Ester-Functionalized Polycarbonates Obtained by Copolymerization of Ester-Substituted Oxiranes and Carbon Dioxide: A MALDI-ToF-MS Analysis Study

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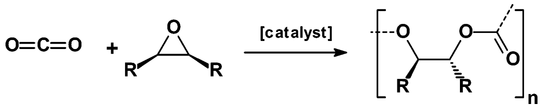
ABSTRACT: Two ester-functionalized cyclohexene oxide monomers (3,4-cyclohexene-oxide-1-carboxylic acid methyl ester (**1**) and 3,4-cyclohexene-oxide-1-carboxylic acid phenyl ester (**2**)) could be copolymerized with CO_2 using the β-diketiminato zinc catalyst (EtBDI)ZnOEt (EtBDI = 2-(2,6-diethylphenyl)amido-4-(2,6-diethylphenyl)imino-2-pentene) under mild conditions. MALDI-ToF-MS microstructure analyses of the formed aliphatic polycarbonates revealed the occurrence of chain transfer reactions to both monomer and polymer as a result of zinc-catalyzed transesterifications. As a consequence, branched and cyclic polymer structures were formed, which limited the molecular weight development and led to an increase in the polydispersity. The zinc catalyst is also capable of transesterifying carbonate functionalities, albeit that the transesterification rate is considerably lower than that for ester functionalities and only becomes visible at high conversion. This was supported by independent catalytic transesterification reactions of esters and carbonates. Transesterification of carbonate functionalities at the end of the polymerization reaction might explain the observed bimodal behavior for the intrinsically living β-diketiminato zinc catalyst.

Introduction

A quarter of a century after its initial discovery,[1,2] the metal-catalyzed copolymerization of oxiranes and CO_2 (Scheme 1) has undergone a revival and has resulted in various highly active catalyst systems for this reaction.[3−12] Current research is mainly focused on the development of more effective and selective catalysts for the copolymerization of carbon dioxide with propylene oxide or cyclohexene oxide, which are the most reactive oxiranes known for this process. Use of alternative oxiranes and structure property relations and possible applications of aliphatic polycarbonates are only scarcely explored so far.[13]

Scheme 1. Copolymerization of Carbon Dioxide and Oxiranes Yielding Aliphatic Polycarbonates with a C2 backbone



The requirement for this copolymerization process to use oxirane monomers obviously limits the backbone to an aliphatic C2 bridge, and therefore, the polymer properties can only be varied by changing the oxirane substituents. The currently known aliphatic polycarbonates are still of limited use as engineering plastics because the most commonly applied oxiranes ethylene oxide (EO), propylene oxide (PO), and cyclohexene oxide (CHO) do not afford the desired properties such as a high T_g and good impact resistance. The first two monomers give polycarbonates with a too low T_g, and although polycarbonate based on CHO has a higher T_g of 116 °C, it is still considered low for engineering plastic applications.[13] In addition, the low entanglement density of polycyclohexene carbonate makes the polymer very brittle.[13a]

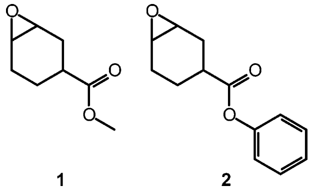


Figure 1. Monomers 3,4-cyclohexene-oxide-1-carboxylic acid methyl ester (**1**) and 3,4-cyclohexene-oxide-1-carboxylic acid phenyl ester (**2**) used for the copolymerization with CO_2.

Some reports can be found in the literature where alternative oxirane monomers are applied. Typical examples are polycarbonates based on styrene oxide, cyclopentene oxide, allyl glycidyl ether, *i*-butyl glycidyl ether, and epichlorohydrin.[14] For most of these oxiranes, the copolymerization with CO_2 is slow and often the obtained carbonate content and T_g of these polymers are low. Because the T_g is related to the rigidity of the polymer chain,[15] oxiranes with substituents on both the α and β positions are expected to give the highest chance of obtaining polymers with a sufficiently high T_g (Scheme 1). Indeed, polycyclohexene carbonate shows with 116 °C the highest T_g of all aliphatic polycarbonates reported and the best chance to obtain polycarbonates with acceptable properties is the use of substituted cyclohexene oxide analogues as monomers. Cyclohexene oxide based oxiranes successfully applied so far are 4-vinyl cyclohexene oxide,[16] limonene oxide,[17] and trimethoxysilane-substituted cyclohexene oxide.[18,19]

In this contribution, we will discuss the CO_2 copolymerization of ester-functionalized cyclohexene oxides (Figure 1). It was argued that the additional functionality might have a positive influence on polymer properties and that it could also be used as a reactive group for postpolymerization modification. With the ester functionality being located at the 4 position, far away from the oxirane functionality, the reactivity of **1** and **2** was expected to be comparable to cyclohexene oxide.

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Experimental Section

Materials. Reactions were performed under an argon atmosphere using a glovebox (Braun MB-150 GI) or Schlenk techniques when necessary. Cyclohexene oxide (Aldrich) was dried on CaH_2, distilled, and then stored under argon on molecular sieves (4 Å) prior to use. Methanol (Sigma Aldrich), dichloromethane (Biosolve), heptane (Aldrich), *m*-chloroperbenzoic acid (Acros), 3-cyclohexene-1-carboxylic acid (TCI Europe), phenol (VWR), DCC (Sigma Aldrich), dimethyl carbonate (VWR), cyclohexanol (VWR), pyridine (VWR), and triphosgene (Aldrich) were used as purchased. Ethyl acetate (Biosolve), methyl propionate (Acros), chloroform-d_1 (Aldrich), and benzene-d_6 (Aldrich) were dried on activated molecular sieves (4 Å). 4-Dimethylaminopyridinium-4-toluenesulfonate (DPTS) was prepared from 4-(dimethylamino)pyridine (Aldrich) and 4-toluenesulfonic acid (Acros) as described.[20] Carbon dioxide (>99.9993% pure) was purchased from HoekLoos and used without any further purification. THF and toluene were dried over an alumina column and stored on molsieves (4 Å). The (EtBDI)ZnOR catalysts (EtBDI = 2-(2,6-diethylphenyl)amido-4-(2,6-diethylphenyl)imino-2-pentene; R = Me, Et, $N(SiMe_3)_2$, O_2CMe) were synthesized according to literature procedures.[5g]

Analytical Techniques. ^1H NMR spectra were recorded on a Varian Gemini 2000 (300 MHz) and a Varian Mercury Vx (400 MHz) spectrometer. Thermal analyses were carried out with a differential scanning calorimeter (DSC Q1000 from TA Instruments). Approximately 2 mg of sample was placed in an aluminum pan. Each sample was heated from 20 to 180 °C at 10 $°C{\cdot}min^{-1}$, held at 180 °C for 2 min, and then cooled at 10 $°C{\cdot}min^{-1}$ to 20 °C. The sample was held at this temperature for 2 min and heated again from 20 to 180 °C at 10 $°C{\cdot}min^{-1}$. 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 $mL{\cdot}min^{-1}$. 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 were performed using Waters Millennium32 software. 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 a literature procedure.[21] Potassium or sodium trifluoroacetate (Aldrich, >99%) was added to the polymer samples as a cationization agent. The matrix was dissolved in THF at a concentration of 40 $mg{\cdot}mL^{-1}$. The potassium trifluoroacetate was added to THF at a typical concentration of 1 $mg{\cdot}mL^{-1}$. Polymer was dissolved in THF at approximately 1 $mg{\cdot}mL^{-1}$. In a typical MALDI-ToF-MS analysis, the matrix, potassium trifluoroacetate, and the polymer solution were premixed in a weight 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. In-house-developed software was used to simulate the spectrum and required the molar mass of (i) repeating units, (ii) possible end groups, and (iii) the cation of the cationization agent as input data. The program makes use of eq a to assign a certain combination of oxirane and carbon dioxide units with a given end group to an experimental value of *m*/*z*.

$$m_{\mathrm{th}} = xM_{\mathrm{Oxirane}} + yM_{\mathrm{CO_2}} + E_{\mathrm{I}} + E_{\mathrm{II}} + M^{+} \qquad \text{(a)}$$

E_{I} and E_{II} represent the masses of the end groups at either side of the chain, M_{Oxirane} represents the mass of the repeating oxirane unit, $M_{\mathrm{CO_2}}$ the mass of the repeating CO_2 unit, and M^+ the mass of the cation.

Synthesis of 3,4-Cyclohexene-oxide-1-carboxylic Acid Methyl Ester (1). 3-Cyclohexene-1-carboxylic acid (125 mL, 1.07 mol) and 2 drops of H_2SO_4 were dissolved in MeOH (200 mL) and refluxed overnight, after which the solvent was removed by distillation and the crude product isolated. 3-Cyclohexene-1-carboxylic acid methyl ester (50.0 g, 0.36 mol) was dissolved in dichloromethane (150 mL) and cooled to 0 °C. A solution of *m*-chloroperbenzoic acid (63.9 g, 0.37 mol) in dichloromethane (600 mL) was added dropwise while keeping the temperature below 10 °C. The mixture was stirred for 2 days at room temperature, and the solids were removed by filtration. The filtrate was then washed with NaS_2O_3 (2 × 100 mL, 10% solution in water), $NaHCO_3$ (2 × 100 mL, 10% solution in water), and brine (100 mL). The solvents were removed on a rotary evaporator, and the obtained product was further purified by distillation. The product was dried over CaH_2, distilled, and then stored under argon on molecular sieves (4 Å). Yield: 47.1 g (0.30 mol, 84%). ^1H NMR (300 MHz, $CDCl_3$): δ = 3.65 (s, 3H, C*H*3), 3.22, 3.14 (m, 2H, C*H*OC*H*), 2.49 (m, 1H, C*H*CO_2), 1.33−2.29 (m, 6H, C*H*$_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.0 (*C*OO), 51.42, 50.59 (*C*HO*C*H), 50.98 (CH_3), 35.15 (*C*HCOO) 26.66, 22.33, 22.25 (*C*H_2).

Synthesis of 3,4-Cyclohexene-oxide-1-carboxylic Acid Phenyl Ester (2). A solution of phenol (44.7 g, 0.48 mol) in dichloromethane (100 mL) was added to a solution of 3-cyclohexene-1-carboxylic acid (50.0 g, 0.40 mol), dicyclohexylcarbodiimide (DCC) (122.7 g, 0.60 mol), and 4-*N*,*N*-dimethylaminopyridinium toluene-*p*-sulfonate (DPTS, 12.0 g, 0.04 mol) in dichloromethane (400 mL). The mixture was stirred overnight at room temperature. Next, the solution was concentrated under reduced pressure, dissolved in ethyl acetate, and filtered trough a Celite pad. The filtrate was evaporated and subjected to column chromatography on silica gel with an AcOEt/heptane eluent (2:9) to yield 3-cyclohexene-1-carboxylic acid phenyl ester. The ester (60.0 g, 0.30 mol) was redissolved in dichloromethane (150 mL) and cooled to 0 °C. Slowly a solution of *m*-chloroperbenzoic acid (64.0 g, 0.37 mol) in dichloromethane (600 mL) was added dropwise while keeping the temperature below 10 °C. The mixture was stirred for 2 days at room temperature, and the solids were removed by filtration. The filtrate was then washed with NaS_2O_3 (5 × 100 mL, 10% solution in water), $NaHCO_3$ (5 × 100 mL, 10% solution in water), and brine (3 × 100 mL). The solvents were removed on a rotary evaporator, and the obtained product was further purified by distillation. The product was dried over CaH_2, redistilled, and stored under argon on molecular sieves (4 Å). Yield: 38.2 g (0.18 mol, 59%). ^1H NMR (300 MHz, $CDCl_3$): δ = 3.65 (s, 5H, Ph-*H*), 3.22, 3.14 (m, 2H, C*H*OC*H*), 2.49 (m, 1H, C*H*CO_2), 1.33−2.29 (m, 6H, C*H*$_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.63 (*C*OO), 150.45 (Ph-*C*-OCO), 129.13, 125.52, 121.17 (Ph*C*), 51.79, 51.06 (*C*HO*C*H), 35.78 (*C*HCOO) 26.86, 22.58, 22.47 (*C*H_2).

A Typical Example of the Copolymerization of Monomer 1 and Carbon Dioxide. (EtBDI)ZnOEt (94 mg, 200 μmol) and monomer **1** (10 g, 64 mmol) were dissolved in toluene (40 mL). After complete dissolution of the catalyst and monomer, the mixture was injected into a preheated (50 °C) autoclave previously dried under vacuum at 120 °C for 12 h. The autoclave was pressurized to 9 bar with carbon dioxide, and the polymerization commenced. The polymerization was continued for 96 h. The conversion to polycarbonate (84%) was determined by integration of the methine peaks in the ^1H NMR spectra. ^1H NMR (300 MHz, $CDCl_3$): δ 4.92 and 4.77 (br, 2 CH (polycarbonate), 4H), 3.22 and 3.14 (m, 2 CH (CHO), 4H). The sample for SEC analysis was prepared as follows: About 0.5 mL of the reaction mixtures was added dropwise to a 10-fold excess of petroleum ether (40−70) upon which the polycarbonate precipitated. After separation, the polymer was redissolved in the SEC eluent THF. Polystyrene standards were used for calibration. $\bar{M}_n$ = 2330 $g{\cdot}mol^{-1}$, $\bar{M}_w/\bar{M}_n$ = 4.4. Polymer solutions for MALDI-ToF-MS analyses were prepared in a similar manner.

A Typical Example of the Copolymerization of Monomer 2 and Carbon Dioxide. Similar to the copolymerizations with monomer **1**, with the only exception that more catalyst (600 μmol) was used. Conversion by ^1H NMR = 30%. $\bar{M}_n$ < 500 $g{\cdot}mol^{-1}$.

NMR Tube Experiment of (EtBDI)ZnOMe, CHO, and CO_2. In the glovebox, an NMR tube was charged with a benzene-d_6 solution of (EtBDI)ZnOMe (28 mg, 62 μmol), CHO (60 μL, 612 μmol). The NMR tube was placed in a steel tube equipped with a needle valve, and the steel tube was charged with 10 bar of CO_2 and placed in a water bath of 50 °C for 24 h. Then the mixture

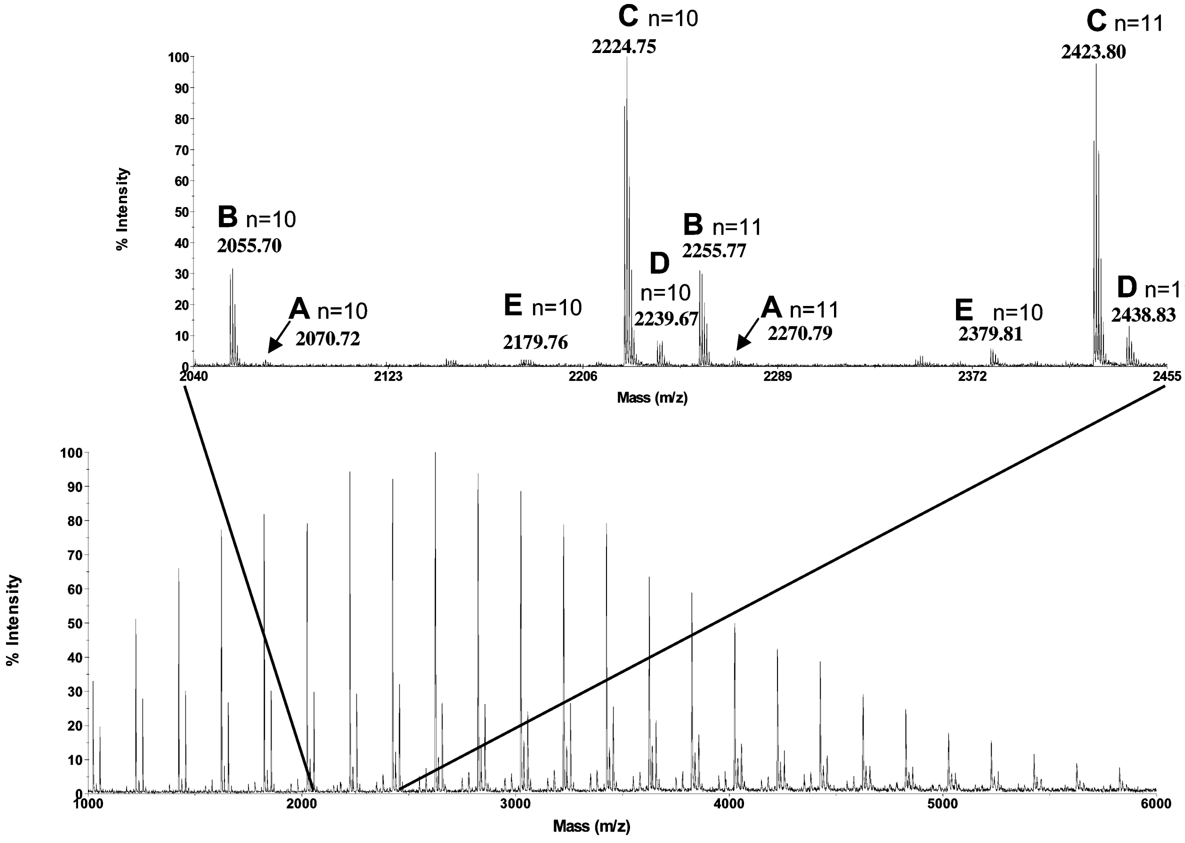


Figure 2. MALDI-ToF-MS spectrum of the copolymer of **1** with CO_2 (cationization ion: Na^+) with "*n*" being the number of repeating units of the corresponding polymer structure as represented in Scheme 2.

was subjected to ^1H and ^{13}C NMR and MALDI-ToF-MS. The NMR spectra revealed the complete conversion of CHO and selective formation of polycyclohexene carbonate.

A Typical Example of a Transesterification Experiment. A toluene (2 mL) solution of (EtBDI)ZnOMe (170 mg, 370 μmol) was added to a mixture of ethyl acetate (1 mL, 10 mmol) and methyl propionate (1 mL, 10 mmol), and the mixture was warmed to 60 °C for 24 h. Samples were taken at set time intervals and analyzed by ^1H and ^{13}C NMR spectroscopy. The same procedure and concentration were used for transesterification between dimethyl carbonate and dicyclohexyl carbonate. The same transesterification experiments were also performed with $[EtBDI]ZnO_2CMe$ and $[EtBDI]ZnN(SiMe_3)_2$ as the precatalyst. The acetate species showed no transesterification activity at all. Dicyclocarbonate was synthesized by reacting triphosgene (6.9 g, 23.3 mmol) at 0 °C with cyclohexyl alcohol (14.2 g, 141.8 mmol) in toluene (200 mL) in the presence of pyridine (12.2 mL, 151.5 mmol), followed by stirring at room temperature overnight. Standard organic workup and vacuum transfer afforded dicyclocyxyl carbonate as a colorless crystalline material (13.1 g, 58.0 mmol, 83%). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 4.61$ (m, 1H, C*H*), 1.93 (m, 2H, CH_2), 1.77 (m, 2H, CH_2), 1.43 (m, 6H, CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta =$ 154.1 (CO_3), 76.27 (*C*H), 31.59, 25.20, 23.74 (CH_2, 2:1:2 ratio).

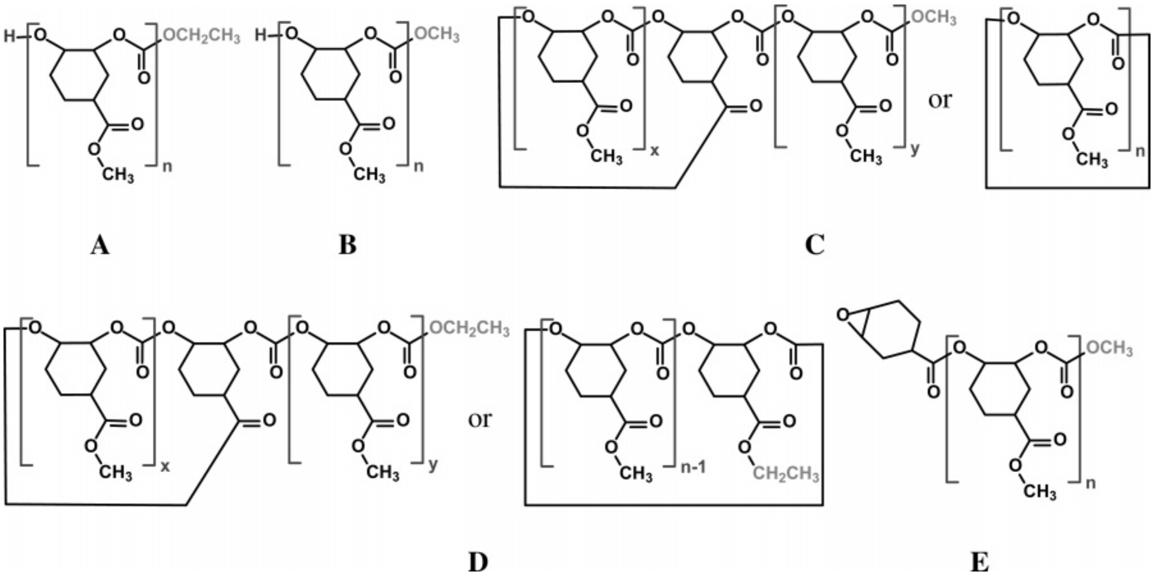
Results and Discussion

The ester-functionalized monomers **1** and **2** were readily synthesized from 3-cyclohexene-1-carboxylic acid by esterification and subsequent epoxidation. Monomers **1** and **2** were copolymerized with the (EtBDI)ZnOEt catalyst for prolonged periods of time.

The copolymerization of monomer **1** with CO_2 resulted in a polycarbonate with a low $\bar{M}_n$ (2330 g·mol^{-1}) according to the SEC analysis. Although the SEC $\bar{M}_n$ values are defined as PS equivalents, the molecular weights observed with MALDI-ToF-MS (Figure 2) do not deviate significantly. Using the SEC values, an estimated average number of thirteen chains per catalyst was found. This is obviously more than the expected one chain per active site for an intrinsically living system as the β-diketiminato zinc catalyst[5] and indicates that chain transfer occurs during the polymerization.[5h] To get more insight into the reactions playing a role in this system, MALDI-ToF-MS measurements were used to determine the end groups of the formed polymers.

A closer look at the MALDI-ToF-MS spectrum (Figure 2) reveals some interesting features. The spectrum shows a perfectly alternating copolymer as no loss of CO_2 could be observed, but there is clearly more than one combination of end groups present. Interestingly, the polymer structure that would be expected in a polymerization with an (EtBDI)ZnOEt catalyst, being a polycyclohexene carbonate with one hydroxyl and one ethyl carbonate end group $H[OC_6H_9(4\text{-}CO_2Me)OC({=}O)]_nOEt$, is only just visible as peak A in Figure 2 (A, Scheme 2).[22] The closest resembling structure of A that is present in significant amounts is B in Scheme 2, which corresponds to a linear polymer with a methyl carbonate instead of an ethyl carbonate end group. The presence of structure B (Scheme 2, Figure 2) indicates that the zinc catalyst readily undergoes transesterification reactions with methyl ester functionalities. Probably, most of the initial zinc ethoxide has been transformed into the corresponding zinc methoxide by transesterification with the ester function of ester-functionalized cyclohexene oxide monomer even before copolymerization starts. This is even more obvious when looking at the polymer structures that correspond to peaks C and D, which are cyclic structures, formed as the result of intramolecular transesterification of either the pendant ester or the carbonate unit (back-biting).

Scheme 2. Possible Structures for the Most Abundant Peaks Found in Figure 2 (C, D: $n = x + y$)



MALDI-ToF-MS cannot distinguish between the ring structures as a result of back biting at another carbonate group and "lasso" structures as a result of transesterification of pendant ester functionalities in C and D. Given that polycyclohexene carbonate synthesized by (EtBDI)ZnOEt only gave linear chains strongly suggests that transesterification of a pendant ester functionality is the principle reaction resulting in cyclic structures.[5h] The exact position in the polymer chain where the transesterification with the pendant ester functionality occurs, resulting in the so-called lasso structure, cannot be determined with MALDI-ToF-MS either. In structure D, an ethoxide group is present. Although in Scheme 2, the ethoxide group in D is positioned at the chain end, it is also likely that, due to transesterification, it is located somewhere along the main chain as an ethyl ester functionality, but also this cannot be distinguished by MALDI-ToF-MS.

There is no reason to believe that this transesterification reaction is limited to ester units in the same polymer chain (intramolecular transesterification) and can just as well occur with an ester functionality of a free monomer or a different polymer chain. In the case of intermolecular transesterification with a free monomer, a polymer structure with an epoxide end group should be formed, and this structure can indeed be seen in Scheme 2 (peak E). The thus obtained macromonomer can in its turn be further copolymerized with CO_2, leading to branched structures. In the case of transesterification with an ester group of a different polymer chain, chain coupling will also occur, resulting in a branched polymer. As the formula and weight of a branched polymer is identical to that of a normal linear polymer chain, it is impossible to discriminate between branched and linear chains using MALDI-ToF-MS.[23] We like to emphasize at this point that MALDI-ToF-MS is a qualitative technique and the relative intensities in the spectra do not necessarily correspond to the product distribution in the original polymer sample.

Zinc-catalyzed transesterification is not unknown,[24,25] but generally more demanding conditions are required before substantial transesterification takes place. Under similar conditions as applied in our study, Coates and co-workers also observed a nonliving behavior of the β-diketiminato zinc catalysts during ring-opening polymerization of β-butyrolactone.[26] The origin for this behavior was attributed to H-elimination leading to crotonate endgroups, rather than zinc-catalyzed transesterification.

To prove the capability of the zinc catalyst to act as a transesterification catalyst under the reaction conditions applied for oxirane$-CO_2$, the copolymerization, a 1:1 mixture of ethyl ethanoate and methyl propionate, was treated with the catalyst at 60 °C (Figure 3). Significant transesterification could already be seen after 1 h, and in about 12 h, a roughly 1:1:1:1 equilibrium mixture of ethyl and methyl ethanoate and ethyl and methyl propionate was formed, which clearly demonstrates that zinc-catalyzed transesterification of ester functionalities is a competitive reaction under the conditions applied. With [EtBDI]-$ZnN(SiMe_3)_2$ as the catalyst, the transesterification is somewhat slower, probably as a result of the poorer nucleophilicity of the bulky amide group. That the transesterification is indeed zinc catalyzed was proven by carrying out the same transesterification with the zinc acetate [EtBDI]ZnO_2CMe. As expected, no transesterification was observed. Triggered by these results, the feasibility of transesterifying carbonate bonds was also studied. As can be seen in Figure 3, [EtBDI]ZnOMe-catalyzed transesterification between dimethyl carbonate and dicyclohexyl

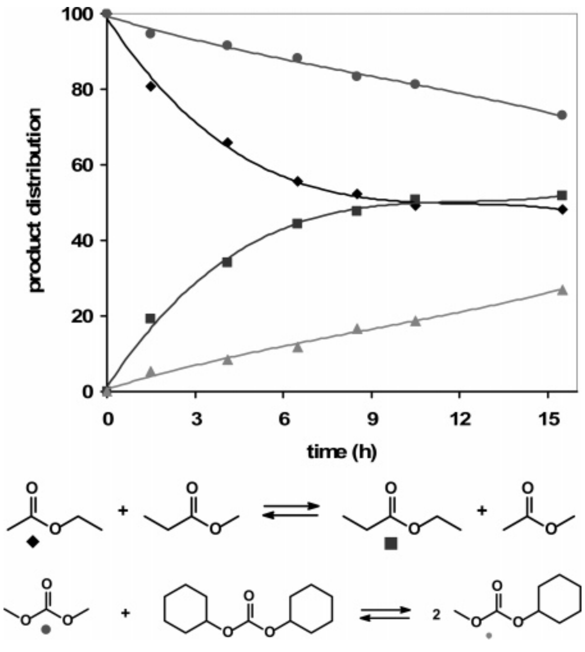
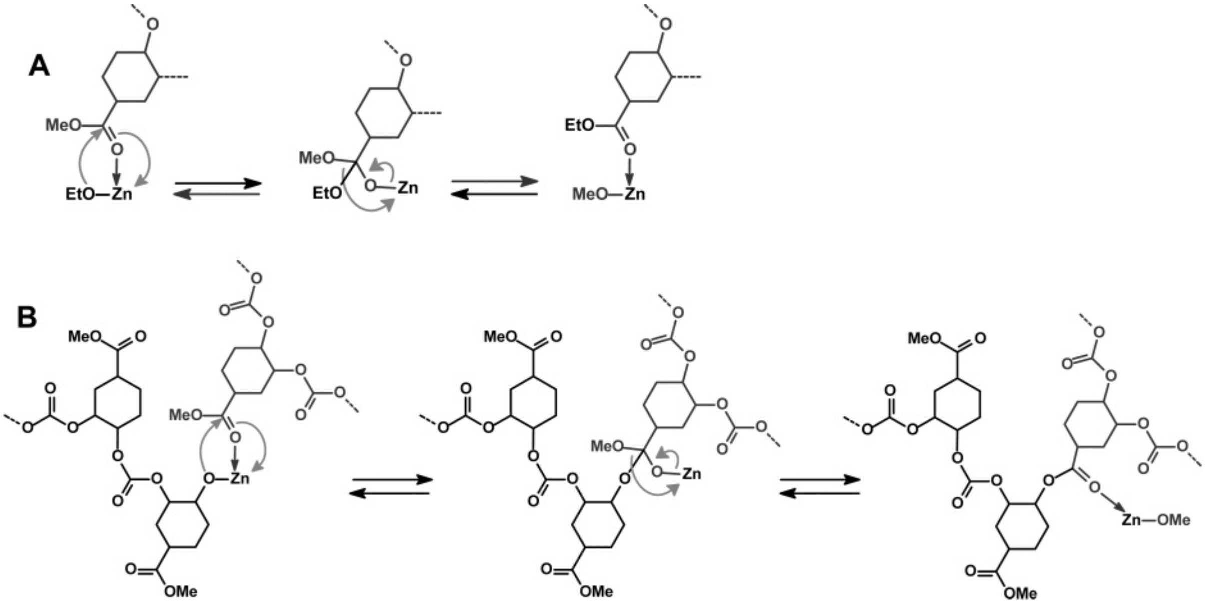


Figure 3. [EtBDI]ZnOMe catalyzed transesterification between $MeCO_2$-Et and $EtCO_2Me$ and between $MeCO_3Me$ and $CyCO_3Cy$.

Scheme 3. Proposed Mechanism for (A) the Chain Transfer Due to Transesterification of a Zinc Initiator with an Ester Functionality) and (B) the Chain Transfer of a Growing Chain with the Subsequent Formation of Either Cyclic Structures (intramolecular transesterification) or Branches (intermolecular transesterification) as Seen in the Copolymerization of Monomer 1



carbonate does indeed take place, albeit that the reaction is considerably slower than the transesterification of ester functionalities.

It is clear that all peaks in the MALDI spectrum are the result of competitive zinc-catalyzed transesterification reactions, which results in various branched products and ring structures. Besides yielding different chain microstructures, transesterification leads to a significant broadening of the molecular weight distribution than expected for an intrinsically living system. The proposed mechanism for the transesterification with the pendant ester functionality is shown in Scheme 3. Scheme 3A represents the transesterification of the zinc ethoxide initiator with one of the ester functionalities in a growing chain (or a monomer), which affords the zinc methoxide precursor that yields the products with structure A, B, or D (Scheme 2). Likewise, nucleophilic attack of the zinc-bonded cyclohexyloxide at an ester-carbonyl group further in the same chain or in another polymer chain will lead to cyclic products or branched polymers, respectively, together with a new methoxide zinc species capable of growing another chain (Scheme 3B). Consequently, the transesterification process described in Scheme 3B results in chain transfer, which explains the average number of thirteen polymer chains per active site for this intrinsically living system. In an earlier study, we reported the ability of alcohols to function as effective chain transfer agents during the copolymerization of cyclohexene oxide and CO_2.[5h] The present study demonstrates that esters show similar behavior but in an aprotic manner.

DSC measurements of the polymer obtained with monomer **1** showed a T_g of 53 °C ($\bar{M}_n = 2330$ g·mol^{-1}). Because the molecular weight of the polymer, especially at lower molar masses, has a strong influence on the T_g, a direct comparison with the T_g reported for PCHC (116 °C) cannot be made.[13a] Two DSC measurements of low-molecular-weight PCHC were performed, and for an $\bar{M}_n$ of 1400 g·mol^{-1}, a T_g of 52 °C was observed, and for an $\bar{M}_n$ of 3500 g·mol^{-1}, a T_g of 85 °C was found.[27] This strongly suggests that the T_g of the polymer obtained with monomer **1** is relatively low compared to the T_g of PCHC of similar molar mass.

As a result of the rigidity of the phenyl substituents, the copolymers of monomer **2** with carbon dioxide were expected to give a higher T_g than for monomer **1**. Although seemingly similar, monomers **1** and **2** clearly show different reactivity. With a conversion to polycarbonate of only 30%, the copolymerization of monomer **2** with CO_2 seems to be significantly hampered. SEC analysis showed only a number of oligomers, and the average molecular weight was too low to obtain reliable $\bar{M}_n$ and $\bar{M}_w$ data. The polymer formed was also analyzed by MALDI-ToF-MS, and the spectrum is shown in Figure 4. The proposed polymer structures are depicted in Scheme 4.

The MALDI-ToF-MS spectrum shows one main peak (A). Like for monomer **1**, the most abundant product A does not correspond to the expected structure, which would be a polymer with one hydroxyl and one ethyl carbonate end group, $H[OC_6H_9(4\text{-}CO_2Ph)OC({=}O)]_nOEt$. Instead, peak A corresponds to a copolymer with one equivalent of CO_2 less than oxiranes and contains exactly two ethyl groups per chain (Scheme 4). Interestingly, polymer chains with one ethyl group or with only phenyl groups were not observed.

When a polymer chain is formed with exactly two ethyl end groups, it is most likely that it is formed by intermolecular transesterification of two polycarbonate chains, both containing an ethyl carbonate end group. The apparent loss of one equivalent of CO_2 can also be explained by transesterification with the phenyl ester (Scheme 5). From the zinc-catalyzed CO_2–oxirane copolymerization, it is known that zinc aryloxide initiators first react with an oxirane,[4] whereas zinc alkoxides primarily insert into carbon dioxide.[5] Transesterification of (EtBDI)ZnOEt with monomer **2** gives the corresponding zinc phenoxide and the ethyl ester functionalized monomer. The zinc phenoxide can now react with an oxirane prior to carbon dioxide, which corresponds to an overall loss of one equivalent of CO_2. The fact that polymers containing only phenyl groups are absent suggests that insertion in the oxirane after transesterification is fast, exclusively leading to $(EtBDI)Zn{-}OC_6H_9(CO_2Et)OPh$ as the actual initiator for the copolymerization (Scheme 5).

Structure A corresponds to a polymer obtained after coupling by transesterification of an ethoxide-initiated chain and a chain with a $OC_6H_9(CO_2Et)OPh$ as the initiating group. The difference between peak A and B is 44 g·mol^{-1}, which corresponds to the loss of one carbon dioxide molecule (Scheme 4). One might

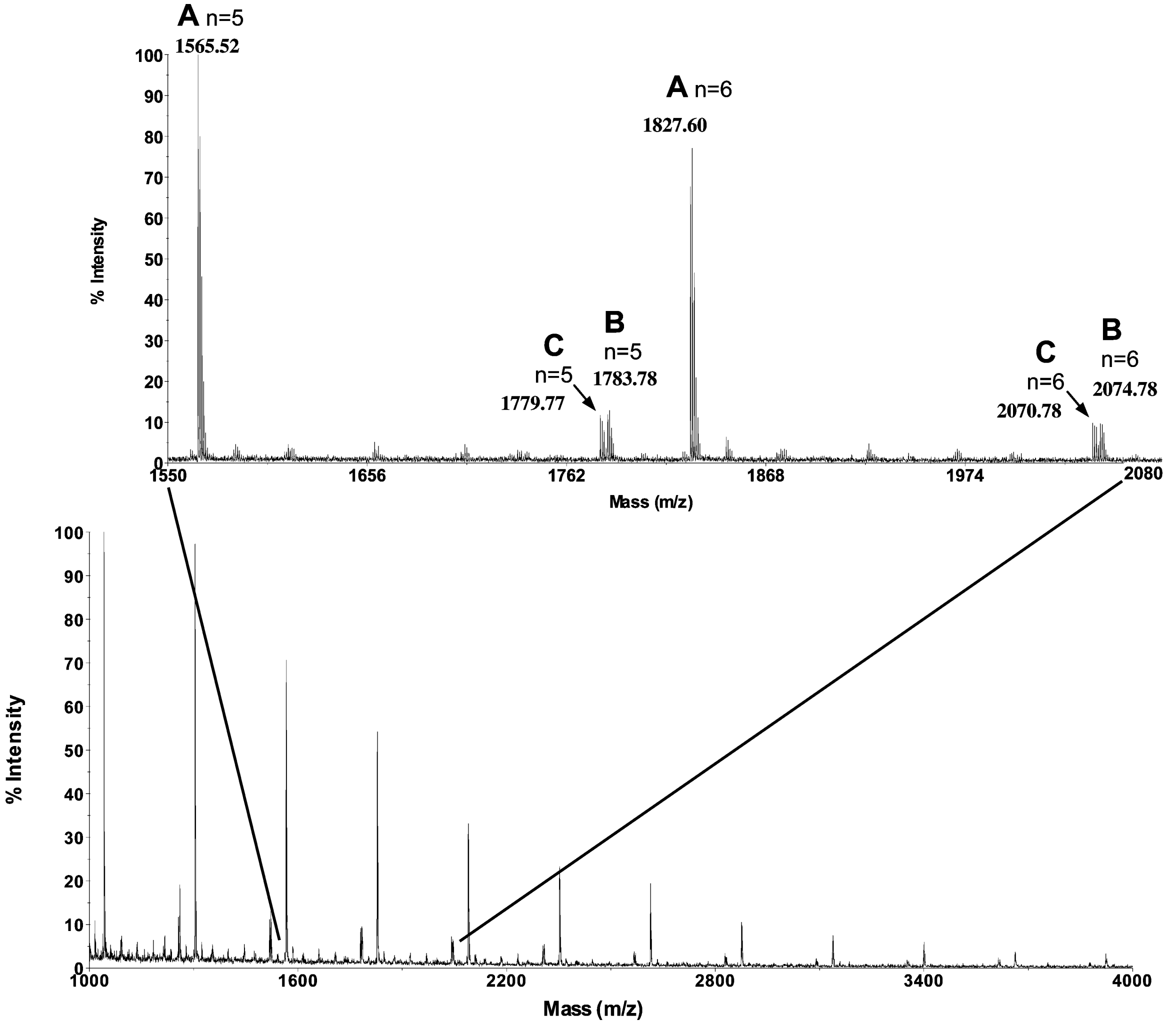
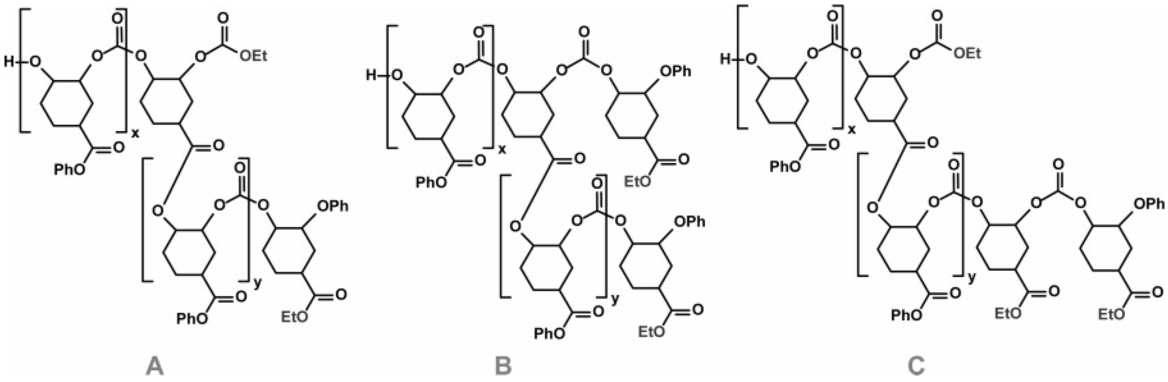
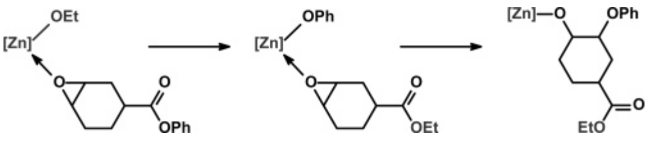


Figure 4. MALDI-ToF-MS spectrum of the copolymer of monomer **2** and CO_2 (cationization ion: K^+), with "*n*" being the number of repeating units of the corresponding polymer structure as represented in Scheme 4.

Scheme 4. Structures for the Peaks Displayed in Figure 4 (A: $n = x + y + 2$; B: $n = x + y + 3$; C: $n = x + y + 3$)



Scheme 5. Transesterification of the Initial Zinc Ethoxide with the Monomer Followed by Subsequent Ring Opening of the Oxirane



assume that the polymer is highly but not perfectly alternating, but on the basis of the observation above, it is more likely that B is the transesterification coupling product of two chains initiated by a $OC_6H_9(CO_2Et)OPh$ group. Finally, there is a third peak in the MALDI-ToF-MS spectrum with a significant intensity. This peak C corresponds to a polycarbonate with the structure of A that has undergone an additional transesterification with an ethyl group of another polymer chain (Scheme 4). While polymers obtained with monomer **1** showed considerable amounts of cyclic structures, with **2**, no cyclic structures were observed. Possibly this is due to a combination of increased steric hindrance resulting in a more rigid chain structure and a lower molar mass of the phenyl-substituted polycarbonates compared to the methyl ester-substituted polycarbonates, which hampers intramolecular transesterification. For the polymer obtained with monomer **2**, no clear T_g could be observed.

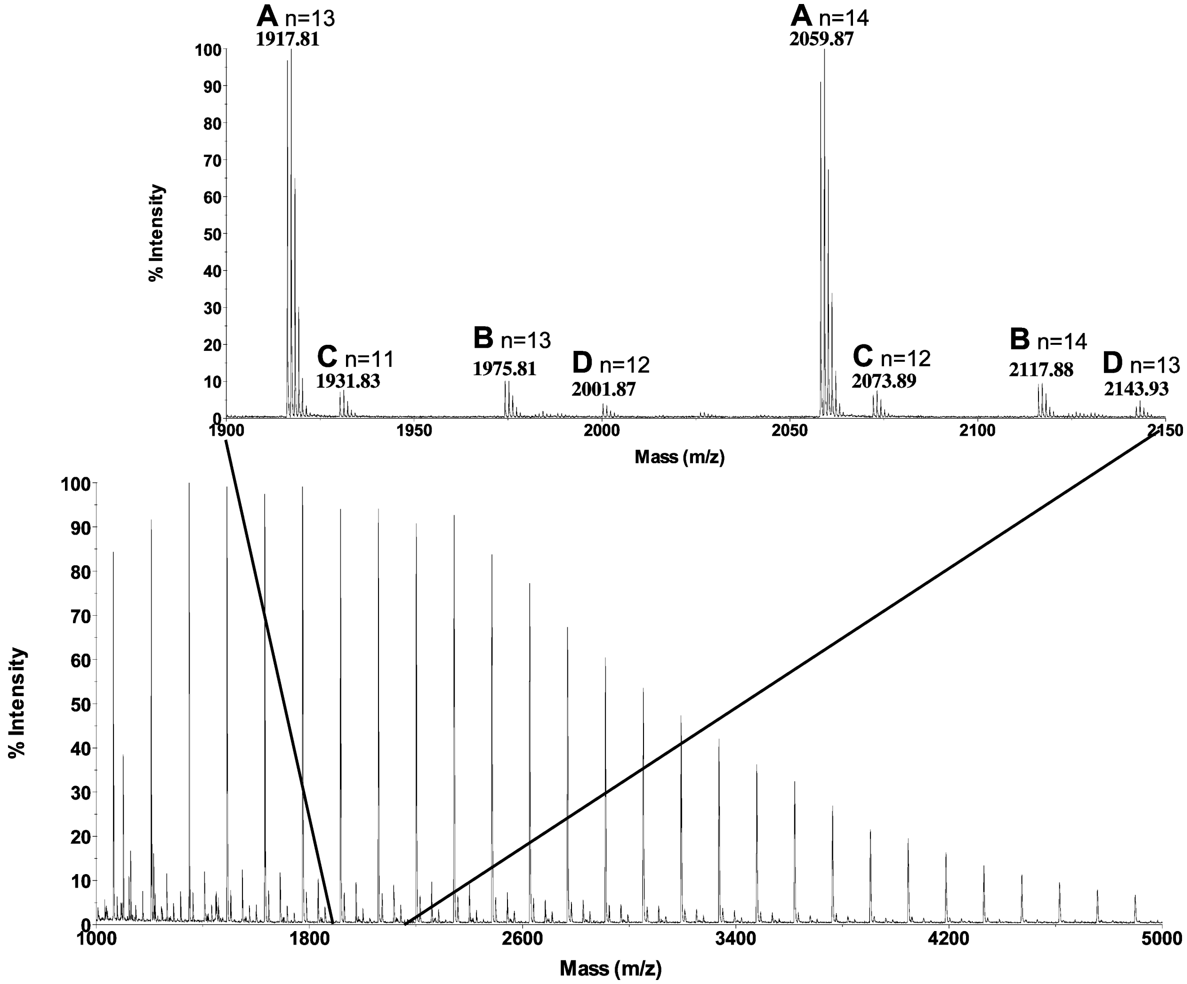
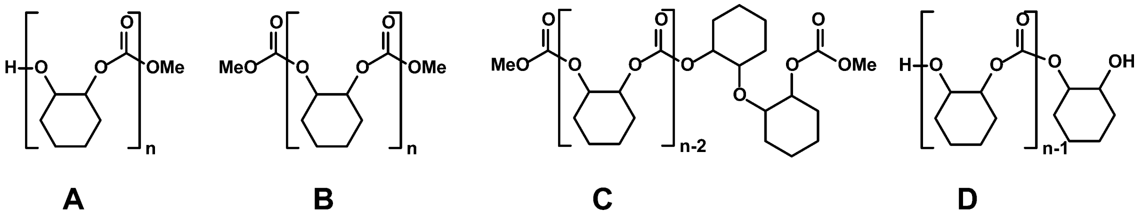
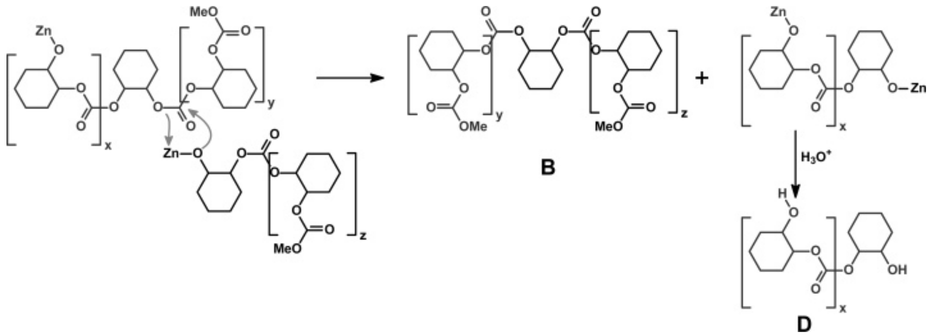


Figure 5. MALDI-ToF-MS spectrum of the polymer obtained after polymerization of CHO and CO_2 in an NMR tube (cationization ion: K^+).

Scheme 6. Structures for the Peaks Displayed in Figure 5



Scheme 7. Proposed Chain Coupling Mechanism of Zinc-Terminated Polycarbonates to Polymer Structures B (Figure 5: $n = y + z + 1$) and D (Figure 5: $n = x + 1$)



Triggered by the results above, we studied whether transesterification of carbonate bonds of polycyclohexene carbonate would also be feasible under the conditions applied. The reason was that, in the past, several reports described a bimodal distribution for polycyclohexene carbonate formed using the single site and intrinsically living β-diketiminato zinc catalyst system. This bimodal distribution has been attributed to monomeric and dimeric catalytic species present in solution.[5f] Because more recent studies have demonstrated that the mechanism requires a bimetallic enchainment,[5g] more or less excluding the monomer–dimer equilibrium of the catalyst as the origin of this behavior, we argued that transesterification could possibly be an alternative explanation for the observed bimodality. The fact that a bimodal distribution is formed indicates that, if transesterification of carbonate functionalities occurs, this process is considerably slower than polymerization and might only become visible at higher conversions or long reaction times.

As MALDI-ToF-MS is a less accurate technique for high-molecular-weight polymers, we performed a reaction in benzene-d_6 in an NMR tube where we treated the (EtBDI)ZnOMe catalyst with 10 equiv of CHO in the presence of CO_2 (10 bar). The reaction was carried out overnight at 50 °C and yielded low-molecular-weight polycyclohexene carbonate. The MALDI-ToF-MS spectrum of the reaction mixture is given in Figure 5, and the corresponding structures are presented in Scheme 6. The main peak corresponds to the expected chain structure with one hydroxide and one methyl carbonate end group (A, Scheme 6). Interestingly, the other less intense peaks correspond to three different types of coupled chain products (B−D, Scheme 6).

A schematic representation of a possible mechanism for the coupling reaction is displayed in Scheme 7,[28] where a transesterification reaction between two zinc-bonded polymer chains would lead to the coupling of two chains (species B, Figure 5) and a polymer end-capped with zinc at each end or, when $x = 0$, a dinuclear zinc species with a bridging cyclohexene diolate (Scheme 7).

The peaks of species C (Figure 5) correspond to a polymer of type B that has lost one carbon dioxide moiety. Although this catalyst system generally affords highly alternating copolymers, loss of carbon dioxide seems to occur. Species D in the MALDI-ToF-MS spectrum (Figure 5) corresponds to a polymer that is formed after transesterification and subsequent hydrolysis (Scheme 6).

On the basis of this NMR experiment, it is obvious that transesterification of carbonates is possible, albeit that the reaction is considerably slower than, for example, for the ester functionality in monomer **1** and it only becomes visible at high conversions. Whether this mechanism is indeed a plausible explanation for the bimodal behavior of the intrinsically living β-diketiminato zinc catalyst system requires more detailed mechanistic studies.

Concluding Remarks

Searching for alternative oxiranes for the production of aliphatic polycarbonates with interesting polymer properties is intriguing and, as this study shows, might lead to unexpected side reactions. Its relatively high reactivity in the copolymerization with CO_2 and the encouraging T_g of polycyclohexene carbonate makes cyclohexene oxide a suitable building block for alternative monomers. The 4-ester functionalized CHO monomers **1** and **2** could indeed be copolymerized with CO_2 using the β-diketiminato zinc catalysts under relatively mild conditions. Whereas the introduced ester functionality did not affect the selectivity in carbonate formation of the catalyst, zinc-catalyzed transesterification with the ester substituents formed a strongly competing side reaction that resulted in branched and cyclic polymer structures, of which the latter considerably suppressed the molecular weight development. The transesterification was not restricted to ester functionalities alone, as chain coupling reactions were also observed for polycyclohexene carbonate. However, the transesterification of carbonate functionalities is considerably slower than the propagation reaction and will only become visible at high monomer conversions.

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(23) Figure 2 shows another small peak 2149.74 and 2349.81 *m*/*z* that corresponds to a structure containing $-OC_6H_9(CO_2Me)OC(=O)-$ as the repeating unit and a $C_7H_9O_2$ end group.

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