Synthesis, Characterization and Post-Modification of Hydroxyl-Functionalized Poly(propylene Carbonate)

Dissertation

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Dedicated to my family

I. List of publications

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II. Table of contents

III. List of abbreviations

AIBN	azobisisobutyronitrile
APCs	aliphatic poly(carbonate)s
ATRP	atom-transfer radical polymerization
BGE	benzyl glycidyl ether
CA	contact angle
CCS	carbon capture and sequestration
cPC	cyclic propylene carbonate
CHO	cyclohexene oxide
DMA	dynamic mechanical analysis
DMC	double metal cyanide (catalyst)
DSC	differential scanning calorimetry
EEGE	ethoxy ethyl glycidyl ether
GPC	gel permeation chromatography
IPN	interpenetrating polymer network
MDI	4,4'-diphenylmethane diisocyanate
OEGMA	oligo(ethylene glycol methyl ether) methacrylate
ONB	*o*-nitrobenzyl
PAPI	polyaryl polymethylene isocyanate
PBAT	poly(butylene adipate-co-terephthalate)
PBS	poly(butylenes succinate)
PC	polycarbonate
PCHC	poly(cyclohexene carbonate)
PCL	polycarprolactone

PPC-OHs	hydroxyl-functionalized poly(propylene carbonate)s
PPC-ONB	*o*-nitrobenzyl protected poly(propylene carbonate)s
PDI	molecular weight distribution
PE	polyethylene
PHBV	poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PHB	polyhydroxylbutyrate
PLA	polylactide, polyactic acid
PLLA	poly(l-lactide)
PO	propylene oxide
PP	polypropylene
PPC	poly(propylene carbonate)
PMMA	poly(methyl methacrylate)
PVC	poly(vinyl chloride)
RAFT	reversible addition-fragmentation chain transfer
ROP	ring-opening polymerization
SEM	scanning electron microscope
sIPN	semi-interpenetrating polymer network
TGA	thermogravimetric analysis
TAIC	triallyl isocyanurate
TBAB	tetrabutylammonium bromide
THF	tetrahydrofuran
TMS	tetramethylsilane
T_g	glass transition temperature
$T_{-5\%}$	temperature of 5% weight loss
$T_{-50\%}$	temperature of 50% weight loss
UV	Ultra-violet (light)

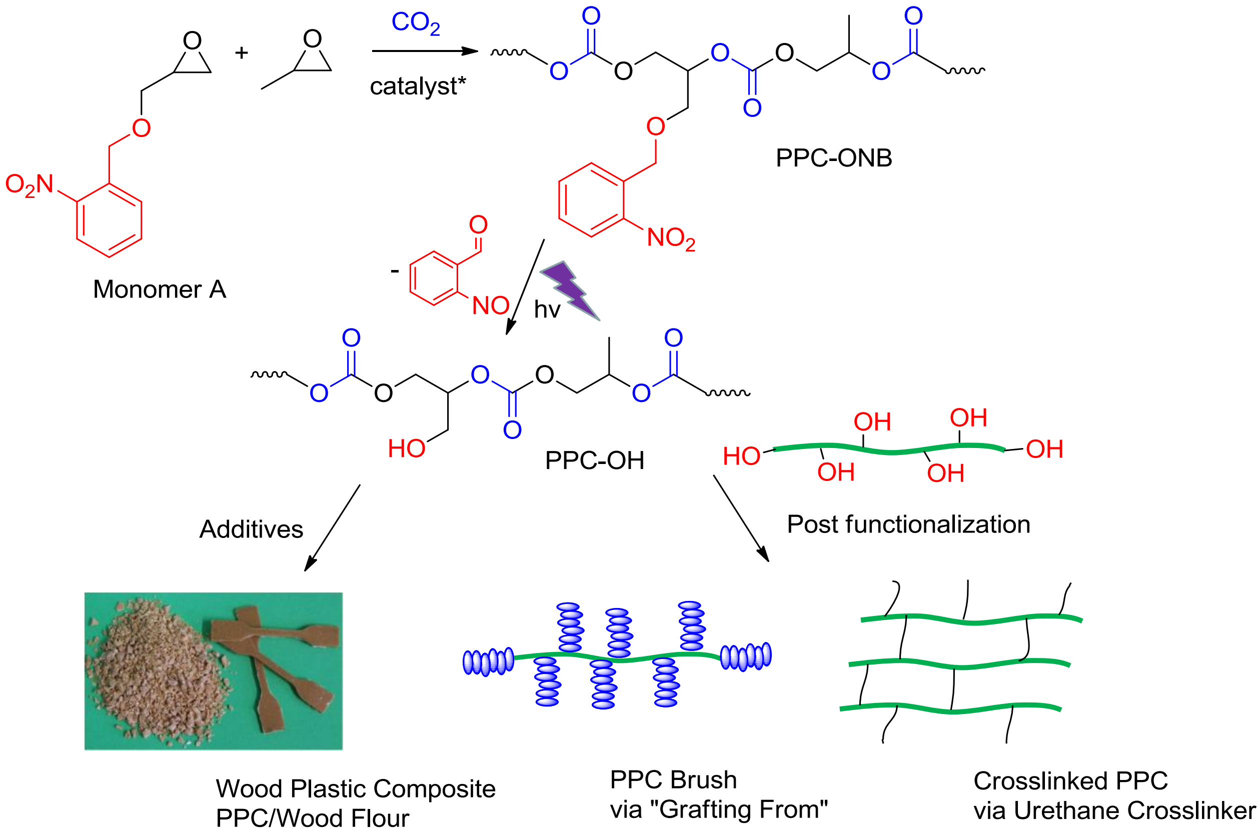
WPCs	wood plastic composites
ZnGlu	Zinc glutarate

1. Zusammenfassung

Hydroxyfunktionalisiertes Poly(propylencarbonat) (PPC-OH) wurde über eine zinkglutarat-katalysierte Terpolymerisation von Kohlenstoffdioxid, Propylenoxid und 2-[[(2-Nitrophenyl)methoxy]methyl]-oxiran (Monomer **A**) erhalten. PPC mit variierenden Gehälte an Monomer **A** (0-10.6%) wurde synthetisiert und konnten ohne Kettendegradation mit ultraviolettem (UV) Licht in hydroxyfunktionalisierten PPC überführt werden. Die Abspaltung der o-Nitrobenzyl (ONB)-Schutzgruppe wurde mit UV-Vis-Spektroskopie verfolgt und erfolgte innerhalb von Minuten. Thermische Eigenschaften und Kontaktwinkel von funktionalisiertem PPC wurden gemessen und zeigten eine erwartete Erhöhung der Hydrophilie und Glasübergangstemperatur mit einem höheren Anteil an Hydroxygruppen. Weitere Anwendungsstudien und Postmodifikation von PPC-OH wurden durchgeführt. PPC-OH wurde als Phasenvermittler in PPC/Holzmehl-Kompositen (70 Gew.-%PPC, 30 Gew.-% Holzmehl) (PPC-basierte *Wood Plastic Composites* (*WPC*)) untersucht. Die Zugfestigkeit der PPC-basierten WPCs wurde durch Zugabe von PPC-OH signifikant erhöht. REM-Bilder gebrochener Proben zeigten eine glattere Oberfläche in Anwesenheit von PPC-OH und lassen eine höhere Kompatibilität zwischen Holzmehlpartikeln und Polymermatrix vermuten. Die thermischen Eigenschaften, die Glasübergangstemperatur und Zersetzungstemperatur der Komposite mit und ohne PPC-OH sind identisch.

PPC-OH wurde modifiziert um PPC-Bürsten und Polymergele über polymeranalogen Reaktionen darzustellen. PPC-Bürsten in Form von PPC-graft-poly(PEOMA) mit kontrollierbaren Bürstenlänge und –dichte wurde über „Grafting from“ aus einem PPC-Makroinitiator dargestellt. Der Makroinitiator war über eine Veresterung von PPC-OH und 2-Bromoisobutyrylbromid zugänglich. Kovalente PPC-Netzwerke in Form von Dioxan-Gelen wurden über die Vernetzung von PPC-OH und 4,4‘-Diphenylmethandiisocyanat (MDI) hergestellt. Rheologische Messungen der Gele zeigten, dass die Netzpunktdichte linear mit der

Anzahl an Hydroxygruppen in PPC-OH zunimmt. Die folgende Figur zeigt den Inhalt dieser Dissertation schematisch.



Figur 1.1. Schematische Überblick über die in dieser Dissertation beschriebenen Entwicklungen.

2. Abstract

Hydroxyl-functionalized poly(propylene carbonate) (PPC-OH) was found accessible via a zinc glutarate catalyst mediated terpolymerization of carbon dioxide, propylene oxide and 2-[[(2-nitrophenyl)methoxy]methyl]-oxirane (monomer **A**). PPC with varying monomer **A** contents (0-10.6 %) were obtained and could be transformed into hydroxyl-functionalized PPC by ultraviolet (UV) light irradiation without backbone degradation. The process of removing the o-nitrobenzyl (ONB) protecting groups was monitored by UV-vis spectrometry and found to proceed within minutes. Thermal properties and contact angles of the functionalized PPCs were measured, showing the expected increase in hydrophilicity and glass transition temperature with increasing content of hydroxyl entities. Further studies on the application and post-modification of PPC-OHs were performed. Firstly, PPC-OHs were considered as compatibilizer in poly(propylene carbonate) (PPC)/wood flour (70/30) composites (PPC-based wood-plastic composites WPCs). Tensile strength of PPC-based WPCs with PPC-OHs present is significantly higher. SEM pictures of fractured samples show that PPC-based WPCs with PPC-OHs addition have a smoother surface and indicate a better compatibility of wood flour particles with polymer matrix. The thermal properties, Tg and decomposition temperature with and without PPC-OH of the composite are basically identical. Secondly, PPC-OHs have been modified to reach PPC-brush and cross-linked polymer gels through post-modification techniques. PPC-brushes in the form of PPC-*graft*-poly(PEOMA) were obtained with controllable brush length and brush density via “grafting from” a PPC-macroinitiator. Latter was prepared by esterification reactions of PPC-OH with 2-bromoisobutyryl bromide. PPC permanent networks in the form of dioxane gels were prepared by cross-linking PPC-OH with 4,4’-diphenylmethane diisocyanate (MDI). Rheological measurement of the gels show that the

cross-linking density scales linear with the hydroxyl group density in PPC-OH. The following figure shows the content of the thesis in a cartoon.

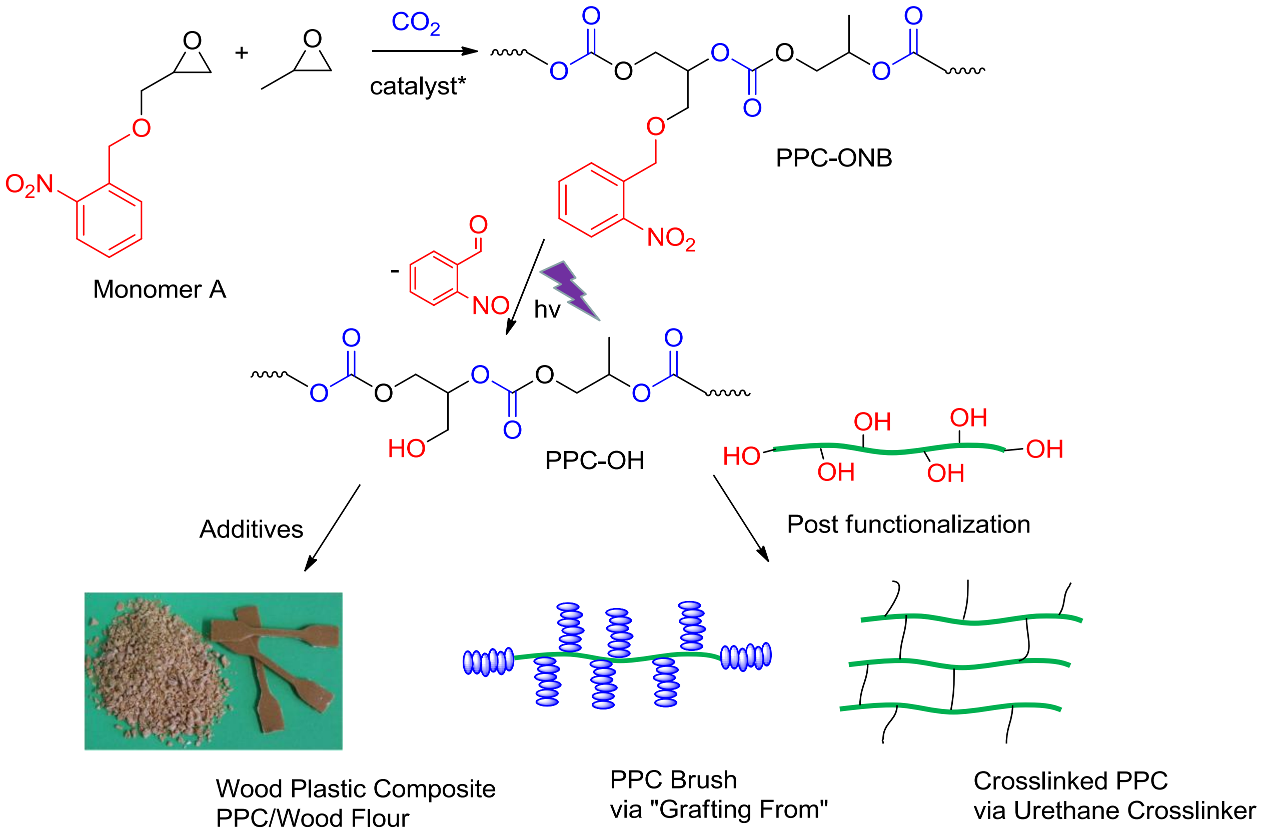


Figure 2.1. Schematic overview of the content of this thesis.

3. Introduction

3.1 Polymer Industry and Green Polymers

Development of Plastics

Since the perhaps first full synthetic polymer — Bakelite, - which was manufactured in 1910 - many polymers have been produced and applied in various areas, comprising electrical appliances as one important exponent.[1] These areas encompass packaging, clothing, automobile parts and light weight aircraft materials, furniture applications, data storage as e.g. magnetic tape and compact discs, surgical instruments. Thus over 288 million tons of plastics were produced and consumed globally in 2012.[2,3] However, as the industry continuous to grow fast, the future manufactures of plastics have to face one or more of the following worldwide challenges. I, plastics production are largely based on petrochemicals, which are derived from nonrenewable fossil resources. Annually, approximately 7% of worldwide oil and gas were consumed by polymer industry.[4] II, most polymers are non-degradable in a natural environment and thus may cause serious plastic pollution if not properly discarded, which has an exponent in form of "white pollution". The accumulation of plastic in the environment adversely affects wildlife, wildlife habitat, and humans.[5] The item of worldwide "white pollution" has attracted more and more attention with the increasing aware of a "natural and healthy" environment, and, also the scale has grown in volume due to increase in plastics usage. Because of the mentioned issues above, markets of biodegradable polymers which may be derived from renewable sources have become of interest to large chemical companies such as BASF SE, Showa Denko, WACKER and DOW Chemicals.[6] A life cycle model of biorenewable polymers shows the transfer of energy and the cycling of mass materials (Figure 3.1).

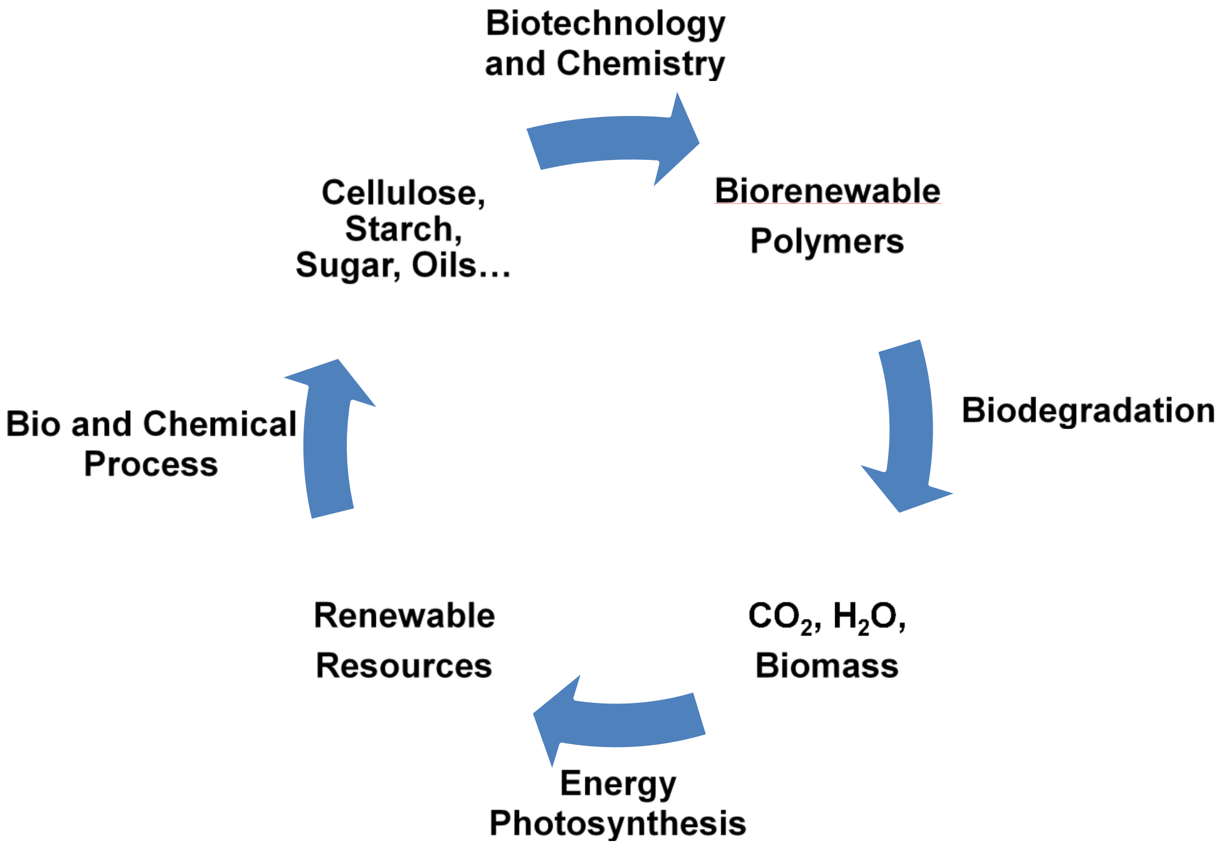
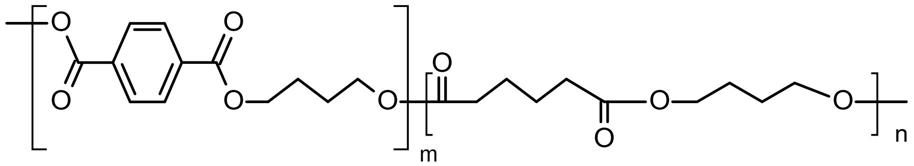


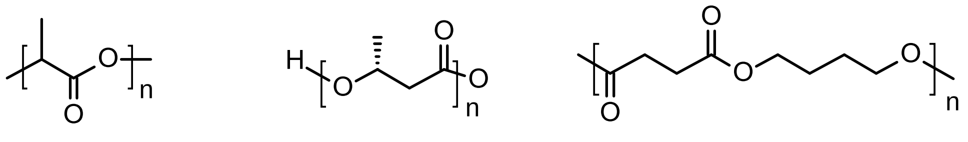
Figure 3.1 Life cycle model of biorenewable polymers according to European Bioplastics.[7]

Biodegradable Polymers

Biodegradable polymers are polymers that can be decomposed by bacteria or other living organisms. Biorenewable polymers are another category of biodegradable polymers whose components are derived from renewable raw materials. Recently, in order to reduce the global plastic pollution, more and more attention has been directed to develop the market for biodegradable polymers.[8,9] Indeed, “green polymers” in form of poly(butylene adipate-co-terephthalate),[10] polylactide, poly(butylenes succinate),[10] poly(3-hydroxylbutyrate)[11] and poly(carbonates)[4,12] are finding some applications in packaging, clothing, carpets and also in automotive engineering, films, and utilities in agriculture. CO_2 based polymers seem attractive due to their advantages of producing biodegradable polymers through utilization of the abundant greenhouse gas – CO_2.[13–15]



Poly(butylene adipate-co-terephthalate)
PBAT



Polylactic acid
PLA

Polyhydroxybutyrate
PHB

Polybutylene succinate
PBS

Figure 3.2 Chemical structures of commercialized biodegradable polymers

3.2 Chemical Synthesis Using CO_2

As reviewed by Aresta, Kühn et al., CO_2 can be activated and used as alternative carbon resource to petrochemicals in chemical industry.[16,17] Annually 125 million ton of CO_2 is industrially utilized as carbon resource for the production of urea-based compounds, methanol and other chemicals.[17,18] Comparing to the anthropogenic production of 38 billion ton per year, CO_2 is an abundant and basically inexhaustible carbon resource for chemical industry.[19] CO_2 is considered as a contributor to the unpopular greenhouse effect next to methane.[20–23] Chemical operations using CO_2 could reduce the global CO_2 emission and thus be a future basis for chemicals.[24,25] Therefore, chemical synthesis using CO_2 has the benefits of producing valuable chemical products and perhaps reducing global CO_2 emission, provided non-fossil based energy is available.

3.3 Polycarbonates Synthesis via Carbon Dioxide and Epoxides

Synthesis of copolymers from CO_2 could be an ideal method that has the potential to solve the combined problems mentioned above. Several polycarbonates can be synthesized by the alternating copolymerization of CO_2 and epoxides[26,27] (Figure3.3). The synthesis of polycarbonates from CO_2 was first reported by professor Inoue in 1969.[28] In the following decades, significant efforts have been devoted to develop of catalysts, adjust material properties and find applications.[4]

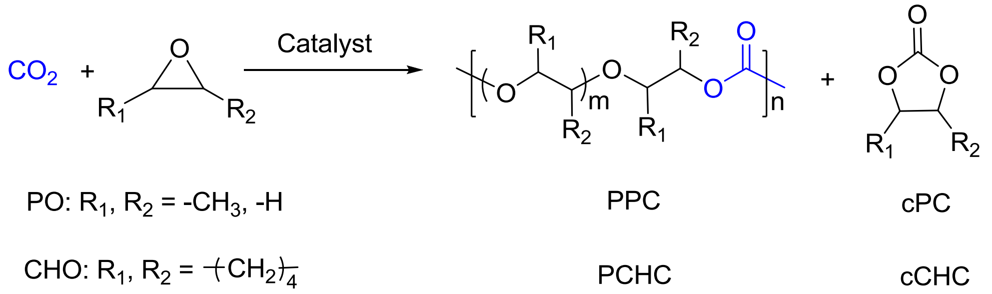


Figure 3.3 Synthesis of polycarbonates from coplymerization of CO_2 and epoxides

Poly(cyclohexene carbonate) (PCHC) and poly(propylene carbonate) (PPC) are the most studied CO_2 based polycarbonates. Compared to PCHC which is generally synthesized by the copolymerization of CO_2 and cyclohexene oxide, PPC has advantages in forms of i) price: propylene oxide is available in large volumes and far cheaper than the specialty chemical cyclohexene oxide and ii) material properties: PCHC is too brittle for application as material (elongation at break of 1-2%).[15] PPC shows some useful properties, high transparency, UV stability, biodegradability and good oxygen and water barrier properties.[29] Therefore, PPC may be considered as the most interesting CO_2 based polycarbonate and also the only commercially available polycarbonates from copolymerization of CO_2. [30,31]

3.4 Copolymerization Mechanisms

The copolymerization mechanism of propylene epoxide/CO_2 was studied with experimental and computational simulation methods. The basic mechanism of epoxide and CO_2 copolymerization is proposed to occur via a coordination and nucleophilic addition.[6] The initiation and propagation steps involved in the coupling of epoxide and carbon dioxide are shown in Figure 3.4. The copolymerization is initiated by coordinating the epoxide and externally attacking it with the nucleophilic group, X (halide, carboxylate), leading to epoxide ring-opening and formation of a metal bound alkoxide. The next step is CO_2 insertion and a metal carbonate is formed in the two monomers propagation process. The copolymerization process leading to 100% carbonate linkages is shown: a metal alkoxide is reformed after epoxide opening, and then followed by CO_2 insertion to form a further metal carbonate. During this propagation cycles, the formation of ether linkages through homopolymerization of epoxides is commonly observed, especially for heterogeneous catalysts based on zinc and other weaker Lewis acids. In addition, cyclic propylene carbonate by-product (cPC) could be formed by one or two back-biting routes. These cyclic propylene carbonates are thermodynamically stable five-member ring that do not undergo spontaneous ring-opening polymerization in the copolymerization process. Chain transfer reactions are observed in the presence of alcohols or water, forming hydroxyl terminated copolymer chain and new metal alkoxide/hydroxide species. Since chain transfer reactions can reduce the number of repeating units of polycarbonate chain, hydroxyl end-capping polycarbonates with lower molecular weight would be obtained. Latter could be applied as polyols for the preparation of polyurethane.[4]

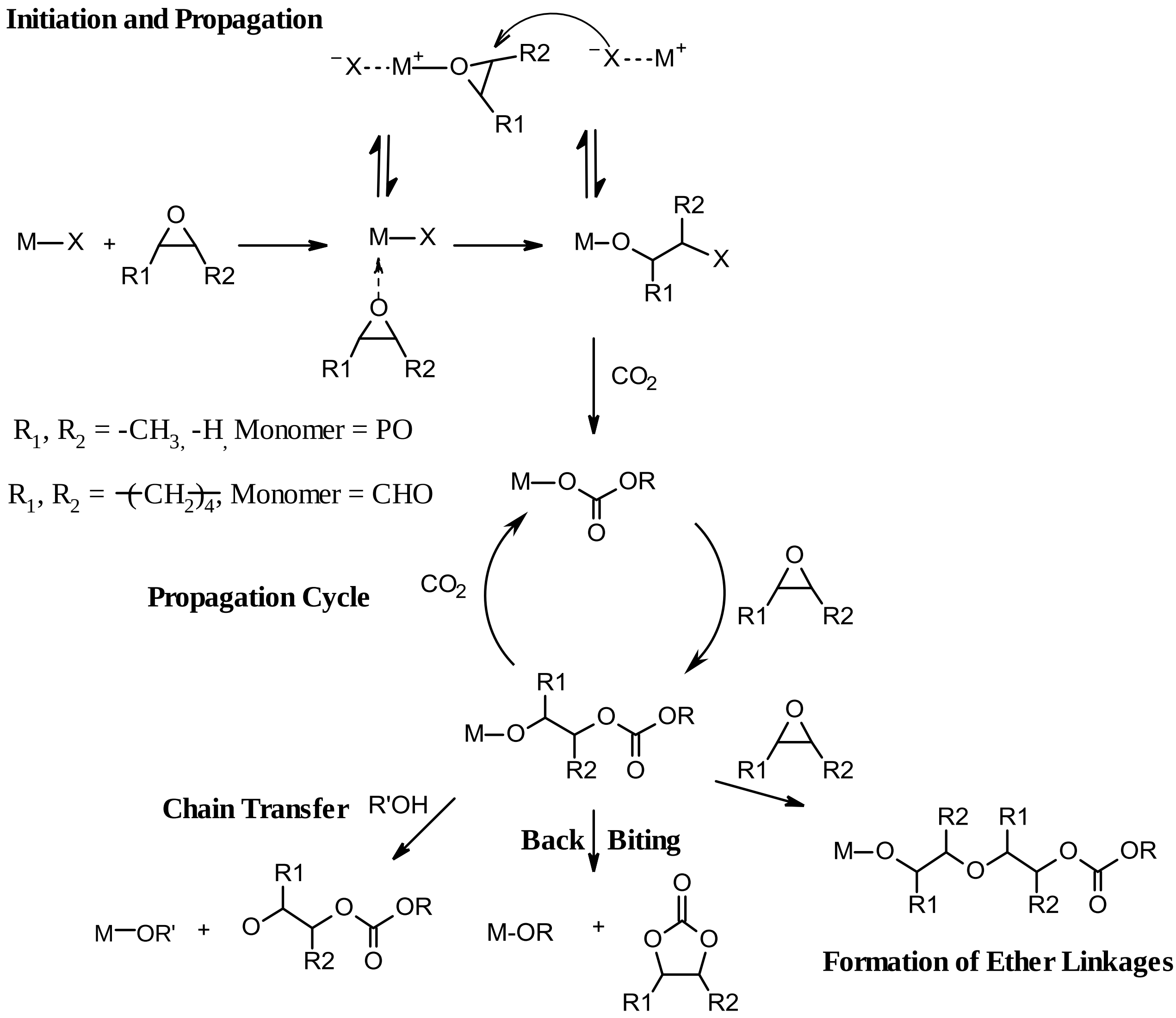


Figure 3.4 Alternating copolymerization of cyclohexene oxide (CHO) and propylene oxide (PO) with CO_2. a, poly(propylene carbonate) (PPC); b, poly(cyclohexene carbonate) (PCHC)

3.5 Copolymerization Catalysts: Homogeneous and Heterogeneous Catalysis

The formation of high molecular weight CO_2 copolymers and production process are critically dependent on the catalyst. Although the copolymerization reaction of CO_2 and epoxides has been known for half a century, preparation of various catalysts with higher activity and selectivity is still one of the major difficulties for commercialization of CO_2 copolymers.

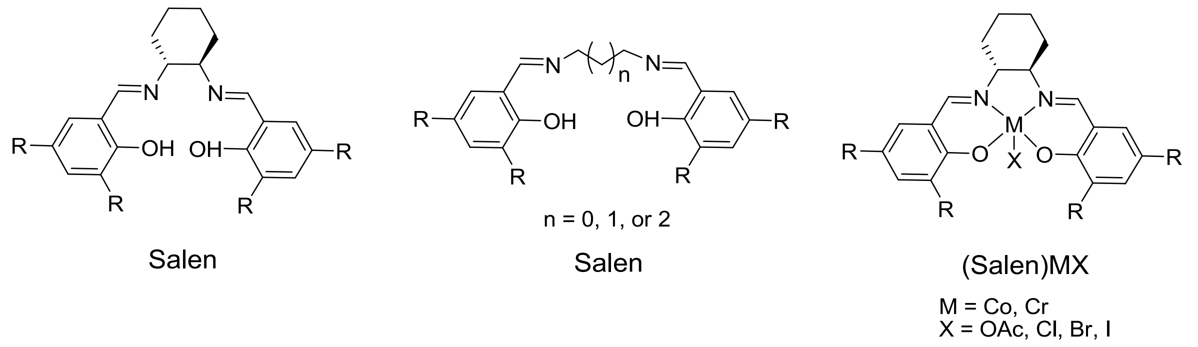
Homogeneous CO_2-epoxide copolymerization catalysts are reported in many papers. They in part have a high activity and selectivity and the ability of producing polymer with generally narrow molecular weight distribution. Their action is understood in terms of structure/activity relationships. Williams[4] notes the following major developments in homogeneous catalysts of CO_2-epoxides copolymerization: the zinc β-diiminate complexes by Coates et. al; the bimetallic complexes by Lee, Lu et. al; the chromium/cobalt salen complexes by Lu, Darensburg, Holmes, Jacobsen et al. These catalysts allow a CO_2-epoxide copolymerization under low pressure of CO_2, with greater higher activity and selectivity [4,32–35] (decades higher) for various epoxides. [33,36]

Studies of (salen)Cr(III) and Co(III) complexes ((salen)MX) have led to the following findings in homogeneous catalysts for copolymerization of CO_2 and epoxides. The major progresses are summarized as follow:

I. (salen)MX catalysts shows very high selectivity for the copolymer production (with greater than 97% carbonate linkages;

II. Copolymers with high molecular weight and narrow molecular weight distributions are produced via (salen)MX catalysts;

III. (salen)MX catalysts show high activity at higher temperature (90 ^oC), for the copolymerization of special epoxide/CO_2 monomers such as styrene oxide.



Salen

n = 0, 1, or 2
Salen

(Salen)MX
M = Co, Cr
X = OAc, Cl, Br, I

Figure 3.5 Complete and partially reduced salen ligands and (salen)MX catalysts

Heterogeneous CO_2-epoxide copolymerization catalysts did not received so much attention recently, mainly due to the difficulty of studying the active sites as well as reaching a structure/activity relationships that would allow catalyst design. Compared to homogeneous CO_2-epoxide copolymerization catalysts, heterogeneous catalysts generally have lower activity and giving production with a wide molecular weight distribution (PDI).[4,15] Research interests on heterogeneous CO_2-epoxide copolymerization catalysis are mainly focus on zinc glutarate[37–39] and double metal cyanides (DMCs) catalysts.[40–42] Due to the research work in new synthesized nano-scale zinc glutarate by Luinstra et al.,[43,44] the activity of heterogeneous zinc glutarate catalysts was improved to over 3 kg PPC per gram zinc. Zinc glutarate catalysts are also adopted for the copolymerization in my work in this thesis.

Comparing to homogeneous catalysts, zinc based heterogeneous catalysts have the advantages as follow:

I. Zinc glutarate complex are easy to prepare and handle, cheap, especially for kiloton scale production of PPC;

II. Zinc glutarate catalyst with higher catalytic activity has become available and has the potential for further improvement;

III. PPCs produced from zinc glutarate catalysts are colorless and contain no heavy metal residues.

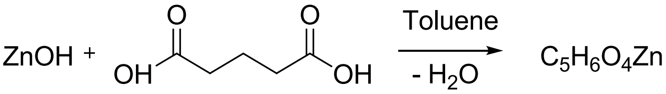


Figure 3.6 Zinc Glutarate synthesis

3.6 Material Properties of Poly(propylene carbonates)

The industrial preparation of PPC has recently reached the volume of over 3,000 ton/year. New PPC plants with productivity of 10,000 ton/year were commissioned recently by China BlueChemical Ltd and Inner Mengxi High-Tech.[45] PPC did not reach large scale industrialization mainly due to the catalyst activity and the "challenging" material properties. The thermal and mechanical properties have restricted the application areas of PPC, mainly because of the easy depolymerization by unzipping and a glass temperature just above room temperature.[15]

PPC starts decomposition via backbiting or unzipping at about 150°C (depending on the route of synthesis and purity). The main decomposition product, cyclic propylene carbonate (cPC) has an atmospheric boiling point around 240 °C. According to the mechanism of the thermal decomposition, the chain ends hydroxyl groups play a role in the decomposition process. Hence, end-capped PPC has an increased decomposition temperature and higher thermal stability.[46,47]

Generally, factors such as the average molecular weight, the molecular weight distribution, and the ether linkage content affect the glass transition temperature of PPC. The glass transition temperature of 35 °C to 45 °C of PPC is too high for usage as elastomer and too low for being used as thermoplastic material. Thus, as put forward by Luinstra et al.,[15] the material property of PPC is unlike that of any large-scale applied thermoplastic polymers and of elastomers including rubbers. To overcome the above disadvantages and to broaden the application area of PPC, there mainly are three approaches:

i) prepare PPC based composites with inorganic fillers such as $CaCO_3$ and glass fibers;[48,49]

ii) prepare blends of PPC with natural starch polymers [50–53] or with other biodegradable stiff polymers such as PHB[54], PHBV[55–57] or PLA[58];

iii) terpolymerize CO_2 and further epoxides to synthesize polycarbonates with advanced properties.[59–63]

3.7 Terpolymerization Polycarbonates and Functionalized Polycarbonates

One way to adjust PPC-polymer properties is to terpolymerize CO_2 and PO with further epoxides. Generally, terpolymer or block copolymer could be prepared through either simultaneously or sequentially polymerization.[4,64] This route relies on the polymerization reactivity of the epoxides. Usually only those without particularly polar functional groups are comparable in coordination strength to the catalyst.[65–67] Hence, derived polymers with very hydrophilic groups (OH, COOH) are usually not accessible directly by a terpolymerization. Terpolymerizations of PO, CHO and CO_2 have been studied under various conditions and catalysts, with various composition ratios to tune the terpolymer properties, e.g. by Darensbourg et al.[59,60,68]

Preparation of "functionalized" poly(propylene carbonate) is an attractive method to modify the polymer microstructure and therefore to tailor the physical and chemical properties for specific applications. Beside copolymerization CO_2 and epoxides with functional groups as mentioned above, another method is introducing functional groups into PPCs by post-functionalization approaches. However, due to the saturated CH and carbonate entities in the backbone, poly(propylene carbonates) are not easily modified. Therefore, preparation of functionalized PPCs bearing functional groups has at least two advantages: I, the option to tailor the structure and therefore improve the properties of PPC based polymers; II, provide potential for post-polymerization modification of functionalized PPC to synthesize new PPC based polymers.

One efficient route of introducing OH or COOH entities is indirectly via de-protection of protecting groups after terpolymerizaton as shown in Figure 3.8. For example, derived polymers with the hydrophilic groups OH or COOH are usually synthesized via ethoxy ethyl glycidyl ether (EEGE) or benzyl glycidyl ether (BGE) as protecting groups (Figure 3.7). As reported by Frey et. al, poly(1,2-glycerol carbonate) was synthesized by copolymerization of CO_2, EEGE or BGE and subsequent deprotection.[64,69–71] However, the deprotection process in acid or base usually results in a degradation of the reactive PPC backbone.[72] Therefore, in this thesis we set out to develop a facile route to synthesize hydroxyl-functionalized poly(propylene carbonate) (PPC-OH) without the risk of backbone degradation. One possible technical pathway is using ultraviolet light (UV light) cleavable *o*-nitrobenzyl (ONB) protecting group for this purpose.[73–77]

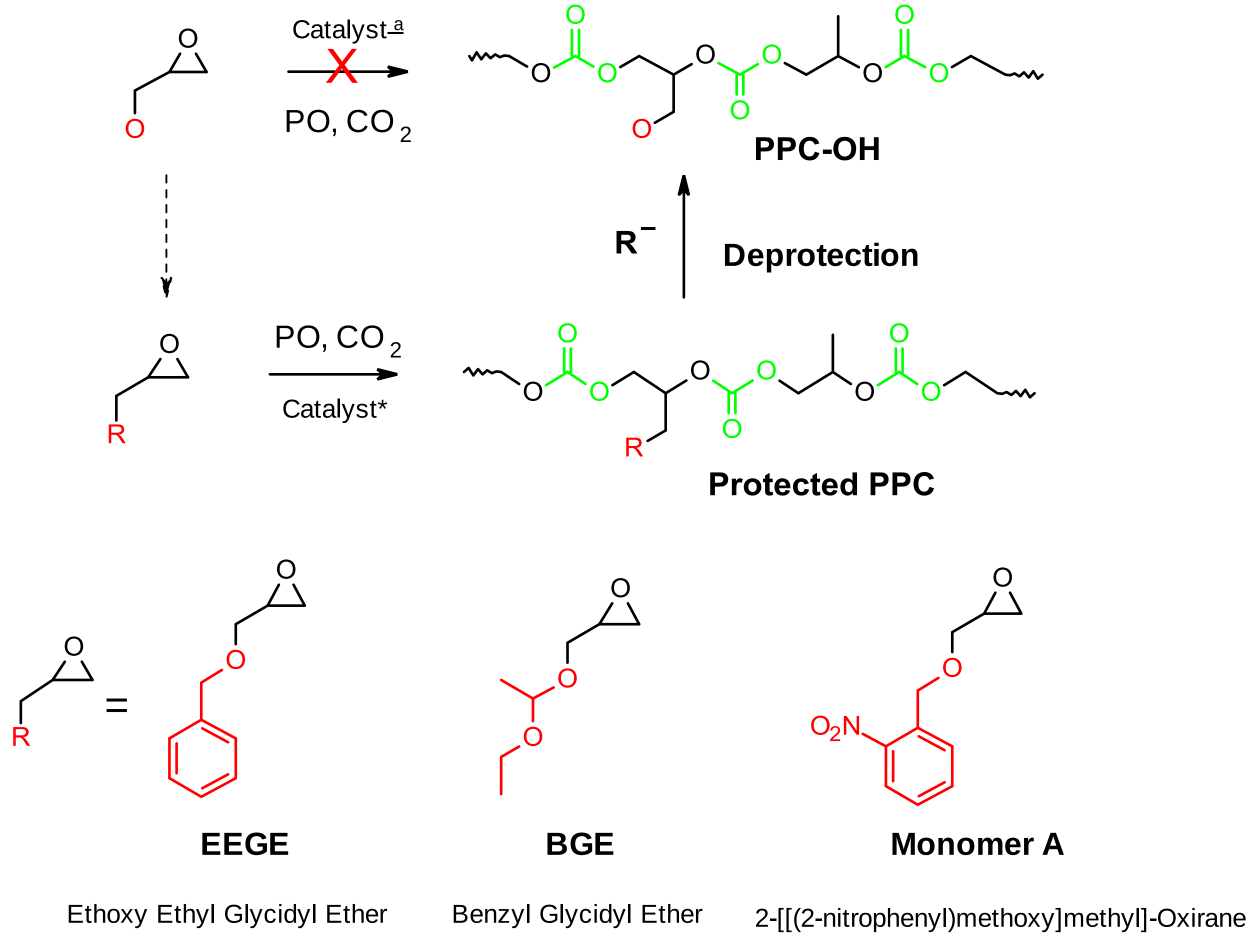


Figure 3.7 Synthetic routes reported and proposed method via photo chemistry to linear hydroxyl-functionalized poly(propylene carbonate)

3.8 Hydroxyl-Functionalized Poly(propylene carbonate)

Aliphatic poly(carbonate)s (APCs) are known biodegradable polymers and have been introduced as integral components of e.g. engineered tissues, medical devices and drug delivery systems.[13,32,33,72,78–82] Tuning the hydrophilic properties of APCs in that regard is important and has been challenging for the fact that the relatively hydrophobic APCs are not easily modified in a post-polymerization process, i.e. functional groups are not easily introduced to the backbone that contains only saturated CH and carbonate entities. There are two established polymerization methods for obtaining functionalized and more reactive APCs, (i) by ring-opening polymerization (ROP) of designated cyclic carbonates[12,32,69,78,83–91] and (ii) by copolymerization of carbon dioxide with functional epoxide comonomers[33,92–97]. Both routes rely on catalysts, which tolerate only a limited number of types of functionalities, and usually only those that are comparable in coordination strength to epoxides and carbonates and thus are not particular polar. A post-polymerization functionalization of the thus prepared functionalized APCs is therefore an efficient route to attain derived polymers with very hydrophilic groups (OH, COOH).[33,71,92,98] This process would allow tailoring the physical and chemical properties of the products for specific applications.

Hydroxyl-functionalized APCs with three or more carbon atoms between the carbonate entities were thus accessible by a sequence of copolymerization of functionalized cyclic carbonates with caprolactone, mediated by stannous octoate and subsequent modification.[70,99,100] Catalysts for preparing APCs with two carbons between the carbonate units from epoxides (majorly propylene oxide) and carbon dioxide have been improved in activity and tolerance of functional groups ever since the first report on poly(propylene carbonate) (PPC) from the alternate copolymerization of carbon dioxide and propylene oxide in 1969 with a catalyst prepared from diethyl zinc and water.[28,33,92] Homogeneous catalysts having metal centers including Cr(III), Co(III), rare earth metal and zinc atoms[4,13,92] are known for their “relatively” high activity and to yield polymer with high carbonate linkage content.[4,16,33,43,44,92,101–103] Also catalysts for stereoselective copolymerization have been reported.[13,104] Some of these catalysts give also access to polycarbonates with functional groups if starting from mixtures of (modified) epoxides.[33,71,102,105]

PPC has been a polymer of continuous interest and newly aroused more interest from chemical industry as well as environmentalists due to its utilization of CO_2 as carbon resource.[13–15] Large scale PPC production capacities have recently been reported, while their application fields remain still comparatively limited.[45] The latter is mainly related to the material properties: benchmarking these to commodity market requirements reveals challenges, in particular the unusual glass transition temperature of about 40 °C, which leads to cold flow at ambient temperatures.[15,29] Introduction of crosslinks would improve the dimensional stability of PPC, for example by the formation of urethanes after reaction with diisocyanates of backbone bound functionalities.[106–109] Therefore we set out to develop a facile route to synthesize hydroxyl-functionalized PPC without the danger of loss in molecular weight. We considered the ultraviolet light (UV light) cleavable o-nitrobenzyl (ONB) protecting group as an effective option for that purpose.[73–77] As shown in Figure 3.8, a series of functionalized PPCs were thus synthesized by terpolymerization of CO_2, PO and ONB-protected glycidol. Cleavage imposed by UV light irradiation leads to hydroxyl-functionalized PPCs without backbone degradation.

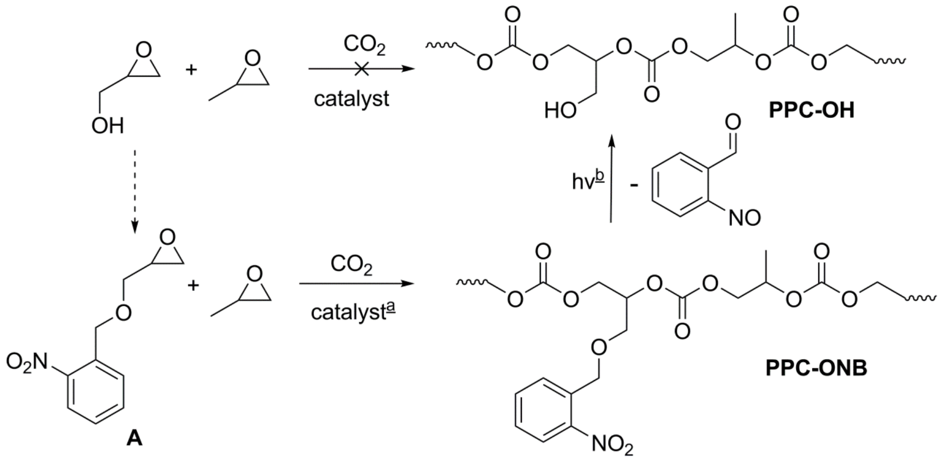


Figure 3.8 Synthesis of hydroxyl-functionalized poly(propylene carbonate). a) zinc glutarate catalyst; b) UV light irradiation with 313 nm UV light

3.9 PPC Based Wood Plastic Composites

Poly(propylene carbonate) (PPC) was synthesized firstly by Inoue *et al.* in 1969 by copolymerization of carbon dioxide (CO_2) and propylene oxide (PO).[28] Recently, PPC has gained a continuous interest from chemical industry and environmentalists due to its content of cheap "greenhouse gas" CO_2 as carbon resource and its application as a biodegradable polymer without causing "white pollution".[13–15] Although, a body of catalysts with highly improved activity have been reported in the past decades,[4,16,33,44,92,102,103,110] there are still a number of challenges for a reliable large scale industrial application of PPC.[45] Besides catalysts with higher activity, the main challenges for PPC application are PPC's low thermal stability and poor mechanical property compared to commodity polymers.[15] The field for applying PPC has been developed comprising the following general methods: i) to blend PPC with other polymers,[111,112] e.g. polyhydroxylbutyrate (PHB),[113] polycaprolactone (PCL), polyactic acid (PLA),[58,114] PMMA,[115] et. al.; ii) to fill PPC matrix with inorganic and organic fillers,[50,53] e.g. $CaCO_3$, starch, wood flour, et. al.; iii) to synthesize PPC derivatives by terpolymerization with a second epoxy monomer,[93,98,116] e.g. styrene oxide,[105,117] cyclohexane oxide[118]. As a result, PPC's thermal and mechanical properties have been largely enhanced and more research in this field is necessary for the reasons mentioned above.

One important goal is approaching the preparation of PPC-based wood plastic composites (WPCs).[119–122] Generally, WPCs are composite materials prepared by blending of wood flour and thermoplastics, e.g. with recycled polyethylene (PE), polypropylene (PP), poly(vinyl chloride) or (PVC).[122–126] PPC-based WPCs has the expectation of complete biodegradability with extended mechanical properties relative to PPC.[8] The miscibility of hydrophilic wood flour and hydrophobic PPC may restrict the attainable mechanical properties of PPC-based WPCs.[55,58,111,113,127,128] Addition of a suitable compatibilizer in PPC-based WPCs could improve the compatibility of the components and eventually enhance the mechanical properties.[50,115,129] Hydroxyl-functionalized poly(propylene carbonate)s (PPC-OHs) were synthesized by a zinc glutarate catalyst mediated terpolymerization of PO, CO_2 and 2-[[(2-nitrophenyl)methoxy]-methyl]oxirane in chapter 3. PPC-OHs are more hydrophilic than PPC because of the primary hydroxyl groups.[130] The polycarbonate backbone of PPC-OHs should have good compatibility with PPC and other polyesters.[29] Hence, the application of PPC-OHs as compatibilizer in PPC-based WPCs would probably enhance the interaction between the components and would change the mechanical properties. Thus prepared WPCs would also be completely biodegradable since PPC-OHs, PPC and wood flour are all biodegradable.

The PPC-OH polymers in this study have a hydroxyl group content from 2.1 mol% to 12.1 mol% with respect to carbonate units in the polymer backbone. The mechanical, thermal and morphological properties of the prepared WPCs were determined.

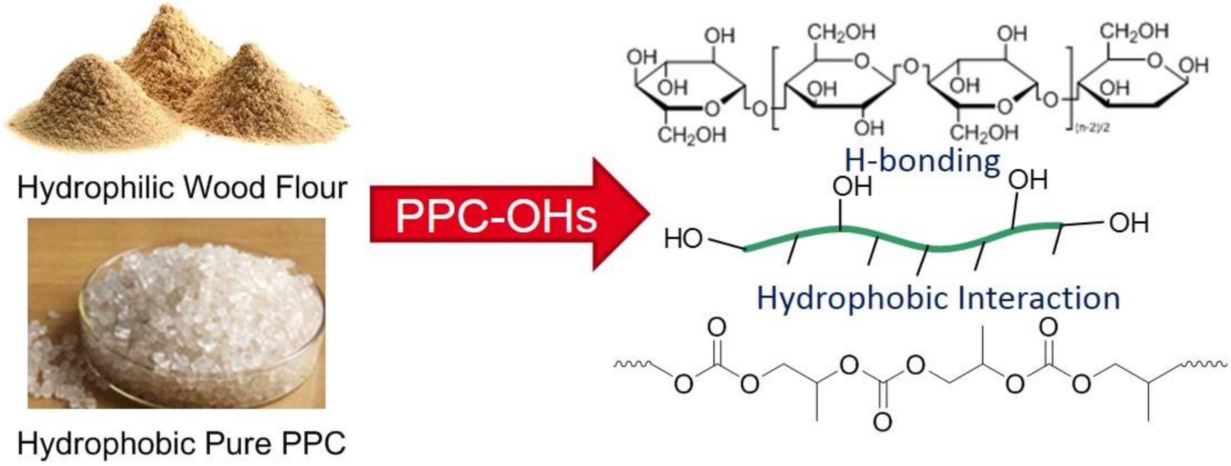


Figure 3.9 PPC-OHs as compatibilizer for PPC-based wood flour composites.

3.10 Post-Modification of Hydroxyl-Functionalized Poly(propylene carbonate)

Post-functionalized polymers could be synthesized based on the hydroxyl-functionalized poly(propylene carbonate). Modification of polymers bearing pendant primary hydroxyl groups was possible to give PPC-brushes and cross-linked PPC network. This thesis focuses on two categories of modifications: a, transferring hydroxyl groups into active centers for living/controlled radical polymerization such as atom-transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT), so that polymer brushes with controllable density and length could be prepared; and, b, direct modification of the hydroxyl groups bound to the PPC backbone to cross-link the linear polymers using diisocyanate to produce highly cross-linked PPC based polymer network. [131–134]

Polymer bushes are accessibly by “grafting to” functional macro monomers or “grafting from” of a functionalized backbone with active sites. [93,135,136] The latter was successful for PPC-OH. Starting from PPC-OHs, various PPC-brushes could be synthesized via atom transfer radical polymerization (ATRP) of various monomers. [136–138] This provided a general method for synthesis of dimensional controllable PPC-brushes with some potentials applications.

Beside of preparing highly cross-linked PPC based polymer network with cross-linker agent, it would be possible to prepare interpenetrating polymer network (IPN) or semi-interpenetrating polymer network (sIPN) which would bring some new properties to PPC. In fact, introducing of network in PPC is very interesting due to the enhancement of polymer mechanical properties with network in PPC matrix. [139–142] In fact, the modification with diisocyanate or triisocyanate based on the urethane reaction with the end-capping hydroxyl groups of pure PPC has been investigated by Wang and Meng et al..[133,134] And their research show that it can truly bring some new properties such as enhanced tensile strength and improved thermal stability.

PPC is linear polymer with hydroxyl end groups. It has also been reported that end-capped PPC with maleic anhydride could significantly enhance the material property and thermal stability.[49,63,115,119,142,143] Moreover, pure PPC treated with diisocyanate or triisocyanate (tolyl diisocyanate, 4,4'-diphenylmethane diisocyanate) as cross-linker were proved and therefore can improved the tensile strength and thermal stability. In this work, pure PPC are also treated with diisocyanate to measure the reaction activity of end-capping hydroxyl groups and isocyanate in solvent. Based on this reaction of pure PPC and diisocyanate, IPN or sIPN would be easily prepared. If then end-capping hydroxyl groups do not react with MDI in solvent, then PPC would keep as linear polymer after reaction, which means only sIPN would be prepared after the following treatment. In this work, semi-interpenetrating polymer network (sIPN) with linear PPC and cross-linked PPC network were prepared. As shown in figure 3.10, controllable PPC based polymer brush and densely cross-linked PPC could be prepared via different post-modification routes.

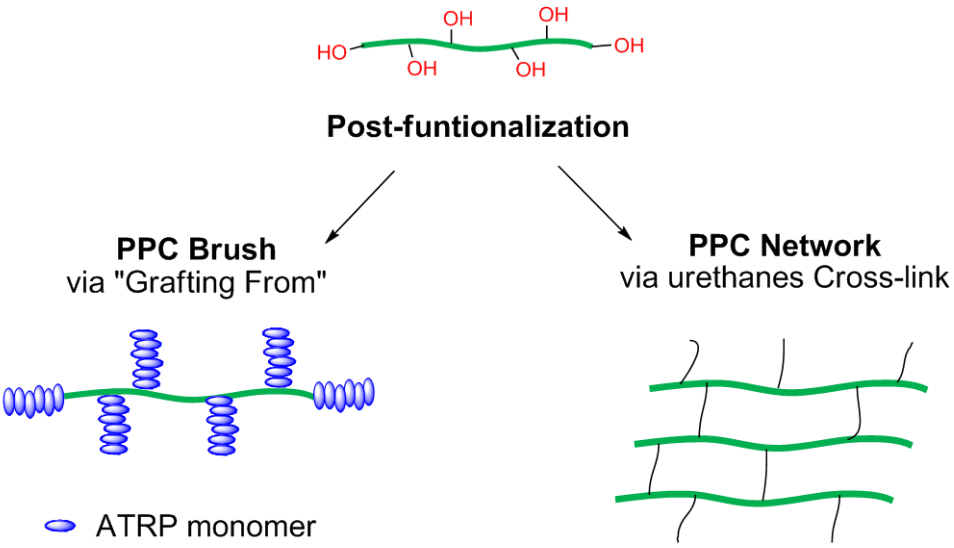


Figure 3.10 Synthesis of PPC brush and PPC network via post-modification of PPC-OHs

4. Motivation

The general targets in this thesis are to establish a general method to synthesize hydroxyl-functionalized poly(propylene carbonate) (PPC-OHs) via terpolymerization of CO_2-, PO-, and ONB protected monomers. In combination of photochemistry and copolymerization of CO_2 and epoxy monomers, PPC-OHs could be accessible after UV-light irradiation. A backbone degradation should not occur under those conditions. In addition, not many polymers are known with hydroxyl moieties in the side chain, and a study of the properties (thermal, spectroscopic, mechanical, rheologic) is of interest.

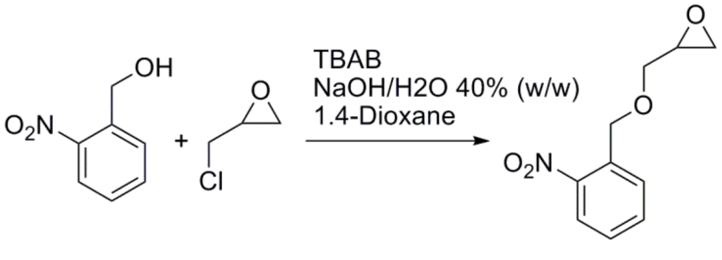
Furthermore, PPC-OH is expected to be biodegradable too and would have a potential for as biodegradable compatibilizer in e.g. PPC/wood flour composites. The preparation of such WPCs is of interest as they would have the potential as fully biodegradable packaging materials. Their property profile has to be acquired and reviewed. PPC-OH is also an interesting polymer to prepare polymer brush and cross-linked PPCs. Orientating studies would allow to assess the potential of these new polyols as backbone for more complex systems.

5. Results and Discussion

5.1 Synthesis and Characterization of Hydroxyl-Functionalized Poly(propylene carbonate)

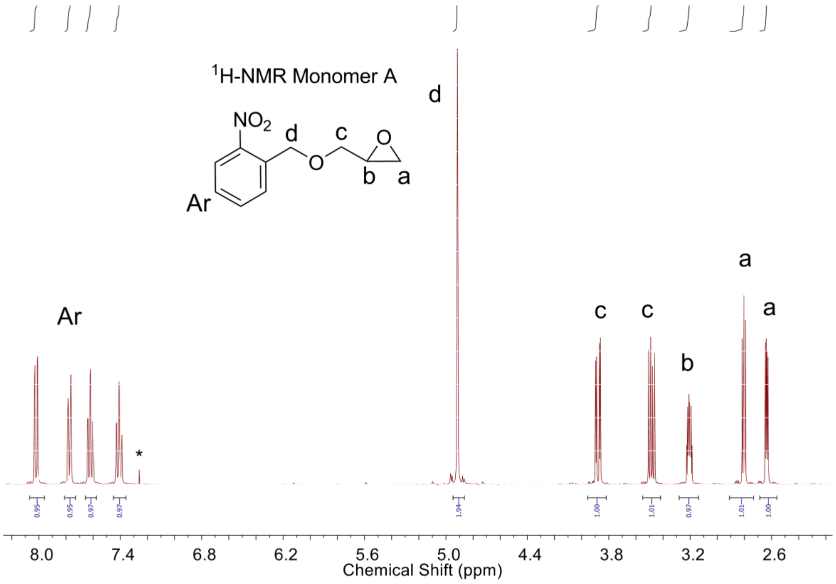
5.1.1 Synthesis of 2-[[(2-nitrophenyl)methoxy]methyl]-oxirane

2-[[(2-nitrophenyl)methoxy]methyl]-oxirane (monomer A) is successfully synthesized in one step reaction as shown in Scheme 5.1. With a yield of 27.2 % (27.2% mole ratio based on *o*-nitrobenzyl alcohol), monomer A is characterized in ^{1}H NMR and ^{1}C NMR spectra. (Figure 5.1)



A

Scheme 5.1 Synthesis of 2-[[(2-nitrophenyl)methoxy]methyl]-oxirane (monomer A); TBAB = tetrabutylammonium bromide .



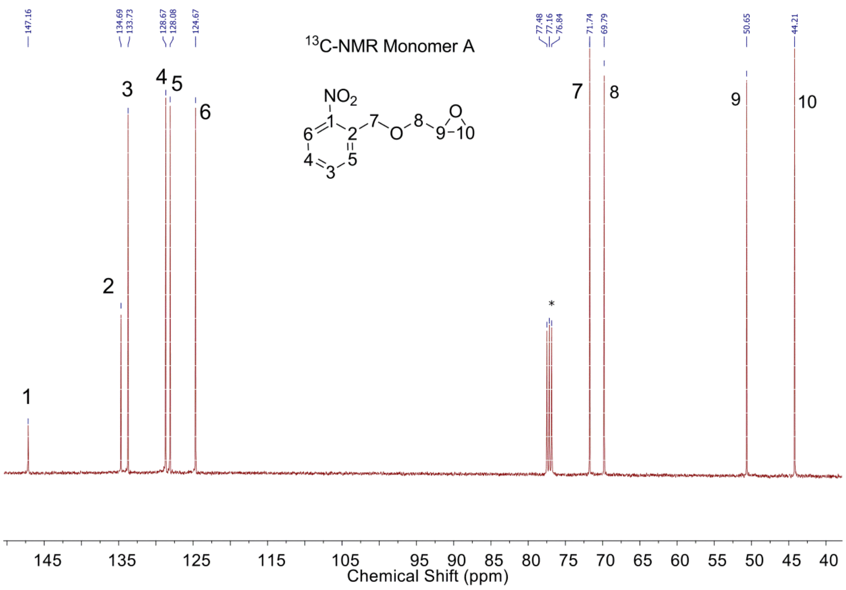


Figure 5.1 ^{1}H NMR and ^{13}C NMR spectra of 2-[[(2-nitrophenyl)methoxy]methyl]-oxirane (monomer **A**). (in $CDCl_3$)

5.1.2 Synthesis of hydroxyl-functionalized Poly(propylene carbonate)

Terpolymers of 2-[[(2-nitrophenyl)methoxy]methyl]-oxirane (monomer **A**), PO and CO_2 were prepared in toluene using a zinc glutarate as catalyst.[43,44] Zinc glutarate is a heterogeneous catalyst that we prefer to use, it has a moderate activity for the copolymerization, is easy to prepare and handle, contains no heavy metals and residues are readily removed. Reaction times of about 8 h at 60 °C and 3 MPa of pressure (CO_2) with 100 mg ZnGlu catalyst typically yielded 10 to 20 g of terpolymer. These conditions are in the optimum range for PO/CO_2-copolymerizations mediated by zinc glutarate.[36] Larger scale preparations (65 g) were successful too (Table 5.2). The terpolymers were readily purified from residual **A** and the formed cyclic carbonate by precipitation into methanol.[144,145] The molar ratio of **A** to PO was varied in a range from 0 to 0.2 to give a range of products **P1** to **P6** (Table 5.1). An analysis by ^{1}H NMR shows that the resulting polymers were polycarbonates with 89 % to 93 % of carbonate linkages. The composition with respect to **A** entities and PO related units ranges up to 10.6 % of **A** when the feed **A**/PO had a molar ratio of 20/100. Higher concentrations of **A** entities in the polymer could not be reached under these conditions as a higher ratio of **A**/PO in the feed (> 30/100) deactivated the catalyst.

The productivity of the catalyst is strongly dependent on the concentration of **A**. It decreases from 15.6 g PPC/g ZnGlu$\cdot$h^{-1} to 8.1 g PPC/g ZnGlu$\cdot$h^{-1} at a concentration of **A** of 0.72 mol/L (Table 5.1). It is assumed that **A** coordinates stronger to zinc centers than PO, i.e. next to the epoxide also with (nitro and) ether moieties thereby blocking the surface.[146] Epoxides are known to be weakly coordinating and are readily displaced from Lewis acids by many functionalities.[147] Without coordination and concomitant activation, epoxides are not undergoing ring opening at the reaction conditions used.[101,148] The molecular weight of the products varied between 22700-62600 g$\cdot$mol^{-1} and molecular weight dispersity (M_w/M_n = 3.1 to 3.9) were in the typical range of zinc glutarate based polypropylene carbonates.[149,150] The number average molecular weight of the samples decreases congruently with the yield at higher concentration of **A**. This is thus probably related to a lower rate of insertion of the monomers affected by the coordination of **A** to the catalyst. Larger scale preparation results show the same trends in productivity and molecular weight. A Fineman-Ross analysis gives the copolymerization reactivity ratios r_1 and r_2 of PO resp. of **A** at 1.46 and 0.64 (Figure 5.9). There is thus a mild preference for incorporation of PO into the terpolymer, nevertheless it may be expected that the functional groups are more or less randomly distributed in the terpolymer.

Table 5.1 Characterization data of copolymer samples.

Sample	**A/PO** feed %	**A/PO**[a] in polymer %	**Conv A.**[b] %	**Conv PO.** %	**Activity** g PPC/ g ZnGlu·h^{-1}	**Carbonate linkages**[c] %	**M_n**[d] PPC-ONB g·mol^{-1}	**M_w/M_n**[d] PPC-ONB	**M_n** PPC-OH g·mol^{-1}	**M_w/M_n** PPC-OH
P1	0	0	0	86.5	15.6	92	89600	3.9	87600	3.9
P2	2.5	0.9	61.0	90.1	18.9	93	62600	3.1	63400	3.1
P3	5.0	2.2	66.3	90.3	18.1	92	35500	3.6	37800	3.4
P4	10	4.6	55.0	65.4	14.1	89	32300	3.6	32700	4.0
P5	16	7.0	44.0	69.7	15.6	90	27000	3.3	26400	3.4
P6	20	10.6	35.7	34.5	8.1	92	22700	3.4	23600	3.6
P7[e]	30	-	-	-	-	-	-	-	-	-

a) Comonomer **A** content, calculated from ^{1}H-NMR spectra of the PPC-ONB polymer samples; residual **A** could be recycled from the precipitation solvent residue, residual PO was removed in vacuum; b) Calculation based on ^{1}H-NMR spectra of samples after polymerization and yields; c) by ^{1}H-NMR spectroscopy; d) by gel permeation chromatography (GPC) calibrated to polystyrene standards in THF at room temperature; e) No polymer obtained.

Table 5.2 Data for copolymer samples prepared in large scale

Sample	**A/PO** feed mol %	**A/PO**[a] in polymer mol %	**Conv. A** %	**Conv. PO** %	**Yield** Polymer g	**Carbonate linkages**[b] %	**M_n**[c] PPC-ONB g·mol^{-1}	**M_n/M_w** PPC-ONB	**Mn** PPC-OH g·mol^{-1}	**M_n/M_w** PPC-OH
R43	2.5	2.1	55.5	87.1	65.5	95	85300	1.8	78500	1.9
R41	5.0	3.7	48.0	71.9	55.3	92	76900	1.8	70400	1.8
R42	10	5.9	47.7	63.2	49.9	91	44300	1.7	47700	2.1
R45	15	6.7	44.0	63.2	50.4	92	27700	2.7	27400	2.9
R50	20	12.1	35.7	47.3	40.0	94	22200	2.7	26400	2.9
R48[d]	30	-	-		-	-	-		-	-
R49[d]	50	-	-		-	-	-		-	-

a) Comonomer **A** content, calculation based on ^{1}H-NMR spectrum of the PPC-ONB polymer; b) by ^{1}H-NMR spectroscopy; c) by gel permeation chromatography (GPC) calibrated to polystyrene standards in THF at room temperature; d) No polymer obtained.

The ONB groups can be readily removed from the polymer in THF solution by irradiation with UV light of a wavelength around 313 nm. The product of this reaction is a poly(propylene carbonate) with hydroxyl groups on the methyl substituent (PPC-OH; Figure 5.2). It was found possible to quantitatively transform the ONB groups into hydroxyl entities. The progress of the reaction is obvious from a color change to dark brown, the typical color of the side product (and decomposition product of) nitroso benzaldehyde.[74,151] The polymer could effectively be separated from the reaction mixture by repeated precipitation from acetone into ligroin, yielding purified PPC-OH.

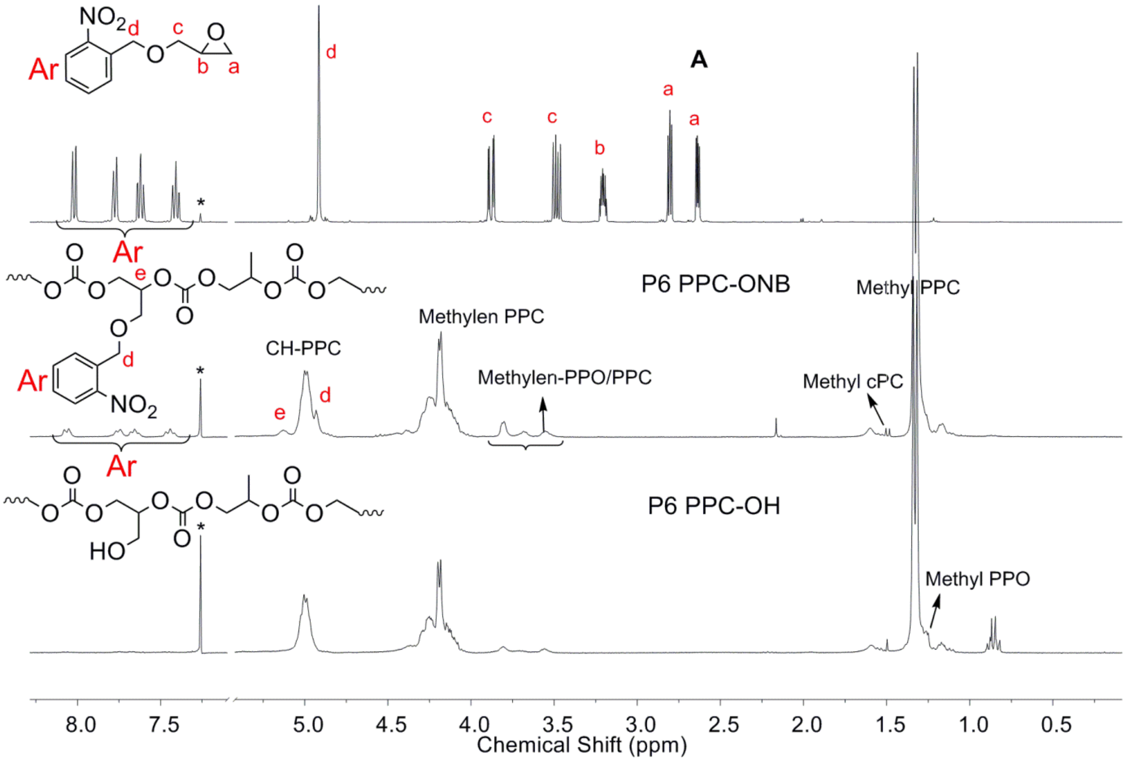


Figure 5.2 ^{1}H NMR spectra of monomer **A**, ONB-protected polymer **P6 PPC-ONB** and deprotected polymer **P6 PPC-OH**.

The transformation of **P6 PPC-ONB** to **P6 PPC-OH** was also monitored by UV-Vis spectrometry (Figure 5.3). A THF solution of the polymer **P6 PPC-ONB** with **A**/PO at 10.6% in molar ratio (2.0 mg/mL) under UV light irradiation was sampled at intervals and spectra immediately recorded. A characteristic absorption related to the ONB-protecting group is found around 260 nm (present before UV light irradiation at 0 s). An isobestic point is observed of spectra recorded from samples in the first minute, indicative of a direct transformation to hydroxyl groups. The photoreaction is very effective as after 1 minute the vast majority of the ONB-protecting groups are already cleaved. Change of absorbance band at 290 nm and 315 nm in Figure 5.3 can be attributed to the formation of nitroso benzaldehyde derivative as a byproduct of the released protecting groups.[151] The nitroso side product is very reactive, leading to consecutive reactions not including the polymer as irradiation is prolonged and the concentration of the nitroso compound decreases.[74,152–155]

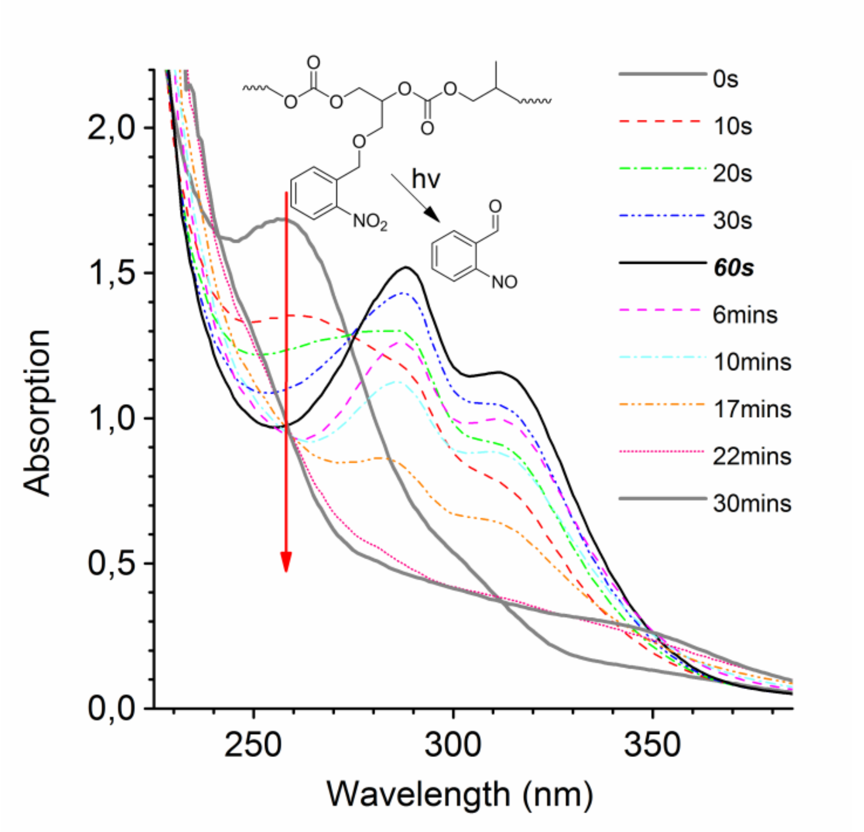


Figure 5.3 UV-Vis spectra of the irradiation process on **P6 PPC-ONB** at room temperature in THF.

The molecular weights determined by GPC of the PPC-OH samples were very comparable to corresponding PPC-ONB samples (Table 5.1). It may thus be anticipated that main chain degradation is not notably taking place during UV light irradiation. Note that the molecular weight should have decreased after UV light irradiation due to the loss of the ONB-protecting (max of 12.3 wt% for polymer **P6).** The molecular weights obtained from GPC are nevertheless almost equal to those of the corresponding PPC-ONBs, which is attributed to a larger hydrodynamic volume of PPC-OHs samples with increasing hydroxyl amount. A similar small increase is documented for other post-modification polycarbonates[71,90,148] and hydroxylated polyesters[156]. A severe degradation of poly(glycerine carbonate) has been observed in solution of organic solvents.[25,27] We find that **P6 PPC-OH** is stable in THF for at least 2 weeks. This attributed to the lower concentration of reactive hydroxyl groups and the mild (neutral pH) conditions of the preparation procedure.

PPC-ONB polymers show a single glass transition temperature (T_g) in the same range as for neat PPC.[149,157] The glass transition temperature of PPC-ONB samples increases from 29.3 °C of neat PPC **P1** to 30.9 °C of **P4 PPC-ONB** with 4.6 % ONB content and then decreases to 27.7 °C (Table 5..3) of entities **P5** and **P6** with a higher content of ONB. The small changes may be explained by the opposing effect of the ONB groups acting as bulky side groups increasing T_g and the decreasing molecular weight decreasing T_g.[158] The glass transition temperatures of hydroxyl-functionalized PPC-OH polymers are somewhat higher than those of PPC-ONB polymers. The shift of T_g (ΔT_g) increases with the increasing content of hydroxyl groups in PPC-OH polymers. This could be explained by the presence of the increasing number of hydrogen bonds.[70,148,159,160] IR spectra of **P1**, **P6 PPC-ONB** and **P6 PPC-OH** were obtained (Figure 5.4) and show e.g. in **P6 PPC-OH**, broad absorptions in the 3500-3000 cm^{-1} region. These are attributed to self-H-bonded O-H groups (3350 cm^{-1}), inter-H-bonded O-H groups (3340 cm^{-1}) and free O-H groups.[112,161–163]

Table 5.3 Contact angle and glass transition temperature of polymer samples.

Sample based on	**A/PO**^{a} in polymer %	**CA**^{b} (°) **before UV** PPC-ONB	**CA** (°) **after UV** PPC-OH	**ΔCA**^{c} (°)	**T**$_{g}^{d}$ (°C) **before UV** PPC-ONB	**T**$_{g}$ (°C) **after UV** PPV-OH	**ΔT**$_{g}^{e}$ (°C)
P1	0	76.8	76.4	-0.4	29.3	29.4	0.1
P2	0.9	75.9	71.8	-4.1	30.8	32.9	2.1
P3	2.2	74.1	70.4	-3.7	30.9	35.3	4.4
P4	4.6	74.4	68.5	-5.9	30.3	35.1	4.8
P5	7.0	73.6	65.1	-8.5	25.9	31.4	5.5
P6	10.6	73.8	60.8	-13.0	27.7	35.8	8.1

a) Comonomer **A** content in polymers; b) Contact angle; c) Contact angle change by deprotection; d) Glass transition temperature (T_g) determined by DSC; e) Glass transition temperature change, $\Delta T_g = T_{g\,(PPC\text{-}OH)} - T_{g\,(PPC\text{-}ONB)}$.

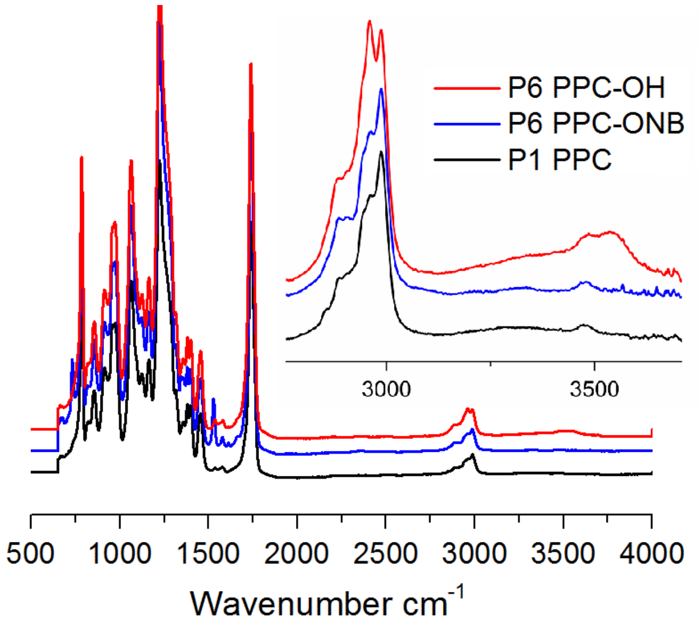


Figure 5.4 FTIR spectra of **P1** (PPC), **P6 PPC-ONB** (before UV light irradiation) and P6 **PPC-OH** (after UV light irradiation).

Consistently, the polarity of the respective polymers **P1-P6 PPC-ONB** and **PPC-OH** are different. The change in polarity is for example expressed in the contact angle of polymer thin films to water. Water contact angles on polymer surfaces were measured on spin-coated films (Table 5.3). Contact angles of PPC-ONB polymers are found in the narrow range of 73.8° to 76.8° close to those reported for water contact angle on PPC films.[164] The PPC-OH polymers have a significantly decreased contact angle. The higher the content of comonomer units in the PPC-OH polymers, the lower the contact angle is (Figure 5.5).

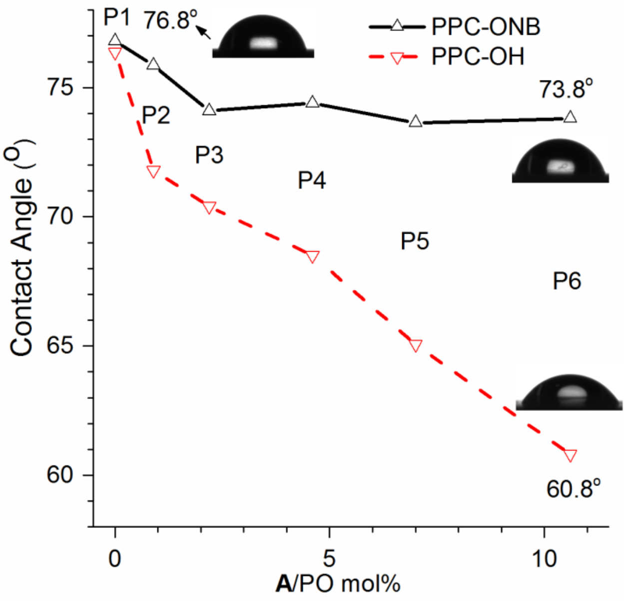


Figure 5.5 Contact angle analysis of PPC-ONB and PPC-OH samples.

5.1.3 Spectroscopic details of the PPC-OH prepared

^{1}H NMR is a suitable method to characterize the copolymers and the polymerization reactions. Spectra of pure samples of **P1-6 PPC-ONB** and **P1-6 PPC-OH** are shown in Figure 5.6 and 5.7. The presence of ONB groups can be deduced from the resonances in the aromatic region (δ = 7.42 - 8.08 ppm). The polymer constitutions were derived from the integral values of the resonances at 1.20 - 1.40 ppm. The molar quantities of benzyl units increased with the concentration of **A** in the feed. Exposure to ultraviolet (UV) light led to a complete cleavage of the ONB groups. The poly(propylene carbonate) (PPC) backbone was not affected as was concluded from a comparison of the ^{1}H-NMR spectra and gel permeation chromatography (GPC) results of PPC-ONB and PPC-OH samples (Figure 5.8). Signals of the methylene and methyl entities attributed by PPC are conserved, whereas signals related to the ONB groups disappear. GPC results in Figure 5.8 show that UV light irradiation was harmless to backbone of PPC samples.

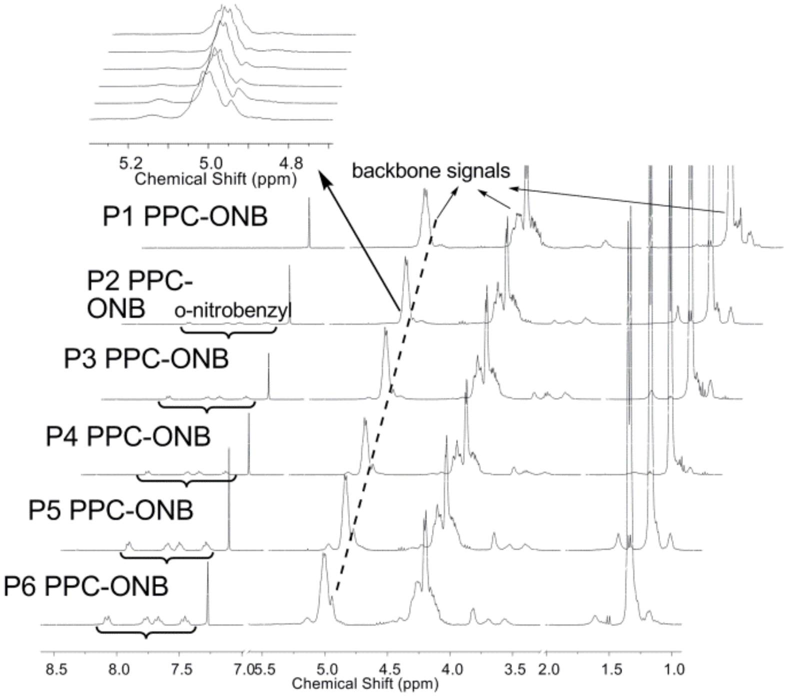


Figure 5.6 ^{1}H NMR spectra of ONB-protected polymers **P1-P6 PPC-ONB**.

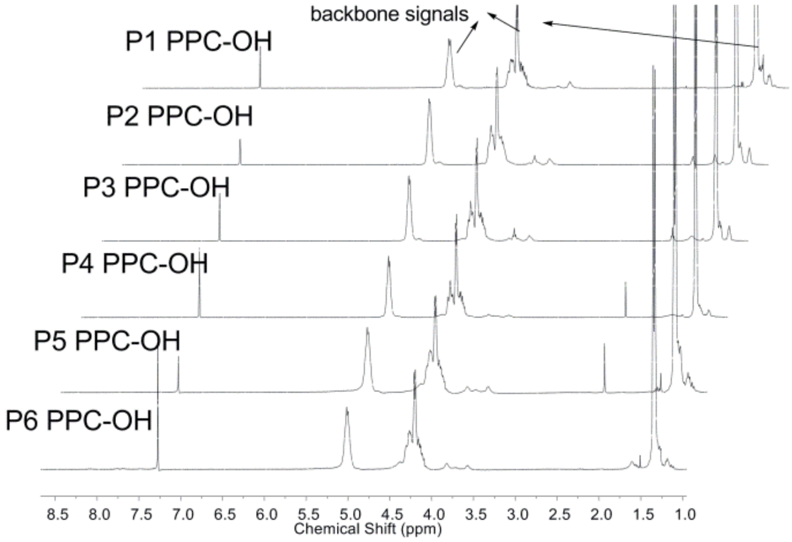


Figure 5.7 ^{1}H NMR spectra of UV light deprotected polymers **P1-P6 PPC-OH**.

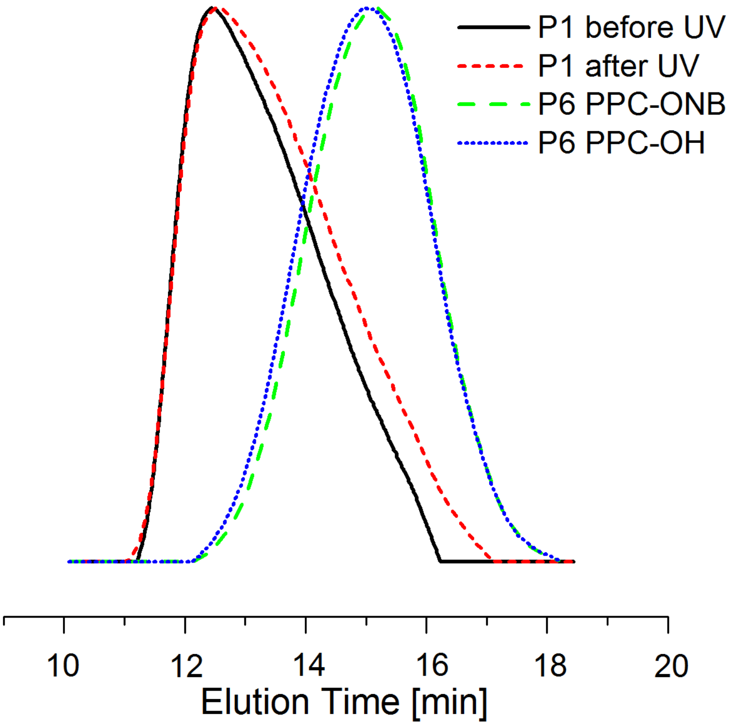
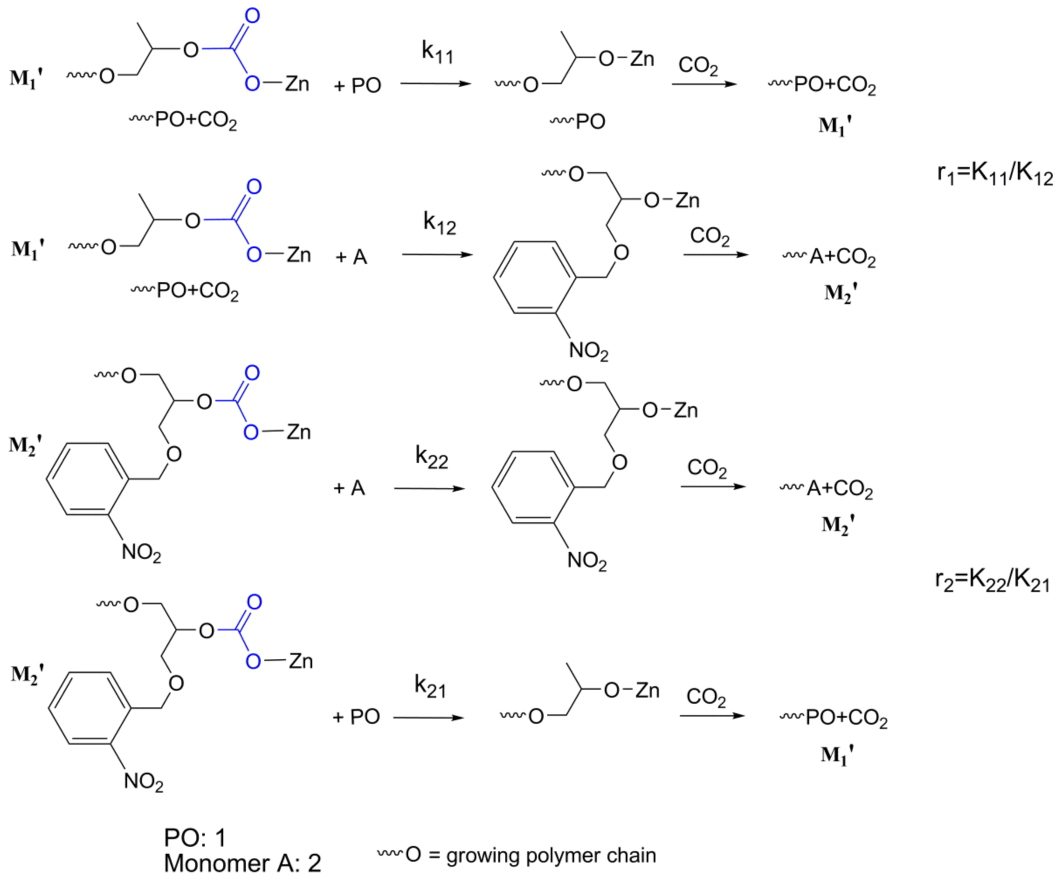


Figure 5.8 GPC trace of polymers before and after UV light irradiation. **P1**: pure PPC; **P6 PPC-ONB** (10.6 % of **A**) and **P6 PPC-OH**.

5.1.4 Fineman-Ross analysis

The analysis was performed on polymerization products from reactions with conversion lower than 5% of monomer **A**. The small differences in the high carbonate content (± 90%) in the respective polymers were neglected. The analysis thus corresponds to the following four propagation reactions (Scheme 5.2). Terpolymerization of **A**, PO and CO_2 was conducted to conversions lower than 5 mol%. The resulting solid was sampled for NMR analysis. The data are in Table 5.4 and form a basis for a Fineman-Ross analysis.



Scheme 5.2 Reactivity ratios, the relative tendencies of the monomers (PO and Monomer **A**) to self-propagate or cross propagate.

Table 5.4 Mole fraction ratios of PO and Monomer **A** in the feed (f) and in the resultant copolymer (F)

Sample	f(PO/**A**)	F(PO/**A**)[a]	Conv. **A**[b] (%)	x=f²/F	y=f(1-F)/F
P81	40	53.76	3.23	29.762	-39.256
P82	20	30.03	3.39	13.320	-19.334
P83	10	13.30	1.57	7.519	-9.248
P84	6.0	9.86	3.30	3.651	-5.391

a) calculated based on ^{1}H-NMR spectra of the precipitated PPC-ONB samples; b) calculated based on ^{1}H-NMR spectra of crude PPC-ONB samples after polymerization.

Representation of the data according to the Fineman-Ross approach for determining the copolymerization ratios is shown below ($\frac{f(1-F)}{F} = \mathrm{r}_2 - \mathrm{r}_1 \cdot (\mathrm{f}^2/F)$):

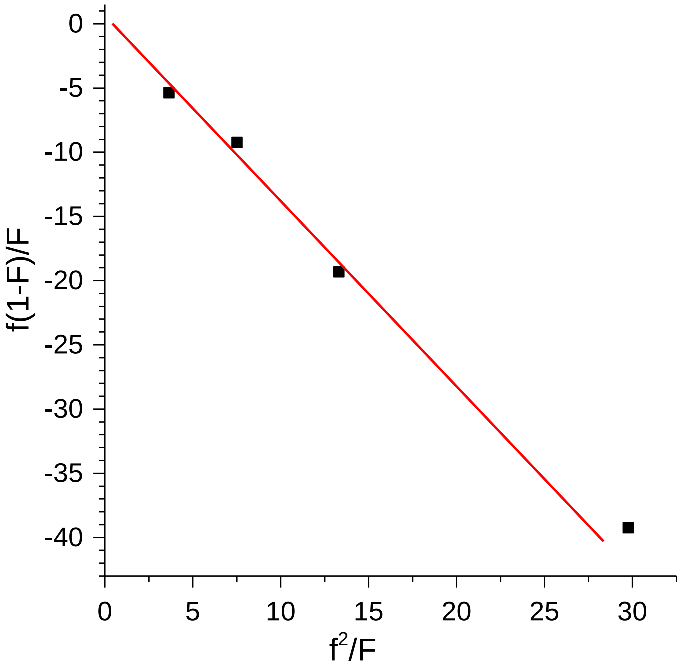


Figure 5.9 Fineman-Ross plot of PO/**A**/CO_2 terpolymerization reaction at 60 °C. The r_l and r_2 values are 1.46(5) and 0.63(9), respectively, with an R^2 value of 0.96(2).

From the monomer feed ratios and the resultant copolymer compositions, the reactivity ratios of PO and monomer **A** were evaluated. The value(s) of $r_l = 1.47$ is greater than 1 and $r_2 = 0.64$ is less than 1 (Figure 5.9). r_l shows that **M_l'** preferentially adds PO instead of monomer **A** while **M_2'** favors cross-propagation over self-propagation.[165] The value shows that PO is generally more reactive than monomer **A** toward both propagating species. The copolymers synthesized contain larger proportion of PO in random placement.

5.1.5 Hydroxyl group assessment in PPC-OH by derivatization

The existence of hydroxyl groups in hydroxyl-functionalized poly(propylene carbonate)s was validated by methylation of polymer **P6 PPC-OH** with methane sulfonyl chloride and pyridine.

(Figure 5.10) In a typical procedure, 100 mg of polymer **P6 PPC-OH** were dissolved in dry dichloromethane. Pyridine (75 mg, 0.7 mmol) was added to the solution which was kept at about 0°C in an ice bath. Methane sulfonyl chloride (80 mg, 0.7 mmol) was then added dropwise to the mixture. The reaction subsided within 3 h, after which the reaction mixture was precipitated into methanol. The product was reprecipitated three times from dichloromethane into methanol followed by drying in an oven at 40 °C for 24 h held under a dynamic vacuum. The purified product (**P6 PPC-Methyl**) was analyzed by ^{1}H NMR to confirm the presence of methane sulfonyl groups. ^{1}H NMR spectra of polymer **P6 PPC-OH** and methylated product **P6 PPC-Methyl** are shown in Figure 5.10. The composition of methane sulfonyl groups to PO in **P6 PPC-Methyl** is quantitatively coincident with that of **A** and PO in polymer **P6 PPC-ONB**.

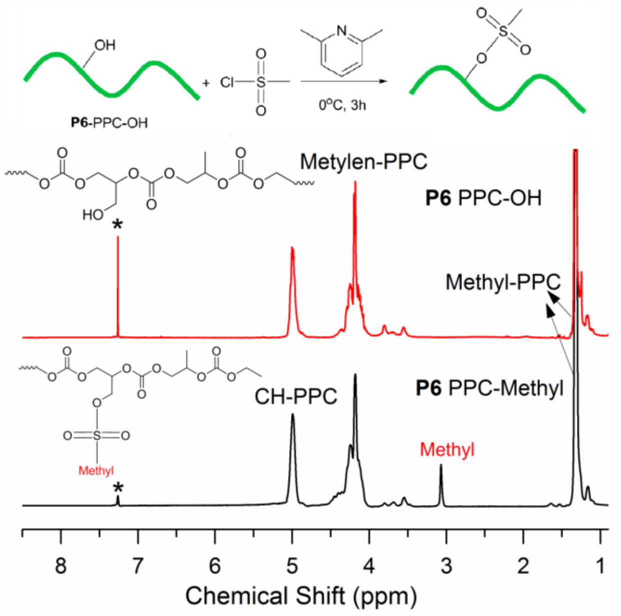


Figure 5.10 Methylation of polymer **P6 PPC-OH** and the corresponding ^{1}H NMR spectra.

5.2 Effects of Hydroxyl-Functionalized Poly(propylene carbonate)s as Biodegradable Compatibilizer of Poly(propylene carbonate)/Wood Flour Composites

5.2.1 Hydrophilicity of PPC-OHs

The change in polarity is expressed in the contact angle of polymer thin films to water which were measured by water contact angle on spin-coated films. Larger scale samples were prepared. Again they show decreasing contact angles of PPC-OHs as the hydroxyl group content in PPC-OHs increases (Figure 5.11).

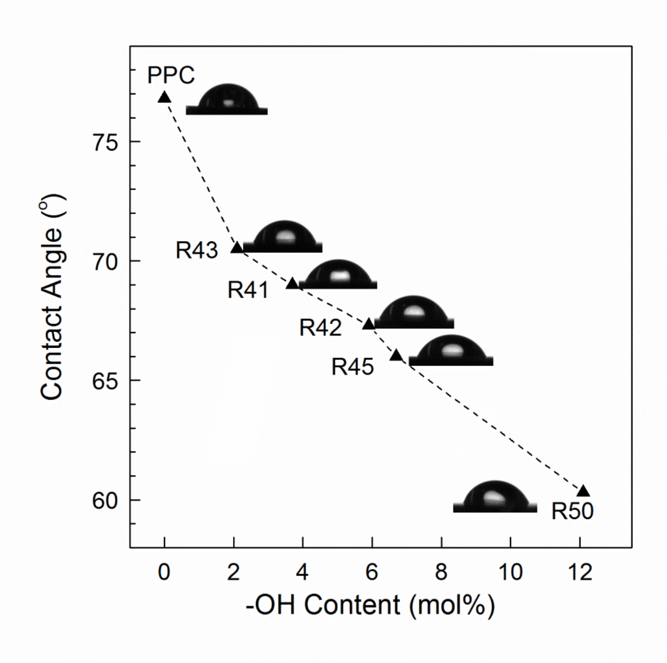


Figure 5.11 Contact angle analysis of PPC-OH samples.

5.2.2 Composite preparation and torque behavior

The typical torque behavior curves during PPC/wood flour (70/30) composite preparation is shown in Figure 5.12. The procedure consists of heating PPC and PPC/PPC-OH mixtures to 140 °C and subsequent addition of wood flour in three equal portions. The torque increases first and then decreases to a constant value due to the temperature increase of the polymers. The torque of the mixture increases after each addition of wood flour as shown in Figure 5.12. The kneading was stopped after 15-20 mins at an about constant torque of the mixture. B1 is a reference WPC of PPC. B2 to B7 are samples containing various PPC-OHs. The final torque values are almost the same for samples B1 to B7.

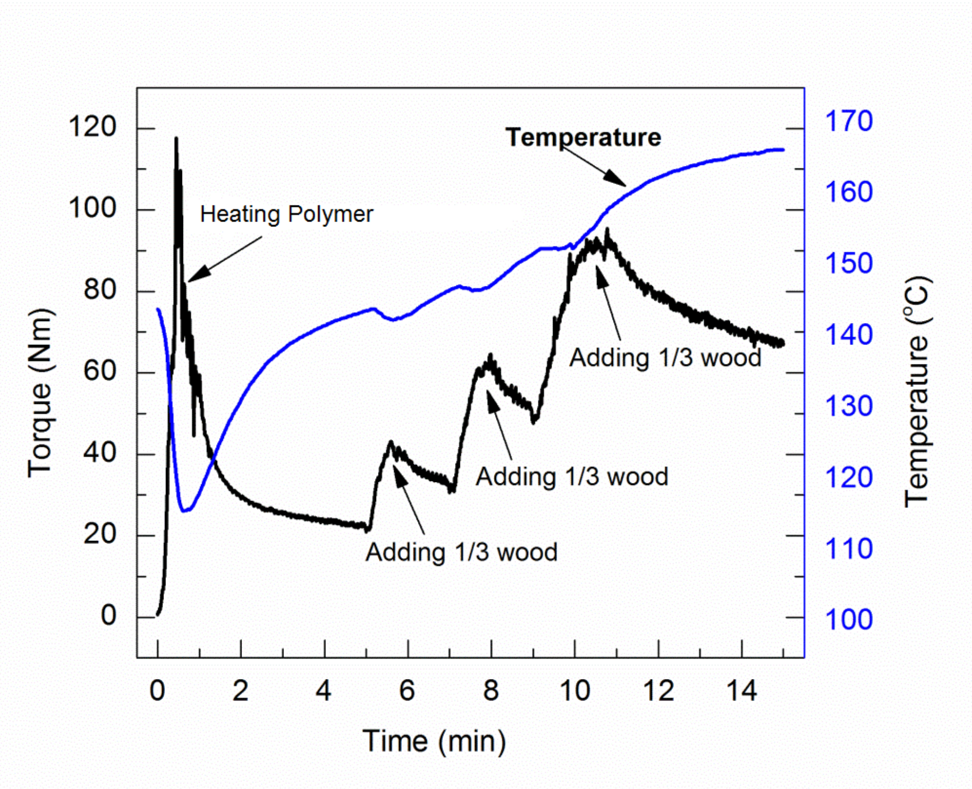


Figure 5.12 Torques of PPC-based WPCs during preparation.

Table 5.5 PPC-based wood flour composites

NO.	**-OH content** in PPC-OHs (mol %)	**PPC-OH /WPC** (wt %)	**Tensile strength** (σM/S MPa)	**Modulus** (Et/S MPa)	**Elongation at break** (%)	**T_g** (°C)	**$T_{-5\%}$** (°C)	**$T_{-50\%}$** (°C)	**T_{max}** (°C)
B1	-	0	41.4 ± 1.5	1890	4.5	29	288	307	299
B2	2.1	5%	42.8 ± 0.8	1780	4.6	28	289	312	298
B3	3.7	5%	44.5 ± 0.7	1910	4.3	28	287	312	298
B4	5.9	5%	46.1 ± 1.2	2040	4.4	29	286	312	298
B5	12.1	5%	44.9 ± 0.6	1910	4.6	29	283	310	295
B6	5.9	1%	42.3 ± 0.8	1960	4.3	29	290	314	298
B7	5.9	3%	44.5 ± 0.6	1910	4.4	29	286	311	298

5.2.3 Thermal properties

The thermal decomposition feature $T_{-5\%}$ (temperature of 5% weight loss) of PPC-based WPCs B1-B7 are found in a small range, from 283 °C to 290 °C. There is no difference between composites with and without PPC-OHs additives. Similarly, $T_{-50\%}$, the temperature of 50% weight loss of composites ranges from 310 °C to 314 °C which is insignificantly higher than that of reference sample B1 (307 °C). Relative to the standard sample B1, composites containing PPC-OHs have no significant different decomposition temperatures. The glass transition temperatures of B1-B7 are found independent on the presence of PPC-OHs in the composites. The thermal decomposition and glass transition temperature characteristics shows that the addition of PPC-OHs with no more than 5 wt% has no significant effect on the thermal properties of the WPCs. This was expected since only a slight portion of PPC-OH ($\leqslant$ 5 wt%) was added. In addition, PPC-OHs and PPC have very similar range of glass transition temperature.

5.2.4 Mechanical properties

The mechanical property of WPCs samples B1-7 were measured. (Table 5.5) The measurement results show that there is no significant change in elastic modulus and elongation at break between the samples. This maybe expected as these properties do not dependent strongly on the matrix-filler interactions. Tensile strength of WPCs samples with 5 wt% of PPC-OHs as additives are shown in Figure 5.13. Samples B1 to B5 have a constant 5 wt% weight portion of PPC-OHs. The hydroxyl group content ranges from 0 of B1 to 12.1 mol% of B5. The tensile strength continuously increases from B1 to B4 to above 46 (± 1) MPa as the hydroxyl group content increases to 5.9 mol%. A further increase is not observed, as the hydroxyl group content increased to 12.1 mol%, the tensile strength remains at the above level. It may be inferential that an approximately 10 % increase in tensile strength is the maximum that can be reached with 5 wt% compatibilizer. The number of interactions among PPC-PPC-OH-Wood flour is increasing with the number of OH groups on the PPC-OH to a maximum. A further increase in polarity of the compatibilizer leads to fewer interactions, indicating that the affinity for wood of PPC-OH is becoming more important than that to PPC. Another explanation may be the lower Mn of PPC-OHs as the OH content increase. As the OH content in PPC-OHs increase from 5.9 mol % to 12.1 mol%, the Mn decreases from 47700 to 26400 (in Table 5.2). The short molecular chain of PPC-OH may reduce the interactions and cause the slight lose in tensile strength from 46.1 MPa (**B4**) to 44.9 MPa (**B5**). All WPCs samples with various PPC-OH additives have improved tensile strength comparing to B1. The tensile strength of the WPCs increases with an increase amount of PPC-OH (5.9 mol% OH content) from 0 part in B1 to 5wt% in B4. (Figure 5.14) The higher concentration of compatibilizer leads to stronger interaction between PPC and wood flour.

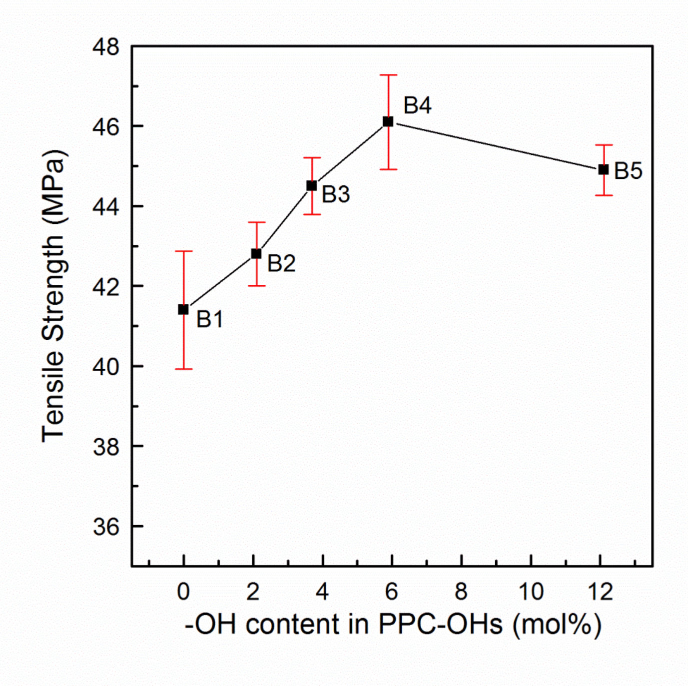


Figure 5.13 Tensile strength of PPC-based WPCs with different PPC-OHs

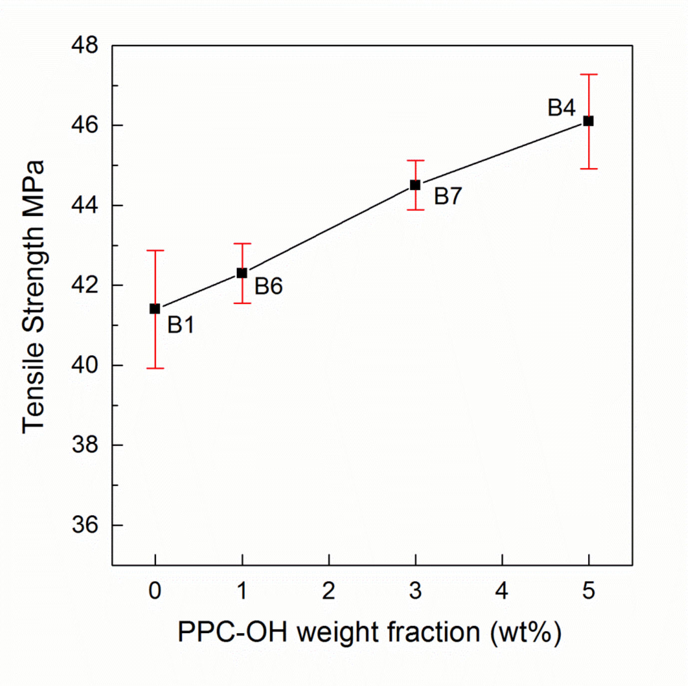


Figure 5.14 Tensile strength of PPC-based WPCs with weight % of PPC-OHs (5.9 mol% OH)

5.2.5 Morphologic characterization

SEM pictures were taken from breaking edges of WPCs. SEM pictures of best tensile strength performance sample B4 and standard sample B1, at a magnification of factor 8000 and 20000 are shown in Figure 5.15.

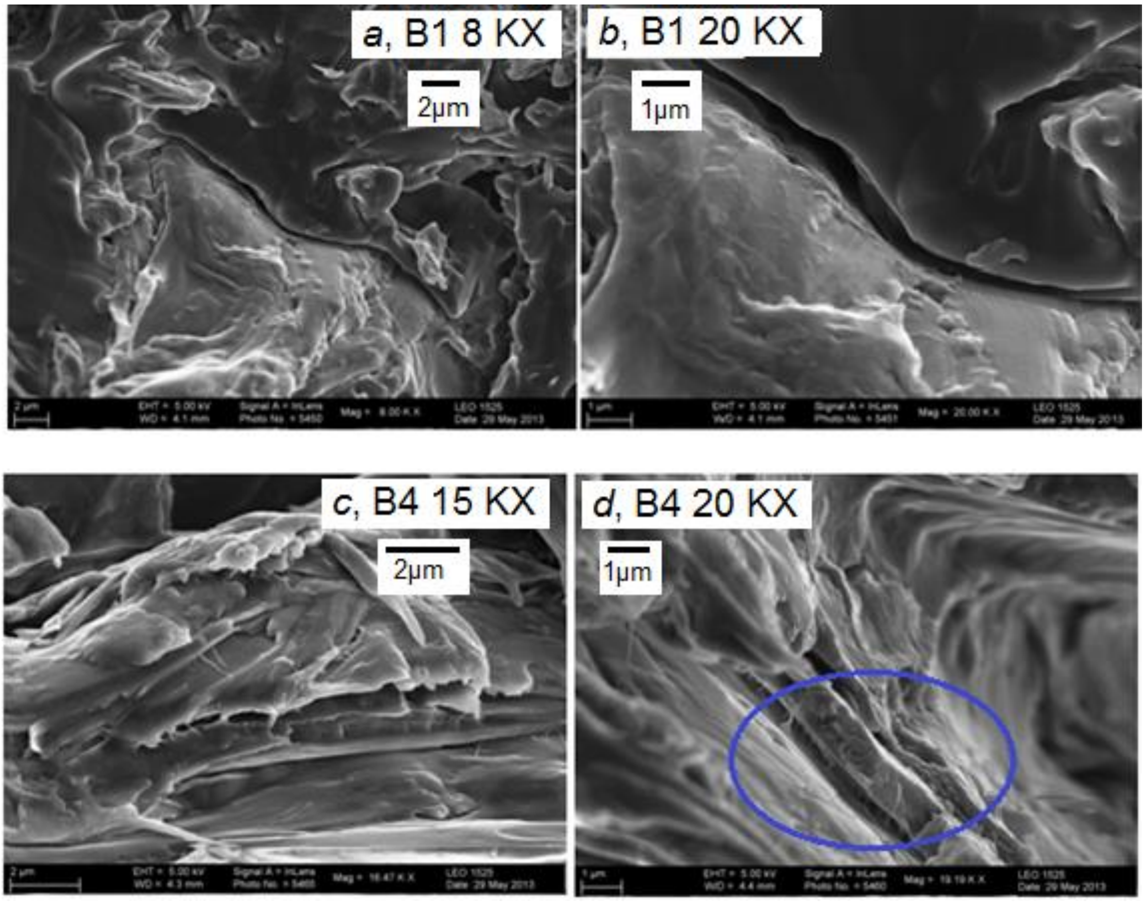


Figure 5.15 SEM micrographs of reference composite B1 and B4

The edges were obtained from breaking testing tensile bars after cooling in liquid nitrogen temperature. The SEM pictures of B1 (Figure 5.15 *a, b*) show voids between filler and matrix and pronounced repulsion of wood fiber and PPC matrix. The SEM pictures also are indicative of an improvement of wood flour and hydrophobic PPC contact in composites with a PPC-OH coupling agent. The SEM picture *c* of B4 which has 5 wt% PPC-OH as additive shows a smoother edge surface, and wood particles are closely embedded in the polymer matrix. There are observable contacts between the interface of PPC matrix and wood flour particles as shown in picture SEM picture of Figure 5.15 *d*.

5.3 Post-Modification of Hydroxyl-Functionalized Poly(propylene carbonate): Synthesis of brushes and gels

5.3.1 Polymer brushes

A PPC based macroinitiator for ATRP was prepared by reacting the hydroxyl groups on PPC-OH with 2-bromoisobutyryl bromide in the presence of pyridine as base (Figure 5.16).[130] The esterification reaction was successful in that most of the hydroxyl entities were transformed into 2-bromomethylpropionyloxy groups. The ^{1}H NMR spectrum (Figure 5.17) of the purified PPC-macroinitiator allows to conclude that the overall functionality of the backbone adds up to 80% mol/mol of building blocks, corresponding to a conversion of over 80% of the initially present OH groups.

It is anticipated that the main chain is not notably degraded during the PPC-macroinitiator synthesis process. The PPC-OH and the corresponding PPC-macroinitiator show about the same hydrodynamic volume according to a GPC analysis in THF (Figure 5.18). The PPC-macroinitiator shows a slightly larger average number molecular mass of Mn = $2{,}9 \times 10^4$, ($M_w/M_n = 2.4$) against PS standards as PPC-OH with an Mn of $2{,}6 \times 10^4$ ($M_w/M_n = 2.9$). Without knowledge of the Mark Houwink parameter, this result is taken as an indication that the main chain was not degraded substantially in the process, i.e. was not attacked nucleophilically by pyridine.

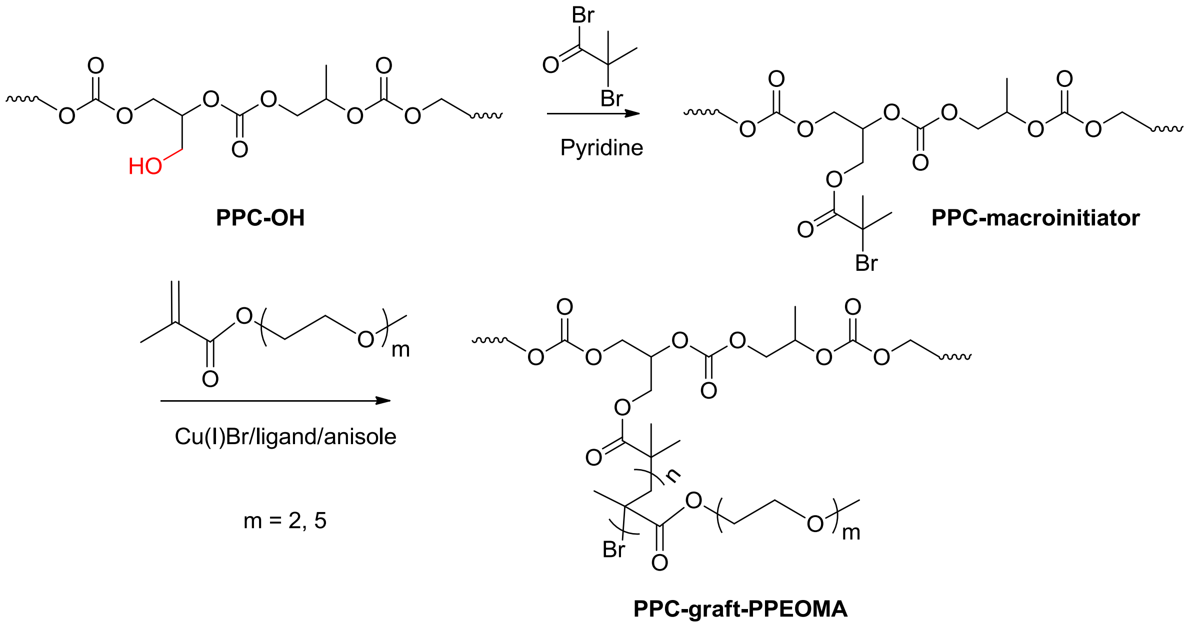


Figure 5.16 Synthesis of PPC-macroinitiator and PPC-*graft*-PPEOMA

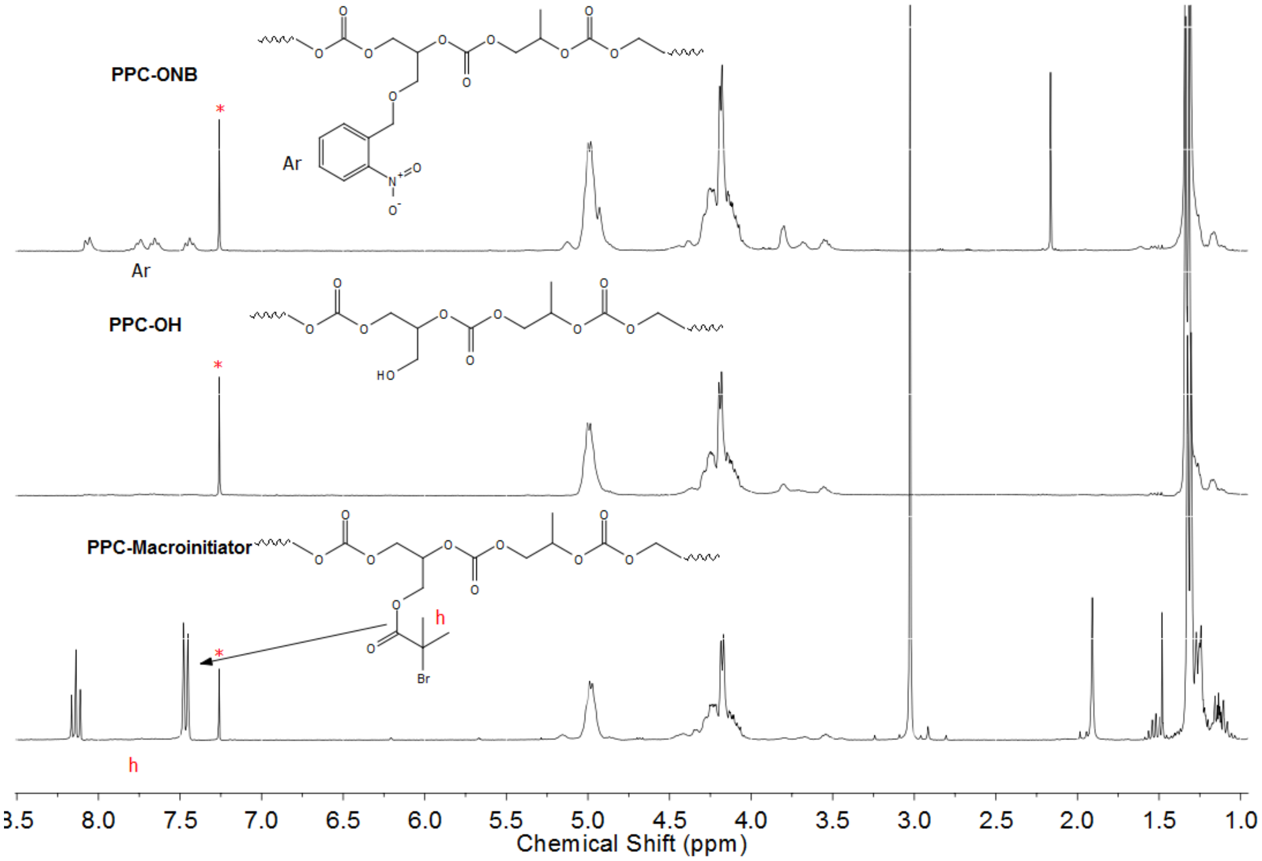


Figure 5.17 ^{1}H NMR spectra of PPC-ONB, PPC-OH and PPC-macroinitiator.

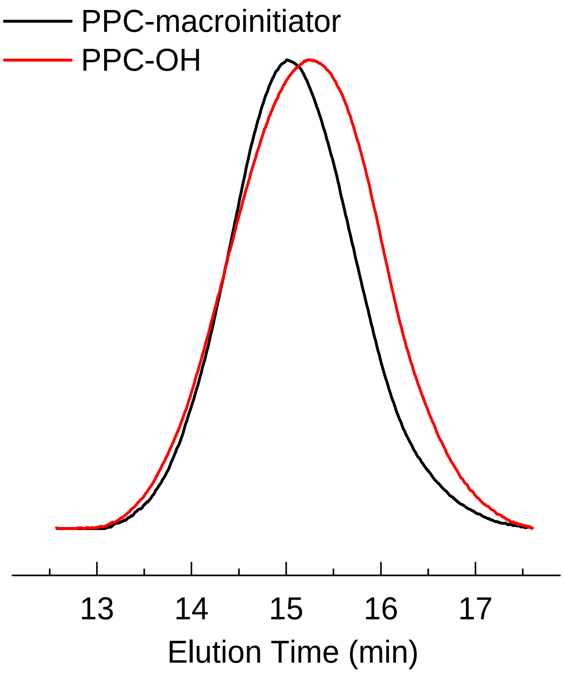


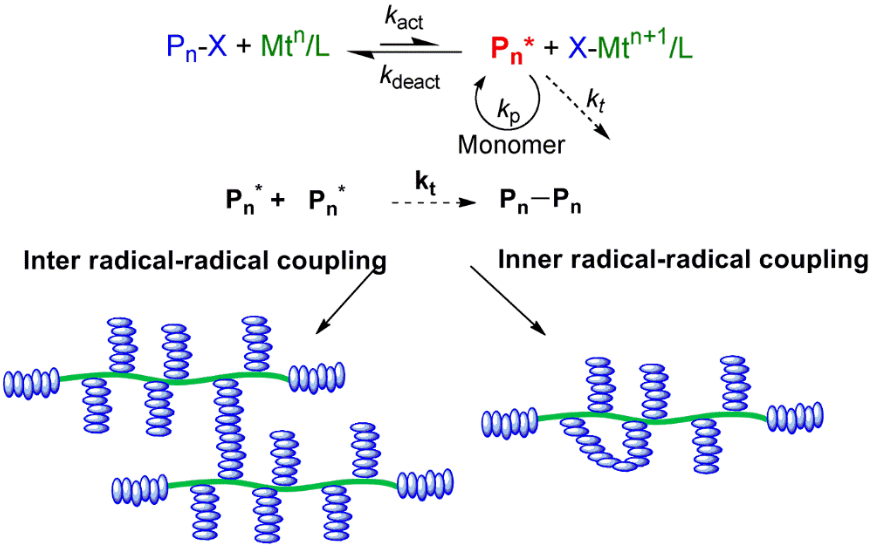
Figure 5.18 GPC trace of PPC-OH (**R46**) and the corresponding PPC-macroinitiator.

A grafting from the PPC-macroinitiator was accomplished under ATRP conditions with polyethylene oxide methyl ether methacrylate PEOMA with Mn = 188 g/mol and Mn = 300 g/mol as monomer (Figure 5.16). The products appear partially as gels (Table 5.6), in particular when using lower ratios of monomer to initiator and at longer reaction times. This gelation is attributed to reactions of the ethylene oxide side chains due to the inner and inter radical-radical coupling reactions[138,166] as shown in Scheme 5.3. The radicals are known to readily form after alpha hydrogen abstraction reactions at the polyethylene oxide entity. Radical-radical coupling terminations are more likely to happen intramolecular due to the high concentration of grafted chains which extend from the PPC back backbone.[167] Various polymerization conditions were screened with the objective to prevent the formation of interchain cross-links. These involve lowering the temperature from 60 °C to 40°C, decreasing the catalyst concentration and screening various monomer/initiator ratios (from 100:1 to 300:1).[167,168] The radical-radical coupling reaction could be minimized (**PA4** and **PA5**) at temperature of 50 °C and with molar ratios of M:I:CuBr:dNbpy = 300:1:1:2 in 5 mL anisole as solvent and short reaction times (2 hours). This leads to lower monomer conversion. The ^{1}H-NMR spectrum of **PA4** shown the presence of PEOMA units after purification of the polymeric reaction product (Figure 5.19). The average degree of polymerization in the brushes was calculated to be 7 for **PA4** and **PA5** by comparing the integral values of signals of PPEOMA and the PPC backbone. The GPC trace of **PA4** and **PA5** is indicative of some residual “macroinitiator” (Figure 5.20). This could be explained by the presence of residual PPC-OH which was not or only partially functionalized by the acyl bromide, probably because it was not completely dissolved in the reaction with bromoisobutyryl bromide (only 80% of initial hydroxyl groups were converted successfully). The GPC trace of the polymer brushes tend to a multimodal distribution. This may be the result of sterical crowding growing during reaction and intramolecular terminations, leading to an unequal distribution of the monomer PEOMA over the initiator entities.

Table 5.6 GPC results of PPC-OH and PPC macroinitiator

NO.	PEOMA^a DPPEO	M:I:CuBr:dNbpy mole ratio	Temp °C	Time (h)	Mn × 10^{-4} (GPC)^b	Mw/Mn (GPC)	DP n=
PA1	2	100:1:1:2	60	6	Cross-linked Gel		
PA2	2	100:1:1:2	50	4	Cross-linked Gel		
PA3	2	150:1:1:2	40	4	Cross-linked Gel		
PA4	2	300:1:1:2	50	2	15.5	2.6	7
PA5	5	300:1:1:2	50	2	17.5	2.9	7

a, PEOMA, DPPEO = 2, MWav = 188 g/mol, DPPEO = 5, MWav = 300 g/mol; b, PPC-macroinitiator, Mn = 2,9 × 104, Mw/Mn = 2.4



Scheme 5.3 Cross-linking reactions from radical-radical coupling. (Partially reprint with permission from ref([138])© American Chemical Society.

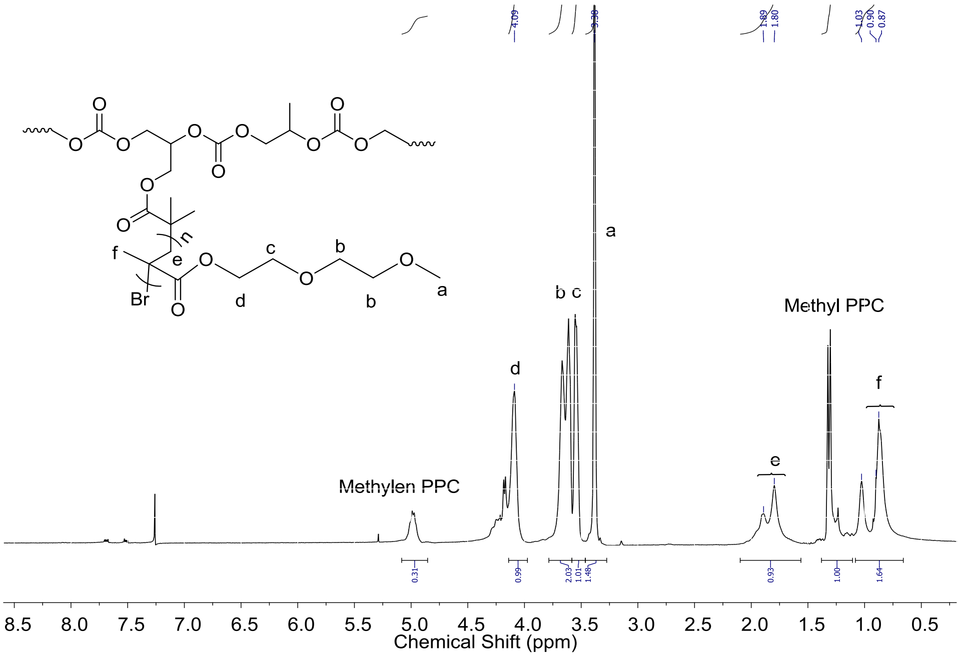


Figure 5.19 ^{1}H NMR spectra of PPC-*graft*-PPEOMA brush (sample **PA4)** n = DP_{PEO} = 7)

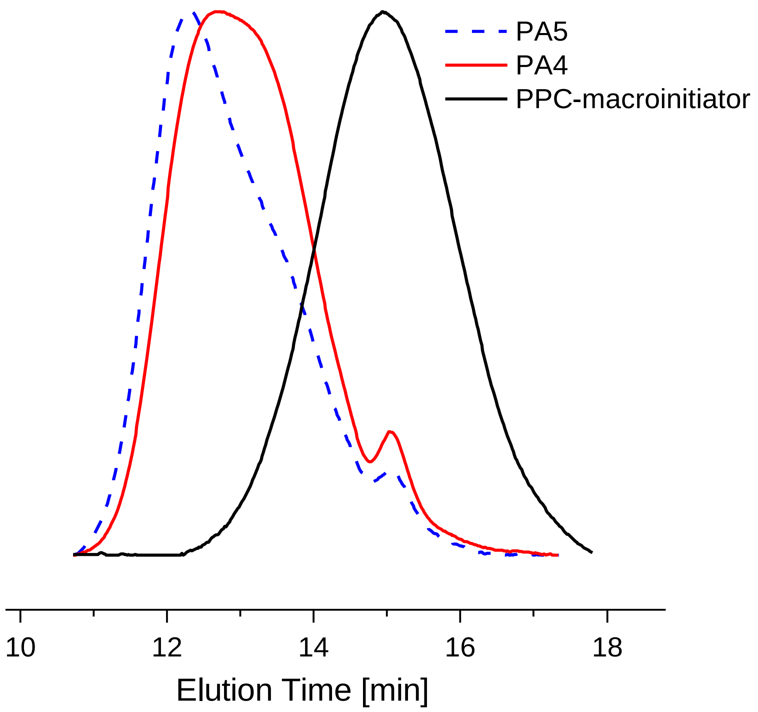


Figure 5.20 GPC trace of PPC-macroinitiator and PPC-brushes

5.3.2 Networks based on PPC-OH

PPC-OHs with a hydroxyl group content from 2.7 mol% to 7.1 mol% of the C2 units in the backbone were selected to prepare gels (Figure 5.21). The facile urethane formation between alcohol and isocyanate moieties were used to cross-link PPC-OH. Methylene diphenyl diisocyanate (MDI) was selected as agent to interconnect PPC-OH chains. It was found possible to prepare gels of PPC-OH and MDI by performing the cross-linking reaction in 1,4-dioxane as medium (Table 5.7). Tin(II) octoate was used as a catalyst. The glass transition temperature of the duromer is found at about 30°C, close to that of PPC.

Table 5.7 Cross-linking of PPC-OHs with MDI in 1,4-dioxane*

entry	PPC-OH	-OH content (mol %)	-NCO/-OH (mol/mol)	T_g (DSC)
1	R64	2.7	1:1	32.3
2	R43	3.3	1:1	30.2
3	R41	6.0	1:1	32.6
4	R47	7.1	1:1	31.3

*Conditions: 10 % g/ml PPC-OHs in 1,4-dioxane, 2-4 h reaction time at 70°C.

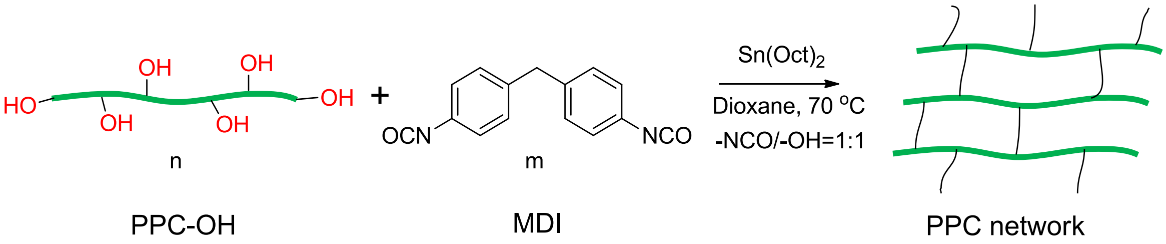


Figure 5.21 Synthesis of cross-linked PPC-OHs using MDI as cross-linking agent

The formation of a cross-linked PPC network was evident from the rheological properties of the gel (Figure 5.22). The storage modulus G’ of the mixture of PPC-OH and MDI before cross-linking shows a Newtonian behavior as expected for a dilute polymer solution. The loss modulus G” is consistently larger than G’ (Figure 5.22a). After cross-linking, as shown in Figure 5.22b, a typical gel behavior is found with the storage modulus G’ of the mixture nearly independent of the angular frequency and at least one decade above the loss modulus G”.

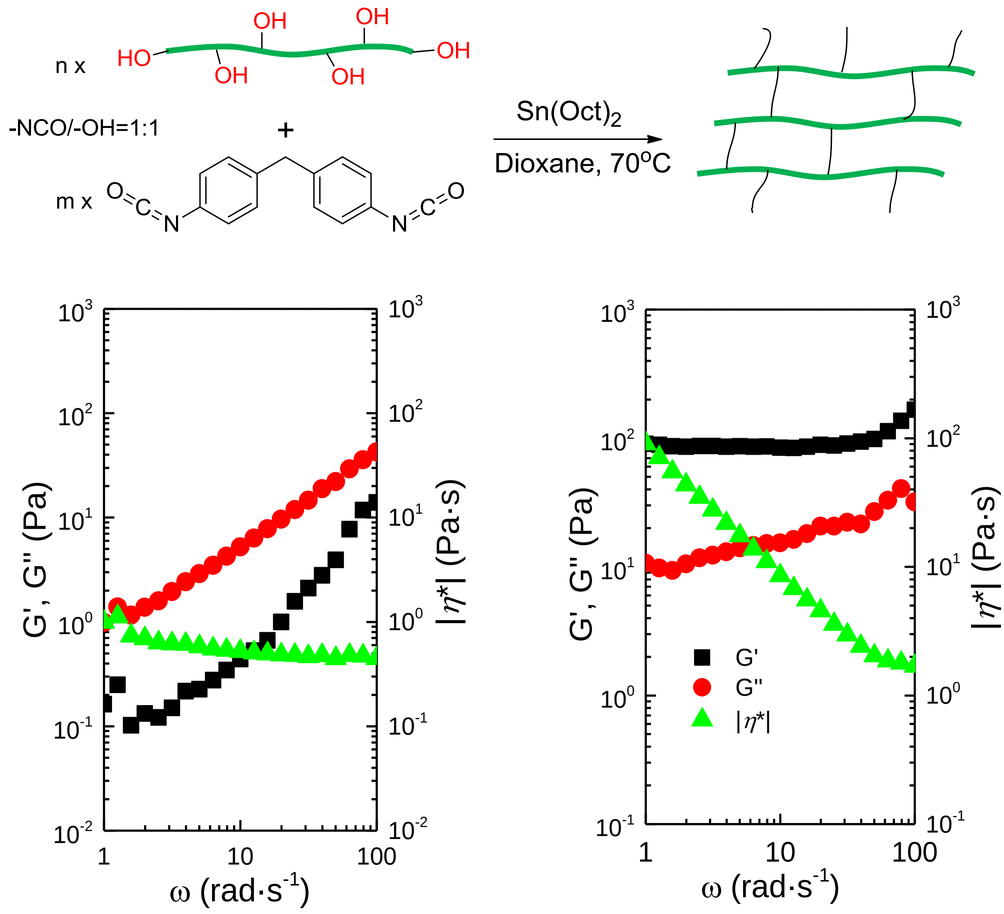


Figure 5.22 Rheology on the mixture before and after cross-linking

The formation of the gel results from the presence of OH functionalities on the backbone. Several reactions were performed to cross-link PPC with MDI (Table 5.8). PPC itself has hydroxyl end groups that may induce cross-linking chemistry.[84,174] PPC was treated with MDI at various –NCO/-OH ratios to study the possibility of reaction between end hydroxyl groups and isocyanate in the solution of dioxane (Table 5.8). No gel formation was observed in the mixture after 12h reaction at 70 °C, and no increase in molecular weight was found in GPC analysis (Figure 5.23). Therefore, PPC itself could not cross-linked by MDI in dioxane at 70 °C.

Table 5.8 Results of reactions of PPC with MDI

NO.[a]	-NCO/-OH mol/mol	MDI g	M_n[b] $\times 10^{-4}$	M_n/M_w[b]
PPC	-	-	5.9	1.74
MP1	0.5/1	0.061	5.7	1.75
MP2	0.8:1	0.098	5.6	1.74
MP3	1:1	0.122	5.9	1.74
MP4	2:1	0.245	5.8	1.75
MP5	3:1	0.366	5.8	1.74

a, In each sample, 20 g PPC was treated with MDI in 1,4-dioxane at 70 °C; b, Molecular weight were determined by GPC calculation in THF

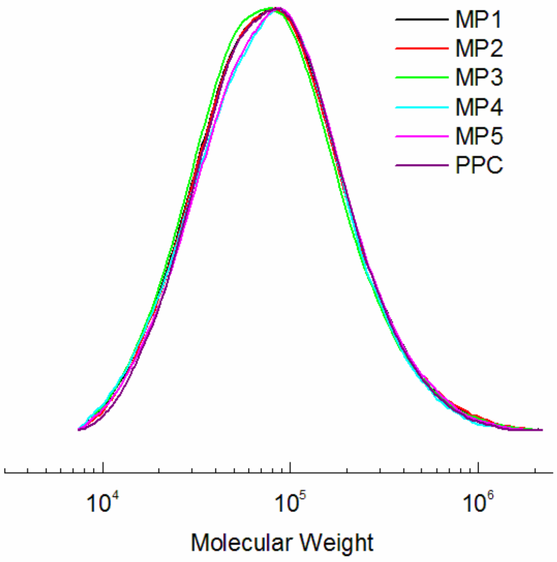


Figure 5.23 GPC trace of PPC after treating with MDI

A series of PPC-OHs with various hydroxyl contents could likewise be cross-linked by MDI using an -NCO/-OH ratio of 1:1. In all cases gels were formed (Figure 5.24). The glass transition temperatures of the products were basically independent of the starting material PPC-OH. The gel strength is increasing about linearly with the density of the OH functions on PPC-OH. The logarithm of the plateau storage modulus G_p' (taken at angular frequency $\omega = 1$ rad·s^{-1}) is linear proportional to the concentration of the OH functionalities. The clear linear behavior results are also because of the molecular weight of the starting materials is basically the same. The cross-link density is thus linear to the hydroxyl content in the polymer PPC-OH. The system is thus well behaved and in combination with the fact that PPC itself is not cross-linked by MDI, the possibility of preparing sIPN of PPC is given (Scheme 5.4). [171–174]

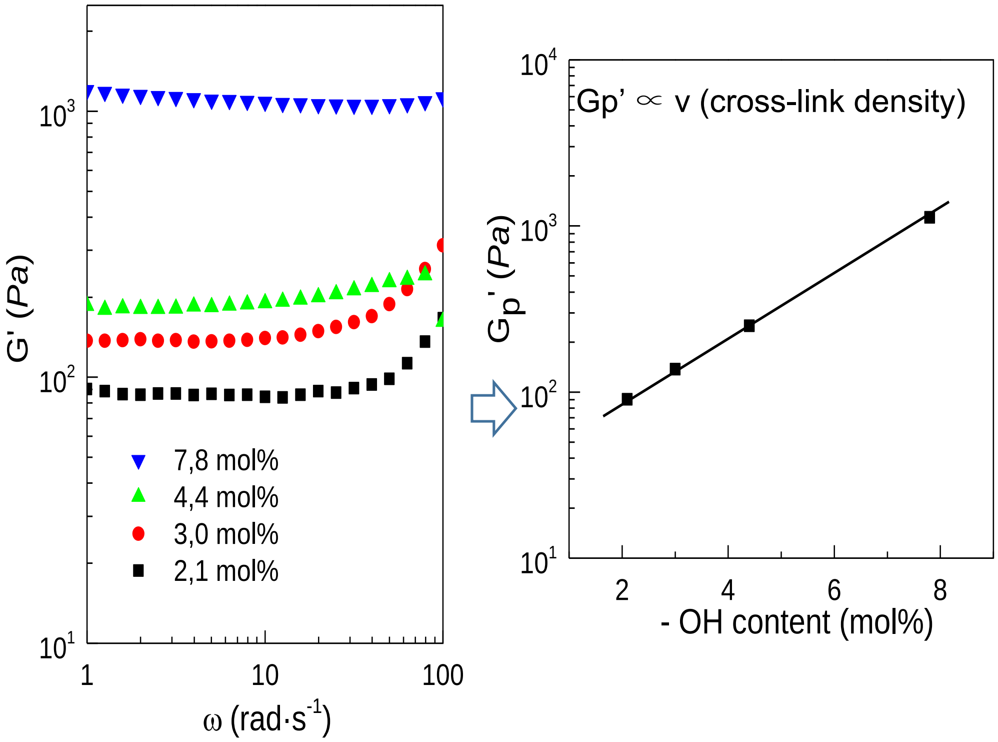
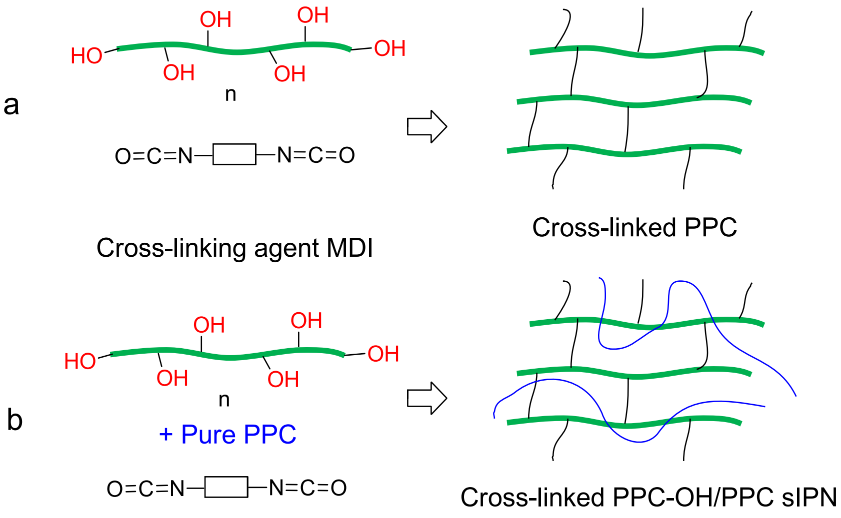


Figure 5.24 Rheology of PPC-OH/MDI gels with increasing cross-link density (OH content corresponds to mol%/mol building blocks of PPC).



Scheme 5.4 Preparation of cross-linked PPC-OH network and the technical pathway of synthesis PPC based sIPN

6. Experimental

6.1 Materials and Methods

All chemical products were obtained from Alfa Aesar, Aldrich or Merck and used as received unless stated differently, polymerizations were performed with dry and purified solvents.

PPC used in this study was produced from PO and CO_2 with zinc glutarate catalyst.[44,119] The number-average molecular weight (Mn) and weight-average molecular weight (Mn) of PPC are respectively 41 000 g/mol and 100 000 g/mol. The polymer PPC has 95 mol% carbonate linkages. The glass transition temperature (Tg) is 27.3 °C. This PPC was dried in a dynamic vacuum at 25°C over night. The wood flour which was grinded with ball milling (Retsch MM 200) in the Institute of Wood Sciences, University of Hamburg, with particle size of about 120 mesh was used in this study. Prior to compounding, the wood flour was dried in dynamic vacuum at 103°C for 72 h as referred in references.[50,124] In this study, 50 g scale of each hydroxyl-functionalized PPC with hydroxyl group content from 2.1 to 12.1 mol% were prepared as described in chapter 3.[130] Poly(ethylene glycol) methyl ether methacrylates, $H_2C{=}C(CH_3)COO\text{-}(CH_2CH_2O)_nCH_3$ (PEOMA, MW_{av} = 188 g/mol, DP_{PEO} = 2; MW_{av} = 300 g/mol, DP_{PEO} = 5) were acquired from Sigma-Aldrich and used after purification by distillation. Solvent dichloromethane and 1,4-dioxane were purchased from Sigma-Aldrich, purified by distillation and dried over 4A molecular sieves. 4,4'-diphenylmethane diisocyanate (MDI) was from BASF and distilled shortly before application.

6.2 Characterization

^{1}H NMR spectra (300 MHz) and ^{13}C NMR spectra

^{1}H NMR spectra (300 MHz) and ^{13}C NMR spectra (75 MHz) were recorded on a Bruker 300 MHz FT-NMR spectrometer in chloroform-d1. The chemical shifts (δ) are reported in ppm relative to tetramethylsilane (TMS).

Gel permeation chromatography

Gel permeation chromatography (GPC, Agilent: Intelligent pump AI12, RI detector RI 101, set of two columns 2 x 5 μm Polypore from Varian) was used to determine the molecular weights distribution of the polymer samples relative to polystyrene standards in tetrahydrofuran as solvent.

Differential scanning calorimetry

Differential scanning calorimetry (DSC, Mettler instruments) was used to determine the glass transition temperature of the polymer samples.

UV spectra

UV spectra obtained on a Jasco V-630 were used in the ONB group cleavage process. An Oriel LSH3023 500W UV-lamp equipped with a 313 nm filter was used to generate UV-radiation.

Contact angle (CA)

Static water contact angle measurements were performed with contact angle system OCA 15plus (Dataphysics Instrument) recorded by a CCD video camera. 2 μL of water were dropped on to the film surface of each polymer samples at dosing rate of 1 $\mu L \cdot s^{-1}$ and at least three measurements were made on each sample. CA measurements were performed on thin films of PPC-OH samples. These were prepared by spin-coating on a silica wafer from THF solutions of the polymers (10% w/v).

IR spectra

IR spectra were recorded on a Thermo Scientific Nicolet iS10 FTIR Spectrometer. Typically, 16 scans were signal-averaged to reduce spectral noise.

Mechanical properties

The static tensile properties were measured according to DIN EN ISO 527-1 using Zwick Z1.0 material testing machine with a video extensometer at 22.5 °C and relative humidity of 31%. The cross-head speed was set at 1 mm/min for the elastic modulus determination and 50 mm/min for tensile strength determination. The tensile bar specimens were prepared with Haake Minijet injection mold. WPC samples were melted at 145 °C before injected at 760 bar into the mold at 70 °C. At least 6 specimens of each sample were tested and the averages are reported.

Thermal characterization

Differential scanning calorimetry (DSC, Mettler instruments) was used to determine the glass transition temperature of the materials by fast heating the to 150 °C at a rate of 10 °C/min to erase their previous thermal history and then cooled down to -20 °C at 10 °C/min followed by a second heating cycle to 150 °C. The glass transition temperatures (Tg) were obtained from the second cycle.

Thermogravimetric analyse (TGA, Netzsch STA 409 TG analysator) was used for studying the thermostability of all WPC samples. Small pieces of WPC samples were dried under a dynamic vacuum oven at room temperature for 24 h before any measurement. 15-25 mg of each WPC samples were put in the furnace determination started at 50 °C to 500 °C at heating rate of 10 °C/min under nitrogen flow of 50 mL/min. Both the thermal degradation temperature of 5% weight loss ($T_{-5\%}$) and 50% weight loss ($T_{-50\%}$) were obtained from the weight versus temperature scanning. The maximum weight loss temperature (T_{max}) was determined by differential thermal analysis (DTG).

SEM

Tensile specimens were fractured after cooling in liquid nitrogen. The resulting pieces were dried in vacuum oven at 25°C for 72 h before coating with carbon. The SEM pictures were generated with a LEO Gemini 1525 scanning electron microscope operated at 10.0 kV and 20.0 kV.

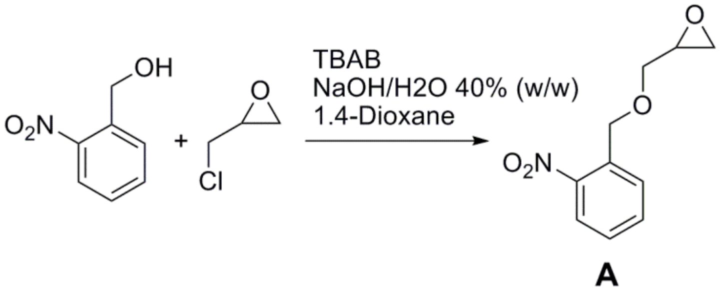
Rheometry

Rheometry was performed on a AR 2000 ex controlled stress rheometer (TA Instruments, New Castle, Germany, USA) by using a cone-plate geometry (diameter = 60 mm, angle = 2°). SAOS experiments were performed in a frequency range from 0.1 to 100 rad•s^{-1} and the applied strain was kept within the limits of the linear viscoelastic regime.

6.3 Experimental Section

6.3.1 Monomer A synthesis

o-Nitrobenzyl alcohol (100 g, 0.65 mol) was dissolved in 300 mL 1,4-dixoane followed by addition of tetrabutylammonium bromide (10.5 g, 32.7 mmol) and 200 g of a 40 wt% aqueous sodium hydroxide sodium (80 g (2 mol) of NaOH in 120 g of H_2O). Epichlorohydrin (200 mL, 2.6 mol) was subsequently added dropwise to the cold mixture (0 °C), and the resulting mixture was allowed to warm to room temperature. The progress of the reaction was monitored by thin layer chromatography (ligroin (50-70) / diethyl ether (5/3 by volume)). After stirring for 48 h, the reaction progress had subsided, and the mixture was extracted with two portions of 500 mL of diethyl ether. The combined ether fractions were extracted with excess of water, saturated sodium bicarbonate and saturated sodium chloride and were dried over magnesium sulfate, filtered and concentrated by rotary evaporation. The oily product was purified by column chromatography with solvent (ligroin (50-70) / diethyl ether (5/3 by volume)) on silica resulting in monomer **A** in a yield of 37 g (27.2% mole ratio based on *o*-nitrobenzyl alcohol) of a light yellow liquid at room temperature. ^{1}H NMR (δ, ppm, $CDCl_3$): 8.00 (d, 1H, ONB), 7.75 (d, 1H, ONB), 7.65 (t, 1H, ONB), 7.40 (t, 1H, ONB), 4.92 (s, 2H, $ONB(\boldsymbol{CH_2})OCH_2CHCH_2O$), 3.86, 3.89 (m, 2H, $ONBCH_2O(\boldsymbol{CH_2})CHCH2O$), 3.20 (m, 1H, $ONBCH_2OCH_2(\boldsymbol{CH})CH_2O$), 2.63, 2.81 (m, 2H, $ONBCH_2OCH_2CH(\boldsymbol{CH_2})O$), ^{13}C NMR (δ, ppm, $CDCl_3$): δ 147.16, 134.69, 133.73, 128.67, 128.08, 124.67, 71.74, 69.79, 50.65, 44.21.



Scheme 6.1 Synthesis of 2-[[(2-nitrophenyl)methoxy]methyl]-oxirane (monomer A); TBAB = tetrabutylammonium bromide

6.3.2 Polymerization

Terpolymerization of **A**, PO and CO_2 was achieved using a zinc glutarate (ZnGlu) catalyst. The catalyst was prepared as described in reference.[43] The copolymerization was carried out in a stainless steel reactor of 300 mL volume (Parr). The reactor was charged with 100 mg of ZnGlu and various amounts of **A**. Prior to reaction, a dynamic vacuum was applied to the reactor at room temperature for 1 h to remove any volatiles. Dry toluene (30 mL) was allowed to enter the reactor and the pressure was raised with gaseous carbon dioxide (3.5 N) to 2.0 MPa. Propylene oxide (10 mL) was added using an HPLC pump. The mixture was heated to 60 °C and the final pressure was adjusted with carbon dioxide to 3.0 MPa. The temperature and pressure were held for 8 h after which the reactor was cooled in an ice bath. The pressure was released and the reaction mixture subjected to a dynamic vacuum for 2 h at room temperature to remove the volatiles. The resulting solid was sampled for NMR analysis. The crude polymer was precipitated from acetone into methanol three times, collected and dried in an oven under vacuum for 24 h at 40 °C. The purified products appear as white to dark yellow powders at high content of comonomer **A**. Corresponding series of larger scale polymerization were successfully achieved with the same ZnGlu catalyst. PPC-ONB polymers at a scale of 40 g to 65 g were produced in each batch with various amounts of **A**. (Table 5.2). For a Fineman-Ross analysis, terpolymerization of **A**, PO and CO_2 were carried out in toluene as solvent with 25 mg zinc glutarate catalyst for 2 hours. The conversion was lower than 5% for monomer A.

6.3.3 Hydroxyl-functionalized PPC

The *o*-nitrobenzyl groups were removed by exposing 10% (wt/vol) THF solutions of the purified polymers to 313 nm UV light at room temperature. THF solutions were deoxygenated by stripping with argon gas before UV light irradiation to prevent possible photo-oxidative degradation. The hydroxyl-functionalized PPCs were separated by precipitation into cold ligroin, dissolved in acetone and reprecipitated into ligroin twice, and finally dried as for PPC-OH. The yield was over 90% in all cases. PPC-OH samples were analyzed by proton NMR to assure the absence of aromatic entities.

6.3.4 Polymerization experiments for Fineman-Ross analysis

Terpolymerization of **A**, PO and CO_2 was achieved using a zinc glutarate (ZnGlu) catalyst at very low conversion. (lower than 5% in molar ratio). The copolymerization was carried out in a stainless steel reactor of 300 mL volume (Parr). The reactor was charged with 25 mg of ZnGlu and various amounts of **A**. Prior to reaction, a dynamic vacuum was applied at room temperature for 1 h to remove any volatiles. Dry toluene (30 mL) was allowed to enter the reactor and the pressure was raised with gaseous carbon dioxide (3.5 N) to 2.0 MPa. Propylene oxide (10 mL) was added using an HPLC pump. The mixture was heated to 60 °C and the final pressure was adjusted with carbon dioxide to 3.0 MPa. The temperature and pressure were held for 2 h after which the reactor was cooled in an ice bath. The pressure was released and the reaction mixture subjected to a dynamic vacuum for 2 h at room temperature to remove the volatiles. The resulting solid was sampled for NMR analysis. The crude polymer was precipitated from acetone into methanol three times, collected and dried in an oven under vacuum for 24 h at 40 °C.

6.3.5 Large scale preparation of Hydroxyl-functionalized PPC

Large scale terpolymerizations of **A**, PO and CO_2 were carried out in a stainless steel reactor of 300 mL volume (Parr). The reactor was charged with 200 mg of ZnGlu and varying amounts of **A**. Prior to reaction, a dynamic vacuum was applied at room temperature for 1 h to remove any volatiles. The pressure in the reactor was adjusted with gaseous carbon dioxide (3.5 N) to 2.0 MPa. Propylene oxide (50 mL) was added using an HPLC pump, the amount of monomer **A** was adjusted to reach the ration of Table 5.2. The mixture was heated to 60°C and the final pressure was adjusted with carbon dioxide to 3.0 MPa. The temperature and pressure were held for 24 h after which the reactor was cooled in an ice bath. The products were purified as for smaller scale experiments and appeared as white to dark yellow solids. PPC-ONB polymers of 40.0 g to 65.5 g were obtained in this way. Data of copolymer samples are shown in Table 5.2.

6.3.6 Synthesis of PPC-macroinitiator

PPC-OH with 10 mol% hydroxyl group was dissolved in dry dichloromethane and the solution was then cooled in an ice water bath. 2-bromoisobutyryl bromide (0.75 mL, 6 mmol) was dropwise to the mixture of 1 mL pyridine (0.0084 mol) and a DCM solution (20 mL) of PPC-OH (1.1 g PPC-OH polymer corresponding to 1.2 mmol hydroxyl groups). The reaction mixture was stirred for 6 hours after which it was precipitated in methanol. Three times of reprecipitation from dichloromethane into methanol gave a pure product that was dried under a dynamic vacuum at 40 °C for 24 h before further processing. The PPC-macroinitiator was analyzed by ^{1}H-NMR to confirm the success of synthesis and determine the content of 2-bromoisotuyryl bromide units.

6.3.7 Synthesis of PPC-*graft*-PPEOMA

In the preparation of grafted polymers, typically 120 mg of PPC-macroinitiator (0.08 mmol initiator groups), PEOMA, MW_{av} = 188 g/mol (4.5 g, 24 mmol) or MW_{av} = 300 g/mol (7.2 g, 24 mmol) and 28 mg of ATRP ligand 2,2'-bipyridine (dNbpy, 0.18 mmol) were dissolved in 5 mL of anisole and purged with argon for 10 min. The mixture was transferred to a Schlenk flask with Cu(I)Br (15 mg, 0.1 mmol) as catalyst ($[PEOMA]_0/([Initiator]_0/\ [CuBr]_0/[dNbpy]_0 = 300:1:1:2$). The mixture was heated (40 °C - 60 °C) and stirred for 2 to 6 hours. The reaction was terminated by cooling with cold water and diluting with DCM. The content was then filtered over a short pad of neutral alumina to remove the copper catalyst followed by three times of precipitation from DCM into methanol. After drying in dynamic vacuum at 40 °C overnight, the final product was characterized by ^{1}H NMR and GPC.

6.3.8 Synthesis of cross-linked PPC network with MDI

The cross-linking was carried out by dissolving 2 g of PPC-OH polymer in 20 mL dry dioxane, heating to 70 °C and addition of MDI (-OH/-NCO= 1:1). Subsequently, 0.02 mL of stannous octoate (tin(II) 2-ethylhexanoate) catalyst solution in toluene (0.06 mmol) was added to the stirred mixture. After 2-4 hours, the mixture transformed into a gel. This gel was characterized by its rheological properties. Gel products were also dried under dynamic vacuum at 70 °C for 48 hours before thermal analysis.

6.3.9 Attempts to cross-link PPC with MDI

PPC was treated with MDI in the same process as for PPC-OHs cross-linking reactions. Thus, to a stirring solution with 20 g of PPC dissolved in 100 mL dry dioxane, MDI was added at 70 °C, followed by adding 0.04 mL stannous octoate (0.12 mmol) in toluene. The mixture was allowed to react for 8 h at 70 °C after which the dioxane was evaporated. The product was subsequently dried under a dynamic vacuum at 70 °C for 48 h for further measurement.

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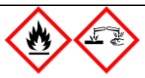
8. Appendix

a. List of hazardous substance used in the study according to GHS

Chemicals **(CAS number)**	**Hazard symbol**	**H-Phrases**	**P-Phrases**
Acetone 67-64-1	 GHS02 GHS07	H066, H225, H319, H336	P210, P233, P240, P241
Acetonitrile 75-05-8	 GHS02 GHS07	H225, H302, H312, H319, H332	P210, P280, P305+351+338
Aluminium oxide 1344-28-1	Not Listed		
Anisole 100-66-3	 GHS02 GHS07	H226 H315 H319	P305+P351 +P338
Acryloyl chloride 814-68-6	 GHS02 GHS05  GHS06 GHS09	H225, H290, H330, H302+312, H314, H400	P210, P280, P273, P301+330+331, P302+352, P304+340 P305+351+338, P309+310
2-bromoisobutyryl bromide 20769-85-1	 GHS05 GHS07	H302, H314	P280 P305+P351+P338 P310
2,2’-bipyridine (dNbpy) 366-18-7	 GHS06	H301+311	P280, P301+310+330, P302+352+312
Chloroform-d$_1$ 865-49-6	 GHS07 GHS08	H302, H315, H319, H351, H373	P281, P305+351+338
Carbon dioxide 124-38-9		H280	P410+P403

Dichloromethane 75-09-2	GHS08	H315, H319, H335, H336, H351, H373	P 261, P281, P305+351+338
Diethylether 60-29-7	GHS02 GHS07	H224, H302, H336	P240, P403+235
Ethanol 64-17-5	GHS02	H225	P210
Epichlorohydrin 106-89-8	GHS02 GHS06 GHS02 GHS05	H 226, H301, H331, H311, H314, H317, H350	P201, P261, P280, P301+310, P305+351+338, P310
1,4-Dioxan 123-91-1	GHS02 GHS07 GHS08	H225, H351, H319, H335	P210, P261, P281, P305+351+338
Dithiothreitol 3483-12-3	GHS07	H302, H315, H319	P302+352, P305+351+338
2-Nitrobenzylbromide 3958-60-9	GHS05	H314	P280
4, 4’-diphenylmethane diisocyanate (MDI) 101-68-8	GHS02 GHS07	H332, H315, H319, H334, h317, H3511, h335, H373	P261, P280, P284, P3014+340+312, P305+351+338, P342+311

Propylene oxide 75-56-9	GHS02 GHS06 GHS08	H224, H302, H312, H315, H319, h332, H335, H340, H350	P201, P210, P261, P280, P305+351+338, P308+313
Petrolether (50-70)	GHS02 GHS08	H225, H304, H340, h350, H361f, H373. H412	P201, P210, P273, P281, P301+310, P308 + 313
Pyridine 110-86-1	GHS02 GHS07	H225, H302, h312, H332	P210, P280
Stannous octoate Tin(II) 2-ethylhexanoate 301-10-0	GHS07 GHS08 GHS02	H317, H318, H361, H412	P273, P280 P305+351+338
Tetrahydrofuran 109-99-9	GHS02 GHS07 GHS08	H225, H302, H319, H335, H351	P210, P233, P280 P370+378, P501
Triethylamin 121-44-8	GHS02 GHS05 GHS06	H 225, H331 , H311, H302, H314	P210, P280, P303+361+353, P305+351+338, P310, P312
Tetramethylsilane (TMS) 75-76-3	GHS02	H224	P210
Tetrabutylammonium bromide (TBAB)		H315, H319, H335	P361, P305+351+338

1643-19-2	GHS07		
Sodium hydroxide 1310-73-2	GHS05	H290, H314	P280
Toluene 108-88-3	GHS02 GHS07 GHS08	H225, H361, H304, H373, H315, H336	P210, P301+310, P331, P302+352
Dimethylformamide DMF 68-12-2	GHS02 GHS07 GHS08	H226, H312, H319, H332, H360	P280, P305+351+338, P308+313
Poly(ethylene glycol) diacrylate 26570-48-9	GHS05, GHS07	H315, H317, H318	P280, P305+351 +338

b. Lebenslauf

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Osnabrück, November 2015

10. Erklärung über frühere Promotionsversuche

Ich versichere, dass von mir, Xiaojun WU, keine früheren Promotionsversuche mit dieser oder einer anderen Dissertation erfolgt sind. Es wurde nur dieser Antrag auf Eröffnung eines Promotionsverfahrens eingereicht.

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11. Eidesstattlicher Erklärung

Hiermit versichere ich, dass ich die vorliegende Arbeit eigenständig erstellt und alle benutzten Quellen ordnungsgemäß zitiert habe. Diese Arbeit ist zuvor in gleicher oder ähnlicher Form keine Prüfungsbehörde vorgelegt worden.

Xiaojun Wu

Osnabrück, November 2015