Kinetic and mechanistic studies of DMC-mediated propoxylation and carboxy propoxylations

Doctoral Thesis

With the aim of achieving a doctoral degree at the Faculty of Mathematics, Informatics and Natural Sciences Department of Chemistry University of Hamburg

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> > 2023

The experimental work presented in this thesis was carried out at the Institute of Technical and Macromolecular Chemistry of the University of Hamburg in the research group of Prof. Dr. Gerrit A. Luinstra from November 2016 to October 2020.

The following referees recommend the acceptance of this doctoral thesis: 1st referee: Prof. Dr. Gerrit A. Luinstra 2nd referee: Prof. Dr. Peter Burger 3rd referee: Prof. Dr. Holger Frey

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Date of thesis defense: 19.07.2024 Date of approval: 19.07.2024

I. List of Publications

Original articles

- <u>S.-F. Stahl</u>, G. A. Luinstra, *DMC-Mediated Copolymerization of CO₂ and PO Mechanistic Aspects Derived from Feed and Polymer Composition*, Catalysts **2020**, 10, 1066. https://doi.org/10.3390/catal10091066
- S.-F. Stahl, M. Wietzer, G. A. Luinstra, DMC-Mediated Propoxylation in Semibatch with an External Loop: Insights into the Catalytic Action, Ind. Eng. Chem. Res. 2023, 62, 29, 11536–11548. https://doi.org/10.1021/acs.iecr.3c01313
- S.-F. Stahl, G. A. Luinstra, Analysis of the Propoxylation of Zinc-Cobalt Double Metal Cyanide Catalysts with different active Surfaces and Particle Sizes, React. Chem. Eng., 2023. https://doi.org/10.1039/D3RE00313B

Conference talks

S.-F. Stahl, J. Marbach, G. A. Luinstra, *Preparation of tailored poly(propylene ether carbonates) with double metal cyanide and zinc glutarate as catalysts*, 13th International Workshop on Polymer Reaction Engineering, **11.- 14.06.2019**, Hamburg, Germany.

Conference posters

- <u>S.-F. Stahl</u>, J. Marbach, G. A. Luinstra, *Characterizing Catalyst Performance of DMCs in Alkoxylation with Propylene Oxide*, Polymer Reaction Engineering X (PRE 10),
 20.- 25.05.2018, Punta Cana, Dominican Republic.
- J. Marbach, S.-F. Stahl, G. A. Luinstra, *Synthesis of novel double metal cyanide catalysts and polymerization of PO and CO*₂, Polymer Reaction Engineering X (PRE 10),
 20.- 25.05.2018, Punta Cana, Dominican Republic.
- <u>S.-F. Stahl</u>, J. Marbach, G. A. Luinstra, *Thermodynamic and kinetic data on the propagation step of PO homopolymerization catalyzed by DMCs; relation to product properties*, 23rd International Congress of Chemical and Process Engineering (CHISA 2018), 25.-29.08.2018, Prague, Czech Republic.
- S.-F. Stahl, J. Marbach, G. A. Luinstra, A new and simple method to obtain easily and quickly kinetic and thermodynamic data via online FTIR-spectroscopy, 7th PhD-Workshop on Polymer Reaction Engineering, 31.08.-02.09.2018, Prague, Czech Republic.
- S.-F. Stahl, G. A. Luinstra, Importance of liquid phase composition for the polymer backbone in the DMC mediated copolymerization of CO₂ and PO, 6th International Symposium - Frontiers in Polymer Science 2019, 05.-08.05.2019, Budapest, Hungary.

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III. List of Abbreviations

ATRP	atom transfer radical polymerization
В	blocking agent
CA	complexing agent
CAOS	continuous addition of starter
CCTP	catalytic chain transfer polymerization
CO ₂	carbon dioxide
CoV	coefficient of variation
cPC	cyclic propylene carbonate
CSTR	continuously stirred tank reactor
СТА	chain transfer agent
DDA	dodecvlamine
DMC	double metal cyanide
EA	elemental analysis
EDX	energy dispersive X-ray spectroscopy
EO	ethylene oxide
FT-IR	Fourier-transform infrared spectroscopy
L	ligand
LDPE	low density polyethylene
MW	molecular weight
MWD	molecular weight distribution
NMR	nuclear magnetic resonance
PA	polyamide
PAC	polv(alkvlene carbonates)
PDI	polydispersity index
PEG	poly(ethylene glycol)
PET	poly(ethylene terephthalate)
PLA	polylactide
PO	propylene oxide
PP	polypropylene
PPEC	poly(propylene ether carbonate)
PPG	poly(propylene glycol)
PS	polystyrene
PU	polyurethane
PVC	polyvinyl chloride
RMSE	root-mean squared error
ROH	hydroxyl
ROP	ring-opening polymerization
SEC	size exclusion chromatography
SEM	scanning electron microscopy
TEA	triethylamine
TGA	thermal gravimetric analysis
TOF	turnover frequency
VOC	volatile organic compound
XRD	X-ray diffraction
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1 Zusammenfassung

Die katalytische Umwandlung von Propylenoxid (PO) zu Poly(propylenglykol) (PPG) mittels Doppelmetallcyanid (DMC) Katalysatoren und die Copolymerisation von PO und Kohlenstoffdioxid (CO₂) zur Herstellung von Poly(propylenethercarbonaten) (PPEC) sind die Themata dieser Dissertation.

Die Arbeit enthält eine Beschreibung einer detaillierten Studie zur Aufklärung mechanistischer Abläufe während der DMC-katalysierten CO₂-PO-Copolymerisation, mit dem Ziel ein grundlegendes Verständnis für den Prozess und seine Einflussfaktoren zu erlangen. Darin wurde festgestellt, dass die Bildung von Polycarbonaten und Polyethern durch DMC-Katalysatoren entlang zwei unterschiedlichen Routen abläuft, die von der Konzentration von aktiviertem PO, der CO₂-Konzentration und der Temperatur beeinflusst werden. Die Einbindung von CO2 in dem polymeren Produkt erfolgt in einem Kettenwachstumsprozess mit Insertionen in einer Metall-Alkoxid-Bindung, während Ether(ver)bindungen schrittweise durch einen externen, von Lewis-Basen-unterstützten nukleophilen Angriff auf ein koordiniertes PO-Molekül entstehen. Demzufolge können nukleophile (basische) Einheiten auf dem Katalysator die CO2-Einbindung fördern. Das vorgeschlagene mechanistische Modell wird durch die Beobachtung gestützt, dass das Molverhältnis F von Carbonat- zu Etherverknüpfungen im Copolymer nahezu konstant ist, wenn ein auf Zinkchlorid basierender DMC eingesetzt wird $(F \approx 0,15)$, während in einem analogen DMC-Komplex mit Nitratanionen auf der Oberfläche der Anteil an Carbonateinheiten höher ist und stärker von der CO₂ Konzentration abhängt $(\max, F = 0.45)$. Die Anwesenheit von zusätzlichen Aminen reduziert die katalytische Aktivität eines DMC mit Chloridanionen, hat jedoch keinen Einfluss auf die Polymerzusammensetzung. Die Bildung von zyklischem Propylencarbonat (cPC) erfolgt parallel zur Polymerisation und ist temperaturabhängig, jedoch unabhängig von der Reaktionszeit. Dies legt nahe, dass eine literaturbekannte Backbiting-Reaktion, die für eine cPC-Bildung angenommen wird, eine höhere Aktivierungsenergie als das Kettenwachstum aufweist.

Im Allgemeinen werden sowohl bei der Copolymerisation von PO mit CO₂ als auch bei der Homopolymerisation Poisson-verteilte Produkte erhalten. Breitere Molekulargewichtsverteilungen entstehen erst, wenn die Kettendiffusionsprozesse langsamer werden als die Propoxylierungsgeschwindigkeit. Dies ist insbesondere bei hohen Temperaturen der Fall und verbunden mit höhermolekularen Produkten mit geringerer Mobilität der Ketten, d.h. verringerter Selbstdiffusion der Polymere. Während der halbkontinuierlichen Propoxylierung verlängern sich Diffusionswege, da durch die Verdünnung der Abstand zwischen den Katalysatorpartikeln zunimmt. Eine schmale Produktverteilung kann nur bei ausreichend kurzen Diffusionswege erreicht werden, d.h. wenn der Abstand zwischen den DMC-Partikeln geringgehalten wird. Dies kann durch hohe Katalysatorteilchenanfangskonzentrationen bevorzugt bei der Verwendung kleiner, feinverteilter Katalysatorpartikel, bestens mit moderater Aktivität, erreicht werden.

Die Erweiterung eines Batchreaktors mit einer Schlaufe inklusive eines statischen Mischers führte zu einer verbesserten Durchmischung des Reaktionsgemisch mit dem dosierten PO in halbkontinuierlicher Fahrweise. Die Propoxylierung in diesem Setup ermöglichte die Erzeugung schmalverteilter PPG-Produkte, selbst bei höheren Molekulargewichten und geringen Katalysatorkonzentrationen. Es wurde gezeigt, dass die Grenzen, an denen die beobachtete "Catch-up" Kinetik ihre Gültigkeit hat, ebenfalls stark von weiteren Prozessbedingungen wie Temperatur und Dosierrate abhängig ist: Gut durchmischte Reaktoren, niedrige Prozesstemperaturen und moderate Dosierraten können helfen länger im Regime der "Catch-up" Kinetik zu agieren, und so Produkte mit geringer Polydispersität zu erhalten.

Ein weiterer Teil der Arbeit beschreibt das katalytische Verhalten dreier Zink-Cobalt-DMCs bei der Homopolymerisation von PO. Es wurde eine Methode vorgestellt die in kurzer Zeit, mittels Stoßdosierungen von jeweils 10 w% PO, Zugang zu einer Reihe katalytischer Merkmale bietet. Die Analyse der Datenpunkte mithilfe der Arrhenius- und Eyring-Theorien ergab, dass bei zwei der drei verwendeten Katalysatoren der Massentransport von PO geschwindigkeitsbestimmend ist, während bei einem der Katalysatoren die Geschwindigkeit der Ringöffnung von PO den maßgeblichen Faktor darstellt. Die kinetischen Parameter sind konsistent mit einer Propagationsreaktion nach dem Eley-Rideal-Mechanismus, bei dem ein koordiniertes PO-Molekül mit einem externen Polymerkettenhydroxylende reagiert. Die Visualisierung von Propoxylierungsraten in Abhängigkeit von Temperatur und Konzentration der Kettenenden [OH] bzw. des Katalysators [DMC] liefert einfache Einblicke in das kinetische und thermische Verhalten der verwendeten Katalysatoren. Es wurde gezeigt, dass die Einteilung in katalytischer Wirkung der drei DMCs nicht mit der Oberflächengeometrie oder -morphologie korreliert werden kann. Stattdessen führte die Betrachtung dispergierter Katalysatorpartikel als individuelle Mikroreaktoren zu einem Verständnis der katalytischen Wirkung: Kleine Kristallite ergeben bei gleicher ppm-Katalysatorbeladung eine größere Anzahl an Mikroreaktoren mit kleineren Interpartikelabständen und führen demnach zu kürzeren Diffusionswegen. Es wurde auch deutlich, dass nicht nur der Diffusionsweg, sondern auch die Aktivität des Katalysators und die Art der Prozessführung einen erheblichen Einfluss auf das Ergebnis der Propoxylierung haben. Das meistgeeignete Katalysatorsystem zur Erzielung von schmal verteilten Produkten mit hohem Molekulargewicht erfordert eine ausgewogene Rate der PO-Umwandlung in Bezug auf den Massentransport des PPGs zur Katalysatoroberfläche.

Zusammenfassend ergibt die Gesamtanalyse der Arbeit, dass Einblicke in die spezifische Wirkung von DMC-Katalysatoren von entscheidender Bedeutung sind, sowohl für die Vergleichbarkeit dieser Katalysatoren als auch für eine gezielte Weiterentwicklung. Die Abhängigkeiten von Faktoren wie Reaktionsraten und Diffusionswegen wurden als wesentlich für die Prozessentwicklung identifiziert. Diese Erkenntnisse tragen dazu bei, die Effizienz und Kontrolle von Reaktionen zur Umwandlung von Propylenoxid in Polymere zu verbessern und ermöglichen eine präzisere Auswahl und Optimierung von Katalysatorsystemen und Prozessfahrweisen für zukünftige Anwendungen.

2 Abstract

The catalytic conversion of propylene oxide (PO) into poly(propylene glycol) (PPG) using double metal cyanide (DMC) catalysts and the copolymerization of PO and carbon dioxide (CO₂) to produce poly(propylene ether carbonates) (PPEC) are the main topics of this dissertation. The work includes a detailed study aimed at elucidating the mechanistic pathways during DMC-catalyzed CO₂-PO copolymerization, with the goal of gaining a fundamental understanding of the process and its influencing factors. It was found that the formation of polycarbonates and polyethers mediated by DMC catalysts proceeds along two different routes influenced by the concentration of activated PO, CO₂ concentration, and temperature. The incorporation of CO₂ into the polymeric product occurs through a chain growth process with insertions in a metal alkoxide bond, while ether bonds are formed stepwise through an external, Lewis base-supported nucleophilic attack on a coordinated PO molecule. Thus, nucleophilic (basic) units on the catalyst can promote CO₂ incorporation. The proposed mechanistic model is supported by the observation that the molar ratio F of carbonate to ether linkages in the copolymer remains nearly constant when a zinc chloride-based DMC is used ($F \approx 0.15$), while in an analogous DMC complex with nitrate anions on the surface, the number of carbonate units is higher and more dependent on CO_2 concentration (max. F = 0.45). The presence of additional amines reduces the catalytic activity of a DMC with chloride anions but has no effect on the polymer composition.

The formation of cyclic propylene carbonate (cPC) occurs in parallel with the polymerization and is temperature-dependent, but independent of reaction time. This suggests that the literature-known backbiting reaction assumed for the formation of cPC has a higher activation energy than the chain growth.

In general, both the copolymerization of PO with CO₂ and the homopolymerization yield Poisson-distributed products. Broader molecular weight distributions only occur when chain diffusion processes become slower than the propoxylation rate, especially at high temperatures, resulting in higher molecular weight products with reduced chain mobility, *i.e.*, reduced polymer self-diffusion. During semibatch propoxylation, diffusion paths lengthen as the distance between catalyst particles increase due to dilution. A narrow product distribution can only be achieved with sufficiently short diffusion paths, which can be attained by using high initial catalyst particle concentrations, especially with small, finely dispersed catalyst particles with moderate activity.

The modification of a batch reactor with a loop including a static mixer improved the mixing of the reaction mixture with the dosed PO in semibatch mode. Propoxylation in this setup allowed the production of narrowly distributed PPG products, even at higher molecular weights and low catalyst concentrations. It was shown that the boundaries where the observed "catch-up" kinetics apply are strongly dependent on additional process conditions such as temperature

and dosing rate: well-mixed reactors, low process temperatures, and moderate dosing rates can help prolong the "catch-up" kinetics regime, leading to products with low polydispersity.

Another part of the work describes the catalytic behavior of three zinc-cobalt DMCs in the homopolymerization of PO. A method was introduced to quickly access a range of catalytic features through pulse dosing PO at a level of 10 wt% of the reactor content.

The analysis of kinetic data using Arrhenius and Eyring theories revealed that in two of the three catalysts used, the mass transport of PO is the rate-determining factor, while in one of the catalysts, the rate of PO ring opening is the dominant factor. The kinetic parameters are consistent with a propagation reaction following the Elev-Rideal mechanism, in which a coordinated PO molecule reacts with an external polymer chain hydroxyl end. Visualizing propoxylation rates as a function of temperature and the concentration of chain ends [OH] or the catalyst [DMC] provided simple insights into the kinetic and thermal behavior of the catalysts used. It was shown that the categorization of the catalytic effect of the three DMCs cannot be correlated with surface geometry or morphology. Instead, considering dispersed catalyst particles as individual microreactors led to an understanding of the catalytic effect: small crystallites result in a larger number of microreactors with smaller interparticle distances, thus leading to shorter diffusion paths. It also became clear that not only the diffusion path, but also the catalyst's activity and process conditions have a significant impact on the outcome of the propoxylation. The most suitable catalyst system for obtaining narrowly distributed highmolecular-weight products requires a balanced rate of PO conversion relative to the mass transport of PPG to the catalyst surface.

In summary, the comprehensive analysis of the work emphasizes the importance of gaining insights into the specific effects of DMC catalysts, both for comparing these catalysts and for targeted further development. The dependencies on factors such as reaction rates and diffusion paths were identified as essential for process development. These findings contribute to improving the efficiency and control of reactions converting propylene oxide into polymers and allow for a more precise selection and optimization of catalyst systems and process modes for future applications.

3 Introduction

Since the development of Bakelite, the first synthetic, industrially produced plastic in 1905, the worldwide production volume of plastics has increased rapidly. This was not in the least due to the fact that the new material, because of its high resistance to electricity and heat, could be used in various areas and was relatively easy to produce.^{1,2} Bakelite is, therefore, the first example to demonstrate the versatility of synthetic polymer materials, laying the foundation for the development of other plastics.

Statistics from 1950 to 2019 show, that the annual production and use increased steadily through the years, reaching a high of 460 million metric tons in 2019 (Figure 1I)^{3,4}. In 2020 the use declined because of COVID-19-related lockdown measures. However, global plastic use is forecasted to continue rising in the coming decades. Key plastic consumption sectors in Europe comprise packaging, building & construction, and the automotive industry (Figure 1r).⁵ Every day examples of plastic applications include LDPE packaging, which extends food shelf life, and PS-based insulation materials for energy-efficient housing. In addition, plastic has made a considerable contribution to resource-efficient mobility by providing lightweight construction materials. Plastics have thus become one of the essential man-made materials useful in all areas of modern life and today's world without plastic *i.e.*, synthetic organic polymers, appear impossible to imagine.



Figure 1 Global plastic production from 1950 – 2015. Included are thermoplastics, thermosets, polyurethanes, elastomers, coatings, sealants and fibers (left)^{3,4} and annual European (EU-28 + NO/CH) plastic demands as of 2018 by segment. Not included are adhesives, coatings, paints, PET fibers, PA fibers, PP fibers and polyacryl fibers (right)⁵.

3.1 Poly(propylene glycol) (PPG)

An important starting material for diverse plastic materials are polyether polyols, which includes the homopolymer poly(propylene glycol) (PPG). PPG is widely used as the "soft component" in the generation of polyurethanes (PU), *e.g.* in form of foams, coatings and sealants.^{6–9} It also finds direct applications as a surfactant, rheology modifier, and antifoaming agent¹⁰. PPGs are

industrially produced on a large scale by ring-opening polymerization (ROP) of propylene oxide (PO) with an alcoholic or acid starter using alkaline catalysts, such as KOH (Scheme 1).^{11,12} Double metal cyanide (DMC) solids were introduced as mediators for chain transfer polymerization in the early 1960s and have since become an effective alternative as they feature several advantages over simple basic catalysts (see below).^{13–15}



Scheme 1 Initiated grafting polymerization of PO onto alcoholic entities to yield PPG.

The identity of the polyether polyol given by the hydroxyl (OH) functionality, molecular weight (MW) and the molecular weight distribution (MWD) has a considerable influence on the properties of the resulting PU. The commonly used classification of PUs in 'elastic' and 'rigid' is mainly based on the properties of the polyol component: Polyols with low functionalities of about 2-3 OH/mol and with a MW of 2,000 to 10,000 Da form elastic PUs, while low MW polyols of 300 to 1,000 Da and higher functionalities (3-8 OH/mol) lead to rigid cross-linked PUs. Also, the MWD of polyols has a significant influence on the physico-mechanical properties of the products, mainly related to the viscosity which is higher for wider MWDs.¹⁶

3.2 Poly(propylene ether carbonate) (PPEC)

Most commercially available plastics are petroleum-based and non-biodegradable. The demand for alternative materials has increased significantly in recent years. An example that meets the requirements is poly(propylene ether carbonate) (PPEC). It is a thermoplastic, amorphous and biodegradable copolymer that results from copolymerization of CO₂ and PO.^{17–} ²⁰ "Bio-PO" can be synthesized from bio-glycerol-derived propylene glycol, which means that it also has a potential renewable basis. Glycerol is a by-product of biodiesel production, and in principle available in sufficient quantities.²¹ The monomer basis of PPEC, its application and recycling form a cycle in which CO₂ can be fixated. Another major advantage of the CO₂ feedstock for PPEC is that its production requires hardly any utilization of agricultural land. Thus, in contrast to most bio-, plant-based polymers, it does not compete with the food chain industry.^{22–25}

The properties of PPECs are strongly dependent on the carbonate-content in the polymer and on the amount of typical by-products of its preparation, such as cyclic propylene carbonate (cPC).^{26–28} Control over the polymerization process and hence the resulting products can be obtained by either the type of catalyst and/or by controlling the process parameters.^{29–33} The

products range thereby from softer poly(ether carbonates) to more hard, rigid polycarbonates (Scheme 2).



Scheme 2 Copolymerization of PO and CO₂ to form PPEC and cPC mediated by a catalytic system and a chain transfer agent (CTA).

Biodegradable, high molecular weight PPEC with a larger carbonate content exhibits noticeable gas barrier properties³⁴, which makes it attractive for short-term applications such as food packaging.^{35,36} One the other hand, PPEC with a lower molecular weight with hydroxyl termini can be used as soft component in the preparation of PUs.^{37–39}

PPEC undergoes a thermal decomposition through random chain-breaking processes and unzipping reactions from chain ends to form the high boiling liquid cPC at temperatures around 170-200 °C.^{40–42} Since cPC is highly soluble in PPEC and acts as a potent plasticizer, it significantly influences the mechanical and thermal properties of PPEC, mostly in an unwanted direction. For example, it lowers the glass transition temperature, reduces tensile strength, and increases the material's elongation at break.⁴³

3.3 Catalysts for the (Co-)Polymerization of Propylene Oxide

The copolymerization of PO and CO₂ is exergonic and, therefore, technologically readily realizable.^{44,45} However, it requires a selective catalytic system to successfully prepare PPEC, given that CO₂ is thermodynamically stable ($\Delta_f H^\circ = -393.51 \text{ kJ/mol}$ at 298.15 K)⁴⁶ and PO features a high chemical potential. INOUE reported the copolymerization of epoxides and CO₂ in 1969, for the first time, using a catalyst based on water and diethylzinc.⁴⁷ Since this pioneering work, numerous studies have aimed to develop novel catalytic systems, resulting in a wide range of both homogeneous and heterogeneous catalysts.

Today, the most well-known and effective homogeneous catalysts consists of metal complexes (such as Co, Zn) with salen^{48–50} or macrocyclic porphyrin ligands.^{51–53} These catalysts yield products with a perfectly alternating structure.^{54,55} Salen based catalysts offer advantages such as stability in air, making them relatively ease to handle and the ease of synthesis allows tuning the steric and electronic properties. ^{55–59} The salen-ligand provides steric shielding for the metal center, preventing aggregate formation. The presence of external nucleophiles, such as amines and chlorides seem necessary for reaching catalytic activity, and the ratio of nucleophile to catalyst is reported to have an impact on product selectivity and the formation

of cPC. Generally, one chain is formed per nucleophile, and a high concentration of nucleophiles leads to cPC formation. This puts some limitations on the salen complexes in their use as catalysts for PPEC formation from CO₂ and PO.

Further highly active catalysts with comparable activities²⁷ are heterogeneous, like double metal cyanide complexes (DMC). DMCs mainly form poly(ether carbonates) with a high content of ether blocks ($f_{carb} << 75 \text{ mol.}\%$).⁶⁰ In contrast, zinc dicarboxylates yield a range of poly(ether carbonates) with polymer compositions ranging from $f_{carb} = 60 - 92 \text{ mol.}\%$, depending on the process conditions.^{61–64} They are less active than DMCs^{65,66} and thus require higher catalyst concentrations for comparable productivity.

Catalysis is applied in about 80% of the global chemical transformations with the majority of the catalysts being in solid form.⁶⁷ This prevalence of the application of heterogeneous catalysis, despite their potentially lower selectivity can be attributed to several engineering advantages. These include the ease of separating catalysts from the product, simple regeneration, and preparation method, as well as their superior stability towards high temperature, pressure, and exposure to air. A heterogeneously catalyzed reaction is mediated at the catalyst surface, with active sites being nonuniformly distributed over the solid surface. Therefore, the catalyst's synthesis procedure has an influence on the number and accessibility of active sites and hence on the catalysts final activity.^{67,68} The following chapters focus on heterogeneous catalysis, since all propoxylation reactions described in this thesis were mediated by DMCs.

3.3.1 Double Metal Cyanide (DMC) Catalysts

Double metal cyanide (DMC) solids were introduced by General Tire Inc.⁶⁹ in the early 1960s as potent Lewis acidic catalysts and have since become known as an effective mediator for catalytic chain transfer polymerization (CCTP) under ring-opening of epoxides, especially of PO, to generate polyether polyols from alcohol or acid starter molecules.^{13–15} They are heterogeneous catalysts and Prussian blue analogues with the general formula $M_m[M'(CN)e]_h$. $xMX_w \cdot yL \cdot zH_2O$ (with e.g. $M = Zn^{2+}$, Fe^{2+} , Ni^{2+} , Co^{2+} and e.g. $M' = Fe^{2+/3+}$. $Co^{2+/3+}$, Ni^{2+} , Cr^{3+}). The complexes are generally precipitated by addition of an aqueous solution of a metal salt (MX_w) to an aqueous solution of hexacyanometallate or vice versa. The non-stoichiometric substances show a variation in electronic properties and vacancies that depend on the oxidation states of the two metal atoms. Organic complexing agents (L) such as *tert*-butyl ether, diglyme and polypropylene glycols are also added during the synthesis, with the aim to interfere with the crystallization.^{70,71} Crystals of Zn₂[Co(CN)₆]₂ formed in the absence of L were found to be catalytically inactive in the ROP of PO.^{72,73} The vacancies and defects in the crystalline structure, caused by ligands and excess of metal salts, are considered to be sites of higher acidity. DMCs have been screened for Lewis-acidic catalytic activity and are

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nowadays not only used in the ROP of epoxides, but also in the copolymerization and terpolymerization with other epoxides,^{74,75} carbon dioxide^{76–80} and/or cyclic anhydrides^{81–84} as well as catalysts for the polycondensation of diols and diacids.⁸⁵

DMCs offer several advantages over conventional alkaline catalysts for alkoxylations, rendering them an effective alternative. They were optimized, especially for PO, to yield lower degrees of olefinic entities. The latter may result from PO isomerization to allylic alcohols, which in turn may act as co-starters. DMC catalysis leads to PPG products with narrower molecular weight distributions and hydroxyl quantities similar to those of the starter molecules.^{86–88} As a result, PU elastomers obtained from polyether diols prepared by DMC catalysts feature improved mechanical properties over those produced using anions.¹⁶ Catalyst concentrations of as little as 15–50 ppm are already sufficient to obtain polyols within short reaction times^{16,89} and ideally enable a continuous process with no need for further purification steps.^{90,91}

A major challenge in performing alkoxylation under DMC catalysis is the occurrence of an induction time with an unpredictable length, during which no substantial chain growth can be observed.^{16,92} A potentially dangerous situation may arise if the epoxide concentration exceeds certain limits, since the ring opening is highly exothermal.⁹³ Consequently, in industrial processes, the DMC solids are activated for catalytic activity after their synthesis which is before the actual monomer feeding is commenced (semibatch reactor operation).^{87,94} The activation is commonly carried out by addition of small amounts of epoxide to a DMC catalyst which is suspended in a starter (typically a diol) of low molecular weight.^{95–97} The induction period significantly reduces the overall space-time yield of the process, however, the reaction rate exceeds that of the conventional KOH-catalyzed alkoxylation once the activation has been secured (Figure 2).¹⁶



Figure 2 Exemplary course of PO conversion (X_{PO}) with reaction time *t* in a PO polymerization with a DMC catalyst and KOH. The DMC-mediated process features an induction period.¹⁶

3.3.2 The Seven Steps of Heterogeneous Catalysis

A heterogeneously catalyzed reaction in the gas phase can be described as a sequence of seven elementary, chemical, and physical reaction steps (Figure 3I). These steps include external diffusion of reactants from the bulk phase to the catalyst particle (1) followed by internal, so-called pore diffusion to its active sites, (2) and the adsorption of reactants (3). Subsequently, surface reaction (4), desorption of the products from the active sites (5) and their diffusion through the catalyst pores (6) and the film diffusion (7) occur. A similar picture can be created for a catalytic process in a liquid (solvent or bulk).

Consideration of all these steps is important for an understanding of the overall rate of the catalytic reaction. The adsorption, desorption and reaction steps cannot be evaluated independently of each other and are hence summarized as microkinetic steps, whereas the macrokinetic steps encompass all diffusion processes. If diffusion is rate-determining, the reaction rate *k* is replaced by an observable, effective reaction rate k_{eff} . Variation in the rate of any one of these steps by changing *e.g.*, temperature, concentration, pore structure or particle size leads to a change in the overall rate. It might also give a change of the rate-determining step of the process.^{98–100}



Figure 3 Schematic diagram of chemical and physical steps involved in a heterogeneous catalytic reaction (I)⁹⁸ and general temperature dependencies of a heterogeneously catalyzed reaction in form of an Arrhenius plot (r).¹⁰⁰

Heat transfer next to mass transfer should be a further point of attention in such a heterogeneous catalytic system. The reaction only takes place at the active sites of the catalyst, and temperature gradients between bulk and catalyst respectively inside the catalyst may exist. Diffusional and chemical reaction rate have different temperature dependencies (Figure 3r). When the overall reaction rate *k* is solely controlled by microkinetics, it is, according to ARRHENIUS,^{101,102} directly proportional to $\exp(-E_a/(RT))$. When the reaction rate is controlled by intraparticle diffusion processes (porous particle), an apparent activation energy of one-half the real activation energy will be found, and the Arrhenius plot gives a straight line of slope $-E_a/(2R)$. Finally when film mass transfer through the external boundary layer

becomes the rate-limiting step, the observable activation energy further decreases to $E_a = 3-5 \text{ kJ/mol.}^{99}$

The reaction step (4) can only occur after adsorption of at least one of the reactants (3). These surface reactions can be described to proceed in a limit through either the Langmuir-Hinshelwood mechanism or the Eley-Rideal mechanism. The Langmuir-Hinshelwood mechanism assumes that both reactants adsorb onto the active sites of the catalyst surface. The surface reaction only takes place between two adjacent absorbed reactants, resulting in the formation of the product, which is subsequently desorbed from the surface. In contrast, the Eley-Rideal mechanism is characterized by a bimolecular reaction in which only one of the reactant molecules is coordinated to the catalyst surface and reacts with an external reactant molecule through direct collision.^{67,68,103-105}

3.4 Process Engineering and Reactor Design

The rate-determining step in a heterogeneously catalyzed reaction is affected not only by the accessibility of the catalyst's active sites, but also by the mixing and dosing conditions in the reactor, with influence on both mass and heat transfer. Concentration equalization through diffusion is typically slow and determined by the diffusion coefficients of the components being mixed.

Generally, DMC-mediated processes yield Poisson-distributed polymers. Nonetheless, broader molecular weight distributions (MWD) can occasionally be obtained, particularly at higher molecular weights and higher dosing rates. Consequently, the broadening of MWD is associated with the reactor setup and process condition.^{106,107} Therefore, mixing is a unit operation that holds significant importance in various industries. The efficiency of mixing, and thereby the uniform distribution of a monomer in the reaction mixture, is determined by factors such as reactor design, dosing points, mixer geometry, phase state and the viscosity.^{108–110} A wide array of apparatuses and mixing units are employed for different mixing operations, adapted to the diverse processes and product requirements. Selection of a mixing geometry for a specific application is dictated by the desired quality of mixing and mixing time. One of the most widely recognized and commonly used mixing apparatuses is the agitator vessel, which can be equipped with various stirrer geometries.^{111–113}

Several dimensionless numbers are used to describe mixing and its quality in different types of reactors. In this context, one widely used number is the Damkoehler number Da_M . It is defined as the ratio of the mixing time to reaction time and indicates whether mixing will be a concern (larger Da_M) or whether the effect of mixing will be of a minor impact for the outcome (smaller Da_M). The latter is targeted and will be the case when the reaction rate is slow compared to the mixing rate.¹¹³

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An important parameter in fluid mechanics is the specific power ϵ which is defined as the power-per-volume unit that is introduced into a system by stirring (= $P/(V\rho)$; ρ fluid density in kg/m³). The Newton number Ne (= $P/(\rho n^3 d^5)$; n rotational speed in 1/s, d diameter of stirrer in m) is a measure of the power introduced into a system by a specific stirrer.¹¹⁴ A further entity of relevance for flow conditions in a reactor is the Reynolds number Re (= $\vartheta d/v = \rho \vartheta d/\eta$). Values above 2,300 are referred to as turbulent flow, whereas lower values are assumed to indicate laminar flow.¹¹⁵ Both the Newton and the Reynolds numbers are dimensionless quantities, which enable a direct comparison between two geometrically similar reactor systems of different dimensions.

The flow in the area of a stirrer is described by the Reynolds number $Re_{R} (=\rho n d^{2}/\eta)$.¹¹⁶ The system is considered as turbulent for values of $Re_{R} > 10,000$. Further dimensionless quantities that are used for the design of reactors are, e.g., the Nusselt number Nu (= aL/k; a convective) heat transfer coefficient in W/(m²K), *k* thermal conductivity in W(mK)), which is used to describe the convective heat flow between a solid surface (reactor wall) and a flowing fluid, and the Prandtl number Pr, (= $\vartheta \rho c_p/k$; c_p specific heat capacity in J/(kgK)), which describes the relationship between kinematic viscosity and thermal diffusivity. The Schmidt-number Sc (= ϑ/D_e) indicates the ratio of kinematic viscosity to the diffusion coefficient.¹¹¹

3.4.1 Commercialized Reactor Designs for Polyether Polyol Synthesis

Most of the polyether polyols are produced in conventional plants on a large scale of about 300 kT per year.¹¹⁷ The synthesis is mainly performed in stirred tank reactors. These have some disadvantages to continuous plants, such as lower space-time yields.^{16,118} Arco Chemical (now part of Bayer) developed the first continuous process in the mid-1990s for a cost-effective production of polyols, propagated as IMPACT Catalyst Technology. The PO monomer in this process is added to a pre-activated starter/catalyst mixture with the option of continuously dosing further hydroxyl compounds (including water) together with PO (continuous addition of starter, CAOS).96,97,119 Its development is based on kinetic studies of DMC-mediated PO polymerization. These studies demonstrated that low mass starters are propoxylated at a high reaction rate without deactivating the catalyst, *i.e.*, when the starter concentration remains below a certain level. The studies also revealed unique catch-up kinetics, leading to a preferred propoxylation of lower molecular weight fractions.¹⁶ The development of this CAOS process has been one of the most important ones in the field of polyether polyol synthesis. Subsequently, numerous modifications based on this technology have been proposed and implemented into industrial processes.^{120,121} Another approach for a continuous process involves combining a loop reactor for PO monomer addition in a plug-flow reactor.122

The rate at which the monomer is added is limited by the plant's ability to dissipate heat from the highly exothermal alkoxylation reaction. Localized overheating during the process promotes formation of by-products, such as allylic compounds from PO isomerization or hydroxide elimination from a metal alkoxide. Optimization approaches focus on improving heat transfer during semibatch operation (PO dosing). This is usually achieved by incorporating a heat exchanger into stirred tank reactors, such as cooling coils, or by increasing the reactor's surface area by circulating parts of the reaction mixtures in a loop through an externally located heat exchanger. Additionally, implementation of nozzles for monomer and/or reaction mixture addition, combined with recirculation through an outer circuit, are described to enhance heat removal and facilitate faster monomer addition, resulting in increased space-time yields.^{123–126} Another patent highlights the beneficial impact of high energy densities of PO dosing during the production of polyether polyols on the foaming properties in the subsequent production of PU foams. In this process, the polyol is pumped through zones with high energy density, primarily generated by mixing units such as static mixers and various nozzles.¹²⁷

Static mixers or motionless mixers were established in the process industry in the 1970s. They have become standard equipment in continuous once-through processes and recycle loops for mixing and heat transfer improvement. They promote homogenization of feed streams with a minimum residence time,^{128–130} require little space, are silent and have low operating and maintenance costs (no moving parts): little to no additional power is needed, *i.e.* except some for pumping against a higher back pressure. A higher fouling potential, limited interchangeability and particle size constraints belong to their drawbacks.^{131,132}

Static mixers consist of a series of identical, stationary guiding elements that are installed reasonably in pipes, plug flow reactors or columns, and influence the flow structure of the fluid as they redistribute it in the direction transverse to the main flow by dividing the laminar product flow into partial streams before they are redirected. The performance of a static mixer is often described by its mixing quality. Quantifying this efficiency is especially of interest for the comparison between mixers from different manufacturers and ensures a reliable design. The relative mixer length (= L/D; L length of mixer, D inside tube diameter) required for a given homogeneity and the corresponding pressure drop are hence basic criteria.¹³³ Nowadays, there are more than 30 commercially available models and more than 2,000 US patents that describe static mixers and their applications, pointing to the versatility of motionless mixers. Most of them are variations of the three basic types: Kenics mixers, consisting of alternating right- and left-handed twisted helices arranged in sequence, interfacial surface generators (ISG) which use four drilled holes through solid sections between axially displaced cavities, and SMV mixer with stacks of corrugated lamellae with open crossing channels.^{129–132,134}

4 DMC-Mediated Copolymerization of CO₂ and PO – Mechanistic Aspects Derived from Feed and Polymer Composition

4.1 Synopsis

As previously outlined in the introduction (Chapter 3.3), there exists a variety of catalysts that can be used for the conversion of propylene oxide (PO) with carbon dioxide (CO₂). These catalysts differ significantly, for example, in their handling, catalytic activity, and notably, in the copolymer composition of the polymers formed during the catalytic PO/CO₂ copolymerization process. The properties of the resulting poly(propylene ether carbonate) (PPEC) products are substantially influenced by the incorporated carbon dioxide (i.e. carbonate content) and the quantity of typical by-products produced, such as cyclic propylene carbonate (cPC). Hence, the choice of catalyst, alongside the selection of process parameters, plays a pivotal role in determining these properties.

Understanding the mechanism of the double metal cyanide (DMC)-mediated copolymerization of PO and CO₂ is of vital importance for the targeted preparation of catalysts, in particular for the aim of producing tailor-made materials. This chapter addresses this very aspect, as the elementary reaction steps involved in the copolymerization of PO and CO₂ under DMC catalysis have not been fully comprehended until now. This understanding is also of importance for the identification of the most suitable process conditions for a specific application.

Process conditions, *i.e.*, pressure and temperature, determine the composition of the coexisting liquid and gas phases in equilibrium. This study examines the correlation of the liquid phase composition N and the incorporation of CO₂ into the polymer chain: three N values and four temperatures are considered. Initial experiments revealed that when chloride - originating from catalyst synthesis - was present at the catalyst surface, N appeared to have little effect on CO₂ incorporation. The impact of process parameters on yield, molecular weight distribution (MWD), and the formation of cyclic propylene carbonate (cPC) is also reported.

Additional experiments were conducted to examine the impact of the presence of nucleophilic amine bases on the resulting polymers, next to the effect of "softer" anions at the catalyst surface by performing an anion exchange of chloride for nitrate. It was observed that the more nucleophilic nitrate ions (by easier dissociation from surface zinc dications) enhanced the basic properties of the catalyst surface, leading to a shift towards carboxylation and leading to a dependence of the polymer product composition on N.

Based on these findings, a mechanism for DMC-mediated copolymerization of PO and CO₂ was proposed. This mechanism encompasses an internal protonation step, which liberates growing polymer alkoxide chains from the catalyst and is influenced by the Lewis acidity of the DMC.

4.2 Copy of Publication



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Article DMC-Mediated Copolymerization of CO₂ and PO—Mechanistic Aspects Derived from Feed and Polymer Composition

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Abstract: The influence of composition of liquid phase on composition of poly(propylene ether carbonates) in the copolymerization of CO_2 with propylene oxide (PO), mediated by a zinc chloride cobalt double metal cyanide, was monitored by FT-IR/CO₂ uptake/size exclusion chromatography in batch and semi-batch mode. The ratio of mol fractions of carbonate to ether linkages *F* (~0.15) was found virtually independent on the feed between 60 and 120 °C. The presence of CO₂ lowers the catalytic activity but yields more narrowly distributed poly(propylene ether carbonates). Hints on diffusion and chemistry-related restrictions were found underlying, broadening the distribution. The incorporation of CO_2 seems to proceed in a metal-based insertion chain process, ether linkages are generated stepwise after external nucleophilic attack. The presence of amines resulted in lower activities and no change in *F*. An exchange of chloride for nitrate in the catalyst led to a higher *F* of max. 0.45. The observations are interpreted in a mechanistic scheme, comprising surface-base-assisted nucleophilic attack of external weak nucleophiles and of mobile surface-bound carboxylato entities on activated PO in competition to protonation of surface-bound alkoxide intermediates by poly(propylene ether carbonate) glycols or by surface-bound protons. Basic entities on the catalyst may promote CO_2 incorporation.

Keywords: double metal cyanide catalysis; ring-opening polymerization; poly(propylene ether carbonate), PPEC; heterogeneous catalysis; propylene oxide; carbon dioxide

1. Introduction

The utilization of carbon dioxide (CO₂) as a feedstock in the chemical industry has been propagated over decades and also as a kind of a soft type of green washing: no current chemical process involving CO₂ has a negative carbon footprint [1]. Nevertheless, it is an inexpensive and nontoxic raw material and indeed may at least help to reduce the carbon footprint of a chemical product [2–4]. Apart from its negative image as a greenhouse gas, it is a readily available waste product of several large scale processes and a utilization in a "chemical Verbund concept" may be economically interesting because of future taxations [5–7]. As it has a high thermodynamic stability ($\Delta_f H^\circ = -393.51$ kJ/mol at 298.15 K) [8], economically processing CO₂ is challenging; reactions with it are bound to be endothermic and are in need of supplementary energy. It thus must not surprise that emission from chemical industry is more than 40 times larger than its use [9]. The copolymerization of CO₂ and epoxides to form poly(alkylene carbonates) (PACs) is in this context an exception, as the copolymerization reaction is spontaneous [10,11]. Especially the combination of CO₂ and propylene oxide (PO) as a commodity chemical to give poly(propylene ether carbonates) (PPEC) is of interest, giving access to biodegradable and biocompatible materials [12–15]. PO could alternatively be prepared from bio-glycerol derived

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propylene glycol, meaning that it has a potential renewable basis but with an unattractive carbon footprint—for other epoxides see [16,17]. Furthermore, PPECs show in dependence on their structure noticeable gas barrier properties [18], which makes it suitable, e.g., for the short-term application of food packaging [19–21]. PPEC diols are also used as soft component in the manufacturing of polyurethanes, adding some slow, sustaining resilience to corresponding coatings and foams [22–26].

Since CO₂ is relatively stable and PO has a high chemical potential and a high kinetic stability, catalytic control is necessary for a reaction between them. Next to effective catalytic systems, an effective process is necessary for a successful commercialization of PPECs to become viable alternatives to current commodities, in particular in a packaging market competing with polyolefins or polystyrene. The material properties of PPECs vary with the carbonate content in the polymer, and with that, the tentative application of the products. A point of concern is also the formation of cyclic propylene carbonate (cPC), which is thermodynamically more stable than the polymer; its formation as a volatile organic compound (VOC) and migrating substance should be avoided [27–29].

Control over the polymerization process can be received by either type of catalyst and/or by process parameter such as temperature, CO₂ pressure, and reaction time [30–34]. The products are ranging from poly(ether carbonates) to polycarbonates (Scheme 1). Ever since Inoue firstly reported on the copolymerization of CO₂ and epoxides in 1969 [35], to today, studies are carried out to develop more selective, more active or better defined catalytic systems. The most active known homogeneous catalysts are (Co, Zn) metal complexes with macrocyclic ligands, like salen [36–38], diketimine [39–42], or porphyrin ligands [43–45]. These homogeneous catalysts tend to yield products with exclusively carbonate linkages as the result of perfectly alternating copolymerization [46–48]. This is a direct consequence of the reaction pathway with typically metal alkoxides that are not reactive towards activated PO [49].



Scheme 1. Transfer copolymerization with a chain transfer agent (CTA) of propylene oxide (PO) and CO_2 to form poly(propylene ether carbonates) (PPEC) diols or cyclic propylene (cPC).

Inoue, in 1995, also introduced the concept of immortal polymerization as an ultimate living polymerization that involves a reversible transfer between an active, propagating chain end and a chain transfer agent (CTA) [50]. End-functional polymers with narrow molecular weight distributions (MWDs) can thus be synthesized when the chain transfer occurs faster than the propagation step. Such a polymerization gives easy control over the molecular weight by the amount of CTA relative to the monomers [51–54]. Such a regime of controlled copolymerization can be reached with the homogeneous catalysts for the perfectly alternating copolymerization of PO and CO_2 with CTAs in the form of acids or alcohols (Scheme 1) [54–56]. The action of the protic CTA is readily understood as resulting from the degenerate protonation of metal bound alkoxide intermediates of the copolymerization mechanism of these catalysts. The total number of chains in such a regime will favorably exceed the number of active catalyst sites. In addition, blockcopolycarbonates can be obtained by the strategy as was recently summarized in an extensive review, comprising many mechanistic considerations [57].

Heterogeneous catalysts, similar to the original system of Inoue is, have their own attractiveness in the PO/CO₂ copolymerization. In contrast to the homogenous predominantly zinc and cobalt catalysts, products with ether linkages as the consequence of consecutive PO additions are also accessible from the combination of PO and CO₂. The effective insertion of PO into a metal alkoxide bond (multiple steps) must then be an additional part of the mechanism. Solid zinc dicarboxylates,

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e.g., allow the preparation of poly(ether carbonates) with an adjustable polymer composition between $f_{\text{carb}} = 60-92 \text{ mol}\%$, attainable by variation of the process parameters [58–61].

The immortal polymerization of PO in the presence of alcohols is a prominent feature of industrially applied double metal cyanide (DMCs) complexes for the preparation of narrow distributed polypropylene glycols [62]. The DMC catalysts for propoxylation may also yield poly(ether carbonates) when CO₂ is admitted, usually giving products with large contents of ether blocks ($f_{carb} << 75 \text{ mol}\%$) [63–65] and with a lower activity [66]. The immortal copolymerization of CO₂ and epoxides can also be mediated by zinc carboxylate and DMC catalysts, giving a product with the signature of both catalysts [67]. Two mechanistic proposals for the action of these DMC catalysts have been put forward: one involving insertion of PO into an intermediate metal alkoxide and one with more evidence comprising an external attack of an alcohol on a coordinated (activated) PO molecule (Scheme 2). The latter reaction step may also be a part of the action of zinc carboxylates in the PO/CO₂ copolymerization [68]. Thus, an interesting mechanistic issue remains on how the action of the heterogeneous catalyst with both ether and carbonate linkage formation is to be understood, and how to relate this to the strictly alternating copolymerization of the homogenous catalysts.



Scheme 2. Proposed reaction routes in double metal cyanide (DMC)-mediated propoxylation of alcohols, external attack of CTA ROH and proton transfer (**a**) and "insertion" of PO in a zinc alkoxide bond after (reversible) RO[–] dissociation (**b**). Formulated in the essence of single zinc site catalysis for simplicity, more interactions will be present; structures would be derived from the 001/100 plane of DMC crystals [69–71].

This study tries to argue that both anionic and neutral nucleophiles are to be considered. It reports on the action of a DMC catalyst on a liquid phase consisting of mixtures of PO and CO₂ and using polypropylene glycols of various molecular weights as CTAs. The immortal copolymerization of CO₂ and PO is thus described in terms of yield, carbonate incorporation, molecular weight distribution, and cPC formation. Based on the extensive study below, a set of interconnected elementary reaction steps for the copolymerization of PO and CO₂ will be presented comprising the importance of basic anions at the DMC surface. The elementary reaction steps of the copolymerization of PO and CO₂ under DMC catalysis are a matter of discussion, several common sense proposals were made [61,72]. Clear seems that before ring-opening, the PO needs to be activated by coordination to the catalyst surface; CO₂ insertion does not seem to require an open coordination site [73]. Idealized free-energy profiles indicate that formation of ether linkages is energetically favored over carbonate linkages, but activation energies may direct the reaction to less favorable products. A consecutive insertion of CO₂ to dicarbonate units is energetically unfavorable and was not observed so far [74].

2. Results

2.1. Homopolymerization of PO and Copolymerization with CO₂ in Batch Processes

Orientating homopolymerization experiments of PO and copolymerization experiments of PO and CO₂ were carried out in batch processes with Caradol ED 56-200, also with the aim to characterize the action of the used batch of the DMC solid in this study (Figures 1 and 2, Table 1, vide infra). The catalyst was kindly supplied to us under restrictions of analysis and non-disclosure obligations, it is known that zinc chloride and the hexacyano cobaltate trianion $Co(CN)_6^{3-}$ were used in its synthesis (c.f. Figure S7). The catalytic chain transfer polymerization of PO to form poly(propylene glycol) (PPG) is a known exothermic process and is potentially dangerous. Care is taken to keep the heat content of the reaction mixture below the reactors' safety limits; it always needs to be assured that the catalyst has been activated and PO is consumed before additional feeding of PO, e.g., to get to higher molecular weights. The products of this study all are liquids—the thermal properties [68] follow the Flory-Fox equation—and are dependent on the molecular weight and the composition. The timeline of a typical copolymerization experiment (Figure 1c) thus comprises (i) a drying procedure at 120 °C, (ii) the initiation by catalyst activation (in the presence of PO and argon respectively CO_2), (iii) for copolymerization, adjustment of CO₂ pressure and temperature to the desired value and addition of PO in batch or semi-batch mode. During the copolymerization (iv), the slope of CO_2 uptake is measured by a mass-flow controller and can be taken as an indicator for the reaction rate.



Figure 1. Reactor logs of batch experiments with 30 g of Caradol and 5 mg of catalyst (a) homopolymerization of PO, set $T = 60 \degree C$ (PPG_1) (b) homopolymerization of PO, $T = 55 \degree C$ (PPG_2) (c) copolymerization of PO with CO₂, $T = 60 \degree C$, p = 10 bar (PPEC), and (d) polymerization during which CO₂ was added at the onset of the exotherm (PPG/PPEC).

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Figure 2. Molecular weight distributions (MWDs) of the polymers of the experiments depicted in Figure 1a–c (Entry 1–3).

Table 1. Molecular weights M_n and M_w of polymers obtained from batch experiments of Figure 1a–d.

Entry	Polymer	M _n [kg/mol]	M _w [kg/mol]	PDI
1	PPG_1	6.7	26.4	4.0
2	PPG_2	5.5	46.3	8.4
3	PPEC	3.5	4.1	1.2
4	PPG/PPEC	4.8	8.6	1.8

(CTA: 30 g Caradol ED 56-200, 300 mL autoclave, 50 mL PO, 5 mg DMC).

The reactor logs of the homopolymerization experiments (Figure 1a) show that the resulting reaction heat cannot be removed from system for isothermal operation once the temperature exceeds ~60 °C. The active cooling of the reactor with a cooling bath of -28 °C does not help, as heat transfer is simply too slow. The runaway reaction results from the moment of the first activated catalyst sites and causes an uncontrollable increase in temperature and pressure (but remains within the safety limits of the reactor). It also leads to broader molecular weight distributions (Figure 2), which is untypical for DMC catalyzed propoxylation in semi-batch with feeding of PO to an active system [75,76]. The initial reaction phase occurs in a chaotic, untypical way with non-equilibrium local conditions.

A homopolymerization experiment in which the temperature was kept at 55 °C could be carried out without resulting in a runaway (Figure 1b, Entry 2), however with the same result with respect to receiving a PPG with a broad molecular weight distribution, be it somewhat smaller. The high molecular tails indicate a process wherein some chains are preferentially growing. This is typically the result of conditions were PO diffusion is faster than that of the chain ends, a process that is self-enhancing as longer chains have a longer diffusion time and then grows faster once in the vicinity of the catalyst and then becomes still slower to diffuse away (and thus to grow further). The presence of various catalytic sites is unlikely an explanation as chains would grow on all centers in an immortal polymerization (which can be achieved with the catalyst).

Polymerization of PO in the presence of CO₂—giving polyether carbonates—favorably does not lead to the strong exotherm of the initiation. This holds true for reactions under otherwise the same conditions as PO homopolymerization, i.e., except for an additional 10 bar (Figure 1c) or 36 bar of CO₂ pressure. The analysis of the products indicate that only small amounts of CO₂ get incorporated into the polymer chain. Incorporation is more or less independent on the process conditions as polymer composition that is described as the ratio of mol fractions f_x of carbonate to ether linkages $F(= f_{carb}/f_{ether})$ adds up to 0.14, both at 10 bar and at 36 bar of CO₂ pressure (Table S1). *F* thus runs from 0 for a polyether to infinitive for alternating PPC and reaches the value of 1 for PPECs with equal molar amounts of carbonate and ether linkages.

The molecular weight distribution of experiment in the presence of CO_2 is much narrower (Figure 2; Table 1). The narrow molecular weight distribution and the absence of a strong isotherm show that CO_2 globally interferes with the rate of PO ring-opening, although incorporation into

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the polymer backbone is only at a low level. It is generally experienced that the presence of CO_2 substantially decreases the activity of the DMC catalysts for PO ring-opening [72], but the advantageous influence on the MWD is not so often reported. Another experiment in which CO_2 was added just after the exotherm started to arise shows that even then CO_2 can be used to slow down the propoxylation. The increase in temperature could be limited to 132 °C instead reaching the 220 °C (Figure 1d). The carbon dioxide dilutes the PO only to a small extent, the major effect is interference with PO ring-opening at the catalyst surface. CO_2 is thus a potential stopper for runaway reactions.

2.2. Copolymerization of CO₂ and PO

Reaching a mechanistic understanding of the reactions of carbon dioxide in the DMC catalysis would profit from a dedicated data basis. We may assume that CO_2 and PO compete for coordination to catalysts surface, and that this is the first step in reaching an understanding. Process parameter pressure and temperature determine the composition of the coexisting liquid and gas phases. The influence of the composition of liquid phase *N* (defined as mol CO_2 /mol PO) on the insertion of CO_2 into the polymer chain was evaluated at four different temperatures and at three values of *N* (Table 2). The gas-liquid equilibrium data were taken from literature (Figure S2) and can satisfactorily be described by the Peng–Robinson equation of state [77–79]. The experimental range regarding values for the composition of liquid phase *N* was limited by a *T* of 120 °C and *p* of 40 bar. The latter was set for reactor safety reasons. It is also reported that temperatures above 150 °C lead to substantial thermal decomposition of PPEC [80]. On the low end, the catalyst suffers in activity at temperatures lower than 60 °C and the conversion of PO and CO_2 proceeds only slowly (vide supra).

Entry	N	<i>T</i> [°C]	<i>p</i> (bar)	Yield [g]	M _n [g/mol]	PDI	<i>f_{cPC}</i>	F
5	0.173	60	18.9	5.7	630	1.2	0.00	0.13
6		80	25.3	6.4	660	1.1	0.02	0.13
7		100	32.6	31.5	1000	1.4	0.11	0.16
8		120	40.0	32.8	1080	1.2	0.08	0.14
9		60	13.6	5.8	630	1.1	0.00	0.12
10	0.115	80	18.2	6.9	660	1.1	0.02	0.15
11	0.115	100	23.6	33.3	1060	1.5	0.08	0.16
12		120	30.9	33.0	1080	1.4	0.07	0.12
13	0.058	60	8.3	5.4	570	1.2	0.00	0.17
14		80	11.0	7.7	660	1.2	0.02	0.15
15		100	14.2	33.5	1070	1.5	0.08	0.13
16		120	19.7	32.5	1100	1.3	0.06	0.11

Table 2. Semi-batch PO/CO₂ copolymerization data received from experiments in 300 mL autoclave.

(CTA: 30 g Lupranol 1200, 300 mL autoclave, 1 h dosing of PO at 0.56 mL/min, 20 mg DMC).

The reactions were run in semi-batch mode, feeding both PO (at constant rate) and CO_2 (keeping constant pressure). Lupranol 1200, a PPG with a molecular weight of 550 Da (against PS) was used as CTA. The low molecular weight enhances the accuracy in determining the composition of the thereon grafted PO/CO₂ by ¹H-NMR. The chain length of the CTA is at a magnitude that does not noticeably inhibit the catalysts' action and is thus useful for these type of experiments. The CO₂ uptake can be taken as a measure of reaction rate and therefore conversion of PO and CO₂. After complete addition of PO taking 1 h, the mixture was kept at a constant temperature and pressure for another 3 h, allowing residual PO to be converted.

The formation of polymer is a strong function of temperature. A kind of light-off temperature can be identified, lying between 80 and 100 °C (Table 2). Temperatures of 80 °C or lower give polymer yields lower than 8 g. The CO₂ uptake in the feeding time here majorly corresponds to the process of

saturating PO with it (Figure 3). The PO concentration increases in these experiments as conversion is slower than addition. The moderate slopes of CO_2 uptake after ending the PO dosing indicate a very slow conversion of CO_2 (Figure 3a; at t = 0 min the monomer feeding was started). The initial uptake increases with pressure, i.e., higher values of N, as a higher volume of CO_2 is needed to reach the equilibrium partial pressure over the reaction mixture. Experiments at temperatures over 100 °C give over 30 g of product, corresponding to about full conversion of PO (Figure 3b, Table 2). At temperatures of 120 °C, the same CO_2 total uptake was recorded as at 100 °C, but the maximum uptake was reached earlier, indicating that in both cases PO was totally converted after the reaction time, at 120 °C with a higher rate.



Figure 3. CO₂ uptake monitored by mass-flow controller from experiments at T = 60 °C (**a**) and N = 0.058 (**b**). PO dosing ended after 60 min (dashed line).

The resulting polymers were subsequently analyzed by ¹H-NMR spectroscopy (Figure S1) and size exclusion chromatography SEC. These data allowed for the calculation of *F* and the cPC content. The ratio *F* between f_{carb} and f_{ether} linkages that were present in the polymer backbone seems to be largely independent on process conditions and therefore on the feed (*N*). The incorporation of CO₂ seems to somewhat increase up to 100 °C, however yields are not comparable, and is lower again at 120 °C (Figure 3b, Table 2). This shows the presence of several competing steps with different activations energies. Note that the incorporation of CO₂ needs to be determined from the molar sums of carbonate linkages in the PPEC and cPC. The formation of cPC is considered the result of a backbiting reaction of a free chain end (vide infra). The backbiting can only proceed if the penultimate entity is a carbonate linkage [81]. The rate of backbiting would be proportional to the rate of formation of the respective copolymer and thus with the catalyst activity and level of CO₂ incorporation.

The activity of the catalyst is consequently somewhat higher at lower CO_2 pressures (Table 2). This confirms that CO_2 slows down reaction rate, consistent with the results from batch experiments described above. The formation of cyclic propylene carbonate is in the range of 2 mol% in the lower temperature range and a factor 4–5 higher at 100 °C and a little lower at 120 °C (possibly as the result of faster PO addition/lower CO_2 content, vide infra). The polydispersity index PDI of polymers synthesized is narrow, showing that the chain transfer polymerization regime of an immortal polymerization is operative. Lower temperatures give a lower PDI, which may be related to the lower viscosities of the reaction mixture at lower polymer concentration and in part to the lower importance of backbiting at those temperature. The molecular weight distribution may broaden through differences in diffusivity of PO monomer and CTA. The difference is smaller for low molecular weight CTAs; otherwise, gradients in molecular weight near and far from the catalyst crystals may arise on account of differences in propoxylation propensity, PO being more mobile and only reacting with catalyst near hydroxyls.

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2.3. Formation of Cyclic Propylene Carbonate

DMCs as catalyst for copolymerization of PO and CO_2 may form cyclic propylene carbonate (cPC) as a side product. The amount of cPC in the final polymer is therefore dependent on process conditions such as temperature, type, and amount of catalysts [82,83]. The dominant formation is a result of a backbiting (unzipping) reaction of a corresponding, free uncoordinated alcohol chain, and proceeds from the chain end. This can continue until two ether linkages constitute the chain end; ether linkages in a PP(E)C lead to a more stable polymer chain end (Scheme 3) [29,84]. In consequence, a relatively fast PO addition to free chains ends lead to less cPC formation (the incorporation of CO_2 will be affected by the relative ratio of the two reactions of the copolymerization and the cPC formation). The formation of cPC is a function of the number of end groups, meaning that more end groups in low molecular weight products tend to give more cPC.



Scheme 3. cPC formation.

As cPC is soluble in PPEC and functions as a typical plasticizer, it significantly influences the mechanical and thermal properties of the resulting polymer by lowering for example the glass transition temperature and tensile strength, as well increasing the elongation at break of the material [85]. It is generally desirable to keep the cPC content of the polymer low during polymerization reaction. Removal of the high boiling side product is not simple, solid–liquid extraction process involving an aqueous maleic anhydride solution was mentioned as alternative to commonly used methods [86], but those procedures mean an additional step for polymer production and higher costs in commercial operation.

Formation of cPC seems not to occur at low temperatures and pressures. This is the case irrespective of duration of an experiment at 60 °C and 18.9 bar of CO₂. The original experiment (Table 2, Entry 5) was modified to extended reaction times (Table 3). Evaluation of ¹H-NMR spectra shows that more PPEC had formed, as methyl protons belonging to carbonate, carbonate ether, and ether carbonate linkages of the graft on Lupranol 1200 could be observed. The cPC content was well below 1 mol% and *F* in the same range as in polymers prepared at other temperatures (Tables 2 and 3). The yield increased thereby with reaction time while the content of cPC remained for all experiments below 1% and did not increase with time. This validates the presumption that the formation of cPC occurs in connection with that of the polymer. The independency on reaction time and dependency on reaction temperature is to be explained by different temperature dependences of the rate of cPC formation and chain propagation. The rate of cyclic carbonate formation is much stronger temperature dependent than chain propagation, i.e., of PO ring-opening [83,87–89].

Table 3. Calculated *F* and determined cPC content in PPEC (PDI = 1.1) synthesized at 60 °C and 18.9 bar CO₂ pressure (N = 0.173).

Entry	Reaction Time [h]	Yield [g]	M _n [g/mol]	PDI	f_{carb}	f_{ether}	fcPC	F
17	6	5.7	600	1.1	0.16	0.84	< 0.01	0.19
18	12	7.8	610	1.1	0.16	0.84	< 0.01	0.19
19	24	8.9	650	1.1	0.15	0.85	< 0.01	0.18

(CTA: 30 g Lupranol 1200, 300 mL autoclave, 1 h dosing of PO at 0.56 mL/min, 20 mg DMC).

2.4. Process Monitoring of Copolymerization of PO with CO2

A more detailed and more accurate insight on the progress of the copolymerization was elaborated with larger equipment. Semi-batch experiments were carried out in 450 mL and 2 L stainless steel autoclaves equipped with an anchor agitator at 10 bar CO_2 pressure (Table 4, Entry 20–22). Such reactions are generally more uniform, and it is easier to secure safety as lower steady concentrations of PO are present. In batch experiments, the generation of a soluble polymer from and in PO gives a transition from a monomer dominated to a polymer dominated solution. The value for *N* given for the batch experiments is one only valid for the monomer, the presence of the copolymer may change it in course of the experiment. In the final dilution with copolymer, the solubility of CO_2 in the mixture of residual PO and product may be also determined by the latter (as the semi-batch experiments of Table 2 have no major differences in product composition, despite the span of yields, the effect of changing medium though may be minor there).

Table 4. Semi-batch PO homopolymerization and copolymerization with CO₂.

Entry	Polymer	СТА	<i>T</i> [°C]	<i>p</i> [bar]	M _n [kg/mol]	PDI	f _{cPC}	F
20	PPEC	Lupranol	120	10	5.5	1.3	0.03	0.11
21	PPEC_1	Caradol	90	10	12.0	7.3	*	*
22	PPEC_2	Caradol	120	10	13.8	1.7	0.02	0.17
23	PPG	Caradol	120	Ar	18.4	1.3		

(CTA: 30 g Lupranol 1200, 450 mL autoclave, 10 h dosing of PO at 0.3 mL/min, 15.9 mg DMC) (CTA: 166 g Caradol ED 56-200, 2 L autoclave, 9–12 h dosing of PO at 0.94 mL/min, 50 mg DMC). Polymer properties given are those of the final polymer. * Evaluation: vide infra.

The experimental set-up allows process monitoring online by FTIR measurements and off-line by tracking the development of molecular weight distributions. Longer feeding times with lower rates of PO additions (0.3 mL/min for experiments in 450 mL autoclave (Entry 20) and 0.94 mL/min in the 2 L autoclave (Entry 21–23)) were performed in this fashion and resulted in the preparation of higher molecular weight products. In the 450 mL set-up, the starting PPG (CTA, Lupranol 1200, Entry 20) with the molecular weight of 550 Da (against PS standards) was used and the polymerization procedure allowed preparation of PPEC with a narrow molecular weight distribution (Figure 4). The *F* value of 0.11 is a little lower than in batch experiments. Apparently, a uniform polymerization proceeds with most of the characteristics of an immortal (co)polymerization process with no indications of major effects of a changing medium form PPG of low mass to PPEG with about ten times that mass (5000 Da). The intermediate minor shoulder at lower mass is typical for "catch up" kinetics and seems to result from a small amount of costarter [90–92].



Figure 4. Development of polydispersity index (PDI) (**a**) and molecular weight distribution (MWD) curves (**b**) of PPECs synthesized at 10 bar CO_2 and 120 °C in semi-batch mode (0.3 mL/min PO feed) in a 450 mL autoclave and with Lupranol 1200 as CTA (Entry 20).

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Caradol ED 56-200, a CTA with a molecular weight of 2900 Da was used in the larger set up with 2 L nominal content (Entry 21–23). The larger PPG was chosen for reaching a medium mass copolymer with a blocky structure. In this system, the number and concentration of chain ends is lower. Runs showing the arising process complexity, one at 90 °C (giving PPEC_1, Entry 21) and at 120 °C (PPEC_2, Entry 22) will be discussed. The CO₂ concentration is majorly determined by the solubility in the polymer/PO mixture at the set temperature. As the copolymers obtained are comparable in composition, the concentration of CO₂ will have been comparable too (and low anyway). The viscosities of the reaction mixture with the respective molecular weights are those of the CO₂ saturated bulk copolymers with some PO. Viscosities also are only little dependent on the composition of the polymer (but will vary strongly with respect to M_w) at temperatures above 90 °C (Table S2), smaller differences in chain end dynamics will be present with a higher mobility at higher carbonate content.

The IR absorbance of the ring-deformation mode of PO at 830 cm⁻¹ is the most useful signal for detecting its concentration (Figure 5 and Figure S3). Taking only this signal as probe for its concentration does not give accurate data, however it keeps the analysis relatively simple. The first sharp increase in intensity of the IR absorbance originates from the catalyst's activation procedure (Figure 5) during which an initial amount of PO was added at 120 °C. The subsequent decrease indicates the successful activation of catalyst. Feeding PO was started as soon as the PO concentration was at the baseline and the set temperature was reached. The IR absorbance of PO then increases until a (semi) steady state concentration of PO is reached. This is reached in case of PPEC_1 after about 50 min and in case of PPEC_2 after 20 min. The steady state concentration of PO was about 0.45 mol/L at 90 °C and 0.15 mol/L at 120 °C. The higher PO concentration at 90 °C and longer time to reach steady state shows that the catalyst is less active at a lower temperature.



Figure 5. IR absorbance of ring-deformation mode of PO (black), cPC (blue), and C=O vibration mode of resulting PPEC (red) during semi-batch experiments in 2 L autoclave at $T = 90 \degree C$ (a) and $T = 120 \degree C$ (b) at 10 bar CO₂ pressure, including the activation procedure and cooling.

The time-dependent (almost steady state) concentration of PO increases about linearly in the experiment at 120 °C. The dilution of the catalyst and the polymer chain ends by grafting of PO/CO₂ results in a slower conversion in time, which in turn leads to a higher PO concentration, inflicted by its constant addition rate. The delicate balance of PO consumption and addition leads to the small increase in the steady state PO concentration. As the PO concentrations are generally on the low side, extraction of the rate constants from the course leads to larger errors and was not pursued. The (about) linear increase in PO concentration is found at 90 °C too, but only until intermediate reaction times. Still later the PO concentration mixture at lower temperatures, however, causes the fluctuations at progressive reaction time, as stirring with the anchor does not lead to a continuous renewal of the layer covering the IR probe window ("fouling", all signals decrease).

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At 90 °C, the appearance of PPEC carbonyl entities—related to the carbonyl vibration mode of poly(propylene carbonate) (PPC) at 1747 cm⁻¹—is clearly delayed from the PO concentration increase up to a volume of 80 mL, giving the concentration of about 0.45 mol/L. It shows that almost no PO conversion occurred in that first span of 50 min. No polymer can form at the low PO concentration against the CO₂ inhibition. Apparently, a certain PO concentration needs to build up first, and as conversion to PPEC commences, the increase in PO concentration by feeding is halted. Then, the copolymer of the very early stage contains more carbonate linkages than the product of later times. This may also hint that at too-low PO concentration, CO₂ cannot be fixated in the chain and effectively no polymerization can take place (vide infra). After the initial larger CO₂ consumption, the expected close to hyperbolic product concentration increase in a semi-batch process with constant intermediate concentration is found.

The cPC concentration increases—following the period of fast carbonate linkages formation—more strongly as later in the process. As discussed above, the carbonate linkages may only be stable when the chain is bound to the catalyst or in the situation when two ether linkages or more are following it in a hydroxyl chain end, precluding easy backbiting. The secondary formation of cPC indicates that instable chain ends exist that are undergoing a slower backbiting in a from polymerization decoupled mode. The unzipping will slow down when ether linkages are the ultimate and penultimate units of a chain. Once the formed part of the copolymer with the higher amount of carbonate linkages have been stabilized by backbiting (or consecutive PO addition), the rate of cPC formation and that of carbonate entities in the polymer backbone becomes a constant lower ratio afterwards until the end of the dosing (with the concomitant dilution).

The decreasing rate of carbonate linkage formation in course of the process may in early stages be related to the chain length. Smaller molecules have a higher local concentration of chain ends and a higher diffusion constant. The higher mobility leads to faster polymerization by chain start and potentially propagation of carbonate anionic chain ends (vide infra) through external nucleophilic attack on PO, and backbiting, a process decreasing the carbonate content of the copolymer, is less competitive. Dilution of the catalyst and chain ends, and possibly lower reaction rate constants on account of the changing medium (polarity and diffusion constants) decrease the propensity of chain end stabilization by consecutive PO insertion(s). As the medium further changes and dilution becomes more extensive, the increase in carbonyl signal intensity further declines, such as the rate of cPC formation. The PO consumption remains at about the level of feeding. The solubility of CO_2 in PPG is higher than in PPEC, which also may contribute some to the lower rate of carbonate generation. The intensity of the C-O-stretching mode of the ether entities ($v = 1100 \text{ cm}^{-1}$) decreases with reaction time as the percentage of ether linkages decreases with ongoing copolymerization (Figure S3). The experiment performed at 120 °C shows the same characteristics, but at a condensed time scale. Thus, in a first phase relatively much CO2 is incorporated with (consecutive) stronger cPC formation indicative of backbiting in free PO-carbonate chain ends, and a second phase with less CO₂ incorporation and cPC formation.

The molecular weight distributions of the products of the experiments at 90 °C, PPEC_1, and 120 °C, PPEC_2 are illustrative of the complex progress of the reaction (Figure 6). Contrasting to the results with the smaller PPG starter Lupranol1200 at 120 °C, where monomodal distributions were obtained (Figure 4, Entry 20), both polymers have a molecular mass distribution that is not the result of a simple/uniform polymerization process, neither a Poisson nor a Flory–Schulz distribution is obtained. The PDI of the PPEC_2 obtained at 120 °C remains distinctly lower than that of the product obtained at 90 °C of up to 8.
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Figure 6. SEC analysis of PPECs synthesized at T = 90 °C, p = 10 bar (**a**, Entry 21) and T = 120 °C, p = 10 bar (**b**, Entry 22) and PPG at T = 120 °C (**c**, Entry 23).

The broadening of a distribution (of an immortal polymerization) may have micro and macro kinetic origins. The latter will not be an issue when the molecular weights remain below the range of about 25 kDa. The preparation of PPG with the same catalyst (no CO_2 present) at 120 °C (Entry 23) gives a uniform, narrow dispersed product (Figure 6c). The development of the MWD of the PPG product follows almost that of an ideal immortal polymerization. The characteristics of a Poisson distribution are thereby maintained almost up to the target molecular mass of about 18 kDa. As the viscosity and hence the dynamics of the PPG and PPEC chain segments are not too different (Table S2; PPEC is even more mobile), we can assume that mixing is ensured also in the presence of low amounts of CO_2 , and thus that deviations have predominantly micro kinetic (chemical) origins in that range.

Although similar behavior at 120 °C, the experiment at 90 °C (Figure 6a) is again most informative as effects are more extensive and easier to recognize. The multimodal molecular weight distribution can be decomposed into three distributions using Gaussian functions with reasonable fits (Table 5; Figure S4; Table S3). The distribution at the highest molecular weight is the dominant product at the end of the dosing. Its content increases with the dosing time, showing that this type of molecules is picking up more than a proportional part of the PO (and with that CO_2). In fact, its final increase in mass is appreciably higher than expected, indicating that substantial amounts of OH end groups did not get carboxy-propoxylated. Contrary, the two other distributions seem almost not or more slowly to increase in weight, suggesting that they do not contain active OH entities, or are not in contact with activated PO. The latter is most likely when comparing the behavior of the system at 120 °C, product PPEC_2 (Figure 6b).

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		PPEC_1 2.5 h	PPEC_1 5 h	PPEC_1 6 h	PPEC_1 7.5 h	PPEC_1 8.25 h	PPEC_1 9 h
	<i>M</i> _n _1 [kg/mol]	3.4	3.6	3.6	3.7	3.7	3.9
Peak 1	$M_{\rm w}$ _1 [kg/mol]	3.9	4.0	4.1	4.1	4.1	4.4
	PDI_1	1.1	1.1	1.1	1.1	1.1	1.1
	<i>M</i> _n _2 [kg/mol]		8.1	8.4	9.0	9.3	9.4
Deals 2	$M_{\rm w}$ _2 [kg/mol]		13.8	13.4	12.5	12.3	12.4
Peak 2	PDI_2		1.7	1.6	1.4	1.3	1.3
	Rel. I (vs. 1)		0.52	0.47	0.36	0.36	0.52
	<i>M</i> _n _3 [kg/mol]	6.7	15.4	16.9	19.2	21.9	23.8
D1-2	$M_{\rm w}$ _3 [kg/mol]	16.4	69.5	80.2	97.2	105.7	106.2
Peak 3	PDI_3	2.5	4.5	4.7	5.1	4.8	4.5
	Rel. I (vs. 1)	0.46	1.69	2.28	3.12	3.36	4.43

Table 5. Molecular weights of PPEC_1 (Entry 21) samples (peak fit using Chromatographica).

The first product containing SEC trace already indicates that some part of the PPG grows in mass more strongly than a major other part. The mass distribution of the arising product has a PDI in the range of 2, more typical for a Flory-Schulz process. Such a distribution would be typical for a chain growth on the catalyst surface with a random termination reaction. This is typical for the homogenous catalyzed PPC formation with anionic active growing chains and with acid base reactions with the CTA (ROH) as termination. This broader mass distribution may be associated to the first phase of the copolymerization with a higher content of carbonate incorporation. The copolymerization does not proceed in an immortal fashion. The broadening then gets more extensive during the experiment, which in part results from the increasing immobility of this fraction close to the catalyst. The exchange with the bulk is slower than PO consumption and hence chain ends in layers around the catalyst crystals grow more extensively (macro kinetic effect). The early phase broadening is typical for the copolymerization. A proposylation of Caradol under the same conditions (90 °C) yields Poisson distributed products, reminiscent of an immortal process (Figure S5). This observation is taken as a clear indication that the products PPG and PPEC are formed along different mechanistic paths (micro kinetic effect). The chain copolymerization at 90 °C is faster than the degenerate acid-base reaction with ROH in the reaction mixture.

A smaller third distribution separates at intermediate chain length. These chains grow at about half the rate of the main distribution. This would fit to chains with only one growing end. Note that parts of the unreacted CTA of the first phase apparently never make it to the catalyst surface. Possibly, this separates from the product PPEC. This is tentatively connected to the choice of the PPG CTA molecular mass and will need investigations beyond the scope of the current report.

The mass distribution of the PPEC_2 product in the initial phase remains close to one. The higher temperature increases the rate of exchange of the chains end near the catalyst, and (if applicable, vide infra), degenerate acid-base termination reactions ensure immortal copolymerization. Most of the CTA is now propoxylated and CO_2 is coinserted regularly over the ensemble (Table 6). The formation of a fraction that similarly grows at a lower rate (half) may be inferred form the shape of the distribution at later times with higher viscosities with a final Mn of 12.6 kDa and a PDI of 1.7. The moderately small weight distributions, allowing calculating *F* of the grafted part of the polymer by simple arithmetics (Table 6). The experiment shows that another stirrer geometry, respectively, mixing quality and PO feed seem not to influence the carbonate content in the final polymer, as it is for PPEC_2 in the same range ($F = 0.16 \pm 0.02$) as before at a smaller scale. The calculated *F* from the experiment at 90 °C is more inaccurate, as the broader molecular mass distribution was not considered in the same simple calculations. The number for *F* is, however, in the same range, in accordance to the observations that neither the composition of liquid phase nor the temperature substantially influences the resulting polymer composition.

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Sample	f_{carb}	f_{ether}	f_{cPC}	F
PPEC_2_2.5h	0.12	0.84	0.03	0.15
PPEC_2_5h	0.13	0.84	0.03	0.15
PPEC_2_7.5h	0.15	0.82	0.03	0.18
PPEC_2_9.5h	0.14	0.84	0.03	0.16
PPEC_2_11h	0.14	0.84	0.02	0.17
PPEC_2_12h	0.14	0.83	0.02	0.17

Table 6. Calculated F and cPC content in PPEC_2 synthesized at 120 °C and 10 bar CO₂ pressure.

2.5. Amines as Cocatalyst/Conucleophile

An important question relating to the action of DMC catalysis for propoxylation vs. carboxy-propoxylation may be related to the base content of the catalyst. The nucleophilic PO ring-opening by an alcohol may profit from the close vicinity/assistance of a base (Scheme 2a), and in case of anionic chain ends, basic entities at the surface are essential (Scheme 2b). Basic entities may either be present on the DMC surface from their synthesis or be generated from nucleophilic attack of a generic nucleophile at PO: ring-opening then gives an alkoxide entity. Therefore, further experiments were carried out to investigate the impact of base on the catalytic action and the polymer composition to gain a deeper understanding of the underlying mechanism. The influence of basic conditions on the copolymerization in terms of induction period, CO_2 incorporation, molecular weight, and distribution was investigated by addition of varying amounts of amines to the suspension of the catalyst in Lupranol 1200. Triethyl amine (TEA) and dodecyl amine (DDA) were used; they differ significantly in chain length, pK_b , and nucleophilicity respective of coordination strength.

It is found that the induction time is not influenced by the presence of TEA or DDA. Propoxylation reactions mediated by DMC catalysts [71–73] generally feature an induction period as substrates from synthesis bind to the catalyst surface, which prevent PO coordination and therefore catalytic activity [93,94]. The catalyst activation is commonly carried out by addition of a small amount of epoxide to a DMC catalyst suspended in a starter (mainly diols as CTA) of low molecular weight [95–98], such as here in form of Lupranol1200. There is a general consensus that during this procedure, complexing agents on the zinc atoms from synthesis (e.g., *tert*-butanol) [99–102] and/or added alcohols are released, respectively, alkoxylated allowing more and more PO to bind to the surface, and thus to become activated for nucleophilic ring-opening [103,104]. The length of the induction period is dependent on, e.g., the catalyst synthesis route and procedure, temperature and epoxide concentration, but is also affected by the content of further nucleophiles with a coordination ability, such as water or added chain starters [75,105,106].

The onset of consumption of PO occurs almost instantaneously respectively after only a couple of minutes at 120 °C (Figure 7; Table 7). This observation is interesting as small molecules usually prolong the induction period. The amines or their reaction products after reaction with PO, however, do have an impact on the catalyst action. The PO partial pressure decreases much slower in the presence of 10 μ L of TEA. Generally, if PO consumption in time is slower, the more TEA is present (Figure 7a, Table 7). This is interpreted as amine or its consecutive reaction products coordinating to the catalyst surface, acting like CO₂ as a spectator ligand and decreasing the available catalytic sites for PO activation. DDA does not show any effect on the induction time or conversion of batch PO. This may be related to either the low coordination strength or the fact that DDA can react with PO to generate a further CTA of low coordination strength [68].

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Figure 7. Pressure curves of activation procedure with triethyl amine (TEA) (**a**) and dodecyl amine (DDA) (**b**).

Table 7. Catalyst activation in the presence of amine.

Entry	n _{amine} [10 ⁻² mol%]	V _{TEA} [μL]	t _{ind} [min]	t _{end} [min]	Δ <i>T</i> [°C]	Entry	m _{DDA} [mg]	t _{ind} [min]	t _{end} [min]	Δ <i>T</i> [°C]
24	0	-	5	45	14					
25	0.66	0.5	13	63	6	30	0.6	8	57	6
26	1.31	1	11	65	6	31	1.3	9	57	4
27	2.62	2	5	75	6	32	2.6	6	>51 #	7
28	6.58	5	5	190	2	33	6.6	8	63	4
29	13.1	10	5	>23 h *	n.d.	34	n.d.	n.d.	n.d.	n.d.

(CTA: 30 g Lupranol 1200, 300 mL autoclave, 4.5 mL PO, 20 mg DMC) * activation phase was not completed, # monomer was not consumed completely. The amount of amine given in mol% refers to CTA. ΔT : max *T* of exotherm.

The copolymer composition seems to be largely unaffected by the presence of TEA or DDA at N = 0.115 and at 120 °C. The carbonate content is still in the range of 14 mol% (Table 8, Entry 35–39 and 45–48). About 60–80% of the incorporation of CO₂ was observed with amines at lower CO₂ pressure (N = 0.058, p = 19.7 bar, $F = 0.08 \pm 0.03$), regardless whether TEA or DDA was added (Entry 40–44 and 49–52). The incorporation was unaffected by the concentration of the amine. This indicates that the amine acts on the surface of catalyst in competition to CO₂. The fact that a dependency on the CO₂ concentration is emerging shows that further smaller effects to concentration in the feed/surface are to be considered.

Table 8. Semi-batch experiments of PO/CO ₂ with amines at 120 °C pe	erformed in 300 mL autoclaves.
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Ν	Entry	V _{TEA} [µL]	M _n [g/mol]	PDI	f _{cPC}	F	Entry	m _{DDA} [mg]	M _n [g/mol]	PDI	f _{cPC}	F
	35	0	1000	1.5	0.07	0.14						
	36	0.5	960	1.8	0.06	0.16	45	0.6	1160	1.4	0.06	0.12
0.115	37	1	n.d.	n.d.	n.d.	n.d.	46	1.3	1210	1.2	0.06	0.09
	38	2	1020	1.6	0.06	0.15	47	2.6	1090	1.7	0.05	0.16
	39	5	1070	1.6	0.06	0.14	48	6.6	1190	1.5	0.06	0.15
	40	0	1100	1.3	0.03	0.16						
	41	0.5	940	1.8	0.05	0.08	49	0.6	1220	1.4	0.03	0.08
0.058	42	1	1080	1.2	0.04	0.07	50	1.3	1230	1.2	0.04	0.06
	43	2	1090	1.5	0.04	0.10	51	2.6	1200	1.3	0.04	0.08
	44	5	1090	1.6	0.04	0.11	52	6.6	1230	1.2	0.04	0.07

(CTA: 30 g Lupranol 1200, 300 mL autoclave, 1h dosing of PO at 0.56 mL/min, 20 mg DMC).

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Monitored semi-batch experiments of PO/CO₂ copolymerization at 120 °C (N = 0.016) in the presence of amines also show that they take no significant influence on the catalyst action. Higher molecular weights were targeted using a low PO feeding rate of 0.3 mL/min in three experiments differing only in the presence and type of amine (feeding time of 10 h; $V_{\text{TEA}} = 2 \,\mu\text{L}$; $m_{\text{DDA}} = 2.6 \,\text{mg}$; 30 g Lupranol1200, Figure S6). The PDI of the blank < DDA < TEA, resulting from minor effects that arise during the first part of the process (Figure 4 and Figure S6). The mass distribution under these conditions is more dependent on the activation procedure than on the process procedure. The amines do not function as a chain starter, e.g., chains of half of the molecular mass should form from the monofunctional TEA, which is not observed (reaction of glycidyl ether with amines is described as very rapid and accelerated by the presence of hydroxyl groups [107]). The molecular mass of the polymers is within experimental inaccuracy equal. In consequence, it can be presumed that the amines or their consecutive products are more or less inert, partly coordinating to the catalyst.

2.6. CO₂/PO Copolymerization with Ion-Exchanged DMC Surfaces

A further attempt to introduce more basic entities into the system was by a post-synthesis modification of the catalyst. The parent DMC (DMC-Cl) was derived from zinc chloride. In this system, chloride is a possible nucleophile that could react with PO and yield a basic entity on the surface. However, the chloride may be effectively little nucleophilic when it is bonded strongly to the zinc center, as alkoxide entities bonded to zinc in the DMC are not basic towards PO, are not readily decoordinating from the surface. The chloride in the DMC was therefore exchanged for the less strongly coordinating nitrate anion by reaction with sodium nitrate. Nitrate would, similar to carbonate, be more prone to react with PO (as was observed for homogenous catalysts) [108]. This initial reaction with PO would lead to a more basic catalyst surface (Scheme 4).



Scheme 4. Coordination and activation steps in DMC-Cl and -NO₃.

The obtained DMC (DMC-NO₃) complex was structurally identical to the chloride derivate. SEM images with 20,000 magnitude of enlargement show the usual plate-like habitus of DMCs [71,109,110] and indicate that the procedure did not influenced the catalyst morphology (Figure 8). The chloride was effectively removed from the parent DMC and sodium could not be detected by EDX, indicating that sodium nitrate was not substantially incorporated into the complex by the procedure (Table 9). The amount of nitrogen and oxygen in DMC-NO₃ also indicated a successful anion exchange. The ratio of Zn and Co was unaffected by the procedure. The isostructural modification of the catalyst is giving the unusual opportunity to assess the importance of the zinc bonded anions, which may be used to tune the action of DMC complexes in propoxylation or other catalytic processes [109,111].

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Figure 8. SEM images with 20,000 magnitude of enlargement of DMC-Cl (a) and DMC-NO₃ (b).

Element	DMC-Cl ^a	DMC-NO ₃ ^a	DMC-Cl ^b	DMC-NO ₃ ^b
C [wt.%]	28.2 ± 2.2	30.2 ± 0.4	22.9 ± 0.1	24.4 ± 1.1
H [wt.%]			2.1 ± 0.1	1.7 ± 0.2
N [wt.%]	8.3 ± 4.5	31.2 ± 2.6	17.6 ± 0.3	21.8 ± 0.7
O [wt.%]	1.5 ± 0.1	5.7 ± 1.4	5.7 ± 0.1	11.9 ± 0.1
Zn [wt.%]	39.1 ± 1.9	21.9 ± 2.4	30.2 ± 0.5	29.8 ± 0.9
Co [wt.%]	17.6 ± 1.7	11.0 ± 1.4	12.6 ± 0.2	15.7 ± 0.6
Na [wt.%]	0 ± 0.0	0 ± 0.0		0.3 ± 0.1
Cl [wt.%]	5.3 ± 1.3	0 ± 0.0	7.4 ± 0.1	0.1 ± 0.0

 Table 9. Elemental composition of DMC-Cl and DMC-NO3.

^a determined by SEM-EDX; ^b determined by elemental analysis (EA).

Semi-batch copolymerization experiments mediated by DMC-NO₃ were performed at 100 °C to find that the CO₂ incorporation is much higher than found for the parent catalyst (Tables 2 and 10, Entry 7, 11, 15 and 53–55). Lupranol1200 was used as CTA. The incorporation of CO₂ into the polymer also became dependent on the composition of the feed (Table 10, Entry 53–55). The carbonate linkage content increases from *F* of 0.25 to 0.45 with increasing pressure of 14.2 to 32.6 bars (*N* of 0.058 to 0.173). The incorporation is still more or less independent on temperature between 80 and 120 °C, as experiments at *N* = 0.173 revealed (Entry 55–57). The yield increases again with temperature and decreasing pressure, just like the previous experience. The distribution of the molecular weights tend to be broader (Figure 9), although the product molecular weight at complete conversion would be in the range of 1200 g/mol (depending on the carbonate content), and diffusion should not be a limitation. The distribution broadens to the high molecular weight side, increasingly with the molecular weight. The broadening is similar to that observed for DMC-Cl (Figure 6b), but much more extensively and already at much lower molecular weights. It is again indicative of a difference in chemical steps at the surface with respect to CO₂/PO addition contra single propoxylation steps.

Table 10. Copolymerization mediated by DMC-NO₃.

Entry	ExperimentT [°C]	<i>p</i> [bar]	N	Yield [g]	M _n [g/mol]	PDI	f_{cPC}	F
53	DMC-NO3_1 100	14.2	0.058	28.2	1000	2.5	0.01	0.25
54	DMC-NO3_2 100	23.6	0.115	26.6	960	2.2	0.02	0.29
55	DMC-NO3_3 100	32.6	0.173	22.0	880	2.3	0.02	0.45
56	DMC-NO3_4 120	40	0.173	36.1	1170	2.0	0.03	0.43
57	DMC-NO ₃ _5 80	25.3	0.173	7.7	640	1.2	0.05	0.42

(CTA: 30 g of Lupranol 1200, 300 mL autoclave, 1 h dosing of PO at 0.56 mL/min, 20 mg DMC).

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Figure 9. SEC traces of DMC-NO₃ catalyzed PO CO₂ copolymerization at N = 0.173.

In addition, the lower cPC content in the product obtained with DMC-NO₃ despite the higher carbonate content. The carbonate entities are of course more clustered, usually leading to an unbraked multiple unzipping, which is not predominantly observed. Apparently, the presence/concentration of instable free chain ends is lower and/or regularly two or more PO molecules are added to the chain ends. This is the case after protonation of a surface bound alkoxide by a free chain ROH entity followed by reentry to the surface by addition to an activated PO. A microstructure analysis will follow in a next report. It also explains why at 80 $^{\circ}$ C, more cPC is formed. The ring-opening of PO has the highest activation energy and cPC formation by backbiting is more competitive than at higher temperature, where ring-opening is faster.

3. Mechanistic Discussion

The perhaps loosely connected appearing observations on the catalytic action of the DMC catalyst of this study and in retrospective of the manifold reported experiences in making PPECs or PPGs using DMCs may be condensed into a comprehensive mechanistic description (Schemes 4–6). The ordering is an attempt to reach a general conception on the epoxide (metal) catalyzed (co)polymerizations and also comprises the insights reached in many in-depth studies using homogeneous catalysts. No new reaction steps are introduced, rather the existing state-of-the-art is reconnected and rearranged with the restriction of considering only low activation energy transformations (Schemes 4–6).



Scheme 5. Propoxylation in combination with carboxylation mediated by "none basic" DMCs, i.e., those with few basic entities.

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Scheme 6. PPEC formation by DMC with anionic sites (alternative CO₂ fixation pathway in grey).

The first part concerns the PO activation and modification of the catalyst (Scheme 4). The formulation of the active sites is chosen in form of binuclear zinc ensemble, following crystal structures and theoretical elaborations [65–67]. It is assumed in the mechanistic proposal that the most of the transformations are at "single sites" with two zinc atoms at the 100 or 001 crystal plane [70]. Similar arguments would hold true for a site with one zinc atom of a cubic crystal slab with tetragonal coordinated zinc atoms, having two free coordination sites [69].

Central and common sense to the propoxylation catalysis is the activation of PO by binding to the zinc centers, PO will not spontaneously react with weak nucleophiles [70]. The catalytic system is further presumed to have no free strong nucleophiles or base; these would bind to the Lewis acidic catalyst in a substantially irreversible way. The absence of free strong base must be assumed as in contrast to KOH catalyzed PPG preparation, isomerization of PO to allylic alcohol is not observed, not even at temperatures as high as 120 °C [94]. The coordination of PO is in competition to the other bases like amine or carbon dioxide (oxygen atoms). The fact that induction times are not influenced by the presence of amine or its propoxylation products, but the rate is, shows that it is (these are) not directly interacting with coordinated PO and not interfering with its reactions. A similar effect is found when CO_2 is present, the behavior of the catalyst system appears in a suppressed way, but not fundamentally different. The usual explanation of fewer sites with activated PO may be extended to absence of obvious cooperative effects between sites at the catalyst. CO₂ addition to the chain end may proceed by either equilibrium coordination to the alkoxide containing site with consecutive insertion or directly insert into the alkoxide metal bond. As CO_2 addition is usual not rate-determining, the impact on the outcome of the copolymerization is basically indifferent (i.e., except when a change between the two options arise; this may underlie the effect at low CO₂ concentration in experiments in the presence of amine).

The reaction sequence leading to the PPG may then be formulated in form of an external attack of a hydroxyl chain end, proton transfer, and liberation of a coordination site for PO activation (Schemes 5 and 6; sequence N1–4). PO is most susceptible to nucleophilic attack at the "back side" anti-bonding C–O orbitals, syn-insertion routes have extensive activation energies. A crucial point in

this sequence is the proton transfer, which perhaps has not received the appropriate consideration in the past with respect to its importance [70]. The intermediate (or only transitional) oxonium will profit from stabilization by basic sites at the DMC surface for its formation. It is proposed here that the chloride anions will likely have this role in DMC-Cl (Scheme 5; N2–3) and assist in the ring-opening and proton transfer, which then leads to the propoxylated ROH through an internal protonation.

The incorporation of CO_2 in this scheme for reaching PPECs with a low carbonate content will, following the insights obtained within homogeneous catalysis [47,74], follow after its insertion into a metal alkoxide bond (N5). Subsequent protonation would lead to an alkyl carbonic acid (N6) that is not particular stable and is bound to decarboxylate to give back ROH and CO₂. This non-productive cycle of carboxylation and decarboxylation must be interrupted for PPEC formation. This is achieved when the intermediate carboxylate is not protonated but reacts with activated PO to regenerate an alkoxide (N7–9 or N7,N10) [112]. This may underlie the observation that a certain PO concentration is necessary for PPEC formation. The carboxylate therefore needs to be a nucleophile, i.e., to decoordinate from the surface zinc center (N7). The sequence of generation a single carbonate linkage in the polymer chain end after consecutive CO₂ and PO additions end after a further (internal, directly in N9) protonation of the intermediate metal alkoxide. The resulting OC(O)- C_3H_6OH chain end may either by further propoxylated, finally fixating the CO_2 molecule in the backbone, or yield cPC by backbiting. Such a sequence where internal protonation is competing with the two step CO₂-PO addition would explain the small dependence on CO₂ pressure and higher cPC content in (none basic, neutral) DMC systems, such as DMC-Cl yielding PPECs with small amounts of carbonate linkages and more cPC. It also indicates that higher PO concentrations (more activated PO) will lead to more CO_2 incorporation through the fixation by alkoxylating the carbonato entities. This all pertains to reactions that give polymers low carbonate content and shows a dominant immortal propoxylation under uniform conditions, i.e., when diffusion of chain end and monomers is faster than reaction. Note that the CO_2 concentration was varied over a factor of 3 in case of DMC-Cl (Table 2).

In the argumentation, the insertion of PO into the carboxylate metal bond also involves backside attack at a coordinated/activated PO to have low activation energies [47]. Homogenous systems make this happen by the interaction of two centers, one holding the carboxylate anion and one activating PO. Dual site catalysts have therefore been in the focus of catalyst development for the alternating copolymerization, as discussed recently [49,113]. In fact, it also explains why these catalysts do not generate ether linkages: the corresponding metal alkoxide chain end is not nucleophilic towards a coordinated PO. The bonding of the alkoxide to the strongly Lewis acidic metal is too favorable, and high activation energies exist for nucleophilic alkoxide activity. External protonation by an ROH on the other hand is fully compatible with the system, and immortal alternating copolymerization can be reached with alcohols or acids as CTAs [108]. The homogenous catalysts are usually already active at temperatures lower than 80 °C, where backbiting in OC(O)- C_3H_6OH chain ends is still slow, and such species can be intermediate products. Although the PO may be more extensively polarized in these more Lewis acidic metal complexes, alcohols are still not nucleophilic towards coordinated PO; no ether linkages are formed. This is one of the arguments to propose that in DMC mediated ring-opening by alcohols, where PO is probably even less polarized, ring-opening transition state stabilizing interactions are required (Scheme 5, N2). At the same time, nucleophiles are bonded less strong to the metal centers in DMCs, amines/propoxylates can be tolerated as external bases. The amines, however, do not seem to change the proton transfer or ring-opening process (i.e., except at low CO₂ concentrations in the feed). Transformation at the surface of the DMC catalyst are too effective to be enhanced by their presence. The centers in DMCs are also arranged quite far from each other for direct assistance in stabilizing transition states [70].

As discussed above, CO_2 insertion is the scheme of DMC catalyzed immortal propoxylation of alcohols is probably restricted to the reaction of carbon dioxide with a metal alkoxide. This implies that CO_2 needs to compete with hydrogen transfer reactions at the surface. This seems particular challenging when the surface contains no permanent towards alcohols basic entities (alkoxides or

nucleophiles that can give an alkoxide after reaction with PO). The insertion of CO_2 in an alkoxide intermediate, before it is protonated also generates a weak basic entity on the surface, which may be generally necessary for substantial CO_2 incorporation. Basic entities can decrease the proton concentration at the surface (by neutralization or delocalization). The latter may make the case for DMC-Cl and not for DMC-NO₃ (Scheme 6).

A further comment in the line of argumentation of only considering elementary reactions steps with low activation energies at the DMC surface follows from the expectation that carboxylato chain end needs to nucleophilically attack at the backside of a coordinated PO. Other than in homogeneous catalysts with mobile partners, this would involve a translation over the "ionic" catalyst surface with (partial) bond breaking of the anionic carboxylato chain end to such a site (Scheme 5, N7–N10) [69]. Intermediate protonation would yield a free alkyl carbonic acid that would potentially decarboxylate. The decarboxylation would decrease the dependence of the outcome of the catalysis on the conditions in the feed. Ion separation in a metal-carboxylato moiety has a lower activation energy than in a metal alkoxide or chloride, tentatively making the carboxylato entity more nucleophilic and capable of opening a PO ring. This is more unlikely for the alkoxide, which is more prone to protonation, internally by the catalyst or by a CTA in a degenerate exchange or by assisting a nucleophilic attack of ROH at a coordinated PO.

Because of the similar charge delocalization to the carboxylato anion, the nitrate anion would show similar ring-opening activity. Nitrate anion would react with coordinated PO to generate surface propoxides (Scheme 4). This reaction has been reported for the stronger Lewis acidic cobalt salen complexes (these however also react with coordinated chloride or phenoxides) [108,114,115]. The change of a weakly coordinating nitrate to an alkoxide gives a basic unit on the catalyst surface, specifically directly at the (di)zinc center that can activate PO. After exchange with hydroxyl compounds in the solution, anionic chain ends are on the surface (Scheme 6, B1). These may now insert CO₂ without the competition for protonation from the surface, i.e., protonation by ROH will only be a degenerate reaction ($B4 \rightarrow B1$; $B7 \rightarrow B1$). Under such conditions, CO_2 insertion rate will become dependent on the concentration in the feed, which is in competition to step propoxylation (B5-7). The alkoxide intermediate will in the productive copolymer formation have the option of external protonation ($B1/4 \rightarrow B1$; $B1 \rightarrow B5 \rightarrow B6$) or CO_2 insertion ($B1 \rightarrow B2$), both followed by a consecutive PO insertion. This explains the impact of *N* on polymer composition in experiments with DMC-NO₃.

In addition, as after insertion of CO_2 and PO the starting alkoxide is regenerated, consecutive carbonate linkages may easily follow, enhancing the carbonate content (chain polymerization). The result is also that chain growth is at the metal, outside the regime of immortal polymerization, i.e., under conditions where external protonation is relatively slow, a broadening of the distribution may arise as external protonation by a CTA becomes a random terminating event. This may underlie the observation in the experiment at 90 °C with Caradol as CTA and DMC-Cl (with/at few basic sites) as catalyst (Entry 21), and at the DMC-NO₃-mediated PO/CO₂ copolymerization with (more) anionic chain ends, where external protonation is chain terminating. That implies that DMC catalyst structure in particular the basic equivalents is an important issue, as it determines an internal rate of protonation. It seems that the importance of the protonation is not adequately considered in the mechanistic description [116–122], and with that the susceptibility of a catalyst to incorporate CO₂ in the backbone. This is, so far as we can understand, the catalytic action today, a crucial extension to mechanisms proposed in the open literature [70,123–126].

4. Materials and Methods

4.1. Materials

Argon (99.999% (5.0) purity, Praxair Deutschland GmbH, Biebesheim am Rhein, Germany), propylene oxide (PO) (99.9%, GHC Gerling, Holz & Co., Hamburg, Germany), carbon dioxide (CO₂) (99.995%, Linde Gas, Hamburg, Germany), triethyl amine (99%, Grüssing GmbH, Filsum, Germany),

dodecyl amine (>97%, Alfa Aesar, Kandel, Germany), sodium nitrate (Merck KGaA, Darmstadt, Germany), Caradol ED 56 (poly(propylene glycol), $M_n = 2900$ g/mol against PS, PDI = 1.12, Shell Chemicals, Pernis, The Netherlands) and Lupranol 1200 (poly(propylene glycol), $M_n = 550$ g/mol against PS, PDI = 1.10, BASF SE, Ludwigshafen, Germany) were used as received. The DMC used was based on cobalt(III) hexacyanide and zinc dichloride; it was a gift from PO-handling industry with non-disclosure restrictions (XRD in Figure S7). General preparation methods of DMCs can, e.g., be found in corresponding patents [127–129]. Surface ion exchange of the DMC was performed in 2 M sodium nitrate and the modified catalyst was received after centrifugation, several washing steps with water and drying in a dynamic vacuum at 80 °C.

4.2. Homopolymerization of PO

The semi-batch catalytic chain transfer polymerization of PO was carried out in a 2 L stainless steel autoclave (serial number 4524, Parr Instrument GmbH, Moline, IL, USA) equipped with an anchor agitator. The autoclave was routinely charged with 166 g of the chain transfer agent (e.g., Caradol) and 50 mg of DMC catalyst. It was then closed, heated to 115 °C and held under a dynamic vacuum $(5 \times 10^{-2} \text{ mbar})$ for 1 h to remove volatiles. Thereafter, the vessel was pressurized with 6.5 bar of argon (for stable pump operation) and 25 mL of PO were added using a HPLC pump (Bischoff HDP PUMP Multitherm 200, 0.01–4.99 mL/min, Bischoff Chromatography, Leonberg, Germany) with a feeding rate of 0.83 mL/min. A rapid increase in temperature and decrease in pressure indicated the activation of the catalyst after an induction period of only several minutes. Once the initial amount of PO was consumed, additional 875 mL PO were added continuously with a feeding rate of 0.94 mL/min. The propoxylation temperature was kept constant at 120 °C, and aliquots were taken at certain intervals through a rising pipe. After complete addition of monomer, the autoclave was rapidly cooled to ambient temperature and depressurized.

The batch homopolymerization experiments were carried out in 300 mL stainless steel autoclaves (Parr Instrument GmbH, serial number 4560) equipped with 4-bladed propeller stirrers. The autoclave was, e.g., charged with 30 g of the chain transfer agent Caradol ED 56 and 5 mg DMC catalyst. After evacuation, the vessel was charged with 10 bar of argon at 120 °C and 2.4 mL PO were added using a HPLC pump (Bischoff HDP PUMP Multitherm 200, 0.1–19.9 mL/min) with a feeding rate of 15.6 mL/min. After activation of catalyst was assured (exotherm), the autoclave was cooled to desired temperatures and 50 mL PO were rapidly added. The product was dried under a dynamic vacuum at 50 °C until the weight was constant. The pressure and temperature were monitored throughout the experiments with the software ProfiSignal 2.2 (Delphin Technology AG, Bergisch Gladbach, Germany).

4.3. Copolymerization of CO₂ and PO

Semi-batch copolymerization experiments were carried out in 300 mL stainless steel autoclaves (Parr Instrument GmbH, serial number 4560) equipped with 4-bladed propeller stirrers. The autoclave was charged with 30 g of Lupranol, 20 mg of DMC catalyst, and in case of amine addition, experiments with additional amounts of amine, then sealed and evacuated to remove all volatiles. Thereafter, the vessel was pressurized at 120 °C with 10 bar argon and subsequently 4.5 mL of PO was added using a HPLC pump (Bischoff HDP PUMP Multitherm 200, 0.1–19.9 mL/min) with a feeding rate of 15.6 mL/min. Once the initial amount of PO was consumed (c.f induction period 4.1), the temperature was adjusted to desired value (60–120 °C), and argon was exchanged against CO_2 (p = 5–40 bar). 30 mL of PO were added with a feeding rate of 0.56 mL/min. The CO_2 pressure was kept at a constant level by a mass-flow controller.

Experiments with amines in semi-batch mode for tracking purposes of MW were carried out in 450 mL autoclaves equipped with an anchor agitator. The activation procedure was performed by addition of 9 mL of PO to a suspension of 15.9 mg of DMC catalyst in 30 g of Lupranol. In total, 180 mL of PO were added with a feeding rate of 0.3 mL/min. In batch processes, the experiments were performed as described for homopolymerization experiments, but argon was replaced by 10 bars of CO₂.

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Experiments monitored by online FTIR spectroscopy were performed in a 2 L stainless steel autoclave (Parr Instrument GmbH, serial number 4524) equipped with an anchor agitator. The vessel was charged with 166 g of CTA (Caranol ED 56) and 50 mg of DMC catalyst, then evacuated and pressurized at 120 °C with 10 bar CO₂. Thereafter 25 mL of PO was added using a HPLC pump (Bischoff HDP PUMP Multitherm 200, 0.01–4.99 mL/min) with a feeding rate of 0.83 mL/min. Once the initial amount of PO was consumed, the temperature was adjusted to desired value (90 °C, 120 °C), and PO was added with a continuous feeding rate of 0.94 mL/min. The pressure was kept constant at 10 bar by a massflow controller using CO₂ gas. The reaction progress was monitored using a ReactIRTM 45m (Mettler-Toledo GmbH, Gießen, Germany) with a diamond probe. Spectra with 128 scans were recorded every minute in the range of $\nu = 650-2000$ cm⁻¹. Copolymerization was terminated by cooling down to room temperature, releasing the pressure and degassing to remove residual PO. The product was dissolved in acetone and the solution cast into an evaporating dish and dried under dynamic vacuum at 50 °C to a constant weight. The pressure and temperature as well as the CO₂ mass-flow were monitored throughout the experiments with the software ProfiSignal 2.2 (Delphin Technology).

4.4. Catalyst Characterization

The DMC catalysts were characterized by scanning electron microscopy (SEM, Gemini Leo 1525 field emission microscope, EHT = 5 kV, Zeiss, Oberkochen, Germany) using the software SmartSEM (Zeiss, Oberkochen, Germany). SEM-EDX measurements were conducted using an octane plus silicon drift detector at 20 kV acceleration. The atomic consistence of the samples given in this study are averaged values of three different spot measurements utilizing the TEAM[™] EDS Analysis System software (V 4.1). Carbon, hydrogen, and nitrogen contents were measured on a Euro EA elemental analyzer (EuroVector, Pavia PV, Italy). Oxygen content was measured on a HEKATech HT Oxygen Analyzer (HEKAtech GmbH, Wegberg, Germany). The combustions gases where quantified by GC with a thermal conductivity detector. The cobalt and zinc contents were determined by ICP-OES (Spectro Arcos, Spectro Analytical Instruments GmbH, Kleve, Germany), sodium content by AAS (Solaar S Series, Thermo Fisher Scientific, Waltham, MA, USA), and chloride by ion chromatography (ICS-1100, Dionex Corporation, Sunnyvale, CA, USA).

4.5. Polymer Characterization

The molecular weight distributions were obtained using size exclusion chromatography (MZ-gel SDplus linear column (5 µm, 300 × 8 mm), Schambeck RI2012 detector, and a Flom Intelligent pump AI-12) in tetrahydrofuran as eluent at 22 °C with a flow rate of 1 mL/min and an injection volume of 20 µm. The MWD curves of experiment PPEC_1 were fitted in Chromatographica V1.037 with a Gaussian function to receive separate molecular weight distribution for each distribution. Monodisperse PS standards (Polymer Standards Service GmbH, Mainz, Germany) were used for calibration and the measured values were referenced against these standards. Data given are relative to these standards. Three ¹H-NMR spectra were recorded for each polymer sample on a Bruker Avance Ultrashield-400 spectrometer in CDCl₃ at room temperature using tetramethylsilane as a reference. The integrals of methyl protons were used for determination of mol fractions f_{CO_2} and f_{PO} , respectively, f_{carb} and f_{ether} that were incorporated into the polymer chain (Equations (S1)–(S4), Figure S1). The impact of starter was thereby negated by calculating the percentage of new linkages from SEC analysis and considering only those for determination of polymer composition. The median values of calculated $F = f_{carb}/f_{ether}$ were used for the discussion.

5. Conclusions

The catalytic action of a DMC complex with chloride ligands was mapped in batch and semi batch PO and PO/CO₂ copolymerizations. Generally Poisson-distributed products are generated. Broader molecular weight distributions with macrokinetic origins are obtained when mixing becomes slower than PO addition to the catalyst at high (local) temperatures with few active centers in the activation

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phase or in high molecular mass products of later stages with lower mobilities of chain ends. CO₂ decreases the activity—useful to control a runaway process—though competition to PO activation, but does not interfere with the course of the reaction. In DMC-Cl complexes, the concentration of CO_2 in the feed is almost invariant to the product composition (such as the presence of amines), whereas in DMC-NO₃ complexes, the CO₂ incorporation is both higher and positive dependent on the CO₂ of the feed composition. This is indicative for a multistep reaction mechanism with competing reaction channels. Indications were found that the formation of carbonate linkages run through an insertion (CO₂) and mobile carboxylato anion species, whereas ether linkages are formed through a Lewis base-assisted nucleophilic attack of an hydroxyl entity at a coordinated PO. The former is a chain growth process, the latter is a step-by-step polymerization. Both the concentration of activated PO and free CO₂ are of importance for the carbonate content. The rate of exchange of metal alkoxides with hydroxyl chains ends in the reaction mixture determines the width of the distribution (microkinetic broadening). This rate is a strong function of temperature. A mechanistic picture was created, comprising the established elementary steps of propoxylation and carboxylation/propoxylation and was extended with a differentiation with respect to the Lewis acidity/basicity of the surface in combination with the presence of surface bound protons and their mobility. The formation of cPC occurs parallel to the polymer and is independent on reaction time, but dependent on temperature, indicating that backbiting has a higher activation energy E_a than propagation.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/10/9/1066/s1, on topics of determination of polymer composition, liquid-gas equilibrium data, full IR spectra of reaction mixtures leading to PPEC-1 and PPEC-2, determination of Newtonian viscosities, peak fit of SEC PPEC-1 semi-batch propoxylation of Caradol at 90 °C, with: Figure S1: Building units and 1H-NMR spectra of methyl protons of a PPEC sample containing carbonate, carbonate ether, and ether linkages, Figure S2: Liquid-gas equilibrium data taken from J. Chem. Eng. Data, 2010, 55, 3379–3382 (red) and Russ. J. Phys. Chem. A, 1973, 47, 895–896, Figure S3: IR spectra of reaction mixture during semi-batch experiment at $T = 90 \degree C$ (a; PPEC_1) and $T = 120 \degree C$ (b; PPEC_2) at 10 bar CO₂ pressure, Figure S4: MWD curve of PPEC_1_2.5h and the sum curve of peak separation (a), curves of separated peaks (b), MWD curve of final product PPEC_1 and the sum curve of peak separation (c), and the curves of separated peaks (d), Figure S5: SEC of the propoxylation of Caradol ED at 90 °C under semi-batch conditions (0.96 mL PO/min), experiment terminated after 6 h, Figure S6: SEC-analysis of PPECs synthesized at 10 bar CO₂ and 120 °C with 2 µL TEA (a) and 2.6 mg DDA (b) in 450 mL autoclave in semi-batch mode (0.3 mL/min PO feed), Table S1: Batch PO/CO₂ copolymerization with Caradol ED 56-200, Figure S7. XRD of DMC-Cl, Table S2: Newtonian viscosities η of PPG (Mn = 5.1 kg/mol, PDI = 1.13) and of PPEC (Mn = 4.9 kg/mol, PDI = 1.19 carbonate content of 12 mol%), Table S3: Total molecular weights of PPEC_1 as measured with SEC and sum of molecular weights after peak fit in Chromatographica (showing a goodness of fit).

Author Contributions: Conceptualization, S.-F.S. and G.A.L.; methodology, S.-F.S. and G.A.L.; formal analysis, S.-F.S. and G.A.L.; investigation, S.-F.S.; data curation, S.-F.S.; writing—original draft preparation, S.-F.S.; writing—review and editing, G.A.L.; visualization, S.-F.S. and G.A.L.; supervision, G.A.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: We wish to acknowledge the efforts of Scheliga in optimizing SEC methods.

Conflicts of Interest: The authors declare no conflict of interest.

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5 Analysis of the Propoxylation of Zinc-Cobalt Double Metal Cyanide Catalysts with different active Surfaces and Particle Sizes

5.1 Synopsis

The kinetic study, described in this chapter, offers further evidence that the propoxylation reaction proceeds by a mechanism along the Eley-Rideal proposal, where only one reactant is activated by coordination to the surface of the catalyst. Additionally, it addresses the question of why some DMC catalysts produce broader molecular weight distributions than others, despite having the same chemical composition. It also shows that the process's outcome cannot be easily correlated with characteristic parameters of heterogeneous catalysts, such as activity, crystallinity, or pore size.

The insights were elaborated by a "pulse" method that allows determination of activation energy data of the catalyst's action in the industrial relevant regime of semibatch operated reactors for the preparation of narrow dispersed PPGs. The data was evaluated along Eyring and Arrhenius theories and thus enabled insights into the underlying mechanism. The outcome of the kinetic analysis conforms to the typical behavior observed in heterogeneous catalysis, with partitioning between macro-diffusion of reagents from and to the bulk phase and microkinetics.

The "pulse" method gives a good basis for a direct assessment of the catalytic actions of DMCs in propoxylations of hydroxyl compounds as is demonstrated for three industrially applied cobalt zinc DMC solids. It is based on multiple pulsed additions of PO to an active DMC-starter-system and uses *inline* FTIR-spectroscopy to obtain kinetic data for a range of diol starter concentrations and temperatures. The rate-determining step of the process significantly influences the resulting molecular weight distribution and that it is strongly affected by particle size, in addition to the catalytic activity for the propoxylation reaction. Charting the kinetic data in a contour plot allows assessing the catalyst performance in one glance and offers valuable information about *e.g.*, decomposition temperatures and activity loss.

The approach offers access to a range of essential catalytic features, aiding in the optimization of a process in terms of product control. The study also highlights factors of significance for directed catalyst development and maps the influence of polymer and monomer diffusion on the polymer properties also in the context of the semibatch feeding of PO.

5.2 Copy of Publication

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Cite this: DOI: 10.1039/d3re00313b

Analysis of propoxylation with zinc-cobalt double metal cyanide catalysts with different active surfaces and particle sizes†

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The action of three different Co/Zn double-metal-cyanide (DMC) catalysts in the propoxylation of polyols was compared in a kinetic study, using pulse-wise feeding of propylene oxide (PO). Key insights are that the catalysis proceeds by an external attack of hydroxyl chain ends on coordinated PO and that the different diffusion rates of PO and polyols result in the broadening of the distribution. This can be visualized by the introduction of finger printing. The initial [PO] decay had a first order dependence on the catalyst, PO and hydroxyl concentrations. The temperature dependence of the characteristic product $k_s K$ (k_s : rate constant for ring-opening; K: equilibrium constant for PO coordination) showed that the rate determining step is most compatible with a PO ring-opening by a direct external nucleophilic attack of a hydroxyl group or one modulated by the diffusion rate of PO. Consideration of the number of crystallites per unit volume (related to the crystal size) and diffusion leads to a consistent description of the catalysis in terms of the rate and polydispersity of the product.

Received 2nd June 2023, Accepted 6th September 2023

DOI: 10.1039/d3re00313b

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Introduction

Double metal cyanide (DMC) complexes were introduced in the early 1960s by General Tire Inc. as industrially viable potent Lewis acidic catalysts.¹ They have become known (in particular to industry) as effective mediators for chain transfer polymerization under the ring-opening polymerization (ROP) of propylene oxide (PO) to generate polyether polyols from alcohol or acid starter molecules (Scheme 1).^{2–6} The high alkoxylation activity of DMC catalysts relative to traditional alkaline catalysts, like KOH, eliminates the need for neutralization and elaborate removal of catalyst residues from the product.7-10 The poly(propylene glycol) (PPG) products prepared with DMC catalysts profit from an almost perfect retention of the functionality of the starter, a low degree of unsaturation (absence of PO isomerization to allyl alcohol) and readily accessible narrow molecular weight distributions.11-15 These properties are advantageous for achieving the lowest possible viscosity for a particular chain length as higher molecular weight fractions, which tend to strongly increase the viscosity, are in small amounts or absent. Low viscosities are of particular importance in applications where mixing and wetting are essential, like in the predominant application of PPGs as soft-phase components in polyurethanes (PU). Application of a PPG with a narrow mass distribution is also advantageous for achieving a clear phase separation in segmented polymers.¹⁶ Challenges in the improvement of the catalyst's major action involve the reliable (robust) formation of narrowly dispersed products with compositions of precatalysts not claimed in current patents, and/or additionally enabling copolymerization with CO2,17 lactones18 or anhydrides.19 Advantageous are also higher value propoxylation products with molecular weights in the range of up to about 20 Da or over, prepared by catalysts with high turnover frequencies and sustained activity (for keeping the PO concentration low at high dosing rates), with no allyl formation and the functionality of starter entities being preserved. A low loading of catalyst is obviously most desirable.

Addressing the challenges would profit from an in-depth knowledge of the alkoxylation in terms of the catalyst's action in connection to the process carried out. The current state of



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[†] Electronic supplementary information (ESI) available: Additional information on the reaction profile and experimental data for the pulse-decay experiments, reasoning for the Thiele modulus, diffusion and M_w dependent viscosity of the reaction mixture at 120 °C, data and discussion of the linearity of the relationship between $\ln k_s K$ (and $\ln k_s K/T$) and 1/T under diffusion influenced rates, calculations of DMC crystals and data on the attainable PDIs in the setup. See DOI: https://doi.org/10.1039/d3re00313b

the art of catalyst and process development more or less relies on experience and on doing a large number of experiments (a Scifinder® search gives about 30 patents with similar titles).¹⁷ A number of efforts to systematically enhance the catalytic action through alternative catalyst synthesis is recognizable, however, general applicable principles have not been extracted yet. Indeed, the outcome of DMC complex synthesis is not very predictable and has many factors of influence, *i.e.* the coprecipitation of, in particular, the $Co(CN)_6^{3-}$ anion with zinc dichloride (or other sources of Zn²⁺)^{12,20,21} may yield several types of precatalyst depending on variables such as concentrations (ratios), solvent (mixtures), auxiliary reagents, temperature, mixing/ stirring rate, application of mechanochemistry and post synthesis treatment (cf. ESI† Fig. S1-S3).^{2,5,17,22-36} In addition, the content and type of complexing agents and residual salts from the synthesis (KCl) may have an impact on the overall activity.^{29,37-42} Efforts for optimizing a catalyst are directed towards increasing the accessibility of active sites by radiation treatment, by trying to control the morphology e.g. using a reverse emulsion synthesis procedure or by supporting the active components and inducing the formation of layered structures.^{31,43-49} Other studies have been directed toward establishing a correlation between catalyst structure and activity - some experimental data point toward the importance of "non-crystalline" fractions of the catalyst for high activity as they may offer improved accessibility of active centers, but also here a convincing general case has not been built.⁵⁰ Some evidence points to the favorable presence of more open "cubic" phases rather than coordinatively saturated hexagonal moieties, however, this was in fact rejected as the bulk phase is merely a hold for the active surface, and also reorganizes in contact with coordinating entities.^{17,29,51,52} Also, theoretical treatises are

Comparing the performance of individual DMC catalysts is limited by the diverging descriptions of catalytic action.^{13,28,42,56–58} Reported catalytic activity is mainly based on the resulting yield (kg per g of catalyst and/or per h) and/ or the overall conversion of monomer.^{25,30,59} These numbers are not a good basis for an analysis or a targeted development. They are determined by manifold, difficult to assess factors such as the number of active sites, the average activity of the sites and diffusion kinetics (polymer/monomer) in heterogeneous catalysis.⁶⁰

difficult to relate to general catalyst activities.34,53-55

The activity of a heterogeneous catalyst needs to be considered in terms of "the seven steps" of heterogeneous catalysis, *i.e.*, reflection of macro and microkinetic barriers, here in a fluid–solid system.⁶¹ Newer models attempt to break down the catalytic action in this context by treating the propoxylation as an insertion polymerization.⁶²

The current description of propoxylation in terms of elementary chemical reaction (microkinetic) steps involves two competing and inherently different pathways: (1) insertion polymerization with a metal-bonded alkoxide as a key feature, and (2) stepwise chain growth with immediate

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release of the chain from the catalyst (Scheme 2). Most of the studies describe the catalyst's action as an insertion polymerization, like polyolefin formation.17,48,55,63-66 PO is treated as a pseudo-olefin that undergoes ring-opening and inserts into a metal alkoxide bond. The final step, giving the immortal polymerization characteristics, involves an acidbase reaction between ROH hydroxyl entities and metalbound alkoxide.67 However, the Lewis-acid catalyzed ringopening of PO involves a backside attack of a nucleophile, resulting in an anti-addition rather than a syn-addition, as observed e.g. in the ammonium chloride catalyzed formation of oxazolidinones from isocyanides and epoxides,^{68,69} or in the catalysis for the formation of poly(propylene carbonate) from PO and CO₂.⁷⁰⁻⁷⁴ This observation is not directly consistent with the first mechanistic description. Only the ring-opening of PO by a strong Lewis acid generates a free carbocation that may lead to syn-addition, but its existence is unlikely in the presence of coordinating alcohols.⁷ An alternative mechanistic description involves the activation of PO by a moderate Lewis acid, followed by an external backside attack of an alcohol ROH and liberation of a propoxylated product in the form of ROPOH after a proton shift (Scheme 2, description 2).²

Kinetic studies of the propoxylation have the potential to distinguish between the alternatives presented in Scheme 2, (depending on the rate-determining step). One particularly comprehensive study, focusing on propoxylation in batch reactions, describes how the induction time and the subsequent propoxylation rate of a PPG diol starter (450 Da) is determined by the DMC content.⁷ It was found that the rate of PO is linearly dependent on the concentration of DMC and PO. The first-order dependence on the catalyst and PO concentration is consistent with both mechanisms in Scheme 2 and does not provide conclusive evidence. Note that this observation may only be taken as an indication, as the same dependence results from a reaction controlled by the rate of PO diffusion (flux of PO to a catalyst particle $J_{\rm PO} = D_{\rm PO} \frac{\partial [\rm PO]}{\partial x}$, where $D_{\rm PO}$ represents the diffusion constant of PO in the medium, and x denotes the thickness of some film around the catalyst particle). The total flux is proportional to the surface area of the catalyst particles, and the time dependence of the gradient in the steady state $\frac{\partial [PO]}{\partial t}$

follows first-order kinetics in [PO] when using standard film theory. The more relevant dependence of the rate on the hydroxyl concentration was not determined in the study. The concentration of hydroxyl entities was almost constant in this study as a molar ratio of PPG to PO of 1:1 was used, leading to only incremental chain growth (facilitating the evaluation and interpretation). A first-order dependence on the catalyst concentration was elaborated for the propoxylation in other cases too, however with a second other dependence on PO.^{63,75} The latter, however, may encompass effects that relate to the activation of the catalyst and the change of the hydroxyl concentration. The Arrhenius activation energy for

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Scheme 2 Competing mechanistic descriptions of the DMC mediated propoxylation of HOR, insertion polymerization (left) and stepwise addition by external nucleophilic attack (right).

the overall process was reported in the range of 60 kJ mol⁻¹. An interpretation was not attempted on account of the complex rate law. Nevertheless, knowledge of the activation parameters can generally provide information about the mechanism.

The distribution of the masses of the products, PPGs, also contains information about the mechanism. The propoxylation of diols mediated by DMCs exhibits a phenomenon known as "catchup" kinetics.76 This term was introduced to describe the observation that low molecular weight diols are preferentially proposylated in the presence of higher mass oligomers. This led to the development of the "continuous addition of starter" (CAOS) process, which enables the production of PPGs with narrow distributions in a continuous stirred tank reactor.77 The "catch-up" kinetics are explained in the context of mechanistic description 1 by assuming larger rate constants for the propoxylation of smaller diols.^{7,62} This explanation, however, contradicts the general assumption of equal reactivity of chain ends and is at least to be challenged for that reason.

Apart from the "catch up" kinetics, broad and multimodal distributions can arise during the propoxylation of diols with DMC catalysts. The undesired formation of these distributions is explained by the interpretation based on the PO-insertion mechanism (1) by suggesting the presence of different sites on the catalyst surface, similar to heterogeneous catalytic polyolefin formation.⁷⁸ It should be noted, however, that the situation is different from polyolefin formation: both PO and ROH need to diffuse to the catalyst surface for chain growth. The self-diffusion of the PPG with slightly different molecular weights must thus keep pace with the rate of PO conversion to achieve balanced growth of an immortal polymerization (Scheme 3).^{79,80} The rate of PO conversion will fundamentally be dependent on its diffusion

to the catalyst and the catalytic action, *i.e.* it is dependent on micro and macrokinetic factors of unknown magnitude.

There is no doubt that DMC mediated propoxylation appears to be of high complexity, which is partly because of the open question of the microkinetic steps in the mechanism and the need for a global understanding of the factors that determine the rate and the mass distribution of the resulting PPGs. Generally, few kinetic data appear to be available on the action of DMCs in the industrial relevant regime of semibatch operated reactors for the preparation of narrowly dispersed PPGs after the initial activation.7 A larger kinetic study was therefore carried out, using three similar DMCs prepared from hexacyano cobaltate and zinc cations, differing in particle size. Given the industrial importance of DMC catalyzed propoxylation and the promise of a knowledge driven optimization of the catalyst performance, a simple method for the mapping of the catalyst's action under relevant conditions seems also of value. The activation parameter characteristics are good indicators for the discrimination between the rate with micro (chemistry) and macro (diffusion) kinetic limitations. The option of performing measurements under temperature control was therefore included.



Scheme 3 Propoxylation at DMC surfaces: concentration and mass transport of PO and PPG. Subscripts b and s refer to bulk and surface near species, respectively, and mt to mass transport.

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The results are interpreted in the context of heterogeneous catalysis and "polymer reaction" engineering, and yield an extended view of the "catch-up" kinetics.^{64,76,77,81–83} Evidence for rate-influencing diffusion and for a chemical reaction are found, showing the importance of micro and macro kinetic steps.^{60,84} The approach intends to decouple the discussion of a sub- or superior catalyst from the difficulty of determining the activity per unit mass, and to map the influence of polymer (PPG) and monomer (PO) diffusion in the context of the semi-batch feeding of PO.

Materials and methods

Materials

Argon (99.999% (5.0) purity, Praxair Deutschland GmbH), propylene oxide (PO) (99.9% purity, GHC Gerling, Holz & Co.) and VoranolTM 2000 L (PPG: poly(propylene glycol), $M_n = 2400$ g mol⁻¹ against polystyrene standards, PDI = 1.10, DOW Chemical Company) were used as received. The DMCs used were gifts from industry with non-disclosure obligations with respect to their identity, some characterization is offered (ESI† Fig. S1–S3). They were formed from similar zinc and cobalt precursors, but differences in the conditions of synthesis (solvent/ligands, quality of mixing, temperature and concentration (gradients), effect of washing procedures, drying conditions and so on) typically lead to divergent morphologies, crystallinities and polarity (*vide infra*).^{20,30} Preparation methods of DMCs can *e.g.* be found in typical patents.^{6,85,86}

Semi-batch propoxylation

The catalytic chain transfer polymerization of PO was carried out in a 2 L-stainless steel autoclave (Parr Instrument GmbH, serial number 4524). The autoclave was charged with a specific amount of the chain transfer (starter) agent Voranol, usually 166 g, and DMC catalyst. It was closed, heated to 118 °C and held under a dynamic vacuum (5 \times 10⁻² mbar) for 1 h to remove volatiles. Thereafter, the vessel was pressurized with 6.5 bar argon (for reasons of pump operational liability) and a small amount of propylene oxide was added using a HPLC pump (Bischoff HDP PUMP Multitherm 200, 0.01-4.99 mL min⁻¹) with a feeding rate of 0.83 mL min⁻¹. A rapid increase in temperature and decrease in pressure indicated the activation of the catalyst after an induction period. Once the initial amount of propylene oxide was consumed, it was added continuously with a feeding rate of 0.94 mL min⁻¹ until the desired molecular weight of the PPG was reached. The pressure and temperature were monitored throughout the experiments with the software ProfiSignal 2.2 (Delphin Technology). PO conversion was monitored by in-line FTIRspectroscopy, using a ReactIR[™] 45 m (Mettler Toledo) equipped with a probe having a diamond window. Spectra of 128 scans were recorded every minute between 650 and 2000 cm⁻¹. The partial least squares (PLS) regression model for multivariate data analysis was used with The Unscrambler X 10.3 (Camo Software) to evaluate the data. The propoxylation temperature was kept constant at 120 °C and aliquots were

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taken at certain intervals through a rising pipe. After complete addition of the monomer, the autoclave was rapidly cooled to ambient temperature and depressurized. The reaction mixture was subsequently transferred to a drying oven and held under a dynamic vacuum at 50 °C until the weight was constant.

Kinetic study

The experiments were conducted as above, only after completion of the activation of the catalyst, 10 wt% PO (with respect to the reactor content) was added with a feeding rate of 30 mL min⁻¹ (Bischoff HDP PUMP Multitherm 200, 0.1–39.9). The rate of PO consumption was determined from the IR signature of the mixture.

Polymer and catalyst characterization

The molecular weight distributions were obtained using size exclusion chromatography (MZ-gel SDplus linear column (5 μ m, 300 × 8 mm), Schambeck RI 2012 detector and Flom Intelligent pump AI-12) with tetrahydrofuran as the eluent at 22 °C. The flow rate was 1 mL min⁻¹ using an injection volume of 20 μ m. Monodisperse PS standards (Polymer Standards Service GmbH) were used for calibration and the measured values were referenced against these standards. Data given are relative to these standards.

The DMC catalysts were characterized by scanning electron microscopy (SEM, Zeiss Gemini Leo 1525 field emission microscope, EHT = 5 kV) using the software SmartSEM (Zeiss). Determination of the surface area was carried out by adsorption measurements using dinitrogen on a Surfer gas adsorption porosimeter (Thermo Fisher Scientific, Software Surfer Acquisition Ver. 1.7.10). The pore size was calculated using the BJH method.⁸⁷ The powdery samples were prepared for measurement by degassing at 70 °C for 2 h. The surface area was calculated with the software Surfer Ver. 1.7.10 based on the BET method⁸⁸ in the range of p/p^0 = 0.05–0.3. The pore size distribution was calculated using the B.J.H. method in the range of p/p^0 = 0.3054-1.003. Powder X-ray diffraction (XRD) measurements were carried out on a MPD X'Pert Pro Powder Diffractometer with Bragg-Brentano geometry (PANalytical, Cu-K_{α}: 0.154 nm). The sizes of the DMC primary particles were obtained from the SEM images by measuring the x,y,z, dimensions of randomly chosen examples.

Results and discussion

Catalyst characterization and propoxylation procedure

The precatalysts used, DMC A–C, are kindly provided samples based on hexacyano cobaltate and a zinc dication source. These DMCs will be treated as "black boxes" with a particular average size and surface area. This approach appears to be sufficient for building a further understanding of the catalysis. DMC A–C commonly show the usual plate-like habitus of these compounds at different dimensions (Fig. 1).^{30,51,89} DMC A

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Fig. 1 SEM images enlarged by a magnitude of 20 000 of DMC A (I), DMC B (m) and DMC C (r).

seems to be the compound with the lowest order, and has the highest number of small primary particles, partly branching away from larger crystal platelets. DMC B and to a lesser extent DMC C have a more homogenous appearance. The X-ray powder diffraction pattern of DMC B displays mostly sharp and intense peaks, as expected, indicating a more ordered structure in comparison to DMC A and C (in accordance with the SEM images; Fig. S3†). The primary platelets of DMC C seem to have a higher state of agglomeration. The agglomerates of primary particles would be expected to break up in the initiation procedure of the propoxylation.

A common issue when using a DMC as a catalyst is activation of the parent precursor solids for alkoxylation activity.90 This is usually achieved in a thermal process by heating the DMC solids with starter hydroxyl compounds and subsequent addition of a small amount of PO monomer. The activation procedure involves an induction period of unknown length,⁵⁶ which depends on several factors such as the composition and preparation procedure of the DMC, temperature, contents of the coordinating entities, and so on.^{7,26,75,91,92} On an industrial, larger scale, usually in a semibatch process, the PO monomer will only be added after the activation has been secured; the concentration of PO may not exceed certain limits as its ring-opening is highly exothermic and potentially dangerous situations may arise when leaving the intrinsically safe operation regime of the reactor.⁵⁶ After the activation, the main part of the propoxylation can be carried out under the control of a PO feeding protocol.

It is a general understanding that coordinating entities (from the catalyst synthesis and/or from the starter and monomer) on the zinc atoms of the surface compete with PO coordination.⁹³ PO is one of the most weakly coordinating agents and the activation procedure involves a displacement of such "blocking agents" from the surface.^{56,65,75,94,95} Neutral agents (like water and alcohols) may be physically removed and/or react with coordinated PO to become alkoxides, which may undergo protolysis if acidic hydrogen moieties are available to become (coordinated) alcohols (Scheme 2, right). The reaction of coordinated PO with decoordinating anionic nucleophiles (CI^{-}) present on the catalyst surface is tentatively also part of the activation process to yield basic, protonatable entities on the

surface.^{55,65,75,96,97} The coordination of PO to the DMC surface becomes progressively more favorable with the increase in the chain length of the coadded starter alcohols in the reaction mixture.^{98,99} It is thus useful to apply alcohol starters as chain transfer agents with a molecular mass that does not effectively inhibit the catalyst.¹⁰⁰ A PPG with a molecular weight of 2000 g mol⁻¹ is satisfactory for this and was used in this study (Voranol 2000 L).

DMCs A-C could be activated for propoxylation reactions at about 120 °C after the dilution of the PPG with \sim 4 mol eq. of PO. This initially added PO was consumed - dependent on the catalyst and conditions - in a time span below 120 min (the activation time). The decay of the PO concentration was monitored in situ with an FT-IR sensor. The induction time is defined as the time interval in which no substantial monomer conversion occurs and describes the phase between the addition of monomer and start of a time phase, where the consumption of PO starts to increase substantially.⁷ It can take up to 30 min. An exothermal peak and a pressure drop in the reactor indicate the beginning of the catalytic action. The temperature increase ΔT was always below 10 °C (Table 1). The latter is important for preventing thermal decomposition of the catalyst and possibly for preventing side reactions like the isomerization of PO to allyl alcohol (vide infra).

Once the DMC precatalysts are activated, PO consumption at temperatures of 100 °C or higher is fast. Monitoring the PO concentration in-line while adding a small feed of PO (about 1 mL min⁻¹ to a suspension of 50 mg DMC in 166 mL of PPG (2000 g mol⁻¹)) shows that its conversion is always basically complete (98 \pm 2%; Fig. 6). The low steady state concentration makes it challenging to obtain an accurate concentration dependent PO conversion profile. The small difference between the integrated feeding rate and a small, time dependent actual concentration would lead to pointless

Table 1 Activation parameters for a suspension of 5 mg of DMCs in 166 g of PPG (M_n = 2400 Da against PS) and 4 mol% PO

Catalyst	Induction time/min	Activation phase/min	$\Delta T/^{\circ}C$
DMC A	23 ± 4	47 ± 5	7 ± 1
DMC B	30 ± 1	117 ± 1	3 ± 1
DMC C	11 ± 5	27 ± 5	6 ± 2

large errors in the consumption rate. It was therefore decided to add PO as repetitive larger pulses by using a relatively high feeding rate (30 mL min⁻¹) and a significantly smaller amount of the DMC catalyst (approx. 5 mg in 166 mL of starter) to have enough time to observe the decline of the PO concentration. The pulses were kept at about 10 wt% of the total mass in the reactor. The actual feeding time added up to less than a minute. The measurements commenced after the PO was essentially mixed into the PPG, *i.e.*, after 2–3 min, allowing the observation of most of the decay. The use of higher concentrations (than in industrial practice) of PO allows the observation of the action of the catalyst, as shown before.⁷ An approach of giving pulses of PO into a reactor was thus used in this study to create an extended map of the catalytic action.

The volume of the PPG starter after the propoxylation by the PO pulse increases in the experiment each pulse, leading to a dilution of the catalyst particles and hydroxyl groups (increasing molecular weight of the PPG). The pulses were accordingly adjusted, *i.e.*, as the reaction volume increased, more PO was added to reach the 10 wt% of the reactor content. This approach limited the temperature increase by the propoxylation and allowed the reactor to be kept within safety limits. The average PPG chain growth at the first pulse was about 4 entities of PO, and it was about 8 for the 7th pulse.

The decline of the PO concentration after the pulse can now easily be detected (Fig. 2). A rate coefficient for the decrease of the PO concentration shortly after the pulse was extracted from the earlier part of the profile with about constant temperature and presuming a first order decay. Plotting the time dependence of the [PO] indeed shows an initial exponential decrease and the linearity of a plot of $\ln[PO]$ *versus* time justifies the 1st order kinetics presumption (Fig. 2, right). A first order [PO] decay is observed in the majority of studies on DMC mediated propoxylation.^{7,60}

The temperature in the reactor cannot (always) be held perfectly constant during the decay of a PO-pulse and increases because of the alkoxylation reaction (Fig. S4†). The observed rate coefficients k_{obs} were consequently evaluated from the early part of the decay of the PO concentration, wherein the temperature was within a few degrees of the starting temperature. The tangent of ln[PO] in that specific interval was always constant within the resulting experimental error (R^2 of linear regression >0.98).



Fig. 2 The concentration of PO decreases exponentially with reaction time *t* (left), linearization allows determination of rate coefficients k_{obs} from the slope of the fit in the initial phase (right).

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The time averaged (corrected) temperature in the reactor at the specific part of the linear decrease of the PO concentration was calculated and used for estimating the activation parameter. The standard deviations of the measured average temperatures for the pulsed additions were mostly below 2 °C (Tables S1–S3†), except for a few experiments with a temperature range of 7 °C in the first pulse (at higher catalyst concentrations). The temperature dependent rates are, as a consequence, only close approximations, leading to some (acceptable) scattering in the overall rate constants.

The initial first order fast decay of the PO concentration is generally followed by a much slower decay of changing rate. The moment of transition of the kinetics is dependent on the catalyst, its concentration, and the temperature. This observation of the slower than exponential decay at starving PO concentrations has been made before, and left undiscussed.^{7,75} A number of arguments, like locally decreasing [OH], change in PO mass transport as a function of molecular weight determined viscosity, change from transient to steady state film diffusion or the formation of a thicker film, may be put forward to account for this (*vide infra*). It indeed contains further information on the catalytic action and will be the topic of a further manuscript with more accurate data for that phase.

The next pulse was only given after the reactor content had reached its set temperature and the PO concentration was close to zero. The procedure also gives some time to allow a self-diffusion equilibration of the PPGs near the catalyst and the bulk, *i.e.* the molecular weights are not too high in the vicinity of the catalyst (Scheme 2).¹⁰¹ The pulseinduced increase of the temperature is larger for the early pulses as conversion is faster (higher [OH] and number of DMC particles/mL) than in later stages of experiments with a higher reactor content. The reaction rate decreases with the number of PO pulses in a run, *i.e.*, with the increase of the molecular mass of the alcohols and the associated dilution with respect to hydroxyl and catalyst concentration (Fig. 2, S4 and Tables S1–S3†).

The observed rate constants $k_{\rm obs}$ from the rate law $\frac{d[PO]}{dt} = k_{obs}[PO]$ of the initial faster pulse decay at a given temperature were found to reduce to a single value after division by the theoretical bulk hydroxyl concentration and the DMC content (in mg per unit of volume) directly after the pulse. This fact suggests that the reaction order with respect to both the catalyst and the hydroxyl concentration is close to one. The constant resulting from the division of k_{obs} by [OH] and [DMC] is denoted by the product $k_s K$ (in L² s⁻¹ mg_{DMC}⁻¹ mol⁻¹), where k_s (in L s⁻¹ mg_{DMC}⁻¹) is understood as the rate constant for the ring-opening of surface coordinated PO per mg of DMC in a 1 L reaction volume and K (in L mol⁻¹) as an equilibrium constant for the binding of PO to the catalyst's surface zinc atoms. These parameters are the outcome of a simple microkinetic mechanistic model for the catalyzed propoxylation as in description 2 (Scheme 2; vide infra).

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It is assumed that the alkoxylation of ROH is of an immortal type, and thus that the number of chain ends remains constant. NMR analysis of the products shows that indeed only traces of allylic or other end groups have formed. The pulsing addition of PO can thus easily be carried out at *in situ* formed PPGs of various molecular masses. The hydroxyl concentration [OH] in bulk corresponds to a particular molecular mass (*cf.* OH-number) and distribution with a specific viscosity, like in a typical situation in a propoxylation production plant operated in a semi-batch mode (but here at a higher PO concentration). Thus, extensive information is obtained on the action of the catalyst as function of [OH].

Kinetic parameter and mechanistic interpretation

The reaction pathway of the DMC-mediated propoxylation of alcohols is, based on the kinetics with first-order dependence on [OH], most compatible with description 2 (Scheme 2). The nucleophilic ring-opening of a coordinated PO (PO_{cat}) may be supposed to reach a pseudo-steady state (i.e., only dependent on the bulk [PO]) once the activation of the catalyst is completed. The kinetic data obtained at several concentrations of DMC particles and hydroxyls (starter ROH) and at various temperatures are of the activated catalyst. The microkinetics of chain growth by the ring-opening step in the mechanism (2) may be formulated as $r_p = k_s[PO_{cat}][OH]$, with $k_{\rm s}$ as the surface reaction constant. [OH] is the concentration of the ROH entities near the catalyst's surface. This concentration may become increasingly different from the concentration in the bulk during the pulse decay. PO will be faster to diffuse than the self-equilibration of the PPGs (Scheme 3; cf. ESI[†]). Hence, the PPGs close to the catalyst will grow in length faster, decreasing the local [OH] (at least temporarily at the end of a pulse; vide infra).

The PO ring-opening by a nucleophile may be supposed to be the slowest of the chemical steps and thus a balanced preequilibrium PO coordination is presumed, involving coordination sites at the DMC surface, coordinated PO and surface-near PO dissolved in PPG. 13 [PO_{cat}], the concentration of PO at the catalyst surface, expressed in mol PO per L and mg_{DMC}, may as usual be treated in terms of the fraction of surface coverage, which is denoted by θ_{PO} . The equilibrium constant K for the PO coordination thus can be represented as $K = \frac{[PO_{cat}]}{[PO] \cdot ["free coordination site"]} = \frac{\theta_{PO}}{[PO](1 - \theta_{PO})} \approx \frac{[\theta_{PO}]}{[PO]}$ $\left[\mathrm{PO}_{\mathrm{cat}}\right]$ in L mol⁻¹: PO is a weakly coordinating species, the relative coverage of the free coordination sites by it may be assumed to be small in relation to 1. The interpretation of a rate determining attack of ROH at a PO-surface entity gives the microkinetic propoxylation rate as $r_{\rm p} = -\frac{\mathrm{d}[\mathrm{PO}]}{\mathrm{d}t} = k_{\rm s}\theta_{\rm PO}[\mathrm{OH}] = k_{\rm s}K[\mathrm{PO}][\mathrm{OH}]$ per unit of surface area of DMC with active sites in 1 L, which is proportional to [DMC] in mg_{DMC} L⁻¹. The separation of variables and integration from t = 0 to t = t gives $\ln([PO]_t/[PO]_0)$ $= k_s K[OH]t$ for every mg_{DMC} per liter. The observed rate constant

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 k_{obs} divided by the concentration of DMC in mg L⁻¹ and [OH] in mol L⁻¹ thus gives $k_s K$ in L mol⁻¹ per PO per s. The fact that within experimental error equal numbers for $k_s K$ are obtained under various conditions (DMC and ROH concentrations) indicates that the analysis may be valid. The same expressions would apply to the surface reaction when the rate is diffusioninfluenced (*i.e.*, with a non-zero PO concentration near the surface). The propoxylation rate thus appears not to be fully limited by PO mass transport, where no dependence on the hydroxyl group concentration is expected.¹⁰²

Categorization of the catalyst's action

The action of individual DMCs can be visualized by taking k_sK as a measure. A fingerprint of the catalyst activity (in bulk) as a function of temperature and concentration of hydroxyl end groups can be constructed in the form of contour plots in which [OH] or the catalyst particle concentration is plotted against *T* (Fig. 3; Tables S1–S3†). Note that although the catalyst and hydroxyl concentrations are eliminated by the reduction of k_{obs} to k_sK , different conditions still apply and non-ideal conditions with respect to the "catalyst particle distance" become visible.

The fingerprints are useful to show the difference in the action of the DMCs. The analysis for DMC C shows a straightforward increase in activity with increasing T and the rate constant is independent of the DMC and hydroxyl concentration. This is the expected behavior when the described catalysis applies under conditions where there are no influences from viscosity changes, deactivation, and other factors affecting the reaction rate. This independence is found only partly for DMC A; the rate is at a maximum at a temperature of about 130 °C. Deactivation of the catalyst at higher temperature explains this behavior.

DMC B is thermally robust like DMC C. Here, it is found that the effective $k_s K$ becomes more and more independent of the temperature and [OH] when the latter drops below about 0.55 mol L⁻¹, when the DMC concentration is lower than about 26–28 mg L⁻¹. Such a region in the fingerprint indicates a loss of control over the distribution, as semibatch feeding experiments indicate (see the section Interpreting the action of DMC A–C). The fingerprinting of the dependence of the catalytic action on *T* and [DMC] thus enables descriptive catalyst characterization and categorizing. It also allows a global determination of the process conditions in terms of reaction rates (and the concomitant heat evolution) or indirectly on the molecular mass distribution and provides information on the thermal decomposition of the catalytic species.

Activation parameter, support for the Eley-Rideal mechanism 2

A fundamental insight into the catalyst action is gained by considering the apparent activation parameter obtained from the temperature dependence of $k_s K$ (Fig. 4). The analysis of the temperature dependence of $k_s K$ using the Arrhenius equation gives the apparent activation energy E_a (Table 2) as the slope

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Fig. 3 Fingerprints of bulk propoxylation with DMC A, DMC B and DMC C (left to right) with respect to catalyst (top) and calculated hydroxyl (bottom) concentration.

with respect to 1/T after taking the natural logarithm as $\ln k_{\rm s} + \ln K = \ln A_{\rm exp} - \frac{E_{\rm a}}{RT}$.^{103,104} The data were also interpreted in terms of the Eyring equation for transition state theory, $k_{\rm s}K = \exp(-\Delta H^{\ddagger}/RT) \times (k_{\rm B}T)/h \times \exp(\Delta S^{\ddagger}/R)$ (Fig. S6†).^{105,106}

Evaluation of the relevant data with respect to the dependence of the initial fast PO consumption on the temperature indeed gives a linear plot with sufficiently high confidence to discriminate between the three types of DMC catalyst (Fig. 4, S5 and S6†). The uncertainty of the (average) temperature after the pulse gives some limitations with respect to the accuracy, *i.e.*, possibly most of the scattering is from the non-isothermal propoxylation during the decay of the PO pulse in combination with the limited sampling



Fig. 4 Arrhenius plot for propoxylation of Voranol 2000 L with DMCs A–C.

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speed of the spectrometer. It is higher for fast rates, however, the global linear dependence of $\ln(k_s K)$ or $\ln\left(\frac{k_s K}{T}\right)$ on 1/T for the data collected at varying [OH] and [DMC] shows that the pulse and decay method is adequate to reach consistent and meaningful values for E_a and ΔH^{\ddagger} for the propoxylation (Table 2). The linearity indicates that a simple, uniform situation underlies the observations in the temperature range for the evaluation of the experimental data.

The data obtained when applying DMC A at temperatures above 130 °C are clearly outliers from the behavior observed below that temperature. The deviation is taken as evidence of substantial catalyst deactivation (*e.g.* simple extrapolation of the activation parameter indicates that more than 80% of the sites are lost at 140 °C). Data from these experiments were not considered in calculations of the kinetic parameters. In the case of DMC B, data obtained at molecular weights with [OH] below 0.55 mol L⁻¹ were also not used in calculations of the general kinetic parameters. The effective [OH] near the catalyst is not known under conditions of strong PPG gradients between the bulk and the vicinity of the catalyst (Scheme 2), and no meaningful outcome of the calculation of *k*_s*K* from *k*_{obs} is obtained (see the section Interpreting the action of DMC A–C; see ESI† for data displayed and used for regression).

The temperature dependence of the product $k_s K$ may mainly originate from the temperature dependence of k_s , *i.e.*, the reaction step with the highest activation barrier. As noted before, PO is a weakly coordinating substrate,^{107,108} and the temperature dependence of *K* may thus be considered low as ΔH , and to an even greater extent ΔG , for coordination are quite small. The slope of the plots in Fig. 4 are thus

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Table 2 Kinetic parameters for PPG propoxylation and surface properties of DMC catalysts

(Pre)catalyst	DMC A	DMC B	DMC C
$E_{\rm a}$ in kJ mol ⁻¹	120 ± 10	49 ± 4	59 ± 7
$A_{\rm exp}$ from $k_{\rm s}K/{\rm s}$	$3.4 (\pm 0.3) \times 10^{12}$	$2.3 (\pm 0.5) \times 10^2$	$4.5 (\pm 0.8) \times 10^4$
max A _{ring-opening}	10^{16}	10^{6}	10^{8}
$\Delta H^{\ddagger}/\text{kJ mol}^{-1}$	120 ± 10	46 ± 4	56 ± 6
$\Delta S_{\exp}^{\ddagger}$ from $k_{\rm s} K$ in J K ⁻¹ mol ⁻¹	-15 ± 2	$-2.1 (\pm 1.5) \times 10^2$	$-1.7 (\pm 0.9) \times 10^2$
$\max \Delta S_{\text{ring-opening}}^{\ddagger}$	-4	$-2(\pm 1.5) \times 10^2$	$-1.6(\pm 0.9) \times 10^{2}$
$V_{\rm p}/{\rm cm}^3 {\rm g}^{-1}$	0.20	0.13	0.15
D/nm	75	230	110
$V_{\rm mono}/{\rm cm}^3 {\rm g}^{-1}$	25	32	5.2
$S_{\rm BET}/{\rm m}^2 {\rm g}^{-1}$	107	140	22.8
$V_{\rm p(cum)}/{\rm cm}^3~{\rm g}^{-1}$	0.30	0.17	0.31
A_{exp} and $\Delta S_{\text{exp}}^{\dagger}$: pre-exponential factor an	nd entropy of activation based on $k_s K$, t	the "max" values are results when <i>K</i> is	set to 10^{-4} L mol ⁻¹ .

effectively associated with the temperature dependence of $k_{\rm s}$ of the ring-opening event.

 A_{\exp} and $\Delta S_{\exp}^{\ddagger}$ are based on the intercepts of the *y*-axes in the plots of $\ln(k_s K)$ and $\ln\left(\frac{k_s K}{T}\right)$, respectively, against 1/T, where 1/T becomes zero. These numbers are, in contrast to the slope giving " $-\frac{E_a}{R}$ " and " $-\frac{\Delta H^{\ddagger}}{R}$ ", quite dependent on *K*. An estimate for *K* is made from the consideration that propoxylation is evident under the conditions in which the coordination of PPG to the DMC surface will lead to a low number of free coordination sites. The coordination constant for the epoxide will be much smaller than 1, as epoxide adducts are not readily observed in the catalytic chemistry of epoxides and Zn^{2+} . DFT calculations also show this; other entities like ester carbonyls coordinate more strongly.¹⁰⁹

The presumed value of *K* is now set to the larger range down to a minimum of 10^{-4} L mol⁻¹. In that scenario, the values for ΔS^{\ddagger} from the $k_s K$ data will be a maximum of about 10 J K⁻¹ mol⁻¹ too low for the true value for the ring-opening. Concomitantly, the values of the pre-exponential factor of the Arrhenius equation would be higher by a maximum of a factor of 10^4 . The largest pre-exponential factor for DMC A then ranges up to 10^{16} s⁻¹, already a quite high number.

The activation parameters obtained show significant differences between the three catalysts and two classes may be distinguished (Table 2; Fig. 4). The values obtained for DMC A are in the range of a molecular reaction. The kinetic data of the experiments are likely to predominantly represent the elementary process of PO ring-opening at the catalyst surface by ROH. PO is a monomer with a rather high kinetic barrier for nucleophilic attack, and coordination to a Lewis acid is a prerequisite for reaction with weak nucleophiles like hydroxyl moieties.^{110–112} Also, the large pre-exponential factor A is typical for a two particle collision, 113,114 and the negative value of ΔS^{\ddagger} is in accordance with a two component reaction with a moderately early transition state.^{115,116} The activation energy and enthalpy of activation in the range of 120 kJ mol⁻¹ indicate a partial (C-O) bond breakage towards the transition state. The action of DMC A is thus readily interpretable in terms of microkinetic chemical steps.

Chemical surface reactions can, descriptively, proceed either by a Langmuir-Hinshelwood mechanism, in which both reactants are assumed to be adsorbed at the catalyst surface, or an Eley-Rideal mechanism, where one reactant that is coordinated to the surface reacts with an external reactant molecule.61,113,117-120 The kinetics of the ringopening of a coordinated PO molecule activated by DMC A are thus compatible with the external nucleophilic attack of a hydroxyl chain end OH in a transition state with a higher order of mechanistic description 2. The negative entropy of activation and the large pre-exponential factor found for the alkoxylation suggest that the propagation step is more along an Eley-Rideal type of mechanism, like the one depicted in Scheme 2 (right side). It is less likely that both reactants were first adsorbed at the catalyst surface (a syn ring-opening like for the insertion of an olefin Ziegler-Natta catalyst is considered not a viable reaction route).

The activation energies for propoxylation with DMC B and C are found somewhat below half of the value for DMC A, of the same order of magnitude as the reported value for the action of Zn-Co DMC in toluene of 59 kJ mol⁻¹ (Table 2).^{63,121} The preexponential factors $A_{(\max)}$ are atypically low for collisions in the fluid state. The entropies of activation appear as larger negative numbers that have no interpretation as an elementary chemical step. There is no reason to assume that the propoxylation mechanism is different from that at DMC A. The activation parameters rather indicate that the action of DMC B and C is influenced by the diffusion of at least one reagent (Scheme 3). This must be the monomer PO, although its mobility will potentially be higher than that of the hydroxyl chain ends.¹²² In contrast to simple chemical transformations, the polymerization not only yields a product in the form of a longer chain, but at the same time a new hydroxyl starting material at a marginally lower concentration. The diffusion of PPG with OH entities should thus not play a significant role as they would be ubiquitously available anywhere in the reaction mixture, *i.e.*, also close to the DMC crystal surface.

The interpretation of the catalytic action should follow the basics of heterogeneous catalysis in the liquid phase for an immortal polymerization involving the dynamics of the PO monomer, polymer chains and their chain ends.¹²³ The

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apparent activation energies of DMC B and C are at a level of 50% of that for DMC A, which may at first glance be reminiscent of the action of a porous heterogeneous catalyst in the intermediate "chemical and diffusion rate" regime (cf. ESI[†]).¹¹³ However, it seems inappropriate to treat the DMC catalyst as a porous particle system. Adsorption measurements with dinitrogen of the DMC precatalysts give type II van der Waals adsorption isotherms, typical for nonporous/macro-porous materials with a pore diameter larger than 50 nm (Table 2; Fig. S2⁺).^{124,125} The geometric surface extracted properties also do not hold obvious explanations for the differences in the diverse catalytic action. The measurements show that DMC A and DMC B have a comparable surface area, whereas the surface area of DMC C is about 15% of that of DMC B. The gross catalytic activity gives a very different order. The pores in the DMCs are in a similar range of 75-250 nm and the volumes of the pores are also similar. The pore volume in any of the DMCs makes up only a couple of percent of the monolayer, and since the DMCs are bulk solids, the surface outside the pores may contain most of the active centers.

An alternative, more appropriate kinetic description for the action of DMC B and C can be kept simple by assuming a pseudo-steady state flux of PO (proportional to the gradient) to the DMC surface, where it is converted (Schemes 3 and 4). The flux of PO to the surface is describable by Fick's first law as J_{PO} = $k_{\rm mt}$ [PO_b] – [PO_s]), with [PO_b] as the bulk (measurable) PO concentration, and $[PO_s]$ the surface-near PO concentration (relevant to the PO coordination). The total amount of PO transport to the surface is $J_{PO} \times A$, with the total surface area A of DMC crystals in a reaction volume of 1 L. The product $k_{mt} \times A$ can be replaced by a mass transport constant $k_{\rm mPO}$, with units of s^{-1} , that relates to the total DMC surface area per liter, *i.e.* to the concentration of the DMC in mg L^{-1} . The chemical reaction rate at the DMC surface with a preequilibrium coordination of PO and a concentration of ROH close to that of the bulk equals $r_{\rm p} = -\frac{\mathrm{d}[\mathrm{PO}]}{\mathrm{d}t} = k_{\rm s} K[\mathrm{PO}_{\rm s}][\mathrm{OH}_{\rm s}]$ per total amount of DMC in 1 L. The latter should equal the mass transport to the catalyst's $k_{\rm mPO}[{
m PO}_{
m b}]$ surface when $[PO_s] = \frac{k_{mPO}[PO_b]}{k_{mPO} + k_s K[OH]}$. The bulk concentration



 \bigcirc : range of PPG self-diffusion within the time for a fixed amount of PO to reach the DMC surface δ : half of the distance between the DMC particles

Scheme 4 Illustration of the consequences of catalyst particle distances δ in the propoxylation: PPGs inside the range of self-diffusion given by the rate of propoxylation are growing predominantly; more PPGs are outside the range when using larger DMC particles, leading to bimodal distributions. On the right of each case, the concentration of PO is shown as a function of δ .

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$$\begin{split} & [\text{PO}_{b}] \text{ will be the average concentration of PO in the reactor. The observed rate for the total amount of DMC in 1 L is described by <math display="block">& -\frac{\text{d}[\text{PO}]}{\text{d}t} = k_{s}K[\text{PO}_{s}][\text{OH}] = \frac{k_{\text{mPO}}k_{s}K[\text{OH}]}{k_{\text{mPO}} + k_{s}K[\text{OH}]} [\text{PO}_{b}]. \quad \text{The observed rate } k_{\text{obs}} \text{ for the total amount of DMC per L is therefore related to the more fundamental rate constants according to } \frac{[\text{DMC}]}{k_{\text{obs}}} = \frac{1}{k_{\text{mPO}}} + \frac{1}{k_{s}K[\text{OH}]}, \text{ or in the form of temperature dependencies as } -\ln\frac{[\text{OH}][\text{DMC}]}{k_{\text{obs}}(T)} = \ln\left(\frac{[\text{OH}]}{k_{\text{mPO}}(T)} + \frac{1}{k_{s}(T)K(T)}\right). \text{ The temperature dependencies of } k_{\text{obs}} \text{ and } k_{s} \text{ are clearly not connected simply anymore in the case of a diffusion-influenced rate of PO conversion. The temperature dependence of <math>\left(\frac{k_{\text{obs}}}{[\text{OH}][\text{DMC}]}\right)$$
 in

the small interval of 30 K, however, may (deceptively) still show up with a linear dependence between $\ln k_s K$ (and $\ln k_s K/T$) and 1/T (ESI[†]). An interpretation in terms of elementary reaction steps will, however, not be possible.^{7,63}

Interpreting the action of DMC A-C

An explanation of the differences in the kinetics between DMC A on the one side, and DMC B and C on the other, results from a consideration of the PO diffusion path length under the conditions of an almost uniform distribution of PO in PPG that should arise within minutes after the pulse (Table 3). The measurement of the decay of the PO concentration reflects such a situation, *i.e.* the mixing of PO in PPG is considered complete at the start of the measurements. This seems viable: the action of DMC A is not limited by diffusion, and the overall rate for DMC B is lower, while that of DMC C is of the same order of magnitude as that of DMC A. The bulk [PO_b] may be assumed to be at a value given by the height of the pulse, the elapsed reaction time since the PO addition and the volume of the reaction mixture (Scheme 4). The DMC crystals can thus be treated as individual microreactors for the transformation of the immediate surrounding PO rich phase. This description has also been applied in a theoretical treatise of DMC catalyzed propoxylation, but with a metal bound alkoxide as the resting state and molecular weight dependent rate constants for propagation.62

Based on the weight (= volume multiplied by density of 1.8 t m^{-3}) of the primary catalyst particles, the number of particles per unit of reaction volume may be calculated under the premise of a complete dissociation of the aggregates of primary catalyst particles (Table 3). The break-up of the aggregates is expected when they are suspended in Voranol 2000 L with stirring shear and the (initial) polymerization reaction, pushing the primary particles away from each other as the polymer locally takes up more volume with PO consumption.

The minimum distance of PO diffusion may in a first approach be set to half of the distance between the crystals (Scheme 4). This allows the ranking of the length of the diffusion pathway for PO in the order DMC A, DMC C, DMC B,

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Table 3 Calculations for selected propoxylations with DMC A-C as micro reactors

	DMC A	DMC B	DMC 0
Averaged crystal weight 10^{-12} g ^{<i>a</i>}	0.05	4	0.4
Pulse 1 (PPG 2250)			
T (°C)	124	121	126
DMC in mg L^{-1}	23.8	39.7	23.19
$d_{(\text{cryst-cryst})}$ in μ m (= 2 δ)	13	46	26
Relative time constant for diffusion over δ	1	13	4
TOF PO per crystal linear regime 10^{-14} /s	1.6	28	17
Exponential PO consumption ^b /% of decay	93	58	76
Pulse 3 (PPG 2800)			
T (°C)	125	122	128
$V_{\rm p}/{\rm cm}^3 {\rm g}^{-1}$	19.27	30.49	18.19
DMC in mg L^{-1}	14	49	28
$d_{(\text{cryst-cryst})}$ in μ m	76	34	67
Exponential PO consumption ^b /% of decay	125	122	128
Average exponential PO consumption ^c /% of decay	80	47	71

^a Calculated from an average crystallite as rectangular, cuboid with flat surfaces (see ESI[†]). ^b Error is in the range of 10%. ^c From all pulses of 2 separate runs.

by choice of the experimental conditions and the composition of the catalysts (Table 3). First order estimates of the relative time constants for Brownian movements as mean squared displacement ($\langle x^2 \rangle = 2D \times t$) over half the distance between the crystals indicate that diffusion to the surface of DMC B and C is half an order of magnitude slower than that to DMC A. This applies to the diffusion of PO and of the PPGs, the latter is of importance for the distribution of the molecular mass.

Taking the total amount of PO consumption per unit time (k_{obs}) as a basis, the breakdown per crystallite shows that the number of molecules of PO converted by crystallites of DMC A is about one order of magnitude lower than for DMC C, and lower still than for DMC B (Table 3). The attainable flux of PO is thus clearly high enough to account for the absence of mass transport influences on the PO consumption in the action of DMC A with its shorter diffusion pathway and its lower propoxylation rate per crystal. The higher number of its crystallites per mg compensates with respect to the overall rate for the lower activity per particle over DMC B. The action of DMC B and C on the other hand is determined by sufficiently extensive PO activation and becomes influenced by PO mass transport. The much lower number of DMC B particles per L leads overall to a much lower overall activity than for DMC C.

It is worth returning to the change of the kinetic regime during the pulse decay from the initial exponential decay and put this into the perspective of the kinetics and the diffusion length for the PPGs. The change should be related to the "black box" of the catalyst, it seems not to be very dependent on the PO concentration (Table 3). The initial exponential decay is prolonged the longest for DMC A, followed by DMC C and B. This holds true for single evaluations under comparable conditions, but also for a gross average over a larger number of PO pulses (>10) at various OH and catalyst concentrations (Table 3, last entry). The order is in agreement with the distance between the crystals, and most probably is caused by an imbalance between the rate of PO diffusion and PPG self-diffusion as the width of the mass distribution also increases in the order DMC A to C to B. A straightforward argument for the decay in rate towards the end of a pulse would be a (ninterpulse) formation of a lower concentration of hydroxyls near the surface by dilution from the propoxylation.

The "catch-up" kinetics, which help to keep the distribution of mass low, would only apply to the growth of PPGs in the range of the self-diffusion space given by the time PO needs to diffuse to the catalyst.¹²⁶ Note that the observation of "catchup" kinetics in DMC catalyzed propoxylation supports the interpretation of a rate determining ROH attack at an activated PO on the DMC surface. Thus, as long as the PPGs are "sufficiently" fast in self-diffusion (e.g., at low mass) and the distance between the catalyst particles is small, a sustained simple exponential decay of the PO pulse decay is expected. Accordingly, the linear regime is maintained the longest for DMC A, then for DMC C, with DMC B coming in last. Any loss of exponential decay in the limited chain growth of the pulse (growth of 4 to 7 units to the polymer with more than 40 to 55 units) indicates that the amount of DMC was not enough to keep the exchange of surface-near and -far PPGs within the same order as that of the frequency of propoxylation (Scheme 4). In other words, the distances between the particles were too large for the "catch-up" kinetics to be operative for the full bulk of the PPGs.

The percentage of the bulk PPGs outside the range of selfdiffusion would be expected to be higher for large particles (at the same catalyst loading), leading to broader distributions tailing to higher masses. The PPG product distributions determined by SEC indeed show this global behavior, and with expected trends with respect to the catalysts and experimental conditions (Fig. 5). The products from DMC B mediated propoxylation even tend toward bimodality. The PPGs closer to the surface become propoxylated more extensively. The lower dynamics of the PPGs with longer chain lengths (eventually

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Fig. 5 Exemplary molecular weight distributions of the final PPG products of pulse experiments with DMC A–C.

leading to entanglements) will result in a broadening of the distribution by a tailing at high mass.^{127–129} Concomitantly, the PDI will tend to increase progressively during the sequence of pulses as some longer chains are formed, and the pulse decay will deviate from exponential decay sooner. The effect is on the other hand somewhat compensated for by the fact that the overall rate of propoxylation decreases on account of the local lower [OH] (*cf.* Fig. 3 middle). Longer PPGs with a lower [OH] close to the DMC will pick up more PO per pulse for their fewer chain ends, which in turn are slower to equilibrate with the bulk. This self-enhancing behavior leads to the indifference to the global [OH] in the contour plots of DMC B.

As a result, the products from the propoxylation by DMC A tend to contain the lowest percentage of long chains. The fact that the initial exponential decay is lost at the end of the pulse indicates that also here the PPG self-diffusion cannot hold pace with the propoxylation rate, and that a broadening of the distribution occurs under the conditions of the measurements (relatively low catalyst concentration; Fig. 5). Note that the SECs in Fig. 5 are the result of products formed under conditions that are not comparable (number of pulses, temperature, catalysts loadings).

Semi-batch propoxylations with DMC A and DMC B

The analysis above pertains to conditions of relatively high PO concentrations with respect to conditions of standard semibatch propoxylations. The latter would be more like the low PO concentration in the fading of the rate at the end of the pulse (after the first order decay), *i.e.*, added PO is converted relatively fast to reach the low steady state concentration: a higher concentration cannot build up because of the limitations set to the feeding rate for safe operation. The flux of PO to the catalyst is lower because of the lower gradient and the propoxylation rate may be influenced by the mass transport for all DMCs. The resulting lower propoxylation rates should be favorable for the equilibration of PPGs between the bulk and catalyst near molecules by self-diffusion, and hence for keeping a low PDI in semi-batch reactions with a limited catalyst amount.

A further set of experiments with DMC A and B was carried out at relatively low PO concentrations in semi-batch

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mode to assess the relevance of the pulse experiments. As rates and conversion are not useful discriminators under such conditions, the development of the molecular mass distribution was monitored.¹³⁰ The self-diffusion of PPGs in relation to the PO diffusion should be a prominent factor for the outcome and with that the distance between the catalyst particles. It is shown that the insights from the pulse experiments for a good product can be transferred to the performance in semi-batch PO feeding experiments.

PO was thus fed continuously to the reactor at such a rate that the temperature could be held constant at 120 °C (Fig. 6). Starting from Voranol (2000 g mol⁻¹; 2500 g mol⁻¹ after activation against PS standards in the shown SEC traces), PO was admitted to give a final number average molecular mass of 20 kg mol⁻¹ (against PS standards; Fig. 7). The increase in pressure (mainly of argon) is proportional to the increase in the volume of the reaction mixture (and decrease of the empty reactor volume). The small pressure drops at regular times giving rise to the "saw tooth" profile originating from the sampling of about 20 mL of the volume. In-line IR-spectra showed that the conversion of PO was always basically complete, *i.e.*, the steady state PO concentration has almost no contribution to the pressure above the reaction mixture.

The pathway taken by PO after admittance to the reactor is macro-kinetically determined by the mixing to the smallest possible domain dictated by the reactor setup, and the subsequent diffusion into the medium and towards the catalyst particles. The setup with an anchor stirrer and the PO dosing rate fundamentally gives access to products with a low mass dispersion (Fig. S9†), showing that the mixing of PO is generally good enough for a low PDI of the PPG.

The PDI of the PPGs obtained with 50 mg of catalyst DMC A remains decisively lower than that for the product obtained from a reaction using 50 mg of DMC B (Fig. 7). The development of the PPG molecular mass distribution with PO consumption in the presence of DMC A is almost that of an ideal immortal polymerization. This observation is taken as further evidence of the importance of short



Fig. 6 Temperature and pressure profiles and conversion of PO during the semi-batch process with DMC A (PO was dosed to the non-activated catalyst after about 2 h, giving a spike of PO, which disappeared, showing that the catalyst had become active. PO semi-batch feeding started after about 3 h).

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Fig. 7 SEC-analysis of PPGs synthesized by PO homopolymerization with 50 mg of DMC A (l), 50 mg of DMC B (m) and 450 mg of DMC B (r), with number average (M_n) (black) and weight average (M_w) (grey) molecular weights of PPGs synthesized by propoxylation.

diffusion distances. This is the regime of "catch-up" kinetics, where the end groups of lower molecular weight fractions with their higher hydroxyl concentrations are preferentially propoxylated, favorably enhanced by their higher diffusion constants.^{100,131} The narrow distribution is maintained almost up to the target molecular mass. Only a slight broadening of the distribution is observed. Thus, a PPG with $M_n = 20$ kg mol⁻¹ (against PS) and a PDI of 1.2 could be achieved.

The PPG obtained under the same conditions (T and feeding rate) with DMC B (50 mg) shows a steadily increasing PDI to about 1.7 with the increase of the molecular mass in the reactor. The eventual formation of a multimodal distribution is indicated by tailing of the distributions at higher masses. The slower diffusion of the PPG chains relative to the rate of PO mobility and propoxylation results in a gradient between catalyst near, longer chains and those at half the distance between the DMC crystals. This gradient will be stronger the longer the diffusion pathway, i.e., the distance between the catalyst particles. The dilution of the catalyst in the experiment enhances the distance and the differences in PO and PPG mass transport. Additionally, the diffusion constant for the self-diffusion of PPG will progressively decrease with the molecular mass, whereas the PO mass transport rate may decrease less as this is probably mainly related to the segment dynamics (cf. ESI⁺).¹³² This increases the difference between the rate of self-diffusion and propoxylation. The effect of the "catch-up" kinetics would also become smaller (in the interpretation of mechanistic description 2) at higher masses of the PPGs (smaller differences of [OH] in products of higher molecular mass), and effectively a much broader distributed product is obtained: the formation during the feeding of even a second distribution is indicated.^{21,77} A low concentration of DMC crystals thus increases the PDI as has been noticed before.⁷

The broadening of the distribution with the degree of propoxylation is not a property of the surface (in terms of PO activation or polymer binding) of DMC B, but of the reaction conditions. If the propoxylation of PPG 2000 is carried out in the same setup with the use of 450 mg of DMC B, the broadening of the distribution is not found. The distance between the DMC crystals is then in the same ballpark as for DMC A in the pulse experiments. The product distribution in these experiments even has less tailing to higher mass than that for DMC A (a smaller shoulder at the low molecular weight side at about half the mass of the main product indicates that some polymers grow from one end only, possibly started from nucleophilic entities on the catalyst, *vide supra*).

The observations in the semi-batch propoxylation experiments mediated by DMC A and B as extremes in terms of small and large crystal sizes thus follow the insights from the pulse experiments. The outcome of the pulse experiments allows one to understand and predict the outcome of propoxylations with a DMC catalyst in industrial settings. A good catalyst for obtaining a narrowly distributed product will have a long phase of exponential decay of the PO pulse and will show a fingerprint like DMC C with a higher rate at higher temperature. Catalysts of smaller particle sizes will

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generally be favorable for propoxylations at low concentrations: the rate can be higher when the crystal sizes are smaller, keeping the distribution narrow. Effectively, the preparation of a supported DMC catalyst or the physical breaking up of the primary particles follows this strategy.^{31,48,74,89}

Conclusions

The monitoring of the DMC mediated pulsed propoxylation of low molecular weight PPGs gives access to a set of characteristics of the catalyst's action. The outcome of the kinetic analysis is typical for heterogeneous catalysis with its known partitioning in macro - diffusion of reagent from and to the bulk phase - and microkinetics. Analyzing the kinetic data using Eyring and Arrhenius theories indicates that mass transport of PO is of importance to the propoxylation rate in the case of DMC B and DMC C, whereas the action of DMC A is determined by PO ring-opening. A derived rate of PO diffusion shows that the latter is feasible. The kinetic parameters are consistent with a propagation reaction according to an Eley-Rideal mechanism, *i.e.* a PO molecule coordinated to the catalyst surface reacts with an external polymer chain end. The catalytic action of the catalyst particles is more readily understood by considering them as individual "microreactors" than from surface geometry or morphology. Small crystallites give more "microreactors" at the same ppm level of catalyst loading and lead to small diffusion lengths.

The imbalance between catalyst near and catalyst far PPG chain growth increases with the square of the distance between the catalyst particles, and should be kept within limits to keep the product distribution low. This distance lies in the range of 10 μ m in the current study. The most suitable catalyst system for obtaining a narrowly dispersed product of higher molecular weight would have a rate of PO conversion balanced with the dynamics of the PPGs. DMC A, where PO ring-opening seems to be rate determining, gives narrow molecular weight distributions (PDI = 1.2 at $M_{\rm p}$ = 20 kg mol⁻¹), provided that the reactor is well-mixed with an appropriate PO dosing protocol. The action of DMC B, where diffusion has a more prominent contribution to the reaction rate, leads to broader distributions, even with a PDI of up to 1.7, when propoxylation is carried out at the same rate of PO dosing as for DMC A.

A fingerprinting system was developed that allows description of the propoxylation reaction rate dependence on the temperature and concentration of chain ends [OH]. The catalyst activity is visualized in a T vs. [OH] or [DMC] rate constant k_sK contour plot. This provides essential information on the catalyst's kinetic and thermal behavior and helps to identify essential parameters for preparing narrowly dispersed PPGs. A further consideration is the percentage of PO that can be converted in the exponential regime: this should be as high as possible. These insights are relevant to standard semi-batch propoxylations with a much

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lower steady state concentration of PO. The overall analysis shows that for the comparison of DMC catalysts and for directed catalyst development, insights into their specific action are necessary, and that the dependencies are relevant to catalyst and process development. It should also not be too surprising that no simple correlations between activity and overall catalyst composition exist.^{133–135}

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors. The authors want to acknowledge the efforts of Dr. Marbach in the early phase of the study (*e.g.*, performing the first pulse experiments (some data in Fig. 3), establishing the distribution in the setup as a function of the dosing time) and of Dr. Szopinski, performing rheology at high temperature on PPGs of various masses and establishing general relationships between viscosity, temperatures, and mass. The expertise of Dr. Scheliga on size exclusion chromatography has been of high importance and his support is gratefully acknowledged.

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6 DMC-Mediated Propoxylation in Semibatch with an External Loop: Insights into the Catalytic Action

6.1 Synopsis

The new, extended study shows that the product distribution of PPGs of molecular mass around 20 kDa, prepared in a semibatch mode with a low steady-state concentration of propylene oxide (PO) depends on the reactor setup and PO dosing protocol. It was concluded that, for describing the catalytic behavior of DMCs, their particles should be considered as independent, small microreactors; the distance between two crystallites in the reaction mixture is crucial for the resulting molecular weight distribution (MWD). Their catalytic activity and the process conditions also play a significant role in addition to their particle size and the number of active sites. The dosing rate and reaction temperature for a narrow product distribution should be chosen in such a way that a chain exchange near the catalyst (macro-kinetics) occurs faster than propoxylation (micro-kinetics). A further factor is the mixing of PO into the mixture. A static mixer was incorporated into the semibatch system used before in an added external loop. This ensures a more even distribution of the small PO feed over the reaction mixture with the highly active catalyst.

The publication inserted in this chapter discusses the impact of mixing on the resulting MWD and demonstrates that by implementing a static mixer and thus improving mixing, products with narrower distributions can be obtained at the same reaction temperature and dosing rate. Furthermore, it compares the behavior of two Co/Zn DMC catalysts with different rate-determining steps during the propoxylation process and describes for the first time that the catch-up kinetics effect exhibits limitations at specific molecular weights, respectively chain lengths.

The results underline those presented in Chapter 5 and are interpreted within the context of heterogeneous catalysis theory. Moreover, these findings are of significance for industrial application in the sense that a static mixer can be easily incorporated into a technical polymerization process to improve mixing conditions and facilitate higher monomer feeding rates. As a result, enhanced space-time yields are obtained while maintaining consistent product quality.

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DMC-Mediated Propoxylation in Semibatch with an External Loop: Insights into the Catalytic Action

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mixing due to an imbalance between diffusion of the chain ends and propoxylation rate.

■ INTRODUCTION

Polyether polyols are widely used as the soft component in the production of polyurethanes (PUs) as foams, for coatings, adhesives, sealants, and elastomers (CASE polymers).^{1–6} Historically, polyether polyols were produced by ring-opening polymerization (ROP) of epoxides—mainly propylene oxide (PO) and ethylene oxide (EO)—with an alcoholic or acid dior multifunctional starter in combination with alkaline catalysts, like KOH.^{7–9} Today, double metal cyanide (DMC) solids have become an effective alternative for the chain transfer PO polymerization, also using hydroxyl-containing-molecules as a starter, i.e., as chain transfer agents (Scheme 1).^{3,10–15}

DMC particles were identified as catalysts in the early 1960s by General Tire Inc.;^{11,16} their high alkoxylation activity eliminates the need for neutralization and expensive removal of basic catalyst residues from the product when using KOH.^{13,17} The DMC catalyst action was further optimized, also addressing the rate of nondesired PO isomerization to yield

Scheme 1. DMC-Mediated Chain Transfer Polymerization of PO onto Hydroxyls ROH



allylic alcohols as costarters. The poly(propylene glycol) (PPG) products prepared by DMC technology also profit from the readily obtainable narrow molecular mass distributions.^{18–23} A narrow mass distribution of the polyol results in enhanced mechanical properties of the derived polyurethane products. Their lower viscosities over similar polyols with broader molecular weight distribution (MWD) are one major cause.³ This is especially important in applications where mixing (e.g., diisocyanate with PPG) is essential. Application of a polyether polyol with a narrow mass distribution is also advantageous for achieving a clear phase separation between hard and soft segments in PU products.¹

ARCO Chemical developed the first process for the costeffective production of polyols in the mid-1990s by propoxylation of starter diols with DMC catalysts (IMPACT Catalyst Technology).²⁴ Various options, including the cofeeding of an alkylene oxide and starter alcohol in a semibatch operation, have led to the development of a continuous process called continuous addition of oxy starter (CAOS), wherein the catalyst, hydroxyl starter (thereunder H₂O), and alkylene oxides are dosed into a continuously stirred tank reactor (CSTR) with an external cooling loop

Received:	April 24, 2023
Revised:	June 21, 2023
Accepted:	June 24, 2023
Published:	July 18, 2023



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Scheme 2. Indication of the Elementary Microkinetic Steps of Propoxylation: PO Coordination, (Assisted) Ring Opening by an External Nucleophilic ROH Attack, H-Shift, and Decoordination of ROPOH (R'OH) at the Surface of $(Co(CN)_6)_2Zn_3$. $(ZnCl_2)_x$ DMC with a Cubic Lattice (Formal Charges Not Shown, Some Alkoxide Entities May Be Present after the Activation)⁴⁹



(IMPACT).^{25–29} Other optimizations in the production of PPGs include the use of less conventional reactor types, such as disk and loop reactors, as well as the use of a heat exchanger and a combination of both.^{30–36} These technologies are well established for the synthesis of standard polyetherols with molecular weights lower than about 10 kDa and are preferably used in the range below 5 kDa.²⁹ In the CAOS process, where hydroxyl starters are continuously added during the propoxylation, smaller PPGs grow more than proportionally in mass compared to larger ones ("catch-up" kinetics).²⁵

The description of the catalysis with all of its chemical (activity; selectivity) and physical (mass transport) features and interdependencies still has to be agreed upon. Theoretical and experimental contributions aim to advance the understanding, especially since optimizing catalysts is crucial for industrial applications.³⁷ The following paragraphs give an interpretation of the developing literature as an extended hypothesis that is consistently tested in this study. It appears that three timescales are important in the case of a semibatch-operated reactor for propoxylation.

The PPGs obtained from starter molecules, which are mostly diols, and PO are typically the outcome of a manufacturing process. These products are the result of physical and engineering process constraints next to chemical features. This is evident from the numerous (also) engineering patents claiming improvements over the preceding state of the art. When describing DMC catalysis, it is important to note that DMCs are heterogeneous catalysts and that any of the seven steps of heterogeneous catalysis can be relevant to propoxylation.³⁸⁻⁴⁰ These comprise the microkinetic steps of adsorption, desorption, and reaction steps at the surface, which are crucial when the relevant diffusion processes-the macrokinetic features-are comparable in rate or faster.⁴¹ The microkinetic aspects of the catalysis led to the view that the propoxylation reaction is a polyreaction of an immortal type, involving competitive growth of all chain ends at all times. This is concluded from the fact that narrow-distributed products with a polydispersity index (PDI) below approximately 1.1 can be obtained and that all chain ends remain addressable.⁴⁴ The amount of a hydroxyl entity starter (CTA) used thus controls the molecular weight of the products for a given amount of PO.⁴⁵ The immortal polymerization is not necessarily a Poisson process with equal chances for each chain end to return to a "propagation" state (i.e., to grow with a monomer unit). This applies in particular to the DMC catalysis, which is characterized by the so-called and in this context the introduced concept of "catch-up" kinetics, meaning that chains with smaller masses are alkoxylated faster.⁴⁶

Although not discussed in this way, the "catch-up" effect is most simply explained by the involvement of the ROH chain end in the rate-determining step.³⁷ A smaller ROH chain has a higher concentration of hydroxyl groups per unit volume and thus reacts faster. A situation like one with a rate law $r = -\frac{d[PO]}{dt} = k[PO_{surface}][ROH_{surface near}]$ would arise in the catalysis,¹² wherein PO is activated at the DMC surface for nucleophilic attack by a free ROH end group in an Eley–Rideal type of mechanism (Scheme 2). In accordance, the activated PO has also been described as a cationic surface species, susceptible to nucleophilic attack by ROH.^{12,47} PO activation at other Lewis acidic surfaces in the presence of weak nucleophiles is also formulated for nanoparticulate titania catalysts.⁴⁸

The rate law with a first-order dependence on the catalyst (particle) and the PO concentration was partially elaborated and can further be extracted from available data.³⁵ The higher concentration of the ROH (more OH per volume) of smaller PPGs, potentially enhanced by their shorter diffusion times, then accounts primarily for the differences in the propagation rate of PPGs differing in mass, leading to the observation of the "catch-up" kinetics. The chain ends would thus not be dynamically activated for the reaction with the monomer at the surface and then returned to a dormant state, like in ATRP⁵⁰ (atom transfer radical polymerization) or the living

ring-opening polymerization of lactones⁵¹ by homogeneous tin catalysts but continuously compete for the reaction with surface activated PO. 37,52,53

The overall propoxylation rate in batch reactions is typically affected by the diffusion of PO to the DMC surface due to the high rate of ring opening (fast microkinetics).^{54,55} It follows that narrow distribution of the product can be achieved when the time constants of propoxylation, which are determined by the rate of PO diffusion and the reaction rate, are aligned to the self-diffusion dynamics of the PPGs. This ensures an even distribution of the monomer over the chain ends. The "catchup" kinetics, which allows for compensation of imbalances in the chain length, only operates when the self-diffusion of PPG has a similar timescale as propoxylation. An important factor in that regard is the catalyst concentration, as the diffusion length of both PO and PPG is determined by the average distance between the catalyst particles. The larger particle distances at lower catalyst concentrations lead to a larger imbalance in the chain length of PPGs closer and further from the catalyst: PO is the fastest to diffuse and hence catalyst-near PPGs are preferentially propoxylated.¹² This leads to a broadening as soon as the "catch-up" kinetics cannot compensate for the local fast growth anymore (too long diffusion times resp. pathways at some point of catalyst concentration for bulk PPGs in relation to PO diffusion). Moreover, the broadening of the distribution is self-enhancing, as longer chains have lower dynamics with respect to self-diffusion.

The propoxylation process in the industry is usually carried out in semibatch with a low PO steady-state concentration (for thermal control and safety issues). Mixing of PO into the PPG reaction medium is, under such conditions of a diffusioninfluenced propoxylation rate, also of importance for an even distribution of the monomer over the chain ends. The mixing time thus is, next to the propoxylation rate and self-diffusion of PPG, a third time constant with relevance to the outcome.

Little knowledge on the diffusion rate of PO as a function of its concentration in PPGs of various molecular weights at the reaction conditions of 100-130 °C and also on the mixing time in the diverse semibatch-operated reactors is available. The outcome in terms of the polydispersity index PDI (=mass average molecular mass M_w/number average molecular mass $M_{\rm n}$) will still depend on the relationship between these factors. It was therefore decided to gather information on the importance of PO mixing in typical setups of semibatchoperated reactors used for PPG production, including production of untypical high molecular weights. The experiments also allow us to validate the description of the catalysis given above. It is found that mixing is of importance, which gives some information on the dynamics of propoxylation. Higher monomer feeding rates at more effective mixing were used with the objective to obtain constant product qualities at higher space-time yields. The importance of catalyst particle concentrations in connection to particle sizes completes the view on the propoxylation in semibatch-operated reactors.

Relevant to this study is also a patent describing an improved method for the production of polyether polyols, during which the polyol is pumped through zones of high energy density. These are formed in particular by mixing units in the form of static mixers in combination with various nozzles, generating the flow in a pipe.⁵⁸ The positive influence of high energy densities of mixing during the synthesis of polyols on the foaming properties in the subsequent production of polyurethane foams is highlighted.

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EXPERIMENTAL SECTION

Materials. Argon (99.999% (5.0) purity, Praxair Deutschland GmbH), propylene oxide (PO) (99.9% purity, GHC Gerling, Holz & Co.) and Voranol 2000 L (poly(propylene glycol), M_n = 2960 g/mol against PS, PDI = 1.10, DOW Chemical Company) were used as received. DMCs used were gifts from the PO-handling industry with nondisclosure restrictions.⁵⁹ Preparation methods of DMCs can, for e.g., be found in relevant patents.^{60–63} They were prepared from K₃Co(CN)₆ and a Zn²⁺ source, like ZnCl₂ and contain *t*BuOH and water at the surface (Table S1).

Reactor Setup, Operation, and Reaction Monitoring. The reactor set consists of a 2 L stainless steel autoclave (Parr Instrument GmbH, type number 4524), equipped with an anchor agitator, a rising pipe, and an FTIR probe having a diamond window. Spectra with 128 scans were recorded every minute in the range of 650-2000 cm⁻¹ on a ReactIR 45m (Mettler Toledo). Partial least-squares (PLS) regression model for multivariate data analysis was used with The Unscrambler X 10.3 (Camo Software) to evaluate the data. The PO was added using HPLC pumps (Bischoff HDP PUMP Multitherm 200, 0.01-4.99 mL/min and 0.1-39.9 mL/min). Three different HPLC pumps are incorporated to allow monomer feeding at a larger range of rates. A high-pressure proportional relief valve (47 bar) was used between the HPLC pump and plug valve to ensure accurate feeding rates of PO throughout the process despite increasing the pressure during the process due to an increasing reaction mixture volume in the closed system.

The reactor was also equipped with a loop, containing a gear pump (Mahr Metering Systems GmbH, Dosimar type 0.6 cm³/U, gap length = 0.174 mm, wheel diameter = 27.982 mm, gear motor: SEW Eurodrive, R07 DT56M4/TF) with a frequency converter (SEW Eurodrive, Movitrac B 0XS, 0.25 kW), a gear wheel flowmeter (Profimess GmbH, type number VM-04.2.6.P.R.2.S.0) with a plug-in display (SD-01.2.1.1), and a static mixer (Schuhmacher Verfahrenstechnik GmbH, Kenics mixer, serial number SVMW~ZD~6~10). The flow data were recorded and processed in LabView 2018 (National Instruments) surrounding using an analogue input module (NuDAM ND-6017 with ND 6530 for serial communication with LabView). The pressure and temperature present in the tank reactor were monitored with software ProfiSignal 2.2 (Delphin Technology).

Propoxylation in Semibatch Mode. The activation of the DMC solids was performed in a 2 L stainless steel autoclave. The autoclave was charged with a specific amount of the starter agent Voranol 2000 L and DMC catalyst. It was closed, heated to 120 °C, and held under a dynamic vacuum (5 \times 10⁻² mbar) for 1 h to remove volatiles. Thereafter, the vessel was pressurized with 1.5 bar of argon, and a small amount of propylene oxide was added using an HPLC pump with a feeding rate of 0.83 mL/min (vide infra). A sudden rapid increase in temperature and decrease in pressure within a range of minutes indicated the activation of the catalyst, ending the usual induction period. The alkoxylation of the starter diols as CTAs with PO was performed after the activation phase was completed, and the PO concentration was (close to) zero. In typically semibatch mode polymerizations, the PO was added continuously at several rates (0.94-2.71 mL/min) until the desired, theoretical molecular weight of the PPG was reached (setup 1). In experiments with enhanced mixing (setup 2), the

PPG was pumped at several rates (4–40 mL/min) over a static mixing loop in which the PO was added continuously at the same rate as in setup 1 (Figures 1 and 2). The pressure and



Figure 1. Setup 1 for propoxylation experiments, consisting of a 2 L Parr reactor with an anchor stirrer, IR probe, and three different pumps for feeding PO at Various Rates.

temperature were monitored throughout the experiments with software ProfiSignal 2.2 (Delphin Technology). The reaction mixtures in the tank reactor were stirred at a rate of 300 rpm. The temperature in the reactor was kept constant at 120 $^{\circ}$ C, and aliquots were taken at intervals through a rising pipe. After the complete addition of monomers, the autoclave was rapidly cooled to ambient temperature and depressurized. The reaction mixture was subsequently transferred to a drying oven and held under a dynamic vacuum at 50 $^{\circ}$ C until the weight was constant.

Gear Pump Control by LabView VI Routine. The gear pump was controlled by digital RS232 communication, converted to RS485 for the frequency converter controlling the pump. A LabView SubVI routine was designed to control the pump, based on monitored port communication with MOVITOOLS MotionStudio software (SEW Eurodrive). The duration of one communication cycle was 0.5 s, containing 3 updates of the rotational speed. Hence, the theoretical maximum update frequency for the rotational speed was 6 Hz. In practical use, the rotational speed was updated cyclically with a cycle duration of 1 s and less than 0.5 s until the instructed rotational speed was reached. The actual rotational speed was monitored and used for subsequent flow rate adjustments. Relevant process parameters, including the reactant amount, dosing, measurement data, flow set points, and adjusted values were saved with a time resolution of 30 s.

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A correlation of the flow rate and pump rotation speed was linear during calibration (Figure S1), but the gap between pump gears with possible cavitation tends to cause a deviation in the actual flow. The extent is dependent on the viscosity and rotational speed. As the viscosity increases nonlinearly with the weight average molecular weight (Figure S2) and thus with the molecular weight distribution, an exact flow rate may not be obtained by using gear pump calibration only. The rotational speed rate of the gear pump needed adjustment throughout the process to maintain a defined flow rate. This was achieved automatically by the routine. Thus, an initial pump rate taken from the calibration curve was used at the start of each experiment. After a constant rotation rate was reached (t < 0.5s) and another 5 s of equilibration time, the following 5 measured flow rate values $(5 \times 1 \text{ s cycle duration} = 5 \text{ s})$ were recorded and used to calculate the average actual flow rate. The adjusted rotational speed ω_1 was kept unchanged if the deviation between the desired flow rate Q_{set} and average actual flow rate Q_0 was lower than 1%. Else, the actual rotational speed ω_0 was directly adjusted by multiplication with the ratio of $\omega_1 = \omega_0 Q_{\rm set}/Q_0$. The procedure was repeated, starting with waiting for a constant rotational speed, until the experiments were terminated with corrections being performed every 10 s.

Calibration of the FTIR Probe. Measurement of the conversion X of PO was based on online FTIR spectroscopy measurements. The FTIR probe was calibrated by a sort of "backwards" polymerization procedure, using a 2 L autoclave that was charged with 166 g of Voranol 2000 L (poly-(propylene glycol) with an M_n of 2400 g/mol against PS), heated at 120 °C, and held under a dynamic vacuum $(5 \times 10^{-2}$ mbar) for 1 h, like in propoxylation reactions. Thereafter, the autoclave was pressurized with 1.5 bar argon (for the stability of feeding by HPLC pumps), and five IR spectra were recorded. A defined volume of PO was added with an HPLC pump to establish a PO concentration. The system was equilibrated for 5 min and again five spectra with 128 scans were recorded. The addition of PO and recording of IR spectra were repeated until a theoretical conversion of 60% was reached (Table S1). The spectra of the reaction mixture at various conversions in the range between 719 and 1510 cm⁻ show a decreasing intensity of the ring vibration of PO at 828 cm⁻¹ and an increasing absorbance of the C-O stretching vibration of the PPG at 1100 cm⁻¹ (Figure S3) at higher PO concentrations. A baseline correction was performed and a partial least-squares (PLS) regression model comprising two



Figure 2. Extended setup 2 for propoxylation with dosing into a loop, consisting of a 2 L Parr reactor with an anchor stirrer, IR probe, loop with a static mixer and gear pump, and three different pumps for feeding PO at various rates into the reactor or into the loop.

factors was generated with multivariate data analysis using software The Unscrambler X. The predicted conversions are in excellent agreement with the actual values as indicated by the root-mean-squared error RMSE = 0.11 and the coefficient of determination $R^2 > 0.999$ (Figure S4).

Calibration of the Gear Pump and Gear Wheel Flowmeter. Calibrations of the gear pump and gear wheel flowmeter were carried out at a defined rotational speed of the gear pump with Voranol 2000 L at 25 °C ($\eta = 0.32$ Pas)[63] because its viscosity is in the range of those of the products at process temperature ($\eta = 0.28$ Pas, T = 120 °C, $M_n = 15.8$ kg/ mol, $M_{\rm w}$ = 19.6 kg/mol, PDI = 1.24). The flowmeter output signal obtained from the gear wheel flowmeter was measured and the analogue value (4-20 mA, 0-45 mL/min) was converted to digital with an analogue input module and transferred to a computer MZ-gel SDplus linear column using a USB. The obtained flow data were processed and monitored by a LabView VI program (Advanced Loop Operation section, Figure S5). The actual flow rate was determined by weighing the pumped liquid assuming that the polymer's density is constant ($\delta = 1.00 \text{ g/mL}$). As expected, the flowmeter signal and actual flow rate showed a strong linear correlation (Figure S6), and the calibration curve was used to calculate the flow rate in the process (i.e., the theoretical flow rate).

Polymer Characterization. The molecular weight distributions were obtained using size exclusion chromatography (MZ-Gel SDplus linear column (5 μ m, 300 mm × 8 mm), Schambeck RI2012 detector, and a Flom Intelligent pump AI-12) in tetrahydrofuran as the eluent at 22 °C with a flow rate of 1 mL/min and an injection volume of 20 μ L. Monodisperse PS standards (Polymer Standards Service GmbH) were used for calibration and the measured values were referenced against these standards. The data given are relative to these standards. Viscosities of PPG samples with narrow molecular weight distributions were determined on an AR2000ex rheometer (TA Instruments) using a plate-plate geometry (diameter = 2.5 cm, measuring gap = 1000 μ m). Frequency sweeps were performed at 120 °C and angular velocities of $\omega = 0.1-100$ rad/s.

RESULTS AND DISCUSSION

Reactor Setup and Loop Operation. Two reactor setups and modus operandi are presented, which allow a direct comparison of the development of MWD of resulting polymers in dependence on their preparation methods resp. mixing quality. Two types of DMC were used, one with small particles and one with larger crystallites (about 2 orders of magnitude larger), to probe for the catalyst particle concentration influences. An existing reactor setup (setup 1; Figure 1) for a DMC-mediated PO ring-opening polymerization was revamped to enable enhanced mixing of the catalyst, monomer, and starter with the aim of gaining narrower molecular weight distributions of the final polymer.59 The original setup 1 consisted of a 2 L stainless steel autoclave equipped with an anchor agitator (stirred tank reactor), a rising pipe, and an FTIR probe. The diameter of 7 cm of the anchor stirrer and the approximate density of 1 kg/L at a dynamic viscosity higher than 0.02 Pa·s of the hot reaction mixture leads to Reynold numbers Res well below 10, indicative of the major laminar flow in the stirred reaction mixture.

The extended setup 2 comprises an additional 1 L storage container for PO, thus limiting the maximum amount in the system for higher safety (Figure 2). PO has a high chemical

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potential, and its uncontrolled conversion is potentially dangerous. Setup 2 also allows us to circulate the reaction mixture (consisting mainly of PPG and the catalyst) with a gear pump through an external loop, starting near the bottom of the stirred tank reactor, running over a static mixer, and then returning it to the top of the tank reactor. The pumping rate through the loop is monitored by a flowmeter. The flow is controlled by a LabView VI module that automatically adjusts the gear pump's engine speed to a set flow rate, relating to a calibration. The monomer can either be added directly into the tank reactor, for example, for the purpose of catalyst activation or onto the static mixer for enhanced mixing experiments.

The application of static mixers, also known as motionless mixers, has been widely adopted in process industries since the 1970s. They are now considered standard equipment in oncethrough processes and recycle loops for enhancing mixing and heat transfer. They promote axial mixing and hence homogenization of feed streams with a minimal residence time.^{64–67} The effectiveness of the mixing can be tailored by adjusting the type and number of mixing elements, making them optimizable for specific applications.^{65,68} The mixer in this study consists of Kenics mixing elements with a total mixing length of 184 mm and two inlets that allow addition of PO into the PPG stream (Figure 3). Dimensioning is based on



Figure 3. Configuration of the static mixer.

a PPG ($M_n = 32$ kg/mol against polystyrene standards in SEC, PDI = 1.5) with a viscosity of 2.96 Pa·s at 120 °C. This was the expected maximum value for the targeted products of this study. A laminar flow was presumed and the target mixing homogeneity was between 90 and 94% (Tables 1 and S3).

Table 1. Calculated Operational Parameter at Various PPG Rates with a Viscosity of \sim 3 Pa·s

PPG volume flow rate	10 mL/min	25 mL/min	$40 \ mL/min$			
total volumetric flow rate ^a	12.7 mL/min	27.7 mL/min	42.7 mL/min			
residence time	9.2 s	4.6 s	3.1 s			
mixing homogeneity	90.1%	92.3%	93.4%			
pressure drop	0.7 bar	1.8 bar	2.9 bar			
'PO feeding rate of 2.7 mL/min (c.f. Table S3).						

Values for the mixing homogeneity can be accessed by several parameters,⁶⁹ but typically the striation model for simplified calculation of the mixing effectiveness in the static mixer is used, as it is not dependent on molecular diffusivity.⁷⁰ The distribution of components at the outlet is therefore assumed to be dependent only on the initial distribution at the inlet, the geometry and number of mixing elements, and component viscosities and their volume fraction.⁶⁵

The mixing homogeneity is thereby roughly defined by the coefficient of variation (CoV) that describes the ratio between

the standard deviation of the concentration σ and mean concentration \overline{c} in the outlet stream (CoV = $\sqrt{(\overline{c-\overline{c}})^2/\overline{c}}$) .^{71,72} Values given here are based on the CoV. The dependence of the relative length of the mixer L/D with the length of the mixer (L) and the inside tube diameter (D) on the CoV can be expressed by $CoV = b \times \exp((-Z \times L)/(D))$, where the parameters b and Z are adjustable constants. Parameter b is thereby dependent on the ratio between the volume flow rates of the fluids and Z on the mixing geometry.^{65,73–75} Addition of PO was carried out with the HPLC pumps using 1/16" piping, whereas the PPG was pumped through 6 mm piping (Figure 3).

Two different types of experiments were performed with loop circulation. The first one involved pumping PPG onto the static mixer at a constant flow rate. The second type was one based on a flow with a constant ratio between the molar amount of hydroxyl end groups $\dot{n}(OH)$ and that of the monomer $\dot{n}(PO)$, which kept the amount of reactants in the mixer constant over time. The molar flow rate $\dot{n}(OH)$ was given by the initial concentration of hydroxyl groups [OH]₀ and initial flow rate Q0. The hydroxyl concentration [OH] continuously decreases due to dilution by the addition of monomers, causing the molar hydroxyl concentration in the PPG stream to also decrease over time. The loop volume flow Q_0 was increased in experiments with a constant $\dot{n}(OH)$ to the same extent as the occurring decrease in [OH]. This led to the time-dependent volume flow rate $Q_1 = Q_0 [OH]_0 / [OH]_t$. The $[OH]_t$ was calculated, presuming a constant number of chain ends and a constant density of the PPGs of different masses. The initial reactor filling volume of the starter and the total added volume of PO at a defined reaction time were obtained from $n(OH)_0$, assuming a substantial complete conversion. The LabView routine was used to calculate and record the theoretical number average molecular weight at a specific reaction time.

Initiation and Simple Propoxylation Experiments. Activation is required for DMC compounds before catalysis can become effective. This is easily achieved by treating the mixture of the starter PPG and DMC with 4.3 mol equivalents of PO (relative to PPG) at 120 °C. This standard activation process leads to a noticeable exotherm and decrease of PO partial pressure after which the catalyst can be presumed activated. For safety reasons, it is essential to ensure that DMC compounds are activated before catalysis can become effective. Accumulation of PO should be avoided, and dosing should only commence after activation is ascertained. The activity of the catalyst in relation to the feeding is such that PO is readily converted and larger concentrations are avoided.

An exemplary reactor log of propoxylation using setup 2 shows the several stages of the propoxylation process (Figure 4). Activation (1), i.e., heating to 120 °C under a dynamic vacuum and keeping it for 1 h to remove volatiles is followed by pressurizing the reactor with 1.5 bar of argon. The addition of a small amount of propylene oxide over 30 min gives a pressure increase of about 3 bars (2). The activation of the catalyst is characterized by a rapid increase and decrease in pressure thereafter (3), concomitantly an exotherm and a depletion of the PO concentration within minutes is observed (pressure drop). Then, the circulation of the reaction mixture through the loop containing the static mixer is commenced and maintained for 15 min, allowing the pipes, gear pump, and flowmeter to equilibrate to temperature. The reaction mixture



Figure 4. Temperature and pressure profiles and conversion of PO during 6 h of dosing and loop circulation volume of 10 mL/min (Poly 4); the concentration of PO is given in wt% (Table S2).

cools thereby down to about 115 °C (4). The dosing of PO was started (5), quickly restoring the set temperature of 120 °C by the exothermic reaction. The temperature was held constant until addition of monomers was final (6). The dosing of PO leads to a pressure increase in the reactor as the free volume decreases. Once the dosing is stopped, the few percent of steady-state concentration of PO is rapidly lost, causing a decrease in pressure in the very last part of the process.

The initial volume of the Voranol starter (a PPG with a molecular weight of around 2000 Da) remained constant in all experiments. Similarly, the amount of PO that was dosed remained the same across all of the experiments. A theoretical molecular mass of the final polymer of 12 kg/mol (\approx 17 kg/mol against polystyrene PS standards by SEC in tetrahydrofur-an) was thus targeted. Such polyether polyols are, in combination with diisocyanates, the most important components in elastic polyurethane rubbers (PUR), featuring low glass transition temperatures ($T_{\rm g}$), that are typically in the range of -50 to -86 °C.^{3,76}

The propoxylation process was conducted using setup 1 and setup 2, both of which were operated in a semibatch mode. As the volume increases during the reaction, the concentration of catalyst particles decreases as no additional catalyst is supplied. Consequently, the distance between the catalyst particles increases along with the molecular weight of the PPG. In setup 1, the PO was fed directly into the stirred reaction mixture, whereas, in setup 2, the PO was fed into the loop just before the static mixer. (Figures 1–3). Aliquots taken at preset times from the reactor allow the analysis of the molecular weights (MW) and their distribution (MWD) along the dosing time. The aliquots change the amount of OH entities in the reactor to some extent, and no corrections were applied to account for these smaller disturbances of mass balance.

Generally low, almost steady-state concentrations of PO are found (Figures 4 and 5) in these types of experiments. The conversion of PO (X(PO)), during the propoxylation phase was higher than 98%, indicating that the monomer gets basically consumed at the rate of addition. The instantaneous conversion typically reaches higher values in setup 2. This holds especially true in later stages of the dosing with higher molecular mass PPGs (corresponding to lower hydroxyl concentration) and higher viscosities (Figure 5).

The feeding rate of PO was set to allow complete monomer addition in 17, 10, or 6 h (0.94-2.71 mL/min). Higher PO feeding rates lead to broader distributions: Samples taken from

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Figure 5. X(PO) during 6 h of semibatch PO feeding in setups 1 and 2 (Poly 3 and Poly 4 (@10 mL/min flow rate in the loop)).

the reactor in which only the anchor agitator was used for mixing (setup 1) show that the polydispersity index (PDI) of the final polymer and at comparable molecular weights increases from a PDI of 1.23 to 1.4 and 1.75, respectively, for 17, 10, and 6 h of dosing time (Figure 6, Table 2). The steady-state concentration of PO tends to increase somewhat with dosing time, which suggests that the reaction rate is decreasing. This decrease could be due to lower hydroxyl and catalyst particle concentration or by the mixing quality. The size of the stirrer-induced vortex rings is bound to increase and the flow rate to decrease with the viscosity of the reaction mixture.⁷⁷ This lower rate is beneficial for the equilibration of catalyst surface-near and -far PPGs (as discussed later), which counteracts the broadening caused by a larger PO gradient. The initial increase and later decrease of the rate of change of the PDI may indicate that indeed several factors determine the process (Figure 61).

Similar experiments conducted in setup 2 with PO addition into the loop resulted in products with a significantly lower polydispersity (Tables 3 and 4). Experiments with a constant flow rate of PPG at 10 or 40 mL/min in the loop were carried out with a PO dosing time of 10 or 6 h. Even at low rates of PPG flow (10 mL/min), which resulted in a higher local PO concentration (than operation at 40 mL/min), the polymers obtained had narrower molecular weight distributions than

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those obtained in setup 1. The PDI decreased in experiments with a feeding time of 6 h from 1.75 in setup 1 to 1.36 in setup 2. The PDI value of 1.36 falls within the range of products obtained from polymerization experiments carried out in setup 1 with a feeding time of 10 h. Therefore, the polymerization process could be significantly improved in terms of space-time yields to obtain a similar product by revamping setup 1 with the implementation of a static mixer. In this setup, a product with a PDI of 1.28 was obtained after 10 h instead of 17 h, as required for a similar product (with a PDI of 1.23) in setup 1. Using a larger PPG stream of 40 mL/min in the loop, keeping the PO dosing at the same level gives an even narrower molecular weight distribution (Table 4), but the improvement of the PDI of the final product is not substantial anymore, although the mixing quality is expected to be substantially higher (Figure 7; Table 1).

Nonideal mixing thus significantly contributes to the broadening of the distribution, which is superimposed over the inherent catalysis that needs to be described in terms of macro- and microkinetics.^{12,37,78} The vertical mixing efficiency of an anchor stirrer is limited, and a lower reaction rate set by a lower PO feeding rate in setup 1 gives more time for mixing, a converging reaction rate, and mixing times.⁷⁷ This results in smaller gradients in the reaction mixture, exposing more volume elements of PPGs to PO at the inlet, but obviously decreases space—time yields.

The more effective mixing in the loop of understoichiometric amounts of PO with PPG chains leads to higher conversion, indicative of shorter diffusion pathways for PO (smaller segregation). The mixing time is lower than in setup 1, making the development of PDI less dependent on it. The fact that the loop operation at 10 or 40 mL/min shows only marginal differences in the PDI of the final product indicates that the other timescales of the process are already determining the outcome. A balanced PPG self-diffusion rate to the propoxylation rate is then again more important for keeping the PDI low.

Advanced Loop Operation. The loop operation may also be favorable with regard to the confinement of PO to a small volume element of PPGs where most of it reacts. It should allow the equilibration of catalyst-near and -far PPGs in the reactor's main vessel. Propoxylation with an under-stochio-



Figure 6. Number average (M_n) (black) and weight average (M_w) (red) molecular weights of PPGs synthesized by propoxylation with DMC A in 17 h (Poly 1, left), 10 h (Poly 2, middle), and 6 h (Poly 3, right) in setup 1 (anchor stirring in the reactor).

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Table 2. Molecular Weight Distributions of PPGs Synthesized in Setup 1^a									
Poly 1 (17 h) Poly 2 (10 h)						Poly 3 (6 h)			
$V_{\rm PO}/{ m mL}$	$M_{\rm n}$	$M_{ m w}$	PDI	$M_{\rm n}$	$M_{ m w}$	PDI	$M_{\rm n}$	$M_{ m w}$	PDI
0	2.96	3.27	1.10	2.96	3.27	1.10	2.96	3.27	1.10
220	6.78	7.61	1.12	6.04	6.97	1.15	6.22	7.14	1.15
415	8.74	10.0	1.14	9.18	10.8	1.17	9.02	11.6	1.29
610	13.0	15.1	1.16	12.5	15.4	1.23	11.5	17.5	1.52
805	15.1	17.9	1.19	15.6	20.1	1.29	14.9	23.9	1.60
1000	20.0	24.6	1.23	18.4	25.7	1.40	18.1	31.6	1.75
^{<i>a</i>} The molecula	^a The molecular weights are given in kg/mol against PS standards, and the first entry represents $t = 0$ (Voranol 2000L).								

Table 3. Molecular Weight Distributions of PPGs Using Setup 2 with a Loop Rate of 10 mL/min^{a}

	Poly 4 (6 h, 10 mL/min)			Poly 6 (Poly 6 (10 h, 10 mL/min)		
$V_{\rm PO}/{\rm mL}$	$M_{\rm n}$	$M_{ m w}$	PDI	M _n	$M_{\rm w}$	PDI	
0	2.96	3.27	1.10	2.96	3.27	1.10	
220	6.51	7.36	1.13	6.56	7.38	1.13	
415	9.50	11.1	1.17	9.90	11.4	1.15	
610	12.3	15.4	1.25	12.5	15.1	1.21	
805	15.2	20.1	1.32	15.4	19.4	1.26	
1000	18.1	27.1	1.50	18.1	23.9	1.32	
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^{*a*}The molecular weights are given in kg/mol against PS standards, and the first entry represents t = 0 (Voranol 2000 L).

Table 4. Molecular Weight Distributions of PPGs Operating the Loop at 40 mL/min^a

	Poly 5 (6 h, 40 mL/min)			Poly 5 (6 h, 40 mL/min) Poly 7 (10 h, 4			10 h, 40 m	L/min)
$V_{\rm PO}/{\rm mL}$	$M_{\rm n}$	$M_{\rm w}$	PDI	$M_{\rm n}$	$M_{\rm w}$	PDI		
0	2.96	3.27	1.10	2.96	3.27	1.10		
220	6.35	7.11	1.12	6.65	7.44	1.12		
415	9.19	10.4	1.13	9.56	10.9	1.14		
610	12.0	14.3	1.19	12.5	14.4	1.15		
805	14.7	19.1	1.30	15.2	18.2	1.20		
1000	17.2	23.4	1.36	18.0	23.0	1.28		

^{*a*}The molecular weights are given in kg/mol against PS standards, and the first entry represents t = 0 (Voranol 2000 L).

metric amount of PO in the pipe also ensures a modest growth of only some of the chain ends. A subsequent phase with no substantial chain growth follows in the reactor vessel, giving time for PPG equilibration, i.e., between catalyst-near and -far chain ends (vide infra). This forced regime of mass ratios in a tubular reactor, combined with "catch-up" kinetics, leads to the expectation of a narrower PPG distribution.

The significance of the PO to hydroxyl group ratio in the loop was investigated through a differential PO dosing protocol that maintained a constant ratio over time. The latter was achieved using a LabView VI routine that regulated the flow rate as a function of the theoretical molecular weight, reaction volume, and hence of [OH]. Assuming a constant density of the reaction mixture, the volume flow rate of PPG ranged from $\dot{V}(PPG) = 6.5-39.7$ and 3.9-23.8 mL/min for dosing times of 6 and 10 h, respectively. The experimental realized volume flows were satisfactorily regulated to the calculated hydroxyl concentration (\dot{V}_{theo} ; Figure 81). It is observed that the actual rotational speed of the gear pump (ω_{exp}) was higher than expected (ω_{theo}) after about 2.7 h of feeding (Figure 8r). The latter may be related to an increase of the PDI, leading to a higher viscosity than presumed in the calculation for the gear pump operation (Figures 8r and 9).

The ratio x was kept constant at 0.146 throughout the processes, which corresponds to an average of 15 mol % of the chain ends being able to react with PO. Products with a narrower molecular weight distribution were expected as under-stoichiometric, constant ratios between PO and the hydroxyl end groups/catalyst would enhance a more uniform distribution of PO over the chain ends, irrespective of the dosing rate.

The results show that the PDIs are the same using 6 or 10 h dosing times up to a number average molecular mass of about 9.5 kg/mol (relative to PS; Table 5). Still, a very comparable PDI for the 6 and 10 h dosing times is achieved at a molecular mass of 12 kg/mol. While these results are in fact slightly



Figure 7. SEC analysis of PPG samples of experiments in setup 2 with (left) $t_{\text{feed}} = 6 \text{ h} (40 \text{ mL/min}, \text{Poly 5})$ and (right) of MWDs of final products obtained with a dosing time of 10 h (Poly 2, 6, and 7).

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Figure 8. Actual and set volume flow of the PGG stream (left) and the actual and set rotational speed of the gear pump ω (right) in cycle per minute in Poly 8.



Figure 9. Polydispersity indices at specific number average molecular weights of PPGs synthesized using DMC A in 6 h (left) and 10 h (right) dosing times.

Table 5. Molecular Weight Distributions of PPGs of Experiments with Constant $\dot{n}(PO)$ with a ratio x of 0.146 between $\dot{n}(OH)$ and $\dot{n}(PO)^{a}$

Poly 8 (6 h, 6.5–39.7 mL/min)	Poly 9 (10 h, 3.9–23.8 mL/min)						
$V_{\rm PO}/{ m mL}$	$M_{\rm n}$	$M_{ m w}$	PDI	$V_{\rm PO}/{\rm mL}$	$M_{ m n}$	$M_{ m w}$	PDI
0	2.96	3.27	1.10	0	2.96	3.27	1.10
220	6.48	7.26	1.12	220	6.64	7.46	1.12
415	9.58	11.1	1.16	415	9.47	11.0	1.16
610	12.4	15.2	1.23	610	12.6	15.2	1.21
805	15.1	19.6	1.30	805	15.4	19.10	1.24
1000	17.9	25.3	1.41	1000	17.9	23.60	1.32
The molecular weights are given in kg/mol against PS standards, and the first entry represents $t = 0$ (Voranol 2000 L).							

better than the intermediate results obtained with a constant circulation rate of 10 mL/min, they are not as favorable as those with a rate of 40 mL/min (Poly 4–7; Figure 9). Further experiments are in progress addressing the importance of the ratio x for keeping the PDI low. This study demonstrates that smaller effects can be expected, and more complex dosing profiles may be used to increase space–time yields and keep the PDI low also in the preparation of high molecular PPGs at the low DMC concentration.

Influence of Catalyst Particle Concentration. As indicated above, the broadening of the distribution at higher molecular weights of the PPG and lower catalyst concentrations cannot be avoided by any mixing strategy in setup 1 or

2. The propoxylation seems to enter a phase of faster broadening at an M_n of about 10 kDa (Figures 7 and 9). This may be showing the limits of the "catch-up" kinetics regime, effectively operative at the start of the dosing. The new phase no longer shows (the full extent of) catch-up kinetics, which can be explained by the self-diffusional exchange of the PPG chains near the catalyst surface with those in the bulk seems to becoming a factor of decisive importance. It is noteworthy that the PO conversion remains always almost complete, and the rate of propoxylation is mostly unchanged, even as the concentration of catalyst surface at (almost) the feeding rate. However, as the diffusion path of the "bulk"-



Figure 10. SEC analysis of PPG samples of the experiments with DMC B and 10 h of the propoxylation time in setup 1 (left) and setup 2 (right), corresponding to the data in Table 6.

PPGs of increasing mass to reach the catalyst surface becomes longer, the timescale of substantial equilibration becomes significantly longer than the rate of propoxylation. This results in an additional broadening (next to mixing) of the MWD, which becomes more extensive with increasing degrees of propoxylation and with slower diffusing PPGs and increasing distances between the catalyst particles.⁵⁷

This interpretation of the broadening of the distribution at higher conversion in terms of a lower catalyst concentration of DMC A is supported by using DMC B as the catalyst. The Brunauer–Emmett–Teller (BET) surface areas of DMC A and B are highly comparable at 107 and 140 m^2/g , like the pore diameter of 75 and 230 nm, respectively. The major difference is that DMC B consists of much larger particles, resulting in a system with a larger separation between the catalyst particles at the same catalyst loading. As a result, the timescale of PPG self-diffusion, which is the longest in the propoxylation process, would have increased.

Indeed, the transition away from the "catch-up" kinetics with a sufficiently rapid PPG diffusion, guaranteeing a narrow distribution, is now found at a much lower conversion. The final result is the formation of PPGs with even bimodal distributions (Figure 10), the logical consequence of an increasing misfit between PPG self-diffusion and the propoxylation rate. The monomodal distribution of the starting PPG is only preserved in the early stages, i.e., propoxylation in a regime where a fast (with respect to PO addition) chain exchange between the bulk and catalyst-near PPGs is given.

Catalytic experiments mediated by DMC B in setup 1 with poorer mixing qualities give evidence for the formation of a second distribution after a dosing time of only 4 h of the projected 10 h total (Table 6; Figure 10). This onset can be prolonged somewhat by using setup 2 with the understochiometric compared dosing, using the highest circulation rate in the loop of 40 mL/min. The situation after 6 h of dosing is comparable to the later stages of the propoxylation of Voranol 2000 L with DMC A, where only the onset of bimodal distribution formation is recognizable (Figure 7). This again shows the self-enhancing of the broadening and that preventing the formation of even some high molecular weight PPGs at any time is essential for preserving a low PDI.

Consistent with the description of the DMC propoxylation, the peak molecular mass of the products prepared using DMC B in setup 2 is higher. These fractions of lower molecular mass products are reminiscent of the "catch-up" kinetic regime. The

Table 6. Molecular Weight Distributions of PPGs
Synthesized by Propoxylation Mediated by DMC B and a
Propoxylation Time of 10 h ^a

Poly 10 (anchor agitator)		Pol	ly 11 (lo	op @ 4	ŀ0 mL∕mi	n)	
t/h	$M_{\rm n}$	$M_{ m w}$	PDI	t/h	$M_{\rm n}$	$M_{ m w}$	PDI
0	2.96	3.27	1.10	0	2.96	3.27	1.10
2	6.23	7.56	1.21	2	6.19	7.16	1.16
4	8.54	18.5	2.17	4	8.80	12.0	1.36
6	12.0	44.9	3.74	6	11.2	21.8	1.95
7	13.2	53.1	4.02				
8	13.9	59.8	4.30	8	13.6	38.2	2.81
9 ^b	14.4	62.3	4.33				
10 ^c	15.1	70.0	4.64	10	15.8	53.4	3.38

^{*a*}The molecular weights are given in kg/mol against PS standards, and the first entry represents t = 0 (Voranol 2000L). ^{*b*}Sample taken 1 h after stopping PO feeding. ^{*c*}Sample taken 2 h after stopping PO feeding.

unbalanced growth of a fraction of chains in Poly 10 (setup 1, DMC B) even led to lower steady-state conversions of PO. The online FTIR spectroscopy measurements revealed (Figure 11) that the PO concentration increases substantially after 8 h. Safety reasons and the high viscosity putting high strain on the anchor agitator, led to the termination of the PO addition. However, monitoring the decrease of the PO concentration



Figure 11. Conversion of PO, determined by online IR spectroscopy, during propoxylation experiments with DMC B.

revealed that the catalyst was still active, and the molecular mass continued to increase. The PDI of the PPG after 8 h of propoxylation in setup 2 was only 2.8 (Poly 11). The PO could be added as planned during the 10 h of the experiment, as $X(PO) = 98 \pm 1\%$ (Figure 11). This once again shows that the propoxylation in a loop with good mixing and possibly confinement of PO and PPG is favorable for controlling the PDI.

CONCLUDING REMARKS

Three timescales are to be considered for understanding the outcome of DMC-catalyzed propoxylation. The longest one is the timescale of PPG self-diffusion. It depends on the dynamic properties of the PPG, such as molecular mass, distribution, and temperature, and needs to be related to the distance between the catalyst particles. The timescale increases in the course of the semibatch propoxylation on account of the increase of the average molecular weight and the dilution of the catalyst by the increase in reaction volume. A narrow distribution of the starter PPGs as CTAs can be held if the timescale is in the same order as the rate of propoxylation provided that the mixing of PO into the PPG is fast enough. These conditions will show the "catch-up" kinetics, which results from a higher hydroxyl concentration of low molecular mass products in the relevant volume close to the surface.¹ The end of this initial regime can be detected by the emergence of a high molecular mass tail and an increase in viscosity. The propoxylation rate then becomes essentially faster than the self-diffusion of PPG. The rate of PO diffusion may be substantially linked to the faster segmental movements of the PPGs and be more or less independent of the movements of the center of mass by self-diffusion. The difference between PO diffusion and PPG self-diffusion will strive to larger values along the time (i.e., amount) of PO dosing.^{56,79} The self-diffusion constant of PPGs decreases linearly with increasing chain length in the Rouse regime of masses at ambient temperatures.⁵

Control over the outcome of the propoxylation in terms of the PPG product is gained by adaption to the longest timescale. The latter is adjustable by the temperature and by the catalyst particle distance. The temperature is limited by decomposition processes, but the catalyst particle concentration can be made high. Previous studies in batch operation have found positive effects when using higher catalyst concentrations.¹²

The use of a high concentration of catalyst particles leads to higher residues in the product and to higher costs. A narrow distribution is only reached when the distance between the DMC particles gives a matching timescale of self-equilibration. A catalyst consisting of small, single dispersed particles is to be preferred over a highly active catalyst of larger particles (e.g., DMC A over DMC B). The approach of supporting DMC on silica to submicron particles may be a valid strategy for obtaining a superior PPG.⁸⁴ Dosing of additional catalyst particles in the CAOS process is keeping the short distance between the particles, implying that no activity or deactivation but dilution gives the necessity in the execution to keep the PDI low.

The requirements on reaction engineering for obtaining a PPG product with a small PDI in a semibatch process follow trivially from the description. Mixing of PO and PPG must be achieved on the timescale of the propoxylation rate. An effective mixing was reached in a loop reactor by injection of

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PO into PPG just in front of a static mixer. The rate of PO addition in the range of the equilibration timescale of the centers of mass of the PPGs gives no specific requirements on the residence time in the tank reactor. The practiced addition of a relatively low amount of PO with respect to the number of chain ends and subsequent equilibration of the PPG in the larger vessel gives access to narrowly distributed products with DMC A, but not for DMC B. The product obtained with DMC B obviously has a gradient of chain length between the catalyst surface and the bulk. The PO dosing at later stages was much too fast for keeping the PDI low at the level of the catalyst dimensions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.3c01313.

Data on DMC A and B from EDX and BET measurements (Table S1); formal conversion X of PO from volume V of PO that was added to 250 mL of Voranol (Table S2); calculated operational parameter and flow values in the static mixer at various PPG flow rates with a viscosity of 2.96 Pas and with a PO feeding rate of 1.62 mL/min ($t_{add} = 10$ h) (Table S3); calibration of the gear wheel flowmeter obtained from the measurement of the flow rate output signal and actual mass flow rate (Figure S1); dynamic viscosity at 120 °C of PPG samples with narrow molecular weight distributions in dependence on the weight average molecular weight (Figure S2); FTIR spectra of PPG/PO mixtures (Figure S3); predicted conversion of PO versus experimental data ($R^2 > 0.9999$) from the PLS regression model (Figure S4); interface of the LabView VI module (Figure S5); and calibration of the gear pump obtained by correlation of the measured actual mass flow rate and pump rotational speed at PPG of Voranol 2000 L at 25 °C (η = 0.32 Pas) (Figure S6) (PDF)

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Notes

The authors declare no competing financial interest.

The authors declare no competing financial interest. This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

ACKNOWLEDGMENTS

The authors wish to thank Dr. Felix Scheliga for sharing his competence in the SEC measurements, and Dr. Daniel Szopinski for performing rheology on PPGs of several masses and temperatures. They also acknowledge the great value of discussions and material exchange (PPGs, DMCs) with PO converting industries.

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8 Appendix

A. Hazardous Materials

All hazardous waste materials were disposed in compliance with legal requirements and are listed in Table A1.

Substance	Hazard	Hazard	Precautionary
	pictograms	statements	statements
Acetone		H225-H319-H336	P210-P233-P240-P241-
			P242-P305+P351+P338
Argon	\diamond	H280	P403
Butane-1,4-diol		H302-H336	P301+P312+P330
Carbon dioxide	\diamond	H280	P403
Chloroform-d		H302-H315- H319-H331- H336-H351- H361d- H372	P202-P301+P312- P304+P340+P311- P308+P313
Dodecylamine		H304-H314- H335-H373-H410	P261-P273-P280- P301+P310- P305+P351+P338-P310
Ethane-1,2-diol		H302-H373	P301+P312+P330- P314
Ethanol		H225-H319	P210-P240- P305+P351+P338- P403+P233
Phosphorus pentoxide		H314	P260-P280- P301+P330+P331- P305+P351+P338- P308+P310
Propylene oxide		H224- H311+H331- H302-H315- H319-H335- H340-H350	P201-P210-P280- P302+P352+P312- P308+P313- P403+P233
Sodium nitrate		H272-H319	P220-P305+P351+P338
Tetrahydrofuran		H225-H302- H319-H335- H336-H351	P210-P280- P301+P312+P330- P305+P351+P338- P370+P378-P403+P235
Toluene		H225-H304- H315-H336- H361d-H373	P202-P210-P273-P331- P301+P310- P303+P361-P353
Trieethylamine		H225-H302- H311+H331- H314-H335	P210-P280-P301+P312- P303+P361+P353- P304+P340-P311- P305+P351+P338+P310

 Table A1 Safety data^[1, 2] on hazardous materials.

References

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- [2] Sigma-Aldrich, *http://www.sigmaaldrich.com*, **22.10.2023** (last access).

B. Additional Supporting Information





1 Supplement

- 2 Batch PO/ CO₂ copolymerization with Caradol ED 56-200 at 60°C
- **3 Table S1.** Batch copolymerization of PO and CO₂ with Caradol ED 56-200.

<i>T</i> [°C]	p [bar]	Mn [kg/mol]	PDI	$f_{ m carb}$	$f_{ m ether}$	F
60	10	3.9	1.1	0.13	0.87	0.14
60	36	3.7	1.1	0.12	0.88	0.14

4 Determination of polymer composition

5 The polymer backbone may consist of carbonate, carbonate ether and ether linkages (Figure S1). 6 Three ¹H-NMR spectra were recorded for each sample and the integrals of methyl protons were used 7 for determination of mole fractions f_{CO_2} and f_{PO} , respectively f_{carb} and f_{ether} that were 8 incorporated into the polymer chain (Equation S1 to S4). The carbonate f_{carb} and the ether content 9 f_{ether} were calculated along Equation S3 and S4, comprising the formation of cyclic propylene 10 carbonate (¹H-NMR, δ CH₃ = 1.5 ppm). The cPC content were calculated along Equation S5.

$$\begin{array}{ll} 12 & f_{CO_2} = \frac{n_{CO_2}}{n_{CO_2} + n_{PO}} = \frac{C + 0.5(EC + CE)}{C + 0.5(EC + CE) + C + EC + CE + yE} = \frac{C + 0.5(EC + CE)}{2C + 1.5(EC + CE) + yE} & \text{Equation 1} \\ \\ 13 & 14 & f_{PO} = \frac{n_{PO}}{n_{CO_2} + n_{PO}} = 1 - f_{CO_2} & \text{Equation 2} \\ \\ 15 & 16 & f_{carb} = \frac{n_{carb}}{n_{carb} + n_{ether} + n_{cPC}} = \frac{C + 0.5(EC + CE)}{C + 0.5(EC + CE) + 0.5(EC + CE) + yE + cPC} = \frac{C + 0.5(EC + CE)}{C + EC + CE + yE + cPC} & \text{Equation 3} \\ \\ 17 & 17 & 17 & 17 & 17 & 17 & 17 \\ \end{array}$$

18
$$f_{ether} = \frac{n_{ether}}{n_{ether} + n_{carb} + n_{cPC}} = \frac{0.5(EC + CE) + yE}{C + 0.5(EC + CE) + yE + 0.5(EC + CE) + cPC} = \frac{0.5(EC + CE) + yE}{C + EC + CE + yE + cPC}$$
 Equation 4

20
$$f_{CPC} = \frac{n_{CPC}}{n_{CPC} + n_{PPC}} = \frac{cPC}{cPC + C + 0.5(EC + CE) + 0.5(EC + CE) + yE} = \frac{cPC}{cPC + C + CE + CE + yE}$$
 Equation 5



22 Figure S1. Building units and ¹H-NMR spectra of methyl protons of a PPEC sample containing 23 carbonate, carbonate ether and ether linkages.

24 Liquid-gas Equilibrium Data



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21

- 26 27 Figure S2. Liquid-gas equilibrium data taken from J. Chem. Eng. Data, 2010, 55, 3379-3382 (red) and
- Russ. J. Phys. Chem. A, 1973, 47, 895-896.
- 28 Full IR spectra of reaction mixtures leading to PPEC-1 and PPEC-2



Figure S3. IR spectra of reaction mixture during semi-batch experiment at T = 90 °C (a; PPEC_1) and 32 T = 120 °C (b; PPEC_2) at 10 bar CO₂ pressure.

33 Determination of Newtonian viscosities

34Viscosities of the products were determined on an AR2000ex rheometer (TA Instruments) using35a plate-plate geometry (diameter = 2.5 cm, measuring gap = 1000 μ m). Steady state flow experiments36were performed at 25 °C, 90 °C and 120 °C and angular velocities of $\omega = 0.1 - 100$ rad/s.

Table S2. Newtonian viscosities η of PPG ($M_n = 5.1$ kg/mol, PDI = 1.13) and of PPEC ($M_n = 4.9$ kg/mol,39PDI = 1.19 carbonate content of 12 mol%).

T [°C]	ηPPG [Pa.s]	η PPEC [Pa.s]
25	0.525 ± 0.004	1.036 ± 0.005
90	0.098 ± 0.001	0.120 ± 0.002
120	0.068 ± 0.001	0.076 ± 0.002



40 Peak fit of SEC PPEC-1



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Figure S4. MWD curve of PPEC_1_2.5h and the sum curve of peak separation (a), curves of separated
peaks (b), MWD curve of final product PPEC_1 and the sum curve of peak separation (c) and the
curves of separated peaks (d).

48 Table S3. Total molecular weights of PPEC_1 as measured with SEC and sum of molecular weights
 49 after peak fit in Chromatographica (showing a goodness of fit)

Sample	Mn	$M_{ m w}$	PDI	Mn_sum	$M_{ m w}$ _sum	PDI_sum
	[kg/mol]	[kg/mol]		[kg/mol]	[kg/mol]	
PPEC_1_2.5h	4.5	12.6	2.8	4.4	9.7	2.2
PPEC_1_5h	7.2	44.5	6.2	7.1	40.0	5.6
PPEC_1_6h	8.1	57.2	7.0	8.0	51.4	6.4
PPEC_1_7.5h	9.5	74.0	7.7	9.4	69.4	7.4
PPEC_1_8.25h	10.2	80.3	7.9	10.2	76.9	7.6
PPEC_1_9h	12.0	84.7	7.0	11.9	80.7	6.8

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51 Semibatch Propoxylation of Caradol at 90°C



52

53 Figure S5. SEC of the propoxylation of Caradol ED at 90°C under semibatch conditions (0.96 mL PO/min),

54 experiment terminated after 6 h.Semibatch PO/ CO₂ copolymerization with Lupranol at 120°C in the

55 presence of amines



59Figure S6 SEC-analysis of PPECs synthesized at 10 bar CO2 and 120 °C with 2 μL TEA (a) and602.6 mg DDA (b) in 450 mL autoclave in semi-batch mode (0.3 mL/min PO feed).

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63 Figure S7. XRD of DMC-Cl

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Supplemental Information belonging to

Analysis of the Propoxylation of Zinc-Cobalt Double Metal Cyanide Catalysts with different active Surfaces and Particles Sizes

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Supporting catalyst descriptions 2 Reaction profile and experimental data in pulse-decay experiments 4 On the Thiele modulus 8 Diffusion and Mw dependent Viscosity of the reaction mixture at 120 °C 9 On the linearity of $\ln k_s K$ (and $\ln k_s K/T$) and 1/T under diffusion influenced rates 10 Calculations on single DMC crystals 11 Attainable PDIs in the set up 12 References 13

Supporting Catalyst descriptions



Figure S1 SEM images with 20 000 magnitude of DMC A (I), DMC B (m) and DMC C (r) after thermal treatment (80 °C, 2 h).



Figure S2 Isotherm of DMC A resulted by adsorption measurements with nitrogen.

DMC complexes are based upon [M[M'(CN)₆] frameworks (here M = Zn²⁺, M' = Co³⁺) in which octahedral [M'(CN)₆]ⁿ⁻ complexes are linked by Mⁿ⁺ ions coordinated to nitrogen atom of the cyanides [1], [2]. The major, sharp reflexes of cubic and presumed catalytically inactive Zn₃[Co(CN)₆]₂ at 2θ = 17.0, 23.7, 24.7, 34.3 and 39.9° are found in the XRD of DMC B. DMC A and C show more broadened peaks, obviously on account of the smaller crystallite size, both showing a sharp reflex at 2θ of 23.7° [3]. The XRD pattern of DMC C is consistent with the usual cubic Prussian blue structure type, but intensity and shape of the peaks indicate that parts of the framework have collapsed [4]. The XRD pattern of DMC A shows a resemblance to reported dimorphic cubic and hexagonal structures, in which the zinc metal (M) is octahedral respectively tetrahedral coordinated as it shows considerable reflexes at 2θ = 9.9 and 14.4°, belonging to a semi-crystalline Zn₃[Co(CN)₆] phase [3]. The reflexes at 2θ of 11.3, 16.5 and 21.7° can be assigned to a hexagonal phase (Zn₃Co₂-H) [5], [6].


Figure S3 XRD patterns of the catalysts. Reflexes of cubic $Zn_3[Co(CN)_6]_2$ (green), semi-crystalline $Zn_3[Co(CN)_6]$ (grey) and hexagonal Zn_3Co_2 -H (blue) are highlighted.



Reaction profile and experimental data in pulse-decay experiments

Figure S4 Temperature- and pressure profiles and conversion of PO during pulse-decay experiment including drying procedure, activation phase and pulsed PO additions.

Nr.	k _{obs} / 10⁻³ · [1/s]	[DMC] /	[ROH] /	<i>k</i> ₅·K / 10 ⁻⁴ ·	T / °C
		mg/L	mol/L	L²/(s·mg _{DMC} ·mol)	
1	4.33 ± 0.23	23.87	0.79	2.29	123.6 ± 4.0
1	3.84 ± 0.15	21.30	0.71	2.55	124.8 ± 3.4
1	3.33 ± 0.11	19.27	0.64	2.70	124.7 ± 2.5
1	1.98 ± 0.17	17.21	0.57	2.01	123.9 ± 2.3
1	1.56 ± 0.04	15.52	0.52	1.95	121.9 ± 1.8
1	1.05 ± 0.02	14.00	0.46	1.61	121.7 ± 1.4
2	8.47 ± 0.22	26.48	0.78	4.08	125.9 ± 4.5
2	8.00 ± 0.18	23.85	0.71	4.75	126.6 ± 4.0
2	6.56 ± 0.04	21.45	0.64	4.81	128.2 ± 2.3
2	4.08 ± 0.12	19.32	0.57	3.69	124.4 ± 3.5
2	2.36 ± 0.02	17.28	0.51	2.67	123.6 ± 2.4
2	1.59 ± 0.02	15.53	0.46	2.23	121.8 ± 2.1
2	1.14 ± 0.02	13.92	0.41	1.98	122.5 ± 2.0
3	5.85 ± 0.17	23.97	0.80	3.07	124.3 ± 3.6
3	4.99 ± 0.12	21.56	0.72	3.24	124.1 ± 2.1
3	3.29 ± 0.05	19.17	0.64	2.70	118.9 ± 1.3
3	1.62 ± 0.06	15.39	0.51	2.06	120.3 ± 1.5
3	1.35 ± 0.02	13.72	0.46	2.16	121.4 ± 2.8
3	0.58 ± 0.02	12.22	0.41	1.02	115.0 ± 2.8
4	2.98 ± 0.10	24.81	0.79	1.52	116.8 ± 0.7
4	2.75 ± 0.10	22.32	0.71	1.73	117.9 ± 1.3
4	2.43 ± 0.07	19.89	0.63	1.93	117.9 ± 1.8
4	1.67 ± 0.04	17.88	0.57	1.63	117.2 ± 0.7
4	0.98 ± 0.02	16.09	0.51	1.19	115.2 ± 0.8
4	0.68 ± 0.01	15.19	0.49	0.92	115.5 ± 1.6
5	1.98 ± 0.04	23.61	0.78	1.07	113.6 ± 0.7
5	1.65 ± 0.02	21.18	0.70	1.11	111.5 ± 1.8

Table S1 Parameters and determined reaction rates of all feeding-step experiments with DMC A.

4

5	1.39 ± 0.01	19.10	0.63	1.14	111.7 ± 3.4
5	1.32 ± 0.06	17.14	0.57	1.35	115.7 ± 0.8
5	0.74 ± 0.06	15.40	0.51	0.94	113.5 ± 1.4
6	2.23 ± 0.06	23.64	0.78	1.20	109.1 ± 0.8
6	2.25 ± 0.07	21.54	0.71	1.46	111.6 ± 0.7
6	2.20 ± 0.03	19.36	0.64	1.77	114.0 ± 1.8
6	1.36 ± 0.02	17.08	0.57	1.40	107.6 ± 0.6
6	0.89 ± 0.01	15.57	0.52	1.11	106.7 ± 0.7
6	5.98 ± 0.34	13.99	0.46	9.19	108.0 ± 0.7
7	5.15 ± 0.16	23.82	0.79	2.73	145.0 ± 1.3
7	3.79 ± 0.14	21.51	0.71	2.46	136.1 ± 0.6
7					138.9 ± 1.6
	2.30 ± 0.02	17.20	0.57	2.34	
7	1.68 ± 0.01	15.50	0.51	2.10	138.8 ± 0.7
7	1.40 ± 0.01	13.89	0.46	2.18	138.2 ± 1.5
8	6.68 ± 0.23	23.78	0.79	3.56	134.6 ± 3.2
8	5.26 ± 0.19	21.34	0.71	3.48	131.1 ± 2.1
8	2.63 ± 0.06	17.27	0.57	2.65	129.8 ± 1.4
8	2.29 ± 0.03	15.51	0.52	2.86	132.0 ± 1.8
8	1.61 ± 0.02	13.93	0.46	2.50	133.8 ± 1.0
8	1.29 ± 0.02	12.57	0.42	2.45	135.2 ± 2.1
9	3.47 ± 0.12	17.70	0.52	3.79	129.3 ± 2.1
9	2.29 ± 0.07	15.94	0.47	3.09	130.7 ± 1.3
9	1.71 ± 0.03	14.31	0.42	2.86	131.6 ± 0.9

Tabl	e S2	Parameters and	l determined	reaction ra	ates of al	l feeding	g-step e	experiments	with	DM	CE	3
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Experiment	k _{obs} / 10⁻³ · [1/s]	[DMC] / mg/L	[ROH] / mol/L	k _s ·K / 10⁻⁵ · L²/(s·mg _{DMC} ·mol)	T/°C
1	1.74 ± 0.05	38.14	0.79	5.75	121.5 ± 1.4
1	1.94 ± 0.08	34.06	0.71	8.04	124.1 ± 1.8
1	1.38 ± 0.05	30.49	0.63	7.16	122.1 ± 1.7
1	1.21 ± 0.03	27.38	0.57	7.78	121.2 ± 1.0
1	0.59 ± 0.02	24.64	0.51	4.69	121.0 ± 0.9
1	0.19 ± 0.00	22.10	0.46	1.91	119.8 ± 2.3
2	2.43 ± 0.10	37.58	0.79	8.21	128.6 ± 1.4
2	2.71 ± 0.12	34.17	0.72	11.08	129.2 ± 1.7
2	2.40 ± 0.10	30.33	0.65	12.04	129.9 ± 1.1
2	1.54 ± 0.02	27.24	0.59	9.38	124.6 ± 0.4
2	0.77 ± 0.01	24.51	0.53	5.67	126.1 ± 0.9
2	0.18 ± 0.00	21.94	0.48	1.68	123.5 ± 0.5
3	3.24 ± 0.11	41.17	0.79	9.89	127.5 ± 2.1
3	2.24 ± 0.03	36.98	0.71	8.50	117.0 ± 0.9
3	2.27 ± 0.06	32.93	0.64	10.86	121.3 ± 0.8
3	1.70 ± 0.03	29.60	0.57	10.04	122.3 ± 0.6
3	0.94 ± 0.04	26.62	0.51	6.89	123.0 ± 2.5
3	0.24 ± 0.00	23.92	0.46	2.14	127.8 ± 1.5
4	1.44 ± 0.03	39.70	0.79	4.57	112.7 ± 2.1
4	1.95 ± 0.05	35.84	0.71	7.60	118.1 ± 1.9

4	1.08 ± 0.03	31.72	0.63	5.40	112.3 ± 1.4
4	0.81 ± 0.02	28.46	0.57	5.01	113.5 ± 1.6
4	0.57 ± 0.01	25.61	0.51	4.34	115.4 ± 1.1
5	3.40 ± 0.11	36.30	0.79	11.80	136.3 ± 2.8
5	3.38 ± 0.15	32.36	0.71	14.75	136.0 ± 1.8
5	3.05 ± 0.09	29.12	0.64	16.44	138.3 ± 2.0
5	1.68 ± 0.04	26.18	0.57	11.21	135.7 ± 1.1
5	0.53 ± 0.01	23.47	0.51	4.42	133.5 ± 0.6
6	3.15 ± 0.12	38.90	0.78	10.33	134.0 ± 2.9
6	3.62 ± 0.17	35.12	0.71	14.54	141.0 ± 2.2
6	3.70 ± 0.28	31.62	0.64	18.34	146.1 ± 2.3
6	2.89 ± 0.14	28.42	0.57	17.72	148.1 ± 1.8
6	0.32 ± 0.00	25.52	0.51	2.47	143.9 ± 0.1
7	3.84 ± 0.10	32.80	0.72	16.27	146.1 ± 3.2

Table S3 Parameters	and determined	d reaction rates	s of all feeding-step	experiments with DMC C.
			s of all rooding otop	

Experiment	k _{obs} I	[DMC] /	[ROH]	<i>k_s</i> ⋅K / 10 ⁻⁴ ·	T / °C
	10 [₋] 3 · [1/s]	mg/L	/ mol/L	L²/(s·mg _{DMC} ·mol)	
1	14.61	22.39	0.79	8.25	125.6 ± 7.0
1	9.98 ± 1.48	20.26	0.72	6.88	128.5 ± 5.1
1	6.84 ± 0.59	18.19	0.64	5.85	128.4 ± 2.5
1	6.34 ± 0.63	16.31	0.58	6.75	126.0 ± 3.0
1	4.59 ± 0.23	14.62	0.52	6.08	123.1 ± 2.3
1	3.51 ± 0.09	13.13	0.46	5.77	124.9 ± 2.8
1	2.72 ± 0.06	11.81	0.42	5.52	125.9 ± 2.0
2	6.03 ± 0.49	23.19	0.79	3.31	110.4 ± 1.3
2	5.08 ± 0.16	20.72	0.70	3.49	105.3 ± 1.2
2	5.98 ± 0.65	18.78	0.64	5.01	113.9 ± 1.5
2	4.62 ± 0.23	16.86	0.57	4.80	113.7 ± 1.7
2	4.40 ± 0.11	15.18	0.51	5.64	117.0 ± 1.5
2	2.86 ± 0.07	13.65	0.46	4.53	117.1 ± 1.4
2	3.14 ± 0.07	12.30	0.42	6.13	124.1 ± 1.7
3	13.39 ± 0.54	23.37	0.79	7.23	124.3 ± 4.8
3	17.00 ± 0.86	21.08	0.71	11.30	128.6 ± 5.8
3	19.89	19.06	0.65	16.20	132.8 ± 6.5
3	19.77	17.35	0.59	19.40	139.1 ± 7.0
3	13.70 ± 0.19	15.36	0.52	17.10	147.5 ± 6.9
3	8.14 ± 0.01	13.78	0.47	12.70	139.2 ± 6.7
3	6.73 ± 0.15	12.37	0.42	13.00	135.8 ± 4.0



Figure S5 Arrhenius plots of reaction system with from left to right DMC A, DMC B and DMC C showing 95 % prediction band (light grey) and 95 % confidence band (grey).



Figure S6 Eyring plots of reaction system with from left to right DMC A, DMC B and DMC C showing 95 % prediction band (light grey) and 95 % confidence band (grey).

DMC/Data	displayed	used in the regression
A	All data	Data T < 130°C
В	Data [ROH] > 0.55 mol/L	Data [ROH] > 0.55 mol/L
С	All data	All data

On the Thiele modulus

The chemical rate of propoxylation would be modified by an effectiveness factor η in case of a porous catalyst. The factor η is defined in terms of the generalized Thiele modulus $\phi = \frac{V_p}{k} \frac{k}{k}$.

 $\phi(=\frac{V_p}{S}\sqrt{\frac{k}{D_e}};V_p;$ pore volume *S*: surface area in the pores, D_e : effective diffusion constant near the catalyst; *k*: rate constant, for a first order reaction) for porous heterogeneous catalysts as $\eta = tanh \mathbb{E}(\phi)/\phi$. The η would smaller than one for DMC C and B at high [OH] (low mass of PPG at initial pulses). The Thiele modulus would lie inside the range of about 0.2 (no diffusion resistance) and 5 (diffusion limitation). The activation parameter and the observed rate obtained for DMC C and DMC B at high [OH] would thus need to be interpreted as resulting from the dependence of the square root of $k(T) = \sqrt{A} \cdot exp \mathbb{E}(-E_a/2RT)$ and of (inverse) $D_e(T,\eta)$ [7], [8], [9]. The temperature dependence of the effective diffusion D_e is mainly determined by the temperature dependency of the PO diffusion, *i.e.* in the small temperature range between 370 and 400 K little change in segmental friction factors of the PPG is expected, and thus with activation energy in the range of 20 kJ/mol for the molecular weight range of this study [10]. This leaves the chemical reaction constant with an activation energy for DMC B and C in the range of 120-145 kJ/mol (~ 2 · (49-59) + 20 kJ/mol). These numbers are then very similar to the obtained activation energies of the propoxylation with DMC A.

Diffusion and M_w dependent Viscosity of the reaction mixture at 120 °C

The self-diffusion of PPGs is quite well-documented, in particular at lower temperatures and smaller molecular masses. [10–15] The diffusion constant *D* may be expected to scale exponentially with molecular mass with a mass dependent exponent between -0.6 (M_w (bulk) of ± 2000 Da) to -0.75 (M_w (bulk) of 4200 Da). Diffusion constants extrapolated to higher temperatures give molecular weight dependent values of about 10⁻¹¹ m²/s. Beyond the critical molecular mass M_c of about 7000 Da, *D* will progressively decrease stronger (exponent reaching down to -2) as entanglements become an issue and mass diffusion becomes more and more determined by reptation [16], [17]. The importance of transient networks between PPGs with molecular weights of this study and at the temperature above 100 °C will be negligible [18], [19].

The diffusion of small molecules in PPGs on the other hand is hardly reported upon, a study with camphor quinone (CQ) showed that the Stokes-Einstein dependence reduces to $D_{SE}(CQ) = a(T/\eta_{visc})^{0.75}$, i.e. the diffusion constant decreases more slowly with viscosity than theoretically. This observation was related to rotation-translational coupling to movements of polymer segments. The viscosity of PPG products at *e.g.* 120 °C scales with an exponent of 1.07 (± 0.03) with the molecular weight (s. suppl between $M_w = 2250-16,000$ Da). Assuming that similar holds true for PO, leading to $D_{SE}(PO) \sim M_w^{-0.8}$, polymer and monomer will deviate increasingly in diffusivity with increasing molecular mass. This is also the result from calculations on data acquired at 7 °C: correcting for the different radii of gyration of CQ (0.35 nm) and PO (~ 0.1 nm), PO would have about 1.5 times the diffusion constant of PPG with M_w of 2000 Da and 3 times for a PPG of 4000 Da [10], [18], [20]. The viscosity of PPG increases with the weight average mass with exponent of about 1 at the relevant range of temperature and molecular mass (Figure S7; measurements by Dr. Szopinski at our institute).



Figure S7 Dynamic viscosity on theoretical weight average molecular weight of PPGs.

On the linearity of $\ln k_s K$ (and $\ln k_s K/T$) and 1/T under diffusion influenced rates

Calculations were carried out on the linearity of ${}^{k}{}^{k}{}^{s}{}^{k}$ in the context of derivation that the one can carried out on the linearity of ${}^{k}{}^{k}{}^{s}{}^{k}{}^{n}$ in the context of derivation that the one can carried out on the linearity of ${}^{k}{}^{k}{}^{s}{}^{k}{}^{n}$ in the context of derivation that the one can carried out on the linearity of ${}^{k}{}^{k}{}^{s}{}^{k}{}^{n}$ in the context of derivation that the output of ${}^{k}{}^{k}{}^{s}{}^{k}{}^{n}{}^{n}{}^{n}{}^{n}{}^{k}{}^{k}{}^{s}{}^{k}{}^{n}{}^{n}{}^{n}{}^{n}{}^{k}{}^{k}{}^{k}{}^{n}{}^{n}{}^{n}{}^{n}{}^{k}{}^{k}{}^{k}{}^{n}{}^{n}{}^{n}{}^{n}{}^{k}{}^{k}{}^{k}{}^{n}{}^{n}{}^{n}{}^{n}{}^{k}{}^{k}{}^{k}{}^{n}{}^{n}{}^{n}{}^{k}{}^{k}{}^{k}{}^{n}{}^{n}{}^{n}{}^{k}{}^{k}{}^{k}{}^{n}{}^{n}{}^{n}{}^{k}{}^{k}{}^{k}{}^{n}{}^{n}{}^{n}{}^{k}{}^{k}{}^{k}{}^{n}{}^{n}{}^{n}{}^{k}{}^{k}{}^{k}{}^{n}{}^{n}{}^{n}{}^{k}{}^{k}{}^{k}{}^{n}{}^{n}{}^{n}{}^{k}{}^{k}{}^{k}{}^{n}{}^{n}{}^{n}{}^{k}{}^{k}{}^{k}{}^{n}{}^{n}{}^{k}{}^{k}{}^{k}{}^{k}{}^{n}{}^{n}{}^{n}{}^{k}{}^{k}{}^{k}{}^{n}{}^{n}{}^{k}{}^{k}{}^{k}{}^{n}{}^{n}{}^{k}{}^{k}{}^{k}{}^{n}{}^{n}{}^{n}{}^{k}{}^{k}{}^{k}{}^{k}{}^{n}{}^{n}{}^{n}{}^{k}{}^{k}{}^{k}{}^{n}{}^{n}{}^{k}{}^{k}{}^{n}{}^{n}{}^{n}{}^{k}{}^{k}{}^{k}{}^{n}{}^{n}{}^{n}{}^{n}{}^{k}{}^{k}{}^{k}{}^{n}{}^{n}{}^{n}{}^{k}{}^{n}{}^{k}{}^{n}{}^{k}{}^{n}{}^{k}{}^{n}{}^{k}{}^{n}{}^{n}{}^{k}{}^{k}{}^{n}{}^{k}{}^{n}{}^{k}{}^{n}{}^{k}{}^{n}{}^{k}{}^{n}{}^{k}{}^{n}{}^{k}{}^{n}{}^{k}{}^{n}{}^{k}{}^{n}{}^{k}{}^{k}{}^{k}{}^{n}{}^{k}{}^{n}{}^{k}{}^{$

Table S4 Model calculations on a k_{obs} from a chosen mass transfer constant with an activation energy of 20 kJ/mol and a surface reaction constant $k_s(T)$.

	20 kJ/mol	120	kJ/mol	127 kJ/mol		135 kJ/mol	
T / °C	[OH]/ <i>k</i> _{mPO}	$k_s(T)$	k₅·K	$k_s(T)$	<i>k₅</i> ∙K	$k_{\rm s}(T)$	<i>k</i> ₅·K
110	18.7	43.1	13.1	4.78	3.81	0.38	0.38
120	22.0	112	18.4	13.2	8.24	1.14	1.08
130	25.6	280	23.4	34.6	14.7	3.18	2.83
140	29.5	665	28.3	86.6	22.0	8.43	6.56





Figure S8 Plot of $\ln k_s$ and $\ln k_{obs}$ vs 1/T for activation energies of 120, 127 and 135 kJ/mol.

Calculations on the action of single DMC crystals

Table S5 Action of single DMC crystals at the first pulse (PPG 2250 mol/L).

	DMC A	DMC B	DMC C
DMC in mg/L	23.8	38.14	23.19
averaged crystal weight 10 ⁻¹² g	0.05 ± 0.02	4 ± 1	0.4 ± 0.1
# crystals/L	4.8 · 10 ¹¹	1.0 · 10 ¹⁰	6.1 · 10 ¹⁰
10 ³ crystals in 10 cm line up	7.8	2.2	3.9
d(cryst-cryst) μm	12.8	45.5	25.6
micro reactor volume in µL	2.1 · 10 ⁻⁶	9.4 · 10 ⁻⁵	1.7 · 10 ⁻⁵
Exponential PO consumption / %	93	58	76
T/°C	124	121	126
<i>k</i> / s ⁻¹	4.33 · 10 ⁻³	1.74 · 10 ⁻³	6.03 · 10 ⁻³
TOF pro xtal 1 · 10 ⁻¹⁴	1.6	28.6	17.0
Surface 10 ⁻⁹ cm ² per crystal	8.8 ± 3	102 ± 20	32 ± 7
TOF per area of 1 m ² from crystals	8.5	0.3	3.2
Surface BET /g	107	140	22
Surface of DMC per liter (BET)	2.55	5.34	0.51
total surface of the crystals per L in m^2	0.42	0.11	0.20
ratio surface by BET/crystal calc.	6	50	3
TOF per area of 1 m ² from BET	29.3	5.6	203.4

Attainable PDIs in the set-up

A broadening of a molecular weight distribution can also originate from the reactor set-up. The viscosity of the PPG is increasing with its molecular weight (thus increasing the Kolmogorov smallest domain). making it also more and more challenging to distribute the PO uniformly into the reaction mixture [21]. This effect could be traced using a propeller stirrer in the reactor while propoxylating with DMC A (Figure S9(I)). Latter stirrer is less effective at higher viscosities than an anchor stirrer. Now a tail of high molecular weight products is readily formed. broadening the PDI (Figure S9(m)). The effects are even more pronounced when the dosing of PO is faster with possible higher local gradients of PO concentration. These results are in accordance with the usual observations [21], [22], [23]. An anchor stirrer is more effective and a narrow distribution is maintained (Figure S9(r)).



Figure S9 Broadening of the distribution as function of the stirrer geometry or enhanced PO addition rate using DMC A (50 ppm initially) and PPG 2000 as starter at 120 °C.

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Supplementary Material belonging to:

DMC-mediated Propoxylation in Semi-Batch with external Loop: Insights into the Catalytic Action

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	(Pre)Catalyst	DMC A	DMC B
Surface Atoms in wt.%	С	28.2	30.4
	Ν	8.3	27.4
	0	1.5	8.7
	Cl	5.3	0.0
	Na	0.0	0.0
	Со	17.6	9.8
	Zn	39.1	23.4
	Co/Zn	0.44	0.41
Pore Volume	$V_{\rm p}$ / cm ³ /g	0.20	0.13
Pore size	D/nm	75	230
Volume mono layer	$V_{\rm mono}$ / cm ³ /g	25	32
Surface area from BET	$S_{\rm BET}/m^2/g$	107	140

Table S1. Data on DMC A and B from EDX and BET measurements

Determination of the surface area was carried out by adsorption measurements using dinitrogen on a Surfer gas adsorption porosimeter (Thermo Fisher Scientific, Software Surfer Acquisition Ver.1.7.10). The pore size was calculated along the B.J.H method. The powdery samples were prepared for measurement by degassing at 70 °C for 2 h. The surface area was calculated with the software Surfer Ver. 1.7.10 and is based on the B.E.T. method in the range of $p/p^0 = 0.05 -$ 0.3. The pore size distribution was calculated using the B.J.H. method in the range of $p/p^0 =$ 0.3054 – 1.003.

Table S2. Formal conversion X of PO from volume V of PO that was added to 250 mL of Voranol.

X(PO) [%]	V(PO)total [mL]	V(PO)added [mL]
100	0	0.0
98	6.2	6.2
96	12.6	6.4

94	19.2	6.7
92	26.2	7.0
90	33.5	7.3
85	53.2	19.7
80	75.3	22.2
75	100.5	25.1
70	129.2	28.7
65	162.3	33.1
60	200.9	38.6

Table S3. Calculated operational parameter and flow values in the static mixer at various PPG

flow rates with a viscosity of 2.96 Pas and with a PO feeding rate of 1.62 mL/min ($t_{add} = 10$ h).

PPG volume flow rate	10 mL/min	25 mL/min	40 mL/min
Total volumetric flow rate	11.6 mL/min	26.6 mL/min	41.6 mL/min
Residence time	9.2 s	4.6 s	3.1 s
Mixing homogeneity	90.3%	92.8%	93.9%
Pressure drop	0.7 bar	1.8 bar	2.9 bar



Figure S1. Calibration of the gear wheel flow meter obtained from measurement of flow rate

output signal and actual mass flow rate.



Figure S2. Dynamic viscosity at 120 °C of PPG samples with narrow molecular weight

distributions in dependence of weight average molecular weight.



Figure S3. FTIR spectra of PPG / PO mixtures.



Figure S4. Predicted conversion of PO versus experimental data ($R^2 > 0.9999$) from the PLS

regression model.



Figure S5. Interface of LabView VI module.

It allows to switch the experimental modus before and during the process and gives control

parameter for process monitoring



Figure S6. Calibration of the gear pump obtained by correlation of measured actual mass flow

rate and pump rotational speed at PPG of Voranol 2000L at 25 °C (η = 0.32 Pas).

9 Statutory Declaration

I hereby declare upon oath that I have written the present dissertation independently and have not used further resources and aids than those stated in the dissertation.

Geesthacht, 15.11.2023