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Unexpected Side Reactions and Chain Transfer for Zinc-Catalyzed Copolymerization of Cyclohexene Oxide and Carbon Dioxide

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ABSTRACT: A detailed investigation was conducted into the chain microstructure and reaction mechanisms of polycyclohexene carbonate (PCHC) synthesized with β-diketiminato zinc catalysts (EtBDI)ZnOEt, (EtBDI)ZnOMe (EtBDI = 2-(2,6-diethylphenyl)amido-4-(2,6-diethylphenyl)imino-2-pentene), and a bis(phenoxy)zinc catalyst $[(2,6\text{-}F_2C_6H_3O)_2Zn\cdot THF]_2$. For these complexes several different initiation, propagation, and termination reactions were identified by analyzing the MALDI-TOF-MS spectra of the resulting polymers. The bis(phenoxy)zinc system showed some ether linkages while the β-diketiminato zinc catalyzed system produces perfectly alternating cyclohexene oxide−CO_2 copolymers. The presence of a mixture of cyclopentyl, cyclohexyl, and cyclohexenyl end groups for all three catalyst systems points to an unexpected side reaction that is initiated by traces of water. This study also led to the discovery that, under conditions where traces of water or alcohols are present, the β-diketiminato zinc catalyst is not a truly living system since a very rapid reversible chain transfer mechanism is operating, where alcohols and/or hydroxyl-terminated polymer chains act as the chain transfer agents.

Introduction

The aliphatic polycarbonates synthesized from carbon dioxide and oxiranes (Scheme 1) are receiving an increasing interest from research groups all over the world.[1] The potential of carbon dioxide as a comonomer in aliphatic polycarbonate production was first recognized by Inoue et al., who copolymerized propylene oxide and carbon dioxide with a $ZnEt_2/H_2O$ mixture.[2] About a decade later the same group discovered that active catalytic systems were not limited to zinc-based systems as porphyrinato aluminum compounds in combination with suitable cocatalysts also proved to be effective in the copolymerization of oxiranes and carbon dioxide.[3] After a period of little progress in this field, Darensbourg and co-workers introduced zinc phenoxide catalysts (Figure 1) for the copolymerization of cyclohexene oxide (CHO) and CO_2, in the early 1990s.[4] Molecular weights obtained with these catalysts are generally high, but the polydispersity is not well-controlled (up to 18) while activities are generally low. More recently, Coates et al.[5] developed highly active, single-site β-diketiminato zinc catalysts (Figure 1). This breakthrough has led to a renewed interest in this field which resulted in the development of highly selective and active chromium,[6] cobalt,[7] and manganese[8] porphyrinato and salen systems.[9]

Although various catalysts have been developed for the oxirane−CO_2 copolymerization, the complete mechanism of the polymerization reaction is still not fully understood.[5e,10] For example, there is still some debate about whether β-diketiminato zinc complexes have to be dimeric to be an active catalytic system. Furthermore, termination or chain transfer reactions have never seriously been addressed in the past. In the case of the β-diketiminato zinc catalysts, the absence of any termination or chain transfer mechanism seemed justified as the low polydispersities reported for this system and the linear relationship found between $\bar{M}_n$ vs conversion are indicative for a living nature.[11] The bis(phenoxy)zinc catalysts, on the other hand, do give poly(cyclohexene carbonate) (PCHC) with extremely high polydispersities. The lack of conformity between these seemingly similar polymerizations triggered us to take a closer look at these systems. In our previous research on the catalytic copolymerization of cyclohexene oxide and CO_2 some anomalies were found which could not be explained by the mechanism proposed previously,[5e] and a more detailed investigation of the polymer microstructure was undertaken with triple-SEC and MALDI-TOF-MS. In this contribution we present our results on a mechanistic study of the cyclohexene oxide−CO_2 copolymerization catalyzed by β-diketiminato zinc catalysts and a bis(phenoxy)zinc catalyst (Figure 1) and compared the poly(cyclohexene carbonate) products obtained using the two catalyst systems.

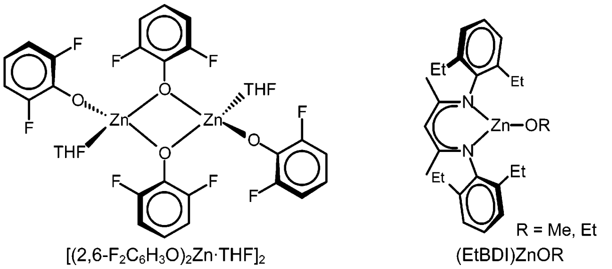
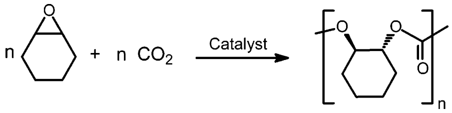


Figure 1. Examples of copolymerization catalysts developed by Darensbourg et al. (left) and Coates and co-workers (right).

Scheme 1. Copolymerization of Carbon Dioxide and Cyclohexene Oxide



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Experimental Section

Materials. Cyclohexene oxide (Aldrich) was dried on CaH_2, distilled, and stored under argon on molsieves (4 Å) prior to use. Carbon dioxide (>99.9993% pure) was purchased from HoekLoos and used without any further purification. Toluene was dried over an alumina column and stored on molsieves (4 Å). The (EtBDI)ZnOR catalysts (R = Me, Et; EtBDI = 2-(2,6-diethylphenyl)amido-4-(2,6-diethylphenyl)imino-2-pentene) and the bis(phenoxy)zinc catalyst $[(2,6\text{-}F_2C_6H_3O)_2Zn\cdot THF]_2$ (Figure 1) were synthesized according to literature procedures.[4e,5b]

Analytical Techniques. ^1H NMR spectra were recorded on a Varian Gemini 2000 (300 MHz) and a Varian Mercury Vx (400 MHz) spectrometer. Size exclusion chromatography (SEC) traces were recorded on a Waters GPC equipped with a Waters model 510 pump and a model 410 differential refractometer (40 °C). THF was used as the eluent at a flow rate of 1.0 mL min^{-1}. A set of two linear columns (Mixed C. Polymer Laboratories, 30 cm, 40 °C) was used. Molecular weights were calculated relative to polystyrene standards. Data acquisition and processing was performed using Waters Millennium32 software. Triple-SEC measurements were performed on a system consisting of a three-column set (two PLgel Mixed-C 5 μ columns and one PLgel Mixed-D 5 μ column from Polymer Laboratories), with a guard column (PLgel 5 μ Polymer Laboratories), a gradient pump (Waters Alliance 2695, flow rate of 1.0 mL min^{-1} isocratic), a photodiode array detector (Waters 2996), and a differential refractive index detector (Waters 2414) as concentration detectors, a light scattering detector (Viscotek), a viscosity detector (Viscotek, dual detector 250), and THF as a solvent. THF was filtered twice (0.2 μm filter) and stabilized with BHT (4-Me-2,6-(t-Bu)$_2C_6H_2OH$). Data acquisition and processing were performed with Viscotek TriSec GPC Software (version 3.0 Rev. B.03.04). MALDI-TOF-MS analysis was carried out on a Voyager DE-STR from Applied Biosystems. The matrix, DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile), was synthesized according to literature procedures.[12] Potassium trifluoroacetate (Aldrich, >99%) was added to the polymer samples as cationization agent. The matrix was dissolved in THF at a concentration of 40 mg mL^{-1}. The potassium trifluoroacetate was added to THF at a typical concentration of 1 mg mL^{-1}. Polymer was dissolved in THF at ~1 mg mL^{-1}. In a typical MALDI-TOF-MS analysis the matrix, potassium trifluoroacetate and the polymer solution were premixed in a ratio of 10:1:5. The premixed solutions were hand-spotted on the target well and left to dry. Spectra were recorded in both the linear and reflector mode.

Example of a Typical Polymerization Using β-Diketiminato Zinc Catalysts. (EtBDI)ZnOEt (194 mg, 295 μmol, 0.06 mol %) was dissolved in a mixture of CHO (50 mL, 495 mmol) and toluene (16.7 mL). After complete dissolution of the catalyst, the mixture was injected into a preheated (50 °C) 200 mL autoclave that was previously dried under vacuum at 100 °C for 12 h. The autoclave was pressurized to 9 bar with carbon dioxide, and the polymerization commenced. After a set polymerization time, a sample was taken for ^1H NMR analyses (300 MHz, $CDCl_3$) to determine the conversion by integration of the methine peaks in the ^1H NMR spectra: ^1H NMR (300 MHz, $CDCl_3$): δ 4.65 (br, CH (PCHC), 2H), 3.11 (s, C*H* (CHO), 2H). The samples for SEC analyses were prepared as follows: About 0.5 mL of each of the reaction mixtures was added dropwise to a 10-fold excess of petroleum ether (40−70), upon which the poly(cyclohexene carbonate) (PCHC) precipitated. After separation, the polymer was redissolved in the SEC eluent THF. Polymers needed for MALDI-TOF-MS analyses were prepared in a similar manner.

Example of a Typical Polymerization Using the Bis(phenoxy)zinc Catalyst. After a mixture of cyclohexene oxide, toluene, and the catalyst was injected into the 200 mL steel autoclave, the reactor was heated to 30 °C and pressurized to 50 bar with carbon dioxide. All valves were closed, and the reactor was further heated to 80 °C, resulting in a pressure of about 80 bar. Analyses and work-up procedures were similar as described above.

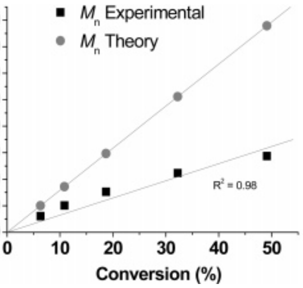


Figure 2. Deviation between $\bar{M}_n$(experimental) and $\bar{M}_n$(theory) for (^{i}PrBDI)ZnN($SiMe_3$)$_2$ catalyst.

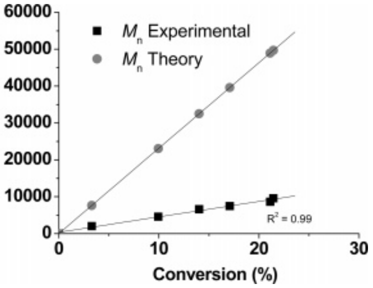


Figure 3. Deviation between $\bar{M}_n$(experimental) and $\bar{M}_n$(theory) for (EtBDI)ZnOMe catalyst.

Results and Discussion

In a recent study on high throughput experimentation, we reported the linear behavior of $\bar{M}_n$ vs time for the (^{i}PrBDI)ZnN($SiMe_3$)$_2$ (^{i}PrBDI = 2-(2,6-diisopropylphenyl)amido-4-(2,6-diisopropylphenyl)imino-2-pentene)) catalyst, pointing to a living character of the system.[11] A closer look, however, showed the $\bar{M}_n$ values obtained by SEC ($\bar{M}_n$(experimental)) to be substantially lower than the values calculated using the ^1H NMR monomer conversion values and the catalyst concentration ($\bar{M}_n$(theory)). The SEC measurements were processed using a polystyrene calibration line, but due to the absence of Mark−Houwink parameters for PCHC, the $\bar{M}_n$ values were validated by means of triple-SEC and MALDI-TOF-MS measurements, which all gave very similar molecular weights. To rule out the occurrence of fortuitous events causing this deviation, similar polymerization experiments with (EtBDI)ZnOR (R = Me, Et) as the catalysts were carried out, which showed a similar (R = Et) or even larger (R = Me) deviation between $\bar{M}_n$(theory) and $\bar{M}_n$(experimental). The behavior of $\bar{M}_n$ vs time for both the (^{i}PrBDI)ZnN($SiMe_3$)$_2$ and the (EtBDI)ZnOMe catalyst is shown in Figures 2 and 3, respectively. The possibility of formation of cyclic carbonate as the origin of the deviation of theoretical from experimental values of the molecular weights could also be excluded. No cyclohexene carbonate was detected by NMR. Furthermore, this would lead to a lower molecular weight but not to an increase in the number of polymer chains. Catalyst deactivation can also be excluded as a possible reason for the deviation between the experimental and theoretical $\bar{M}_n$ values. Fast catalyst deactivation at the beginning of the polymerization would lead to a lower concentration of active catalysts. For a living system, the expected $\bar{M}_n$ would therefore be higher instead of lower than the theoretical $\bar{M}_n$ for the same conversion and yield. Slow deactivation during the polymerization process will not affect the number of chains much but is expected to broaden the molecular weight distribution, which was not observed either.

Table 1. Details of Experimental Conditions and Results for Polymers Analyzed with MALDI-TOF-MS[a]

catalyst	monomer	temp (°C)	P (bar)	time (h)	$\bar{M}_n$ (g/mol^{-1})	$\bar{M}_w/\bar{M}_n$	conv (%)	chains per catalyst[b]	MALDI spectrum
(EtBDI)ZnOMe	CHO	50	9	2	3700	1.11	9	5.6	Figure 5
(EtBDI)ZnOEt	CHO	50	9	2	11600	1.18	40	2.4	
$[(2,6\text{-}F_2C_6H_3O)_2Zn\cdot THF]_2$	CHO	80	80	28	25800	18.4	19	1.7	Figure 6

[a] All polymerizations were performed with 300 μmol of catalyst, 15 mL of CHO, and 35 mL of toluene. [b] Calculation based on both SEC data and conversion data from ^{1}H NMR, assuming that 100% of the catalyst is active.

Table 2. Effect of Catalyst (EtBDI)ZnOEt Concentration and Temperature on Chain Transfer[a]

entry	catalyst (μmol)	CHO (mL)	toluene (mL)	temp (°C)	conversion to PCHC (%)	$\bar{M}_n$ (g mol^{-1})	$\bar{M}_w/\bar{M}_n$	chains per catalyst
1	200	15	35	50	26.4	9729	1.08	2.9
2	300	15	35	50	39.4	11561	1.18	2.4
3	400	15	35	50	45.3	12645	1.09	1.9
4	300	15	35	30	14.4	4058	1.76	2.5
5	300	15	35	80	9.5[b]	2853	1.23	2.3

[a] All polymerizations were performed at 9 bar CO_2 pressure for 2 h. [b] As a result of backbiting around 11% of the CHO was converted to the cyclic carbonate (trans-CHC).

Hence, the found deviation is most probably the result of a nonliving behavior of the catalyst.

The next questions that arise are what kind of chain termination or chain transfer mechanism is playing a role and how for example temperature and catalyst concentration affect these processes. The influence of temperature and catalyst concentration on the number of chains and the $\bar{M}_n$ was investigated, and the results for the β-diketiminato zinc system (EtBDI)ZnOEt are displayed in Table 2.

Changing the temperature does not have a significant effect on the number of chains per active site. However, the temperature does have a considerable effect on the molecular weight and the selectivity of the reaction. Lowering the temperature from 50 to 30 °C resulted in a considerable drop in molecular weight, most probably due to the slow initiation and low activity of the catalyst at that temperature.[5e,10] On the other hand, increasing the temperature affects both the molecular weight and the selectivity of the catalyst toward PCHC formation. At 80 °C, the selectivity drops to around 50%, and a considerable amount of *trans*-cyclohexene carbonate is formed by backbiting of the PCHC chain. This severely reduces the molecular weight, as can be seen from entry 5. A similar change in selectivity was observed by Allen and co-workers during CO_2−propylene oxide copolymerization, which selectively afforded poly(propylene carbonate) at 25 °C, while at 50 °C exclusively propylene carbonate was formed.[5c] Kinetics studies performed by Coates et al revealed a near second-order dependence in zinc for the copolymerization, which indicates the presence of dimeric active species.[5e] At higher temperature, the monomer dimer equilibrium of the catalyst shifts toward the monomer form.[5,10] Regardless of whether the monomeric species is an active catalyst for the copolymerization, the monomeric zinc species can still undergo intramolecular backbiting, yielding cyclohexene carbonate and lower molecular weight polycarbonates. Increasing the catalyst concentration leads to a reduction of the number of chains per catalyst while a small increase in molecular weight is also observed. Although influence of the aforementioned shift in the monomer dimer equilibrium of the catalyst toward the dimeric species at higher concentrations cannot be excluded,[5e,10] the observed effect is most likely caused by the lower effect of poisoning impurities, present in the reactor or in the monomer, at higher catalyst concentrations (vide infra).

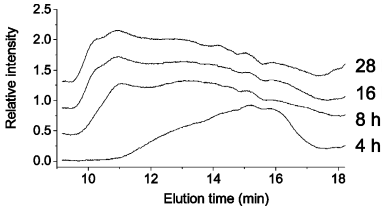


Figure 4. Characteristic SEC plots of polycarbonate samples synthesized with $[(2,6\text{-}F_2C_6H_3O)_2Zn\cdot THF]_2$, taken at set time intervals.

As was reported earlier,[4] the bis(phenoxy)zinc system $[(2,6\text{-}F_2C_6H_3O)_2Zn\cdot THF]_2$ shows very high polydispersities. This broad molecular weight distribution originates from multimodal Schulz−Flory distributions, which are hardly affected by temperature or catalyst concentration. Figure 4 shows characteristic SEC plots of polycarbonate samples taken at set time intervals. Already at the beginning of the polymerization the polydispersity is higher than 6 and increases during the polymerization to a value of 18. Although the polydispersity drops somewhat toward the end of the polymerization, it is clear that the shape of the SEC plots do not change significantly. Similar distributions were also found with the bis(salicylaldiminato)zinc complexes made by Darensbourg and co-workers.[13] Such a distribution pattern is characteristic for multiple nonliving active sites present in the system. Koning et al. already commented upon these broad polydispersities and postulated an influence of different phases during the polymerization.[4b] Slow or incomplete initiation in combination with the formation of aggregates is another probable cause of the high polydispersities for this catalyst system.

To investigate the possible occurrence of transesterification reactions, both catalytic systems were tested in a prolonged polymerization, for which the reaction mixture was kept at polymerization conditions for a long time (10 days) after full conversion had already been reached. Although intermolecular transesterification does not affect the number of polymer chains but randomization should lead to a molecular weight distribution of 2. However, for the bis(phenoxy)zinc system the PDI remained very high (∼9), while for the β-diketiminato zinc catalysts, even after the prolonged polymerization, the polydispersities were as low as 1.12. Intramolecular transesterification, on the other hand, would lead to cyclohexene carbonate or ring structures

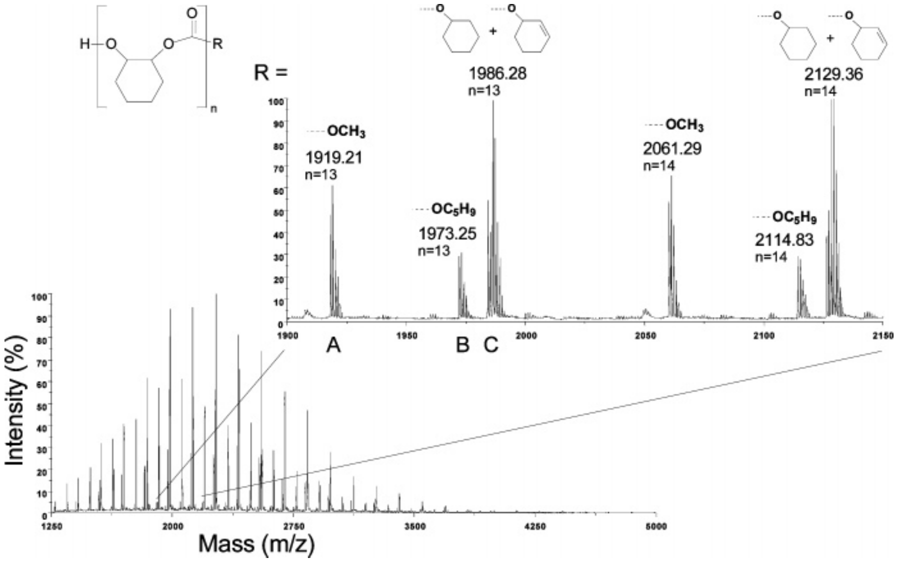


Figure 5. MALDI-TOF-MS spectrum of the K^+ adduct of PCHC obtained with (EtBDI)ZnOMe and an enlargement of part of the spectrum.

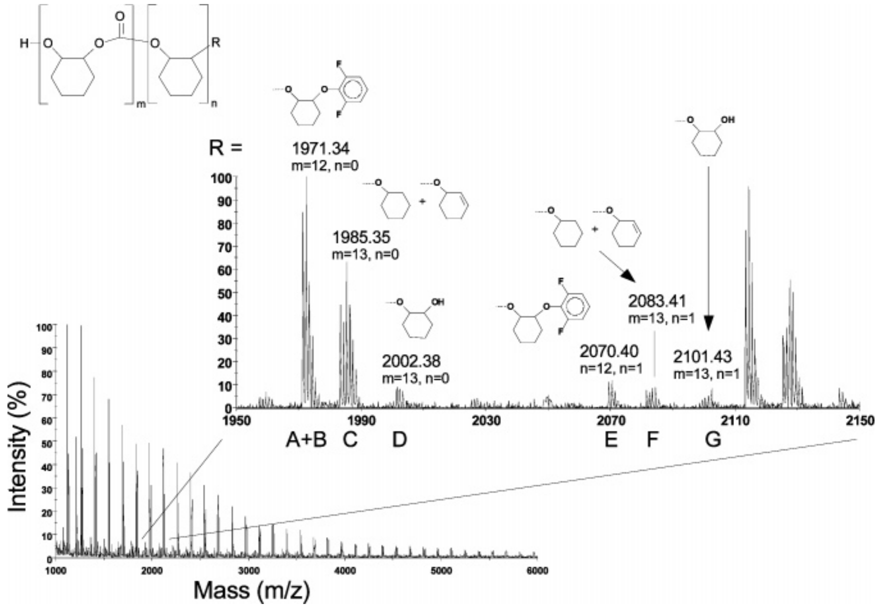


Figure 6. MALDI-TOF-MS spectrum of the K^+ adduct of PCHC obtained with $[(2,6\text{-}F_2C_6H_3O)_2Zn\cdot THF]_2$ and an enlargement of part of the spectrum.

in combination with a smaller chain fragment and thus indeed to an increase of the number of polymer chains per active site. However, the molecular weight of the polymers did not decline, and MALDI-TOF-MS analysis of polymer samples did not show any sign of ring structures or randomization (head-to-head, tail-to-tail structures) of the polymer chains, ruling out any random chain scission/recombination reactions. However, MALDI-TOF-MS did show some unexpected results.

MALDI-TOF-MS Analysis. MALDI-TOF-MS analyses of the polymers produced by the bis(phenoxy)zinc and β-diketiminato zinc systems revealed some interesting features. In Figure 5 a Poisson type molecular weight distribution is found for the PCHC produced with the (EtBDI)ZnOMe zinc catalyst in the experiment described in Table 1. On the other hand, the PCHC formed with the $[(2,6\text{-}F_2C_6H_3O)_2Zn\cdot THF]_2$ catalyst also described in Table 1 shows a Schulz–Flory type molecular weight distribution (Figure 6).

The repeating unit is 142 Da, which is the mass of a cyclohexene carbonate unit. The various peaks (each peak, in turn, is split in its isotope pattern) within a repeating unit are the result of different end groups that are present in the polymer. Since the formation of different end groups *after* polymerization could not be ruled out completely a priori, various work-up procedures were used.[14] However, no changes were observed in either SEC or MALDI-TOF-MS spectra, indicating that the various end groups were formed during the polymerization. In all polymers prepared with a β-diketiminato zinc catalyst CO_2 is the first monomer to insert in the zinc–initiator bond. This is not surprising since homopolymerization of CHO is not possible with this catalyst under typical polymerization conditions.[5] Correspondingly, perfectly alternating cyclohexene oxide–CO_2 copolymers are formed. On the other hand, the MALDI-TOF-MS spectrum of the PCHC made with the Darensbourg catalyst $[(2,6\text{-}F_2C_6H_3O)_2Zn\cdot THF]_2$ (Figure 6) also showed the presence of polymeric chains where

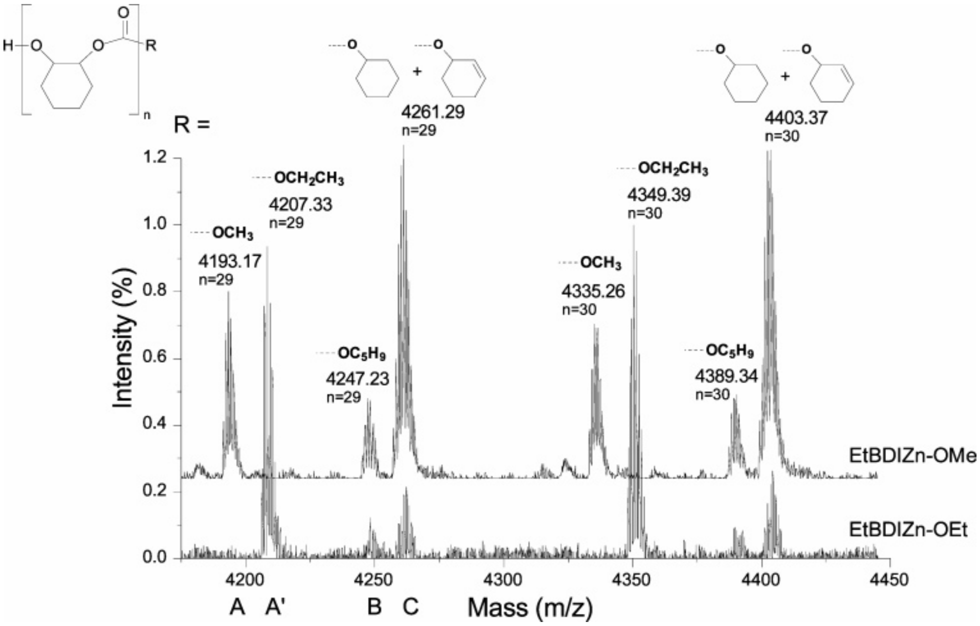


Figure 7. Comparison between MALDI-TOF-MS spectra of PCHC obtained with (EtBDI)ZnOMe and (EtBDI)ZnOEt.

one or more CO_2 units are missing. Interestingly, the phenoxides first react selectively with cyclohexene oxide before inserting a carbon dioxide monomer. This is in agreement with the capability, albeit poor, of $[(2,6\text{-}F_2C_6H_3O)_2Zn\cdot THF]_2$ to homopolymerize cyclohexene oxide to the corresponding polyether.[4]

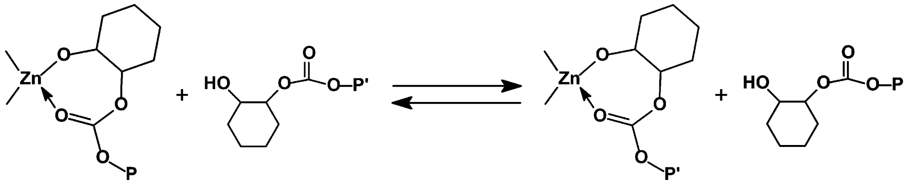
For the PCHC prepared with (EtBDI)ZnOMe (Figure 5), peak A is the expected chain end originating from ionization by K^+ of a normal polymer of 13 cyclohexene carbonate units, with a methoxide group on one side (resulting from the catalyst initiating moiety) and a proton on the other side (originating from hydrolyses of the polymer−catalyst bond after quenching with MeOH/HCl). Similarly, peak A in Figure 6 corresponds to the expected K^+ ionized polymer that contains the initiating phenoxide group $2,6\text{-}F_2C_6H_3O$ of $[(2,6\text{-}F_2C_6H_3O)_2Zn\cdot THF]_2$ and is end-capped by a proton as a result of the hydrolysis after quenching. The incorporation of the phenoxide ligand as an end group in the polymer chain was previously observed by ^{19}F NMR and UV.[4e,15] Polymers with two hydroxyl end groups are also observed for the bis(phenoxy)zinc system (peak D, Figure 6). The origin of these end groups is probably water that can act as a chain transfer agent. Peaks E, F, and G in Figure 6 correspond with polymers (peaks A−D) in which a carbon dioxide unit is missing. Such peaks were absent in the β-diketiminato zinc system, which formed completely alternating copolymers.

More difficult to assign are peaks B and C. Peaks B and C do not appear to be influenced by the initiating group, as can be seen in Figure 7 where the spectra of PCHC prepared with the (EtBDI)ZnOEt and the (EtBDI)ZnOMe are shown. The peak of the polymeric species initiated with the alkoxide groups can clearly be seen as peaks A and A′ for the methoxide and ethoxide, respectively. However, peaks B and C do not shift. Moreover, both (EtBDI)ZnOR (R = Me, Et) and $[(2,6\text{-}F_2C_6H_3O)_2Zn\cdot THF]_2$ (Figures 5 and 6, respectively) show the same peaks B and C at the same mass, which indicates that the corresponding chain structures are catalyst independent. In the case of $[(2,6\text{-}F_2C_6H_3O)_2Zn\cdot THF]_2$ peak B overlaps with peak A (Figure 6), but a similar analysis on the analogous dimethyl-substituted zinc phenoxide $[(2,6\text{-}Me_2C_6H_3O)_2Zn\cdot THF]_2$ clearly shows the presence of peak B. Interestingly, peaks B and C were exclusively found when zinc-based catalysts were used to catalyze the copolymerization. For example, when the porphyrinato chromium complex [TPP]CrCl was used as the catalyst, only polymers with two hydroxyl end groups ($HO[C_6H_{10}OC({=}O)O]_nC_6H_{10}OH$) were observed.

The fact that the fragments B and C were formed, irrespective of the type of zinc catalysts, did point at a catalyst and initiator independent structure like rings formed after transesterification. As already mentioned, no plausible ring structures could be modeled with the mass of peak B or C, and SEC-DV measurements showed a linear Mark−Houwink plot indicating a linear polymer.[4b] Peak B corresponds to a polycarbonate with a C_5H_9O initiating group and a proton end group ($HO\text{-}[C_6H_{10}OC({=}O)O]_nC_5H_9$). So far it is a complete mystery where the C_5H_9O fragment originates from. GC-MS analysis of the cyclohexene oxide showed no impurities, and the fact that only the use of zinc catalysts gives rise to the formation of C_5H_9O end groups strongly suggests some kind of zinc-based side reaction. A careful analysis of the isomer patterns revealed that peak C is a combination of two overlapping isotope patterns with an end group mass corresponding with a $C_6H_{11}O$ and a C_6H_9O fragment, which indicate the presence of cyclohexyl and cyclohexenyl end groups in a 1:1 ratio (Figure 8). Although their presence is evident, the origin of the cyclohexyl and cyclohexenyl end groups is not obvious.[16]

The possibility of chain scission during MALDI-TOF-MS experiments can be excluded, since these peaks were not observed in the MALDI-TOF-MS spectra of PCHC samples prepared by porphyrinato chromium systems.[17] To exclude any zinc-based reactions during sample preparation or MALDI-TOF-MS measurements, some β-diketiminato zinc alkoxide was added to PCHC samples produced with the porphyrinato chromium system. However, this did not lead to the appearance of cyclohexyl/cyclohexenyl (peak C) or the C_5H_9O- end groups (peak B). Hence, the cyclohexyl and cyclohexenyl end groups as well as the cyclopentyl end group are formed

Scheme 2. Schematic Representation of the Fast Reversible Chain Transfer Process[a]



[a] The hydroxyl-terminated chains are dormant while the zinc-bonded polymers are the growing chains.

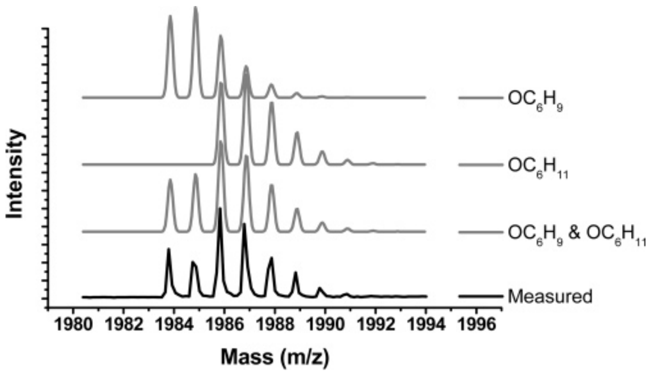


Figure 8. Simulated and measured isotope patterns of peak C in Figure 5.

prior to or during the polymerization reaction as a side reaction where a zinc species plays a crucial role. Various side reactions including β-H transfer and oxiranes rearrangement can be thought of that might explain the presence of a cyclohexenyl end group but not a cyclohexyl end group but to obtain a cyclohexyl end group, a reduction step is required. A possible explanation could be a Meerwein–Ponndorf–Verley type of reduction.

In synthetic organic chemistry, the base-mediated isomerization of oxiranes into ketones and allylic alcohols[18–20] as well as the Oppenauer oxidation/Meerwein–Ponndorf–Verley reduction (collectively denoted as MPVO)[21] are two well-known synthetic transformations. Since zinc was reported to show catalytic activity in both of these reactions,[22] it is not unlikely that the oxirane isomerization reaction in combination with MPVO is also catalyzed by the zinc catalysts (or their hydrolysis products[23]) used in these copolymerization. Assuming this is indeed possible, the cyclohexene oxide rearranges to afford cyclohexanone and 2-cyclohexenol, which via MPVO are in equilibrium with cyclohexanol and 2-cyclohexenone. This could also explain the fact that cyclohexyl and cyclohexenyl end groups were absent during the chromium ([TPP]CrCl)-catalyzed cyclohexene oxide–CO_2 copolymerization, since the abovementioned rearrangement reactions are not catalyzed by chromium.

It is also likely that the presence of different end groups is related to the formation of more chains per active site than expected for a living catalyst such as the β-diketiminato zinc alkoxide system. However, this is only possible if alcohols, generated by the rearrangement reactions, can function as chain transfer agents similar as was found for the porphyrinato aluminum catalyzed ring-opening polymerization of oxiranes.[3e,24] The observation that with time the molecular weight of all the polymer chains increases simultaneously suggests that chain transfer is a reversible process (Scheme 2). Furthermore, since the poydispersities of the polymers are very narrow, this chain transfer process has to be extremely fast.

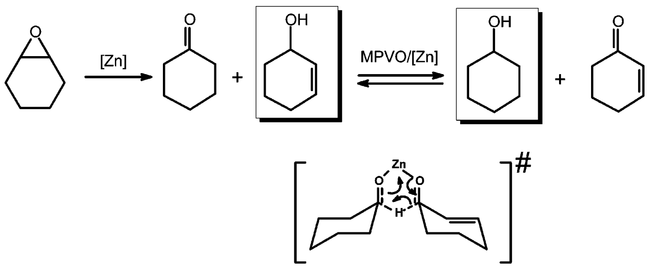


Figure 9. Cyclohexene oxide rearrangements.

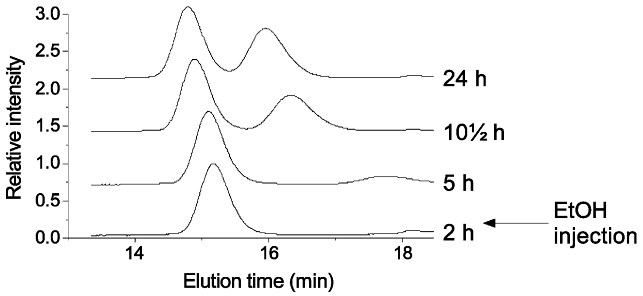


Figure 10. SEC plots of sample before and after EtOH addition.

Reversible Chain Transfer. To prove that alcohols can indeed act as effective chain transfer agents and that chain transfer is a fast and reversible process,[25] two polymerizations with (EtBDI)ZnOMe were carried out in the presence of ethanol. In the first reaction 10 equiv of ethanol was present from the beginning of the polymerization.[26] As expected, MALDI-TOF-MS analyses showed that the polymerization mainly resulted in ethoxy end-capped polycarbonates. Although lower than the theoretical value of 11 chains per active site, the observed average value of 7.1 chains per catalyst proves that alcohols can indeed act as chain transfer agents. Moreover, the narrow molecular weight distribution of 1.1 proves that chain transfer is a reversible and much faster process than propagation. These characteristics are very typical for a quasi-living polymerization.[27] Further proof came from an experiment where 10 equiv of ethanol was added after 2 h of polymerization, after which the polymerization was continued for another 22 h.

After the ethanol addition, a second distribution emerged in the SEC plot at lower molecular weight values (longer elution time, Figure 10). Both distributions continued shifting to a higher molecular weight during the polymerization while the polydispersity index of both distributions remained very low (Table 3), further supporting a reversible and very fast chain transfer mechanism (Scheme 2). To our knowledge this is the first time that this quasi-living behavior, which is similar to that observed by Inoue during oxirane ring-opening polymerization,[3e] is observed for carbon dioxide–oxirane copolymerizations. Interestingly, MALDI-TOF-MS analysis revealed that the low molecular

Table 3. Molecular Weight Data from Chain Transfer Experiment

time	low mol wt fraction			high mol wt fraction			conv
(h)[a]	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	(%)
2				12 635	13 573	1.08	40
5	1088	1283	1.18	13 438	14 872	1.11	46
$10^1/_2$	4131	4596	1.11	16 533	17 332	1.05	70
24	5909	6498	1.10	18 465	19 563	1.06	92

[a] Ethanol was injected after 2 h.

weight fraction exclusively consisted of ethoxide-initiated polymer chains. While present in the originally formed high molecular weight fraction, no cyclopentyl, cyclohexyl, or cyclohexenyl end groups were observed in the new distribution. This indicates that formation of cyclopentyl, cyclohexyl, and cyclohexenyl end groups exclusively takes place prior to or at the beginning of the polymerization. Furthermore, if a β-H elimination type of process would be active, it should occur throughout the polymerization and will result in broadening of the PDI, which was not observed. It is therefore assumed that traces of water or other impurities in the system play a crucial role in the formation of the zinc species that are active in the proposed rearrangement reactions. Since the formation of cyclopentyl, cyclohexyl, and cyclohexenyl end groups is only observed at the beginning of the reaction, it seems that the reaction is stoichiometric rather than catalytic. The exact nature of the zinc species, responsible for these rearrangement reactions, is still unknown and currently under investigation.

Concluding Remarks

MALDI-TOF-MS proved to be a powerful tool to provide more insight into the mechanisms of the various reactions taking place during the zinc-catalyzed cyclohexene oxide–CO_2 copolymerization. Whereas the β-diketiminato zinc alkoxides first reacts with CO_2, the bis(phenoxy)zinc system is initiated by the reaction with cyclohexene oxide. This is in agreement with the observation that $[(2,6\text{-}F_2C_6H_3O)_2Zn\cdot THF]_2$ is also capable of homopolymerizing cyclohexene oxide, whereas the β-diketiminato zinc system is not and produces perfectly alternating poly(cyclohexene carbonate). The results of the SEC measurements of the bis(phenoxy)zinc system suggest that the initiation is very slow and/or different active species are formed that result in an extremely broad molecular weight distribution. Although the β-diketiminato zinc system is intrinsically living, a closer look at the SEC and MALDI-TOF-MS data revealed a quasi-living nature of the catalyst where alcohols can act as chain transfer agents in a very fast and reversible chain transfer process. This process allows the synthesis of multiple polycarbonate chains per active site with a very narrow polymer distribution, thereby removing the one chain per catalyst limitations for this system while retaining good molecular weight control. The number of chains per site depends on the amount of chain transfer agent added, while the molecular weight can be tuned by the polymerization time. MALDI-TOF-MS also revealed a thus far unrecognized side reaction leading to cyclopentyl, cyclohexyl, and cyclohexenyl end groups. Clearly, besides that traces of water or other impurities present at the beginning of the reaction in combination with some zinc species play a crucial role in this process, this puzzle is by far not solved. Various side reactions including β-H transfer and oxiranes rearrangement can be thought of that might explain the presence of a cyclohexenyl end group but to obtain a cyclohexyl end group a true reduction step is required. Oxirane rearrangement in combination with a MPVO type of reaction seems to be a viable explanation for the cyclohexyl and cyclohexenyl end groups. However, the origin of the cyclopentyl end group remains a mystery. Further attempts to understand the origin of this peculiar process is currently in progress.

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