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DMC-Mediated Copolymerization of CO$_2$ 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/CO$_2$ 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 CO$_2$ 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 (CO$_2$) 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 CO$_2$ 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 ($\Delta H^\circ = -393.51$ kJ/mol at 298.15 K) [8], economically processing CO$_2$ 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 CO$_2$ 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 CO$_2$ 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
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 CO$_2$ 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, CO$_2$ pressure, and reaction time [30–34]. The products are ranging from poly(ether carbonates) to polyarbonates (Scheme 1). Ever since Inoue firstly reported on the copolymerization of CO$_2$ 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].

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/CO$_2$ 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 CO$_2$. The effective insertion of PO into a metal alkoxide bond (multiple steps) must then be an additional part of the mechanism. Solid zinc dicarboxylates,
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 \( \text{CO}_2 \) is admitted, usually giving products with large contents of ether blocks \( (f_{\text{carb}} << 75 \text{ mol\%}) \) [63–65] and with a lower activity [66]. The immortal copolymerization of \( \text{CO}_2 \) 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/\( \text{CO}_2 \) 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](image-url)

**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 \( \text{CO}_2 \) and using polypropylene glycols of various molecular weights as CTAs. The immortal copolymerization of \( \text{CO}_2 \) 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 \( \text{CO}_2 \) will be presented comprising the importance of basic anions at the DMC surface. The elementary reaction steps of the copolymerization of PO and \( \text{CO}_2 \) 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; \( \text{CO}_2 \) 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 \( \text{CO}_2 \) 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)₆³⁻ 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 CO₂), (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 CO₂ uptake is measured by a mass-flow controller and can be taken as an indicator for the reaction rate.

![Figure 1](image-url)

Figure 1. Reactor logs of batch experiments with 30 g of Caradol and 5 mg of catalyst (a) homopolymerization of PO, set T = 60 °C (PPG_1) (b) homopolymerization of PO, T = 55 °C (PPG_2) (c) copolymerization of PO with CO₂, T = 60 °C, p = 10 bar (PPEC), and (d) polymerization during which CO₂ was added at the onset of the exotherm (PPG/PPEC).
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 $\sim 60 ^\circ C$. The active cooling of the reactor with a cooling bath of $-28 ^\circ C$ 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 $55 ^\circ C$ 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 CO$_2$—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 CO$_2$ pressure. The analysis of the products indicate that only small amounts of CO$_2$ 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 $F(= f_{\text{carb}}/f_{\text{ether}})$ adds up to 0.14, both at 10 bar and at 36 bar of CO$_2$ 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
the polymer backbone is only at a low level. It is generally experienced that the presence of CO₂ 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 CO₂ was added just after the exotherm started to arise shows that even then CO₂ 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. CO₂ 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 CO₂ 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 CO₂/mol PO) on the insertion of CO₂ 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 a 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 CO₂ proceeds only slowly (vide supra).

| Entry | N     | T [°C] | p (bar) | Yield [g] | M_n [g/mol] | PDI | f_PC | 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     | 0.115 | 60     | 13.6   | 5.8       | 630         | 1.1 | 0.00 | 0.12|
| 10    |       | 80     | 18.2   | 6.9       | 660         | 1.1 | 0.02 | 0.15|
| 11    |       | 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|

(C TA: 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 CO₂ (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.

The resulting polymers were subsequently analyzed by $^1$H-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 $f_{\text{carb}}$ and $f_{\text{ether}}$ 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 CO$_2$ 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 CO$_2$ 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 CO$_2$ 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.
2.3. Formation of Cyclic Propylene Carbonate

DMCs as catalyst for copolymerization of PO and CO₂ 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 CO₂ 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.

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 | \( f_{\text{carb}} \) | \( f_{\text{ether}} \) | \( f_{\text{cPC}} \) | \( F \) |
|-------|------------------|-----------|-------------------|-----|----------------|----------------|----------------|-----|
| 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 CO$_2$

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 CO$_2$.

| Entry | Polymer | CTA        | $T$ [°C] | $p$ [bar] | $M_n$ [kg/mol] | PDI  | $f_{sc}$ | 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    | 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. Long 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](image-url)

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).
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 °C (a) and T = 120 °C (b) at 10 bar CO₂ pressure, including the activation procedure and cooling.](image-url)

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 remains at an almost constant level and then seemingly decreases again. The higher viscosity of the reaction 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).
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 CO\(_2\) 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, CO\(_2\) cannot be fixed in the chain and effectively no polymerization can take place (vide infra). After the initial larger CO\(_2\) 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 (\(v = 1100\) 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 CO\(_2\) is incorporated with (consecutive) stronger cPC formation indicative of backbiting in free PO-carbonate chain ends, and a second phase with less CO\(_2\) 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.
Figure 6. SEC analysis of PPECs synthesized at $T = 90 \, ^\circ C$, $p = 10 \, \text{bar}$ (a, Entry 21) and $T = 120 \, ^\circ C$, $p = 10 \, \text{bar}$ (b, Entry 22) and PPG at $T = 120 \, ^\circ C$ (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).
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 propoxylation 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\textsubscript{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.

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

|        | 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 |
|--------|--------------|------------|------------|--------------|--------------|------------|
| Peak 1 | $M_n$ [kg/mol] | 3.4 | 3.6 | 3.6 | 3.7 | 3.7 | 3.9 |
|        | $M_w$ [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 |
| Peak 2 | $M_n$ [kg/mol] | 8.1 | 8.4 | 9.0 | 9.3 | 9.4 |
|        | $M_w$ [kg/mol] | 13.8 | 13.4 | 12.5 | 12.3 | 12.4 |
|        | 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 |
| Peak 3 | $M_n$ [kg/mol] | 6.7 | 15.4 | 16.9 | 19.2 | 21.9 | 23.8 |
|        | $M_w$ [kg/mol] | 16.4 | 69.5 | 80.2 | 97.2 | 105.7 | 106.2 |
|        | 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 6. Calculated $F$ and cPC content in PPEC_2 synthesized at 120 °C and 10 bar CO$_2$ pressure.

| Sample       | $f_{\text{carb}}$ | $f_{\text{ether}}$ | $f_{\text{cPC}}$ | $F$  |
|--------------|-------------------|--------------------|-----------------|------|
| 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 |

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, alkoxyalted 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 µL 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 CO$_2$ 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].
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 | $n_{\text{amine}}$ [10$^{-2}$ mol%] | $V_{\text{TEA}}$ [µL] | $t_{\text{ind}}$ [min] | $t_{\text{end}}$ [min] | $\Delta T$ [°C] | Entry | $m_{\text{DDA}}$ [mg] | $t_{\text{ind}}$ [min] | $t_{\text{end}}$ [min] | $\Delta T$ [°C] |
|-------|-----------------|----------------|----------------|----------------|----------------|-------|----------------|----------------|----------------|----------------|
| 24    | 0               | -              | 5              | 45             | 14             | 25    | 0.66           | 0.5            | 13             | 6              | 30              | 0.6              | 8                  | 57             | 6               |
| 26    | 1.31            | 1              | 11             | 65             | 6              | 31              | 1.3  | 6              | 5              | 75             | 6              | 32              | 2.6              | 6                  | >51 #           |
| 27    | 2.62            | 2              | 5              | 75             | 6              | 32              | 2.6  | 6              | 5              | 190            | 2              | 33              | 6.6              | 8                  | 63             | 4               |
| 28    | 6.58            | 5              | 5              | 190            | 2              | 33              | 6.6  | 8              | 5              | 5              | >23 h *         | n.d.            | 34              | n.d.            | n.d.            |
| 29    | 13.1            | 10             | 5              | >23 h *        | n.d.           | 34              | n.d. | n.d.           | n.d.           | n.d.           | 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. $\Delta T$: 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 CO$_2$ was observed with amines at lower CO$_2$ 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 CO$_2$. The fact that a dependency on the CO$_2$ 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 performed in 300 mL autoclaves.

| N     | Entry | $V_{\text{TEA}}$ [µL] | $M_n$ [g/mol] | PDI | $f_{\text{PC}}$ | $F$ | Entry | $m_{\text{DDA}}$ [mg] | $M_n$ [g/mol] | PDI | $f_{\text{PC}}$ | $F$ |
|-------|-------|----------------------|---------------|-----|----------------|-----|-------|----------------------|---------------|-----|----------------|-----|
| 0.115 | 35    | 0                    | 1000          | 1.5 | 0.07           | 0.14| 45    | 0.6               | 1160          | 1.4 | 0.06           | 0.12|
|       | 36    | 0.5                  | 960           | 1.8 | 0.06           | 0.16| 46    | 1.3               | 1210          | 1.2 | 0.06           | 0.09|
|       | 37    | 1                    | n.d.          | n.d.| n.d.           | n.d.| 47    | 2.6               | 1090          | 1.7 | 0.05           | 0.16|
|       | 38    | 2                    | 1020          | 1.6 | 0.06           | 0.15| 48    | 6.6               | 1190          | 1.5 | 0.06           | 0.15|
|       | 39    | 5                    | 1070          | 1.6 | 0.06           | 0.14| 49    | 0.6               | 1220          | 1.4 | 0.03           | 0.08|
| 0.058 | 40    | 0                    | 1100          | 1.3 | 0.03           | 0.16| 41    | 0.5               | 940           | 1.8 | 0.05           | 0.08|
|       | 41    | 0.5                  | 940           | 1.8 | 0.05           | 0.08| 49    | 0.6               | 1220          | 1.4 | 0.03           | 0.08|
|       | 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).
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; \( V_{\text{TEA}} = 2 \mu\text{L}; m_{\text{DDA}} = 2.6 \text{ mg}; 30 \text{ g Lupranol1200, Figure S6} \). 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.](image)

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

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

| Element | DMC-Cl a | DMC-NO₃ a | DMC-Cl b | DMC-NO₃ 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 | 2.1 ± 0.1 | 1.7 ± 0.2 | 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 ± 1.1 | 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 | 0.3 ± 0.1 |
| Cl [wt.%] | 5.3 ± 1.3 | 0 ± 0.0 | 7.4 ± 0.1 | 0.1 ± 0.0 |

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 | Experiment | $T$ [°C] | $p$ [bar] | $N$ | Yield [g] | $M_n$ [g/mol] | PDI | $f_{cPC}$ | $F$ |
|-------|------------|----------|----------|-----|-----------|---------------|-----|-----------|-----|
| 53    | DMC-NO₃₁   | 100      | 14.2     | 0.058 | 28.2      | 1000          | 2.5 | 0.01      | 0.25|
| 54    | DMC-NO₃₂   | 100      | 23.6     | 0.115 | 26.6      | 960           | 2.2 | 0.02      | 0.29|
| 55    | DMC-NO₃₃   | 100      | 32.6     | 0.173 | 22.0      | 880           | 2.3 | 0.02      | 0.45|
| 56    | DMC-NO₃₄   | 120      | 40       | 0.173 | 36.1      | 1170          | 2.0 | 0.03      | 0.43|
| 57    | DMC-NO₃₅   | 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).
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 °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. Proxoylation in combination with carboxylation mediated by “none basic” DMCs, i.e., those with few basic entities.
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 CO₂ 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 CO₂ 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 particularly stable and is bound to decarboxylate to give back ROH and CO\(_2\). 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 CO\(_2\) and PO additions end after a further (internal, directly in N9) protonation of the intermediate metal alkoxide. The resulting OC(O)-C\(_3\)H\(_6\)OH 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 CO\(_2\)-PO addition would explain the small dependence on CO\(_2\) 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\(_3\)H\(_6\)OH 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 CO\(_2\) 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-NO$_3$ (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 carboxonic 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 CO$_2$ without the competition for protonation from the surface, i.e., protonation by ROH will only be a degenerate reaction (B4→B1; B7→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→B1; B1→B5→B6) or CO$_2$ insertion (B1→B2), both followed by a consecutive PO insertion. This explains the impact of N on polymer composition in experiments with DMC-NO$_3$.

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/af few basic sites) as catalyst (Entry 21), and at the DMC-NO$_3$-mediated PO/CO$_2$ 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 CO$_2$ 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 (CO$_2$) (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 ($5 \times 10^{-2}$ 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 CO$_2$ 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 CO$_2$. 
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 CO\textsubscript{2}. 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 CO\textsubscript{2} gas. The reaction progress was monitored using a ReactIR™ 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 CO\textsubscript{2} 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 combustion 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 SDbasis linear column (5 µm, 300 × 8 mm), Schambeck RI2012 detector, and a Flom Intelligent pump Al-12) in tetrahydrofuran as eluent at 22 °C with a flow rate of 1 mL/min and an injection volume of 20 µL. 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 \(^1\)H-NMR spectra were recorded for each polymer sample on a Bruker Avance Ultrashield-400 spectrometer in CDCl\textsubscript{3} at room temperature using tetramethylsilane as a reference. The integrals of methyl protons were used for determination of mol fractions \(f_{\text{CO}_2}\) and \(f_{\text{PO}}\), respectively, \(f_{\text{carb}}\) and \(f_{\text{ether}}\) 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 \(F = f_{\text{carb}}/f_{\text{ether}}\) 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/CO\textsubscript{2} 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
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 CO₂ 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 other 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, 885–896, Figure S3: IR spectra of reaction mixture during semi-batch experiment at $T = 90$ °C (a; PPEC_1) and $T = 120$ °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 $\eta$ 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).

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