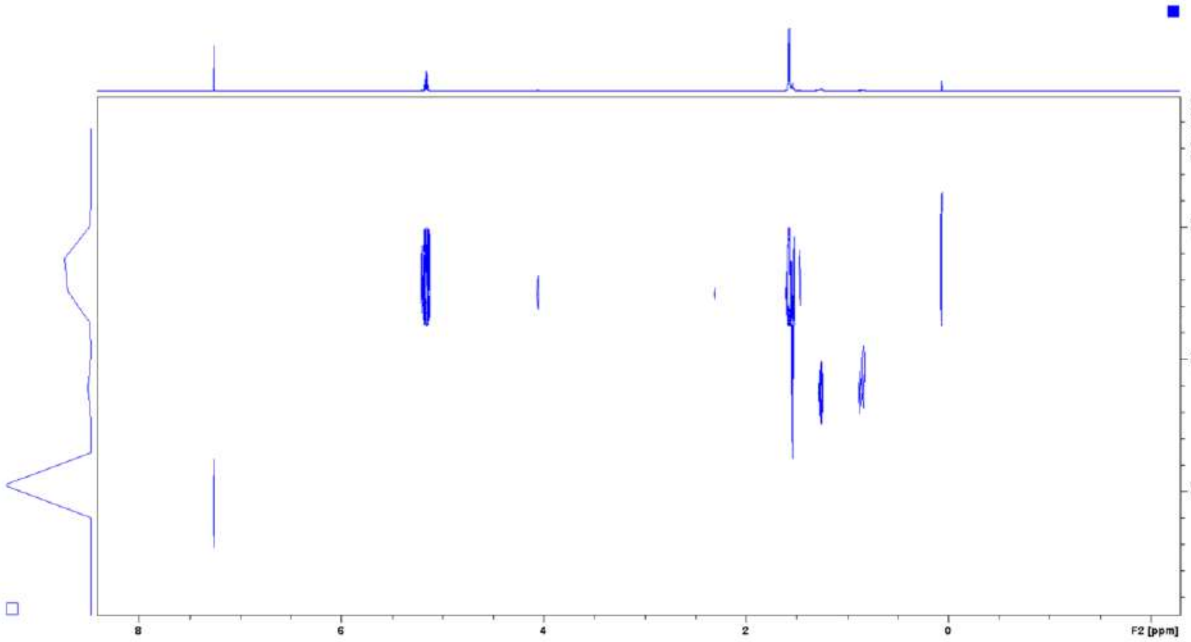
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 °C): δ [ppm] = 68.4 (CH_2OH), 68.0 (*C*HOH), 18.8 (CH_3).


1H NMR of 1,2-propane diol (CDCl3, 25°C, 500 MHz)


13C NMR of 1,2-propane diol (CDCl3, 25 °C, 500 MHz)

DOSY NMR spectrum of poly(lactide) (600 MHz, $CDCl_3$, 25 °C)).

5.17-5.14 ppm (m, 1H, CH_3CH): $D = 4.8 \cdot 10^{-10} \frac{m^2}{s}$

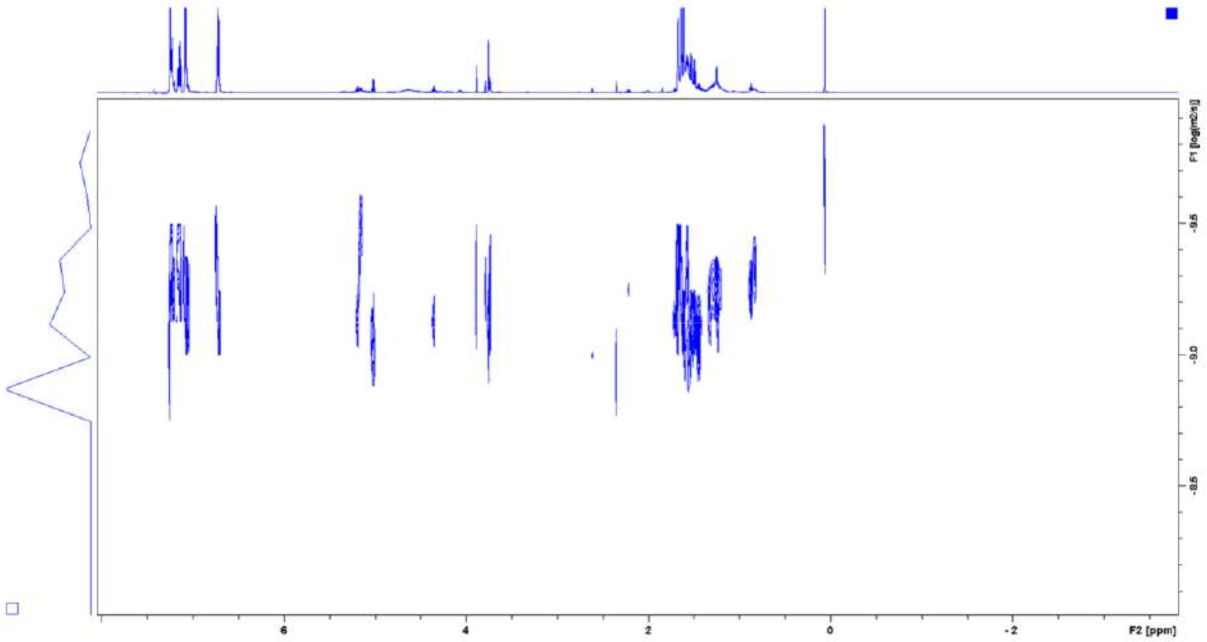


DOSY NMR spectrum of the reaction mixture of poly(bisphenol A carbonate)/poly(lactide), polylactide, (600 MHz, $CDCl_3$, 25 °C)).

5.21-5.18 ppm (m, 1H, CH_3CH): $D = 7.6 \cdot 10^{-10} \frac{m^2}{s}$

5.17-5.14 ppm (m, 1H, CH_3CH): $D = 3.6 \cdot 10^{-10} \frac{m^2}{s}$

5.04-5.00 ppm (m, 1H, CH_3CH): $D = 1.0 \cdot 10^{-9} \frac{m^2}{s}$



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ChemistrySelect

Supporting Information

Ruthenium-catalyzed Chemical Recycling of Poly(ε-caprolactone) via Hydrogenative Depolymerization and Dehydrogenative Polymerization

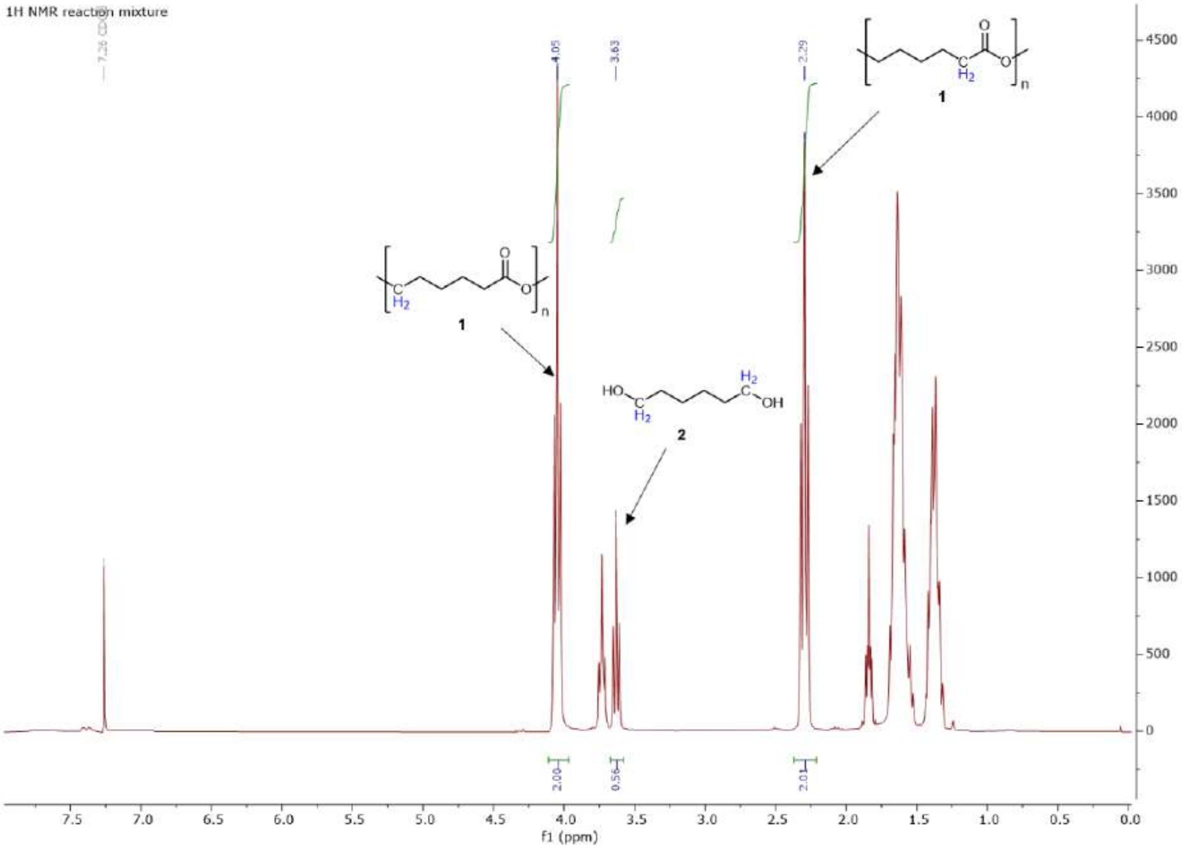
Christoph Alberti and Stephan Enthaler*

General: All chemicals were used as received without further manipulations. Poly(ε-caprolactone) (M_n~80,000 g/mol) was received from Sigma Aldrich/Merck. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a *Fourier 300 MHz* (^{1}H: 300 MHz, ^{13}C: 75 MHz) or *Avance I-400* (^{1}H: 400 MHz, ^{13}C: 101 MHz) by Bruker, using the proton signals of the deuterated solvents as reference or external standards. Mass spectrometry was performed using a *Thermo ISQ LT EI* by Thermo Fisher Scientific. TLC was performed on *ALUGRAM XTRA SIL G/UV$_{254}$* cards from *Macherey-Nagel* GmbH & Co. KG with a thickness of 0.20 mm. Detection succeeded with UV-light (254 nm). For filtration Celite® 545 (particle size 0.02-0.1 mm) from (Merck KGaA) was used. For preparative column chromatography silica gel 60 (particle size 40 – 63 µm) from *Fluka* was used. All catalytic set-ups were prepared in a glovebox under argon. Ru-MACHO®-BH: Carbonylhydrido(tetrahydroborato)[bis(2-diphenylphosphinoethyl)amino]ruthenium(II) (CAS Number: 1295649-41-0) was received from TCI Deutschland GmbH. THF was dried over sodium-benzophenone, was distilled off and stored over molecular sieves 4 Å under a nitrogen atmosphere. The hydrogenations were performed in a Parr autoclave (model: 4774) (Parr Instrument Company). SEC analysis was performed using a "mixed bed" linear SEC-column (5 µm porous styrene-divinylbenzene particles, separation range 200-1000k g/mol) at a flow rate of 1 mL/min in tetrahydrofuran as eluent. Molecular weights refer to a so-called relative calibration based on narrow polystyrene samples supplied by Agilent Technologies. The SEC system was equipped with a Shimadzu LC-10ATvP pump, an AS1000 autosampler from Thermo Separation Products and a RI2012 refractive index detector from Schambeck SFD GmbH. For microwave heating experiments a Microwave Synthesis Reactor Monowave 400 (Anton Paar GmbH) was used.

General procedure for the hydrogenative depolymerization of poly(ε-caprolactone) (optimization of reaction conditions): A mixture of poly(ε-caprolactone) (**1**) (16 mg, 0.14 mmol based on the repeating unit of **1**), catalytic amounts of complex **8** (0–4.2 mg, 0–0.007 mmol based on the repeating unit of **1**) and THF or toluene (2 mL) was placed with a stir bar in a vial. The vial was placed in an autoclave, which was sealed and purged with hydrogen (5 times). Afterwards the desired hydrogen pressure was adjusted (10-45 bar) and the autoclave was heated to the desired temperature (100-140 °C). The temperature was hold for 6-24 hours, while stirring the reaction mixture. Afterwards the autoclave was cooled to room temperature and the hydrogen pressure was carefully released. An aliquot of the solution was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.6 mL). The sample was subjected to ^{1}H NMR to determine the yield of 1,6-hexanediol (**2**). The yield of **2** was calculated on the basis of the HOC*H*$_2$- of **2** and the -C(O)OC*H*$_2$- leftover signals of the polymer/oligomer.

1,6-Hexanediol (**2**)[1]: ^{1}H NMR (400 MHz, C*D*Cl$_3$, 25 °C): δ = 3.62 (t, *J* = 6.52 Hz, 4H, HOC*H*$_2$), 2.05 (s, br, -OH, 2H), 1.49-1.63 (m, 4H, C*H*$_2$), 1.32-1.43 (m, 4H, C*H*$_2$) ppm.

Figure S1. ^{1}H NMR-Spectrum of the depolymerization reaction mixture (400 MHz, C*D*Cl$_3$, 25 °C).



Procedure for the hydrogenative depolymerization of poly(ε-caprolactone) (scale-up): A mixture of poly(ε-caprolactone) (**1**) (200 mg, 1.75 mmol based on the repeating unit of **1**), catalytic amounts of complex **8** (52.5 mg, 0.0875 mmol based on the repeating unit of **1**) and toluene (25 mL) was placed in an autoclave, which was sealed and purged with hydrogen (5 times). Afterwards the desired hydrogen pressure was adjusted (45 bar) and the autoclave was heated to the desired temperature (140 °C). The temperature was hold for 6 hours, while stirring the reaction mixture. Afterwards the autoclave was cooled to room temperature and the hydrogen pressure was carefully released. The mixture was filtered over a short plug of silica. Afterwards the solvent was removed in vacuum. **2** was isolated as colorless solid (yield: 87%, m = 180 mg).

1,6-Hexanediol (**2**): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.62 (t, *J* = 6.52 Hz, 4H, HOCH_2), 2.05 (s, br, -OH, 2H), 1.49-1.63 (m, 4H, CH_2), 1.32-1.43 (m, 4H, CH_2) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 25 °C): δ = 62.7, 32.7, 25.6 pm.

Figure S2. ^{1}H NMR-Spectrum of 1,6-hexanediol (400 MHz, $CDCl_3$, 25 °C).

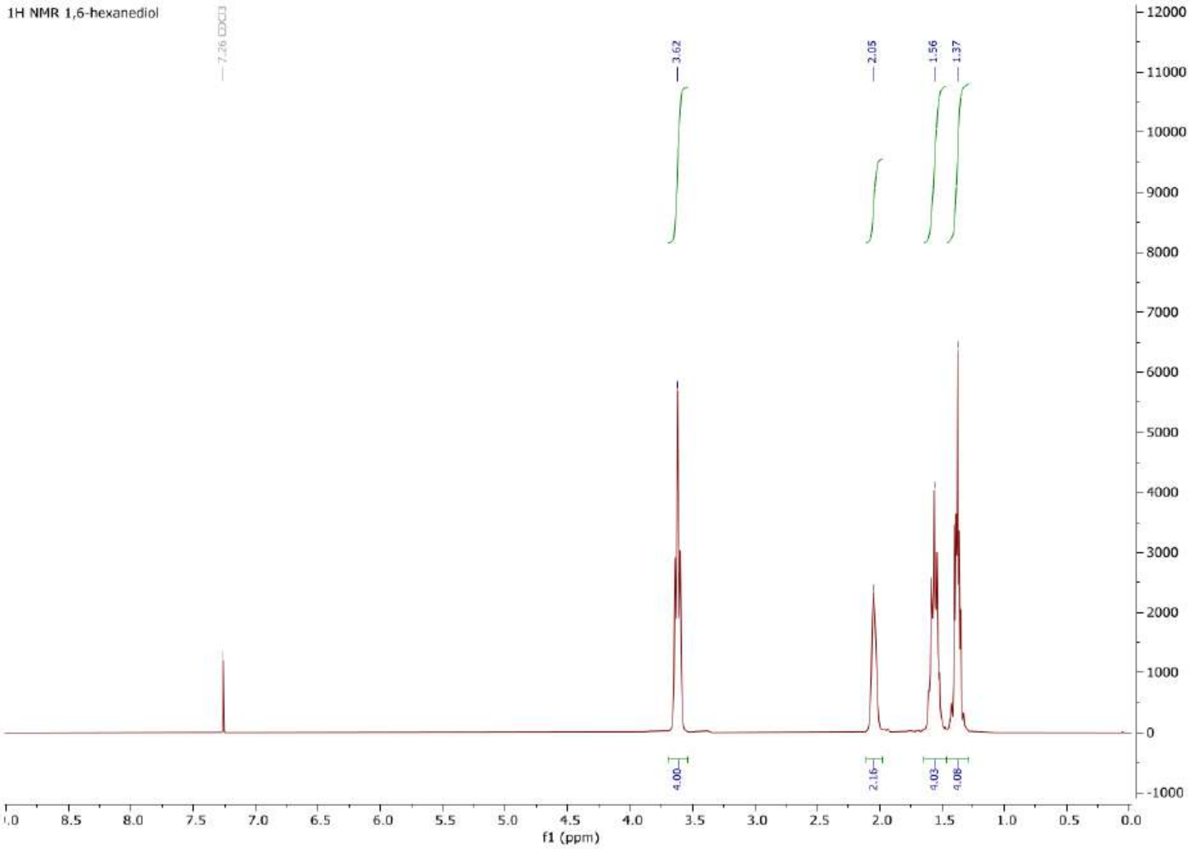
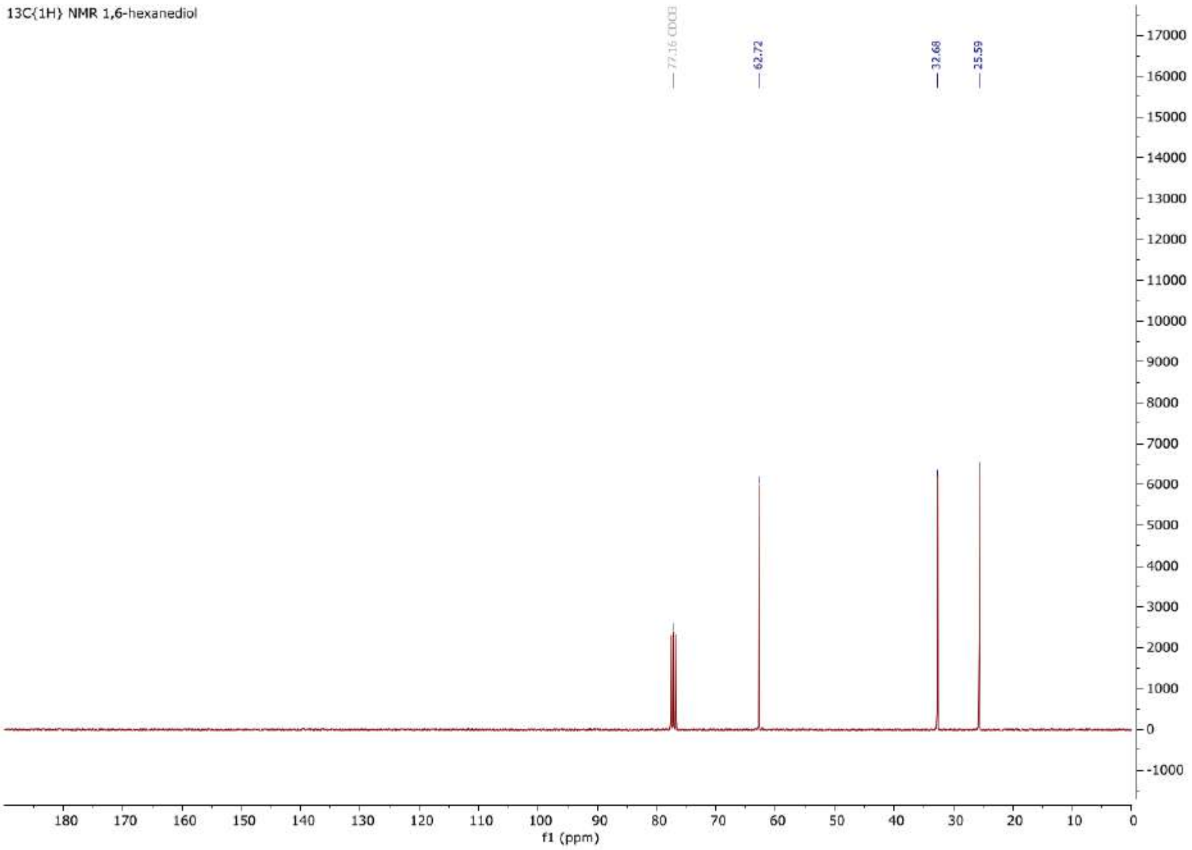


Figure S3. $^{13}C\{^{1}H\}$ NMR-Spectrum of 1,6-hexanediol (400 MHz, $CDCl_3$, 25 °C).



General procedure for the dehydrogenation of 1,6-hexanediol (optimization of reaction conditions): A mixture of 1,6-hexanediol (**2**) (0.369-2.88 g, 2.27-24.33 mmol) and catalytic amounts of complex **8** (0–5.0 mg, 0–0.0091 mmol) was placed with a stir bar in a Schlenk tube under an atmosphere of nitrogen. The mixture was heated at 100-150 °C for 24 hours, while a constant flow of nitrogen was passed through the solution. After cooling to ambient temperature an aliquot was transferred to an NMR tube with $CDCl_3$ (0.6 mL). The sample was subjected to ^{1}H NMR. The yield of **7** was calculated based on the integrals of the OCH_2-group signal of **7** and those signals of leftover 1,6-hexanediol. For GPC measurements the leftover 1,6-hexandiol was removed in vacuum and the leftover in the flask was dissolved in dichloromethane and the solution was filtered over a plug of silica. The solvent was removed and the residue was dissolved in THF for GPC measurements.

Polyester (**7**): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.05 (m, 2H, CH_2), 2.29 (m, 2H, CH_2), 1.58-1.69 (m, 4H, CH_2), 1.33-1.42 (m, 2H, CH_2) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 25 °C): δ = 173.7, 64.3, 34.2, 28.5, 25.7, 24.7 ppm.

Figure S4. ^{1}H NMR-Spectrum of the polymerization reaction mixture (400 MHz, C*D*Cl$_3$, 25 °C).

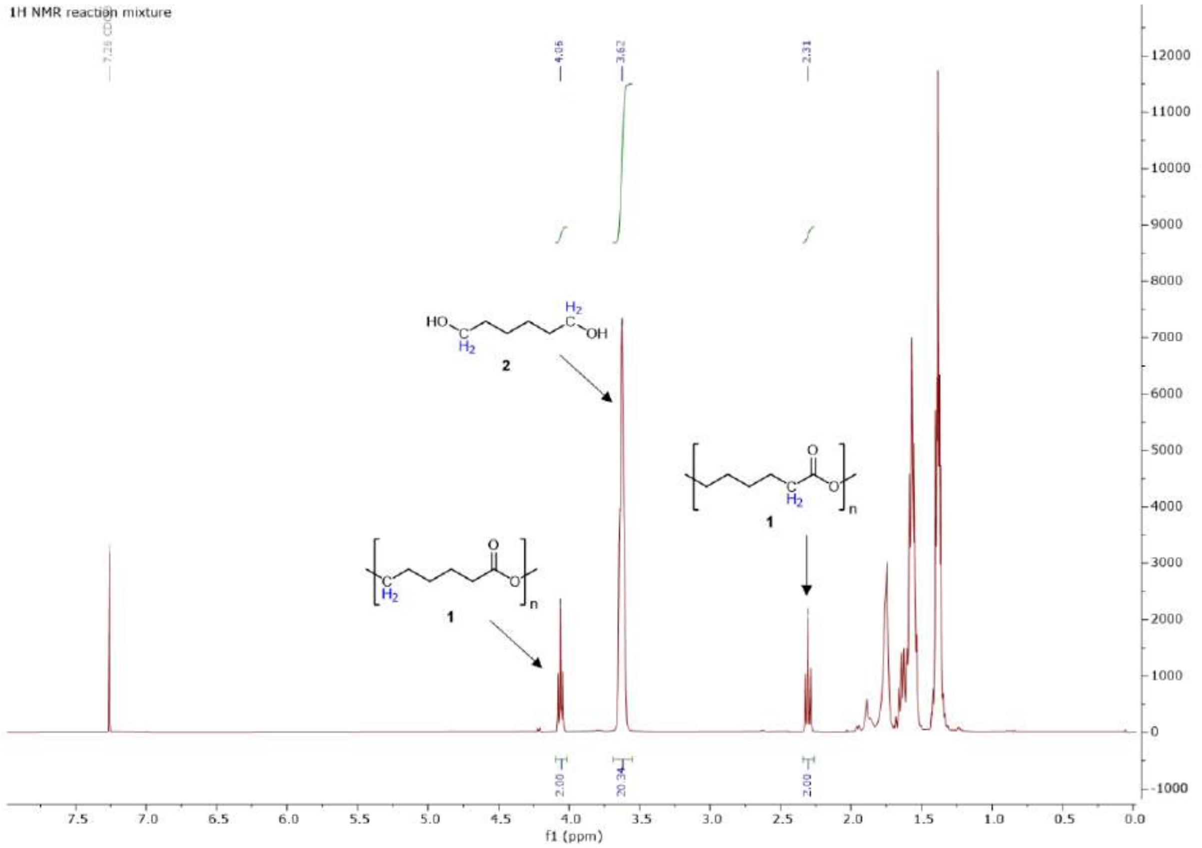


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of the reaction mixture (125 MHz, $CDCl_3$, 25 °C).

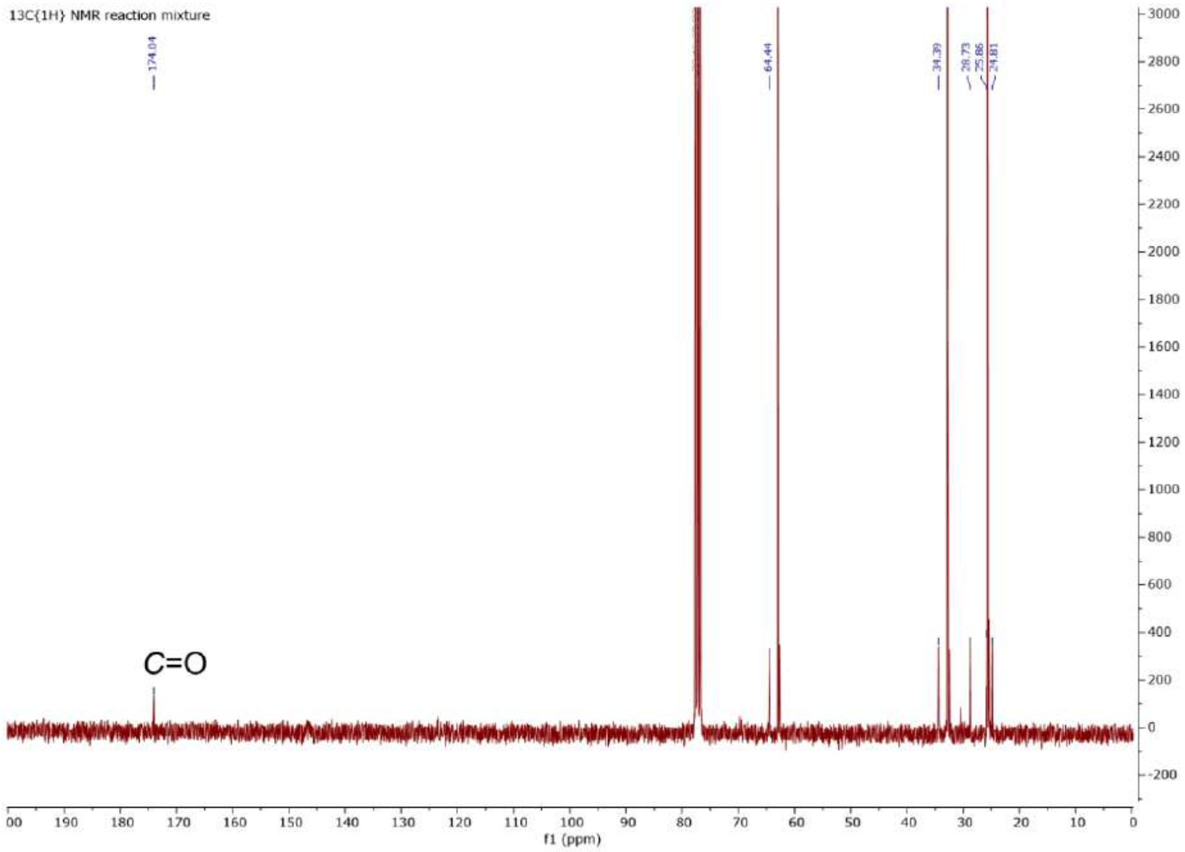


Figure S6. ^{1}H NMR spectrum of **1a** (400 MHz, $CDCl_3$, 25 °C).

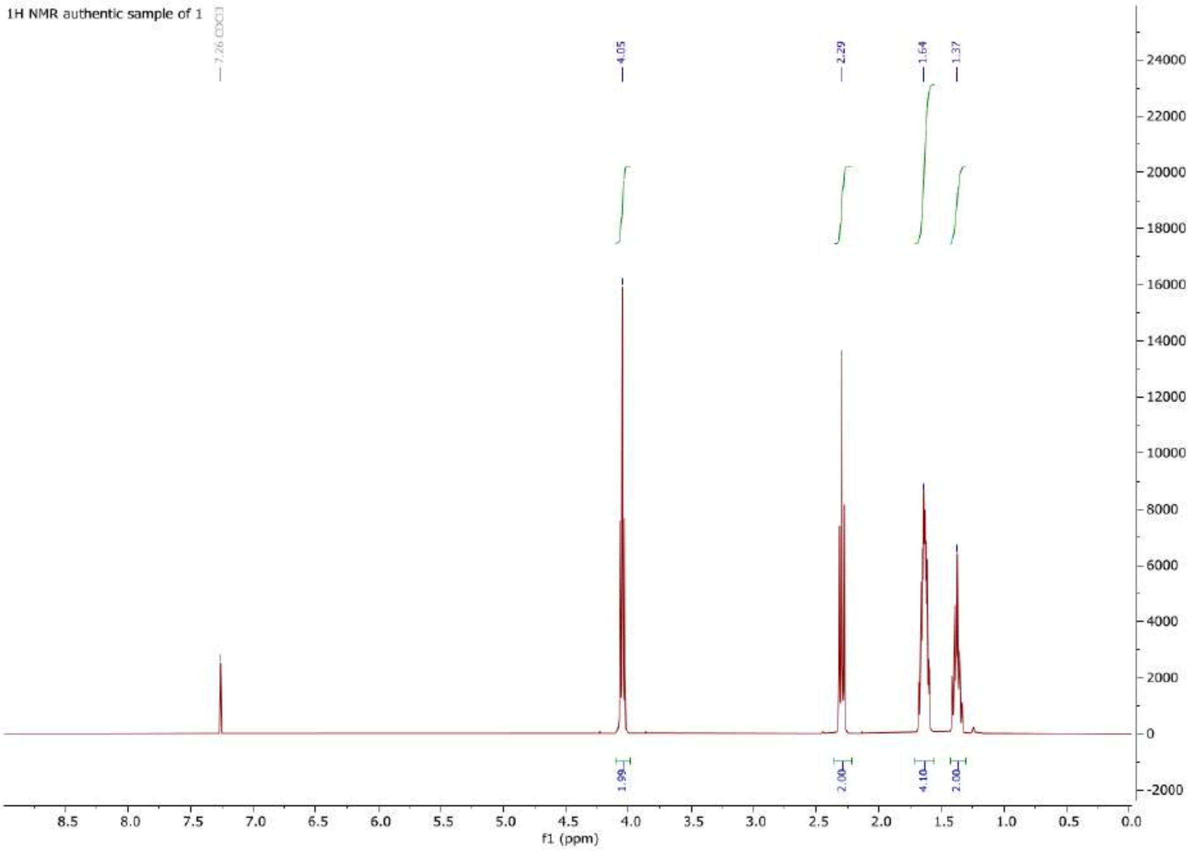


Figure S7. $^{13}C\{^1H\}$ NMR spectrum of **1a** (125 MHz, $CDCl_3$, 25 °C).

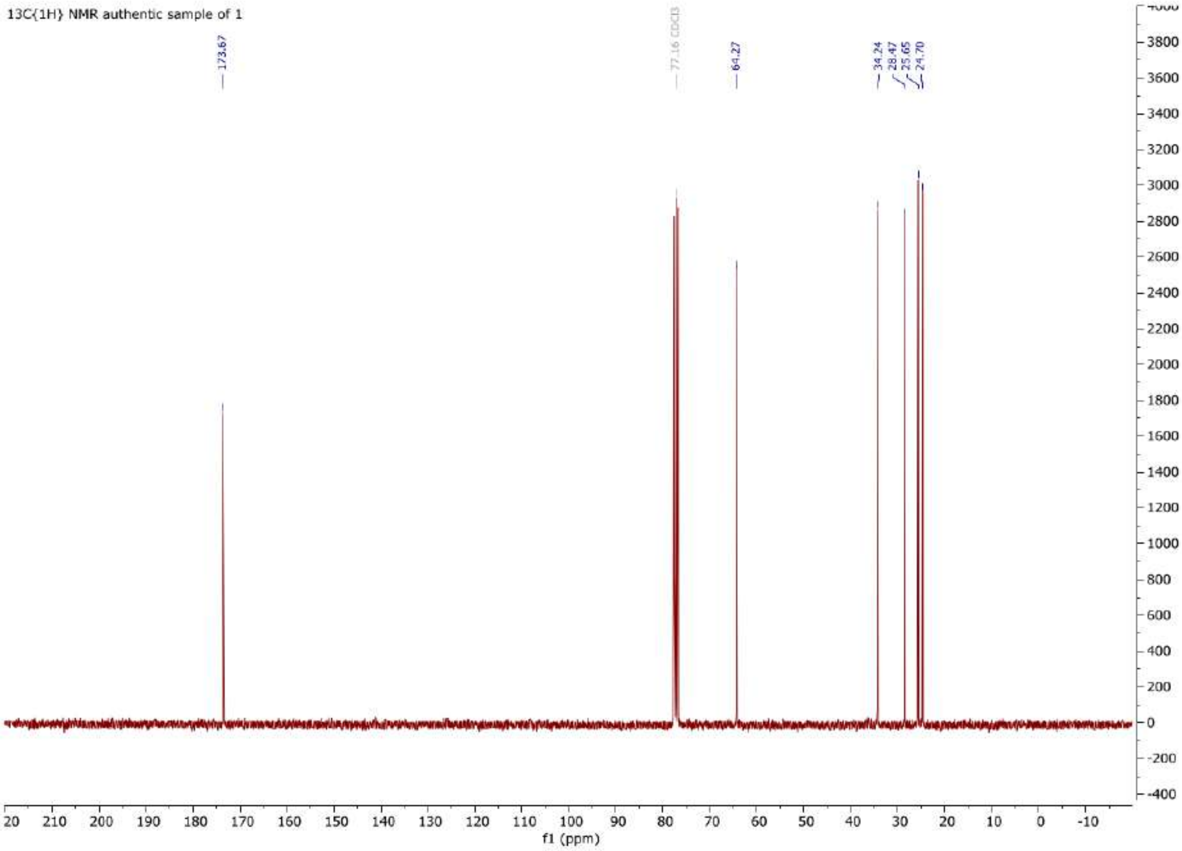


Figure S8. ESI-MS (Table 2, Entry 2).

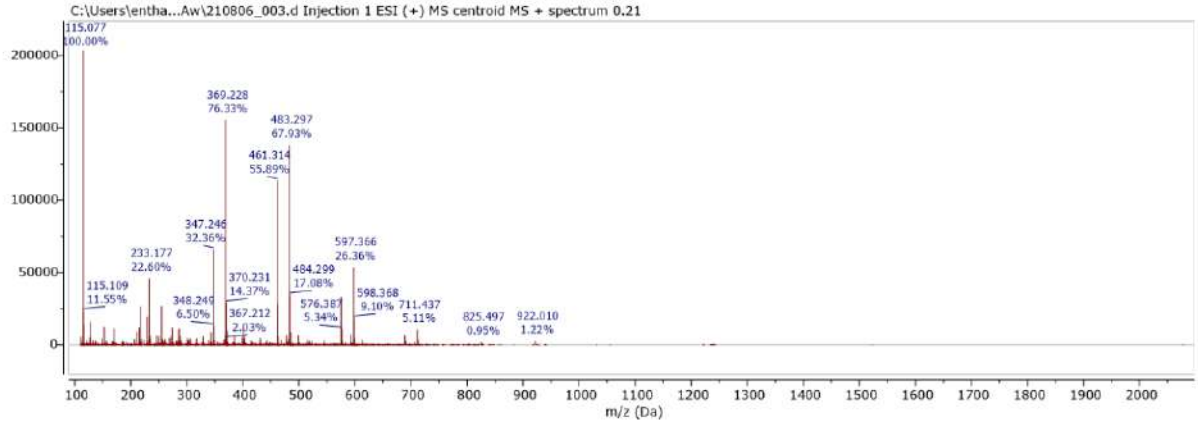


Figure S9. ESI-MS (Table 2, Entry 4).

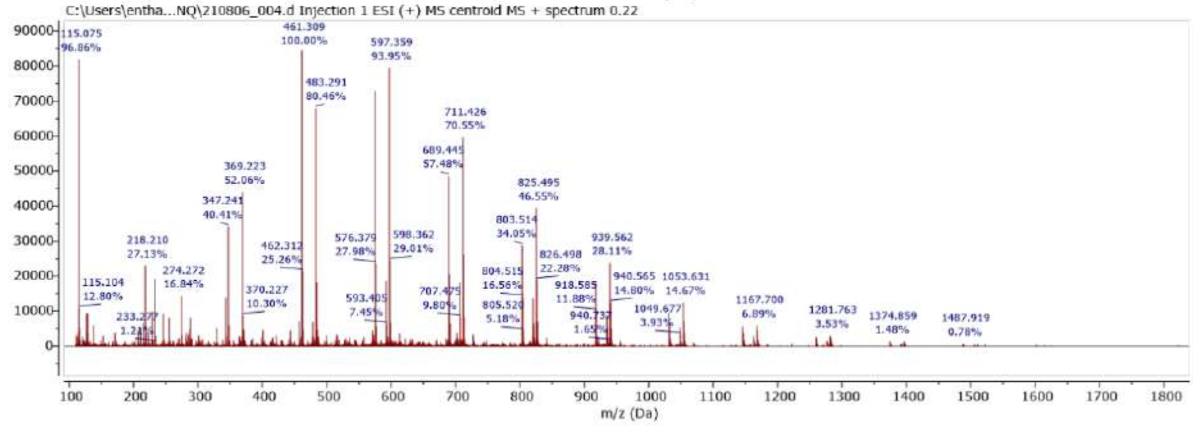


Figure S10. ESI-MS (Table 2, Entry 5).

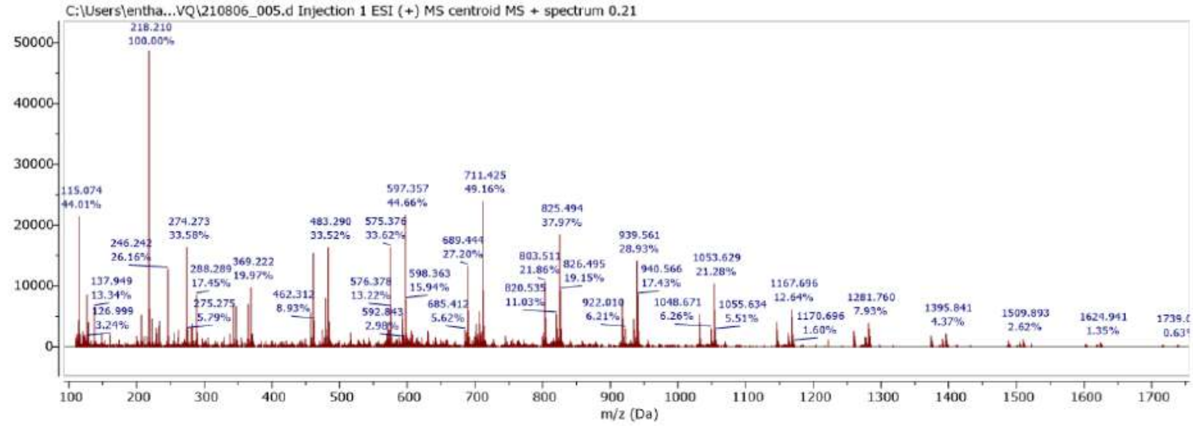


Figure S11. ESI-MS (Table 2, Entry 6).

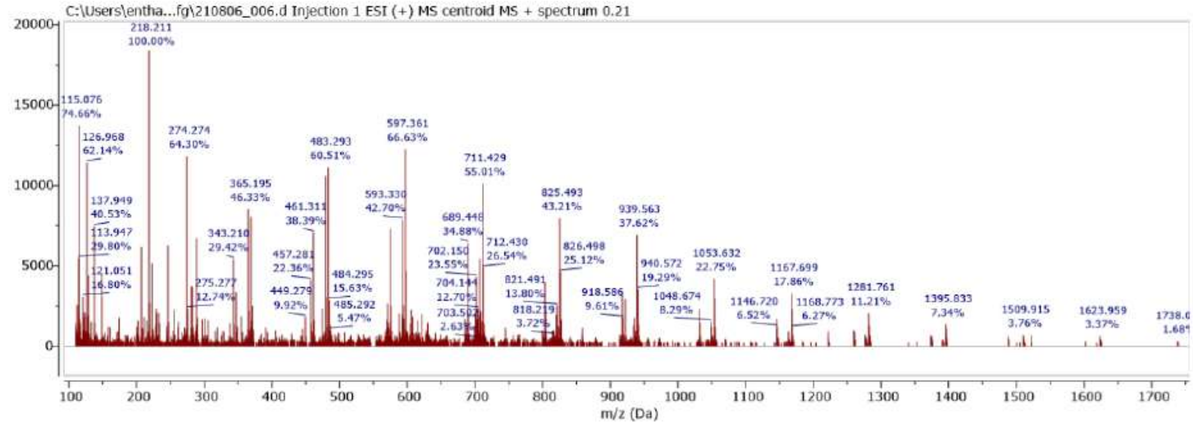
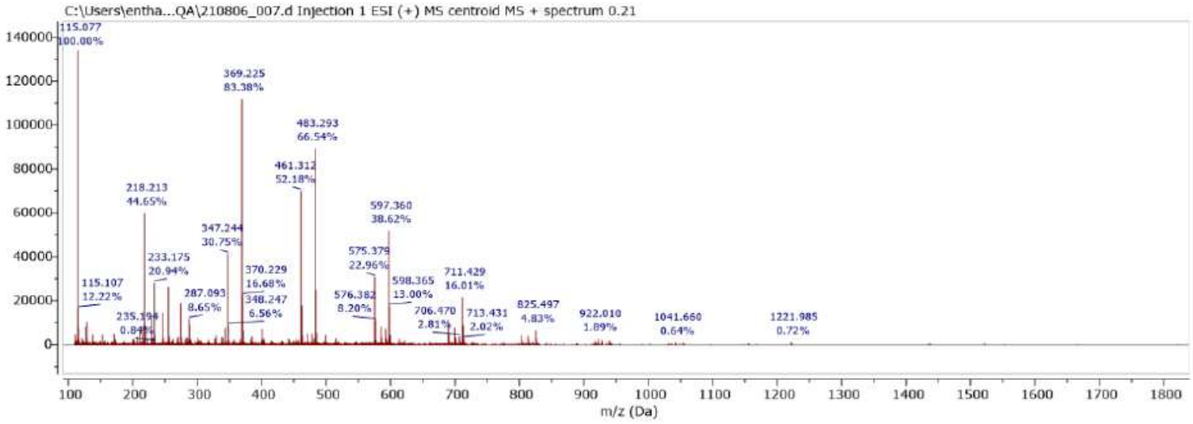


Figure S12. ESI-MS (Table 2, Entry 7).



Scale-up procedure for the dehydrogenative polymerization of 1,6-hexanediol: A mixture of 1,6-hexanediol (**2**) (100 mg, 0.85 mmol, obtained from the depolymerization process) and catalytic amounts of complex **8** (1.98 mg, 0.00338 mmol) was placed with a stir bar in a Schlenk-tube under an atmosphere of nitrogen. The mixture was heated at 130 °C for 24 hours, while a constant flow of nitrogen was passed through the solution. After cooling to ambient temperature an aliquot was transferred to an NMR tube with $CDCl_3$ (0.6 mL). The sample was subjected to ^1H NMR. The yield of **7** was calculated based on the integrals of the OCH_2-group signal of **7** and those signals of leftover 1,6-hexanediol. Poly(ε-caprolactone) (**1**) was obtained as yellow viscous oil/solid in 84% yield (m = 81 mg). The analytical properties are in accordance to the properties reported (see above).

Procedure for the depolymerization of polymer 7 – methanolysis: Polymer **7** (50 mg, 0.438 mmol based on the repeating unit), methanol (1.0 g, 31.2 mmol, 35.6 equiv. based on the repeating unit of **7**) and $Zn(OAc)_2$ (2.0 mol%, 1.6 mg, 0.0875 mmol based on the repeating unit of **7**) was placed with a stir bar in a vial. The vial was sealed and subjected to a Microwave Synthesis Reactor Monowave 400. The reaction was performed for 60 minutes (hold time) at 160 °C and with a stirring of 600 rpm. The reaction temperature was reached within 1-2 minutes (heat as fast as possible). Afterwards the vial was cooled to room temperature. An aliquot of the clear solution was transferred to an NMR tube and was dissolved in $CDCl_3$ (0.5 mL). The sample was subjected to ^1H NMR.

Figure S13. ^{1}H NMR-Spectrum of the methanolysis reaction mixture (400 MHz, $CDCl_3$, 25 °C).

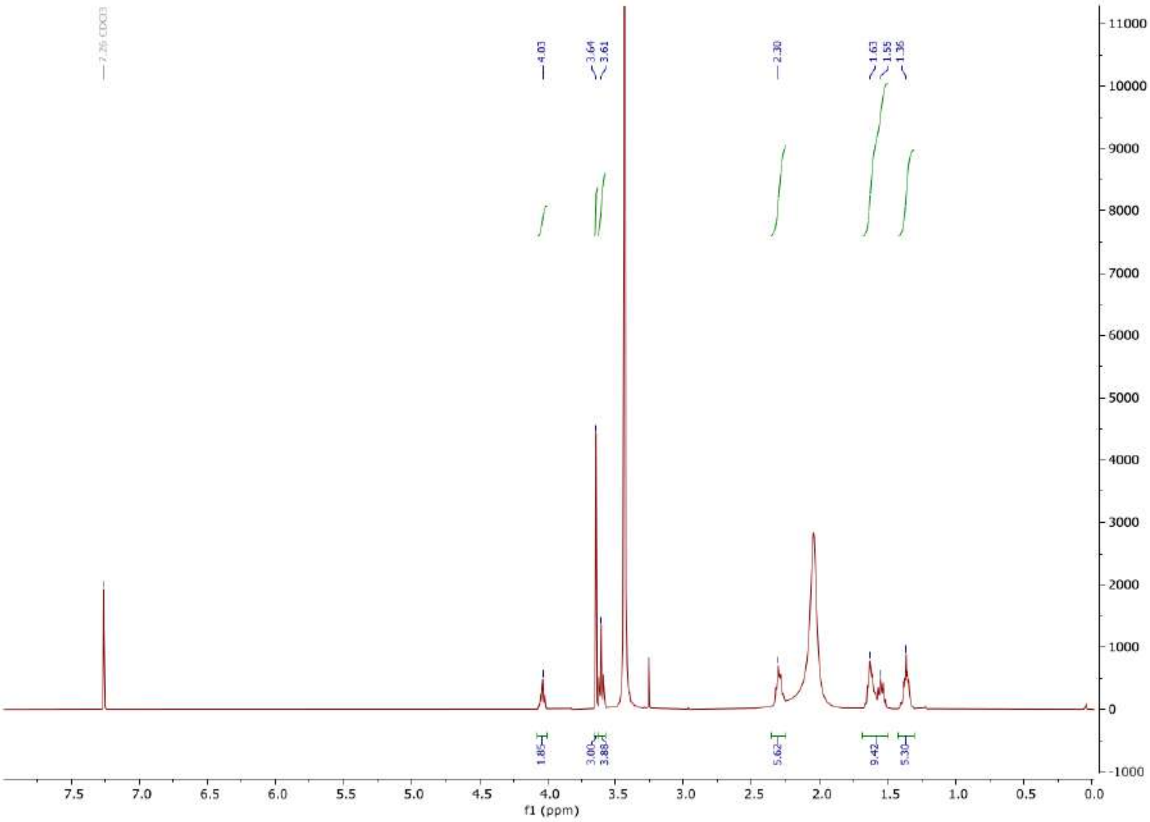


Figure S14. GC-chromatogram of the methanolysis reaction mixture.

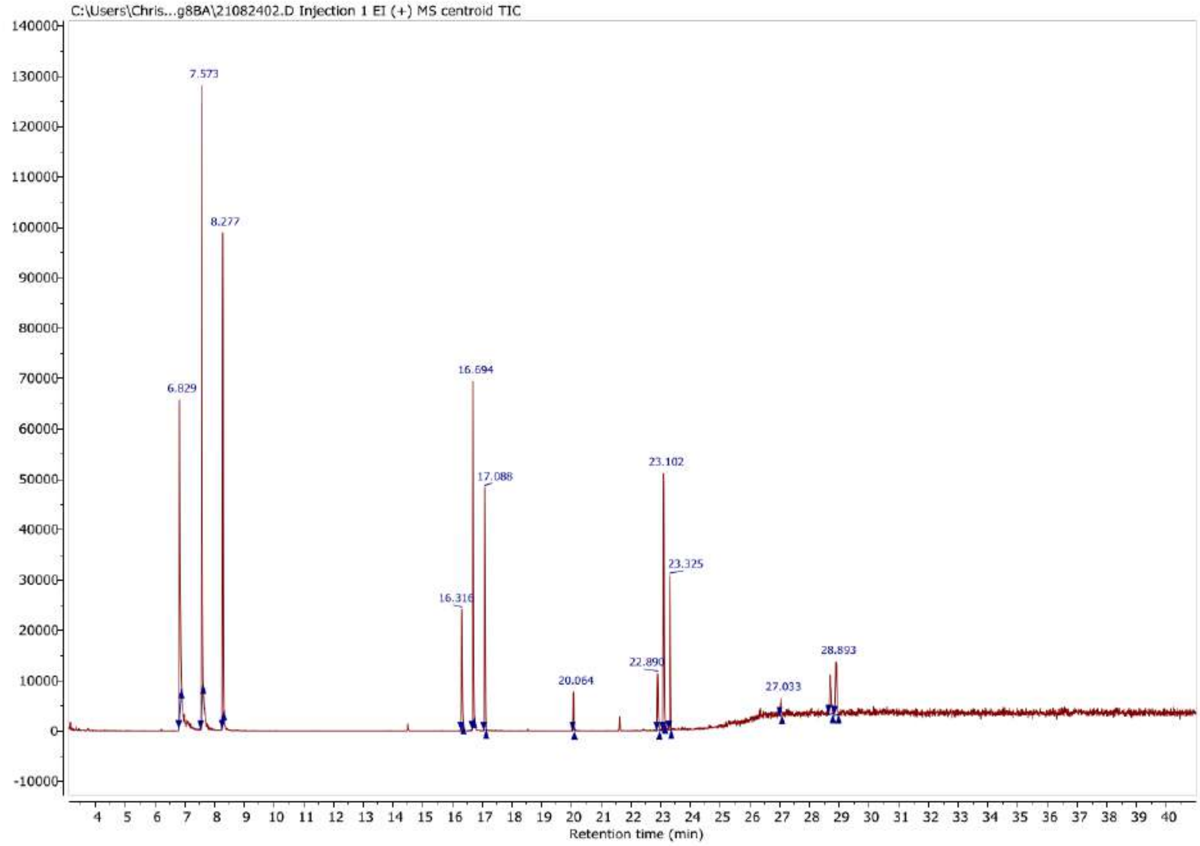


Figure S15. MS-EI spectrum (6.829 min) (Compared with library data).

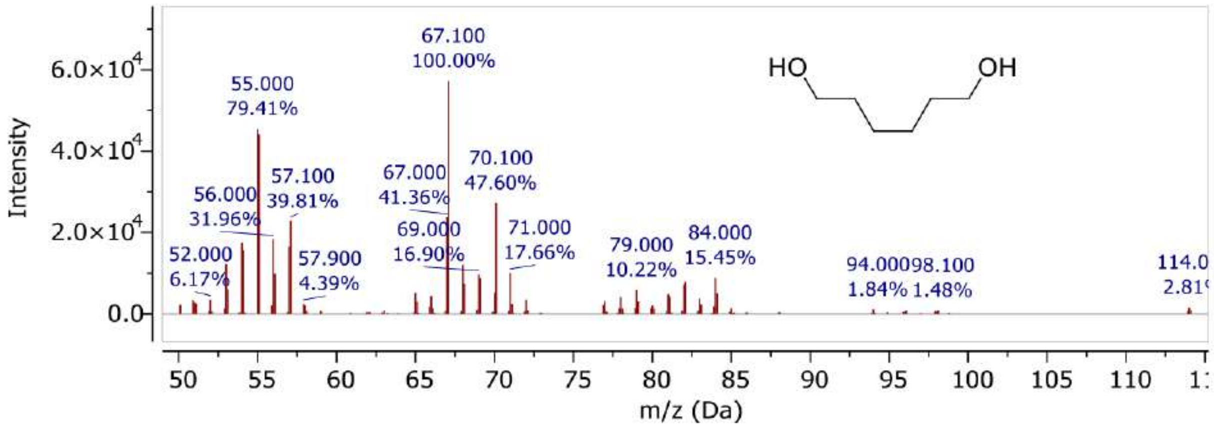


Figure S16. MS-EI spectrum (7.573 min) (Compared with library data).

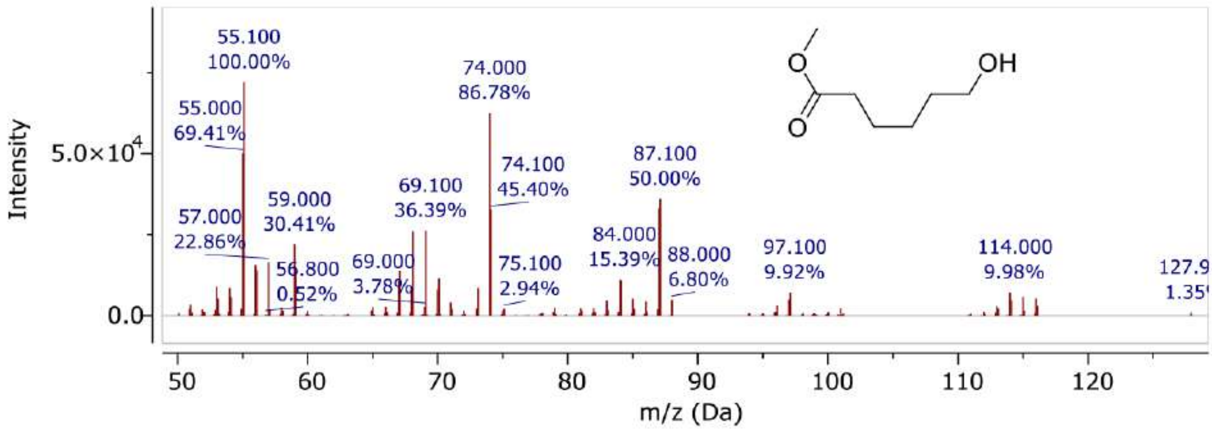


Figure S17. MS-EI spectrum (8.277 min) (Compared with library data).

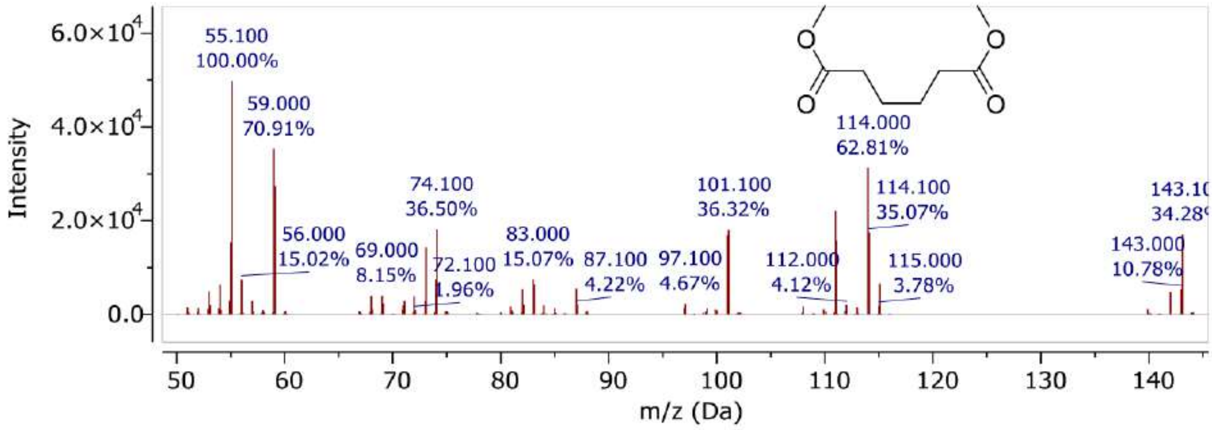


Figure S18. MS-EI spectrum (16.316 min).

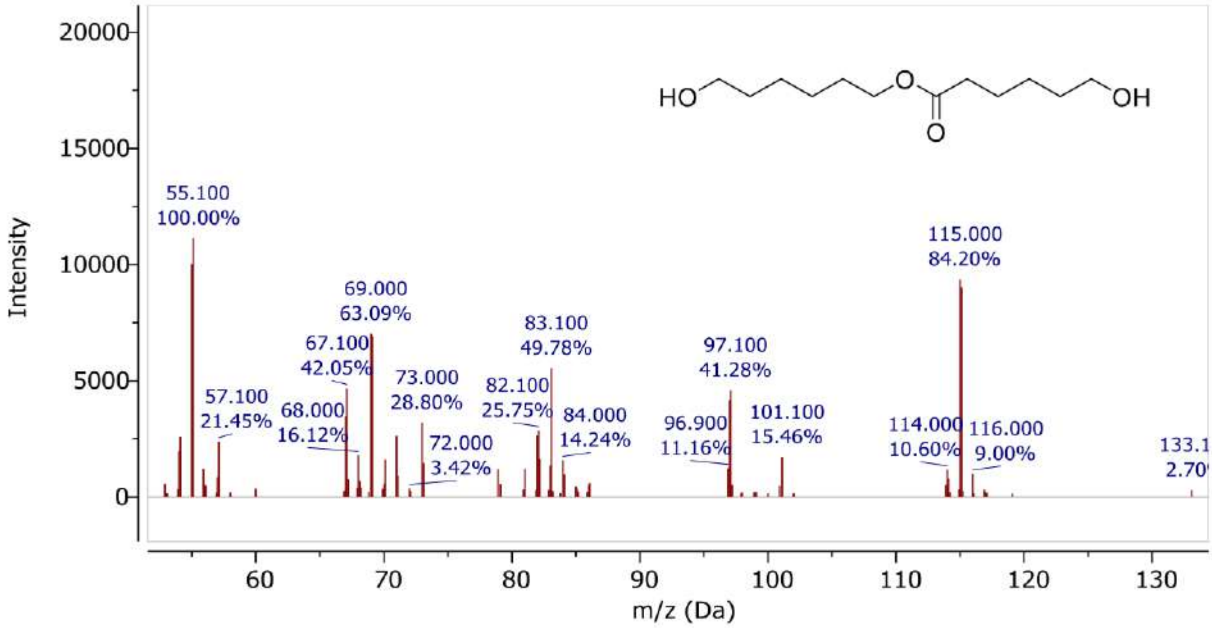


Figure S19. MS-EI spectrum (16.694 min).

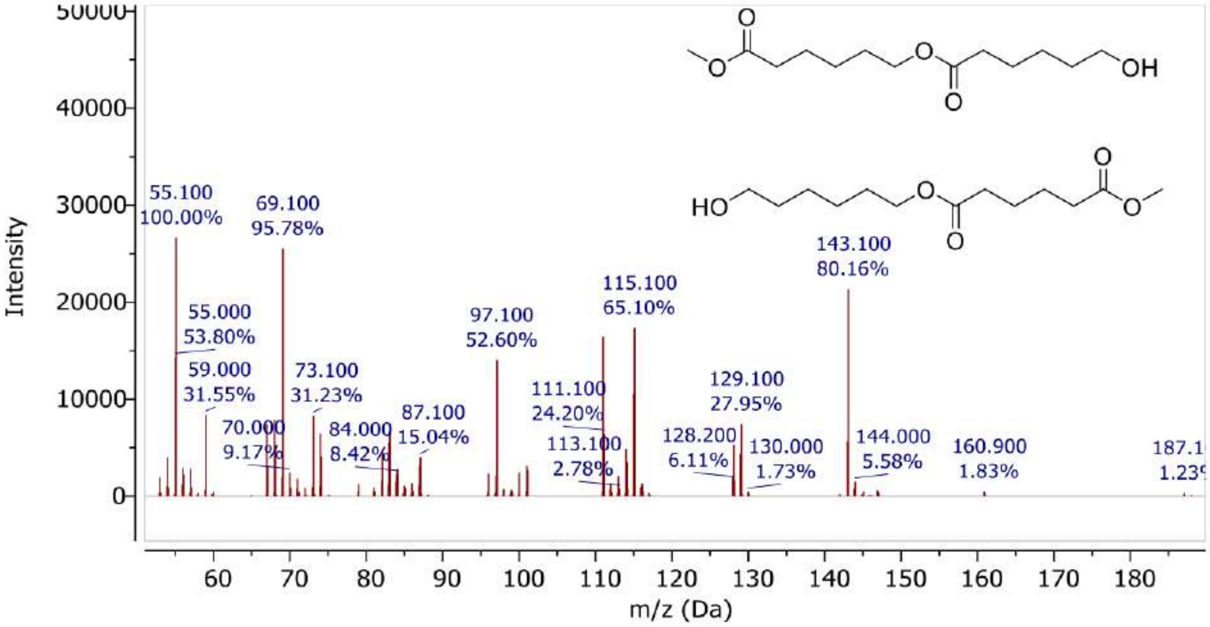


Figure S20. MS-EI spectrum (17.088 min).

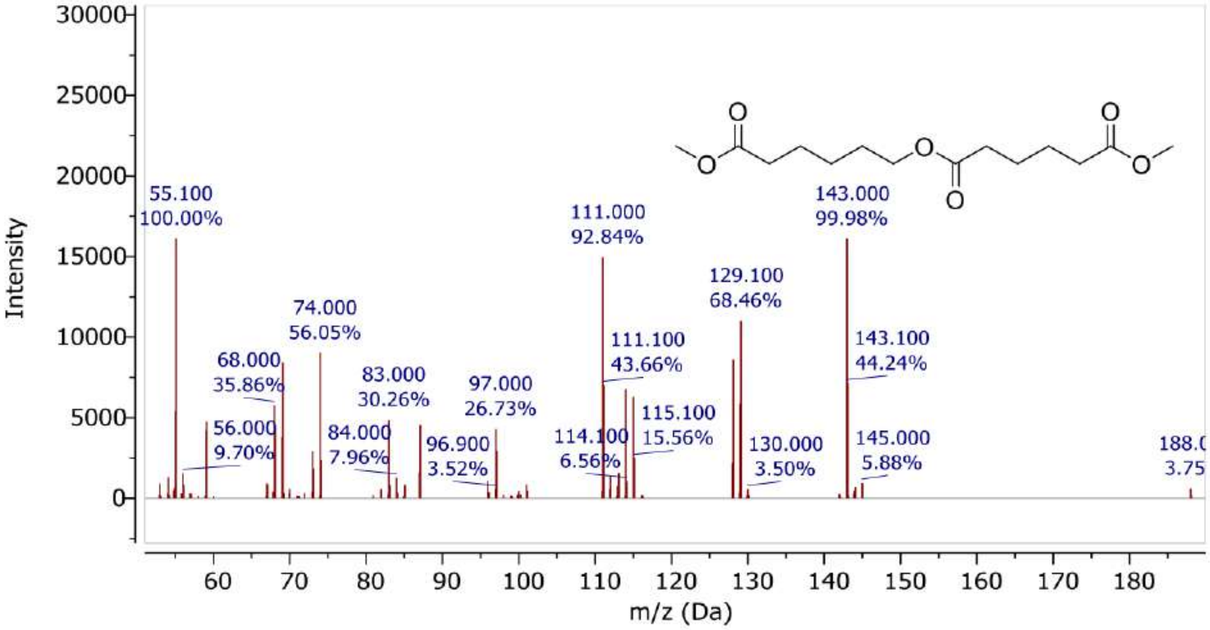


Figure S21. MS-EI spectrum (22.890 min).

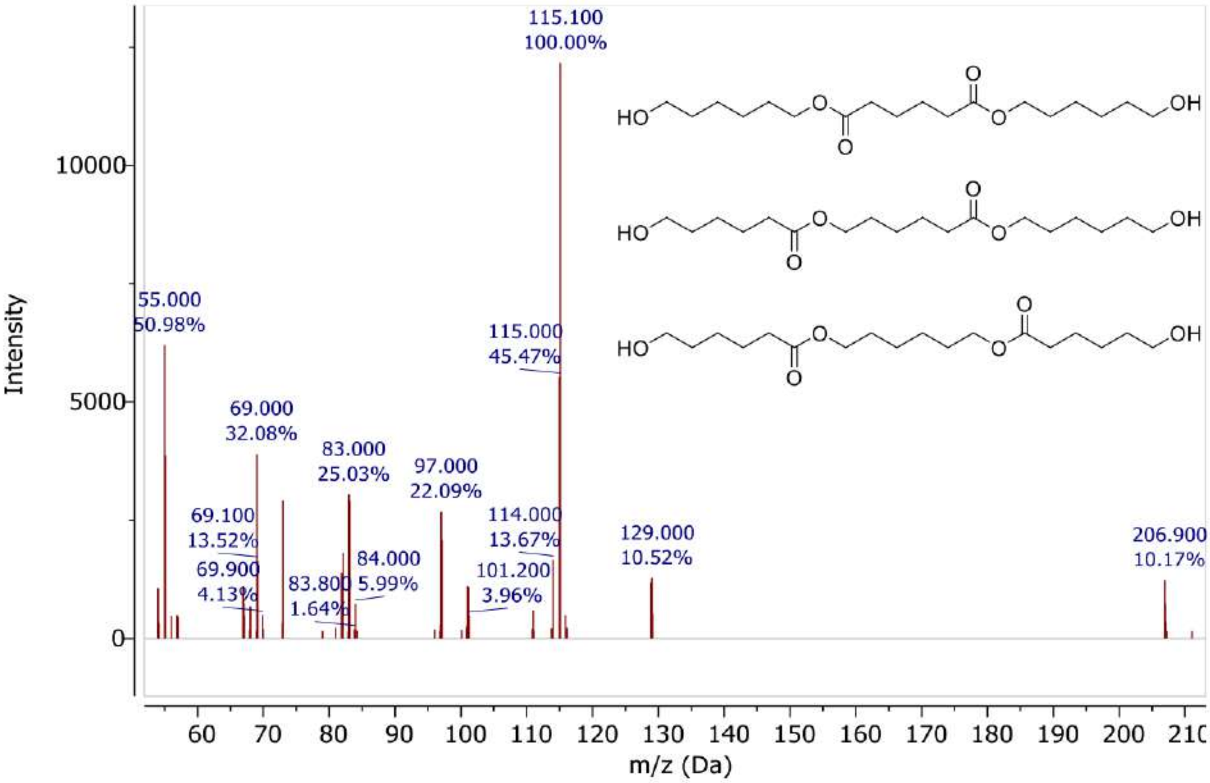


Figure S22. MS-EI spectrum (23.102 min).

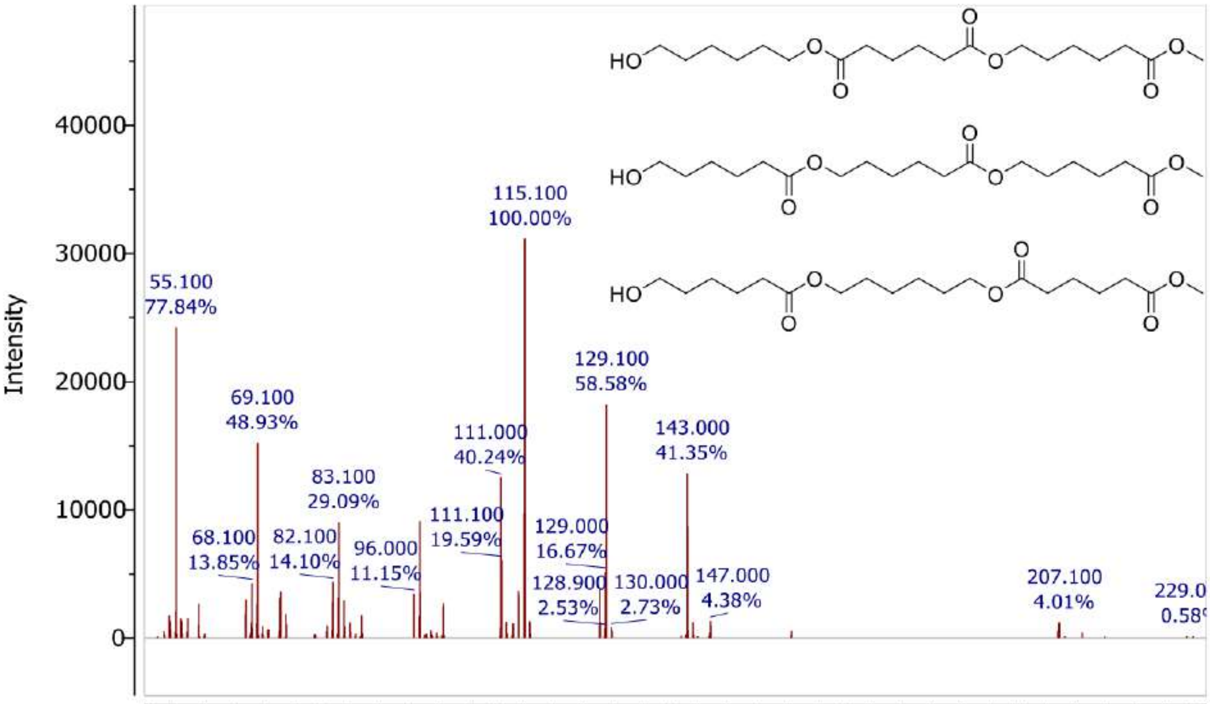
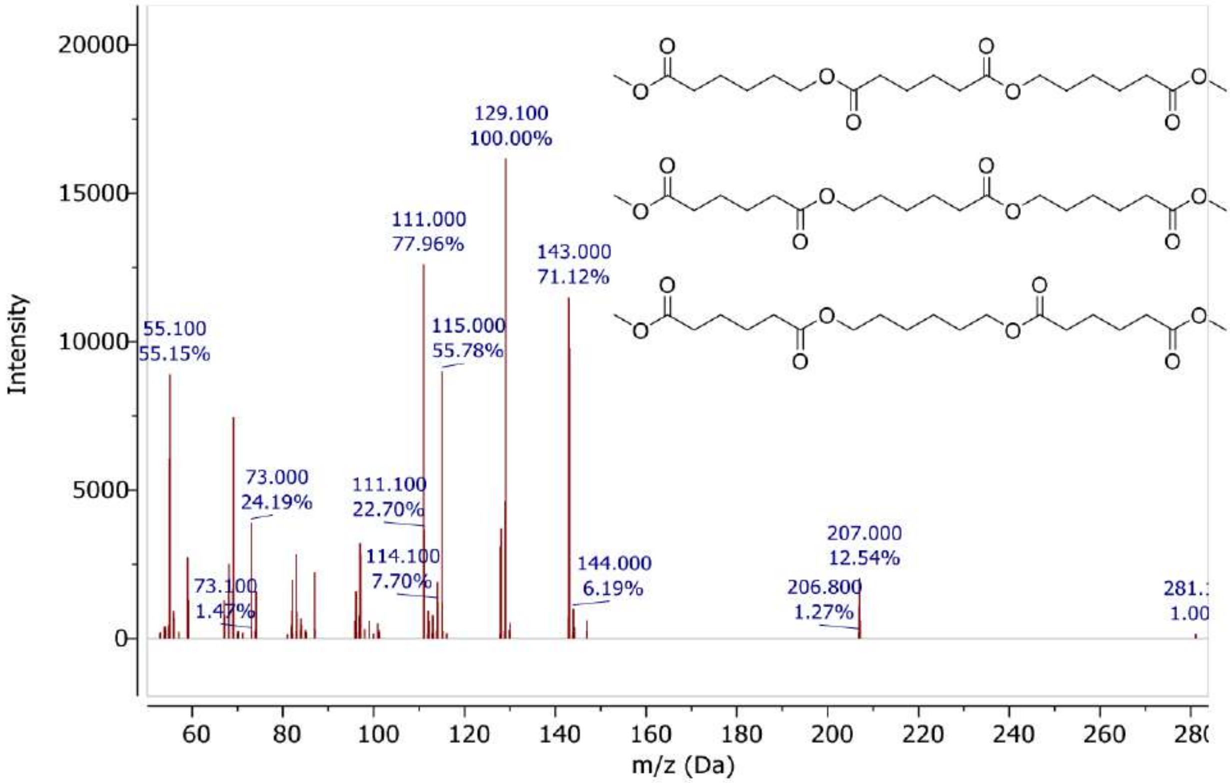
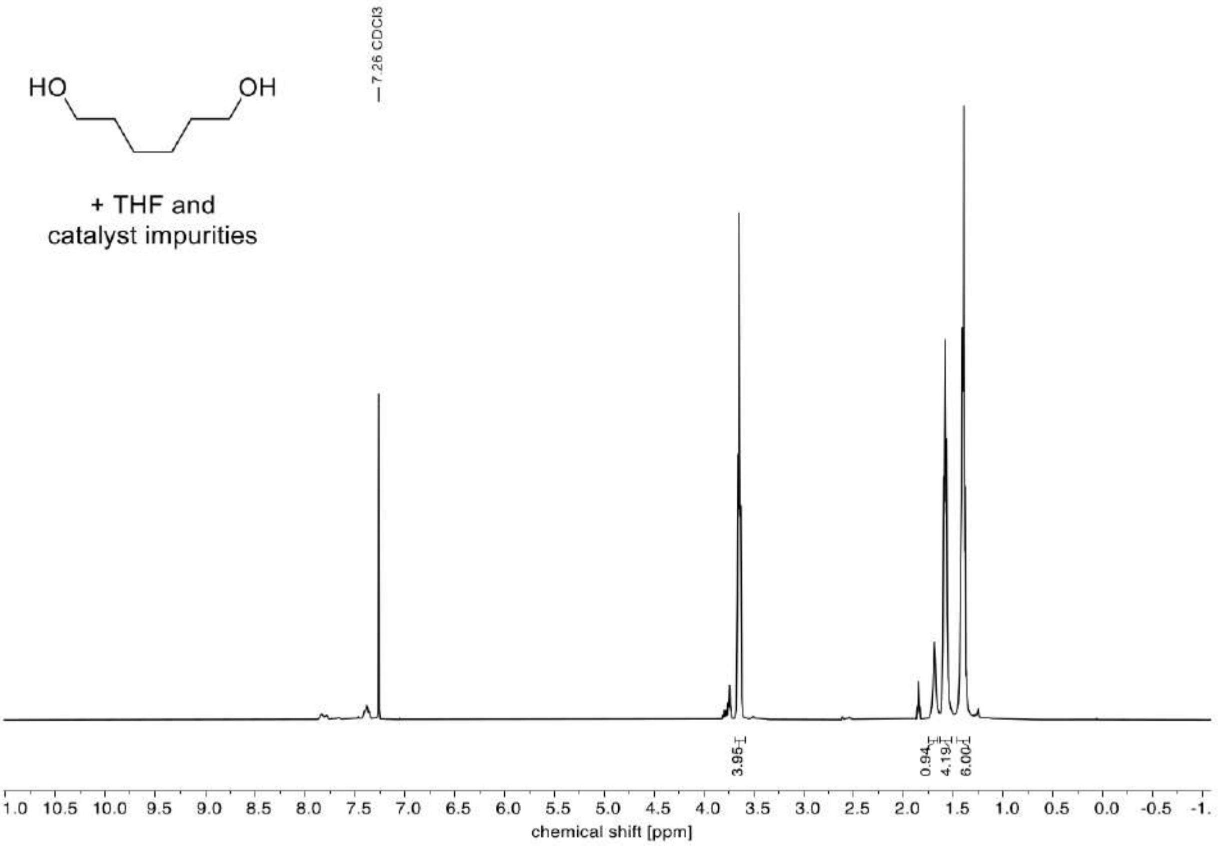


Figure S23. MS-EI spectrum (23.325 min).



Hydrogenation of 7: For the hydrogenation of **7**, the polymerization was carried out according to Table 2, entry 4 with subsequent removal of the solvent in vacuum. A mixture of the polyester (**7**) (50.2 mg, 0.44 mmol based on the repeating unit of **7**), catalytic amounts of complex **8** (12.9 mg, 22 µmol, 5 mol% based on the repeating unit of **7**) and THF (3 mL) was placed with a stir bar in a vial. The vial was placed in an autoclave, which was sealed and purged with hydrogen (5 times). Afterwards the desired hydrogen pressure was adjusted (45 bar) and the autoclave was heated to the 140 °C. The temperature was hold for 24 hours, while stirring the reaction mixture. Afterwards the autoclave was cooled to room temperature and the hydrogen pressure was carefully released. The solvent was partially removed in vacuum and a sample was transferred to a NMR tube and was dissolved in $CDCl_3$ (0.6 mL). The sample was subjected to ^1H NMR to determine the yield of 1,6-hexanediol (**2**). The ^1H NMR spectrum revealed a yield of >99% for diol **2**.

Figure S24. ^{1}H NMR spectrum of the reaction mixture after hydrogenation of **7** (400 MHz, $CDCl_3$, 25 °C).



References

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[1] Compared with an authentic sample.

10. Danksagung

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11. Eidesstattliche Versicherung

Hiermit versichere ich an Eides statt, die vorliegende Dissertation selbst verfasst und keine anderen als die angegebenen Hilfsmittel benutzt zu haben. Die eingereichte schriftliche Fassung entspricht der auf dem elektronischen Speichermedium. Ich versichere, dass diese Dissertation nicht in einem früheren Promotionsverfahren eingereicht wurde.

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