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Chemoselective Alternating Copolymerization of Limonene Dioxide and Carbon Dioxide: A New Highly Functional Aliphatic Epoxy Polycarbonate

Chunliang Li, Rafaeıl J. Sablong,* and Cor E. Koning

Abstract: The alternating copolymerization of biorenewable limonene dioxide with carbon dioxide (CO₂) catalyzed by a zinc β-diiminate complex is reported. The chemoselective reaction results in linear amorphous polycarbonates that carry pendant methyloxiranes and exhibit glass transition temperatures (T_g) up to 135°C. These polycarbonates can be efficiently modified by thiols or carboxylic acids in combination with lithium hydroxide or tetrabutylphosphonium bromide as catalysts, respectively, without destruction of the main chain. Moreover, polycarbonates bearing pendant cyclic carbonates can be quantitatively prepared by CO₂ insertion catalyzed by lithium bromide.

Aliphatic polycarbonates (APCs) have received extensive attention due to their potential recyclability and biodegradability.[1] An attractive method for preparing APCs is the alternating copolymerization of epoxides with carbon dioxide. The number of epoxide monomers and efficient catalysts has increased tremendously since 1969, when Inoue reported the first example of such a reaction.[2] The most commonly studied polycarbonates are two petroleum-based derivatives, poly(cyclohexene carbonate) (PCHC) and polypropylene carbonate (PPC), of which PPC has been marketed as a polyol building block for polyurethane synthesis.[3] So far, PCHC and PPC as such have limited commercial applications because of their unsatisfactory physical and mechanical properties, for example, poor hydrophilicity and low elongation at break.[4] Moreover, the lack of additional functionality in the corresponding epoxides makes it rather difficult to enhance the properties by chemical modification. On the other hand, the selective polymerization of functional epoxides, epoxy monomers with an extra functionality like an alkanyl, carbonate, or hydrophilic group, leads to functional polyurathanes (NIPUs) that exhibit promising properties.[9] So far, PCHC and PPC as such have limited commercial applications because of their unsatisfactory physical and mechanical properties, for example, poor hydrophilicity and low elongation at break.[4] Moreover, the lack of additional functionality in the corresponding epoxides makes it rather difficult to enhance the properties by chemical modification. On the other hand, the selective polymerization of functional epoxides, epoxy monomers with an extra functionality like an alkanyl, carbonate, or hydrophilic group, leads to functional polymers of interest for many applications such as reactive substrates, coating resins, polymeric nanoparticles, and electronic and biomedical materials.[5] Among the functional epoxides, limonene 1,2-monoepoxide (LMO) is derived mainly from the (R)-limonene isomer present in orange oils (see Figure 1), is used as a flavor agent, in the fragrance industry, and as a green solvent.[6] Since the first report in 2002 on the alternating copolymerization of LMO and CO₂ catalyzed by a β-diiminate (BDI) zinc acetate complex, efforts have been made to investigate the specific properties and potential applications of such limonene-based polycarbonates.[5,7]

Limonene dioxide (LDO), the diepoxide counterpart of LMO, normally exists as a mixture of four isomers (see Figure 1a–d). It is widely used as reactive diluent in cationic UV-curing applications.[8] It has also been recently employed in the synthesis of cyclic limonene dicarbonate, a monomer for the production of linear and cross-linked poly(hydroxy urethanes). The reaction of this dicyclic carbonate with polyanimes results in thermoset, non-isocyanate oligo and polyurethanes (NIPUs) that exhibit promising properties.[9] The cycloaliphatic oxirane (1,2-epoxide) and 1,1-disubstituted oxirane (8,9-epoxide) moieties in LDO show a significant difference in their respective reactivity.[9] Using this disparity, we report in this work the chemoselective alternating copolymerization of LDO with CO₂, yielding aliphatic polycarbonates with a high number of pendant epoxide groups, namely, poly(limonene-8,9-epoxide carbonate) (PLOC). To our best knowledge, this is the first report on the synthesis of such linear, non-gelling epoxy-functionalized PCs, at high monomer conversion using a diepoxide and CO₂.[11]

Based on the conditions used for the LMO/CO₂ system, initial copolymerizations with commercially available LDO were performed in bulk at 25°C under 10 bar of CO₂ using 1.0 mol% of the zinc catalyst (Et-BDI)Zn[N(SiMe₃)₂] (see Scheme 1).[5,6] The polymerization results are summarized in

Figure 1. (R)-limonene and the corresponding 1,2-mono- and 1,2,8,9-diepoxides.
Table 1. The molecular weight of the polymers and the monomer conversion first increased rapidly with the reaction time. After 6 hours, the molecular weight reached 19.4 kDa for an LDO conversion of 34% (Table 1, Entry 1). The reaction subsequently slowed down as a result of the decreasing monomer concentration and increasing viscosity of the reaction mixture, yielding an LDO conversion of 44% after 18 h. Increasing the CO₂ pressure to 40 bar slightly enhanced the catalytic activity (Table 1, compare Entries 1 and 3 as well as 5 and 7). The maximum LDO conversion reached was 53% after 48 h (Table 1, Entry 4), as most of the cis-1,2-epoxides (Figure 1c,d) remained unreacted as indicated by ¹H NMR. Coates reported a similar stereo-selective preference for the LMO/CO₂ copolymerization.[7c] The reactions with a high catalyst loading yielded polymers with number average molecular weight values obtained by gel permeation chromatograph, $M_n$ (GPC), higher than the theoretical values, which were calculated using the ¹H NMR monomer conversion and the catalyst concentration, $M_n$ (theory). The observed effect is most likely caused by a monomer–dimer equilibrium of the catalyst, which leads to a high concentration of the active dimeric zinc complex in the reaction solution, as a result of the high initial catalyst concentration.[12] An increase of the [LDO]/[Zn] ratio to 250 resulted in a decrease of the polymerization rate. A conversion of merely 36% was reached after 12 h (Table 1, Entry 5), compared to 34% after 6 h for Entry 1 (Table 1) with [LDO]/[Zn] = 100. $M_n$(GPC) values increased from 19.4 (Table 1, Entry 1) to 24.9 kDa (Table 1, Entry 5) accordingly, but not proportionally to the [LDO]/[Zn] feed ratio. A possible explanation is that the concentration of the dimeric zinc complex decreases with the decreasing initial catalyst concentration. It is worth mentioning that the polydispersities of the polymers were rather narrow (1.3–1.4), suggesting no branching or crosslinking side reactions caused by ring-opening reaction of the 8,9-epoxy group of LDO, not even for the nearly complete trans-LDO conversions (Table 1, Entry 9). The MALDI-TOF mass spectra showed different distributions separated by the molecular weight of a repeating unit (212 Da), exactly the sum of the molar mass of LDO and CO₂ (see Figure S10 in the Supporting Information). These results also point to a chemoselective copolymerization.

The ¹H NMR spectra of the products obtained at the beginning of the reaction (reaction time < 6 h) were consistent with regio-regular copolymers, as illustrated by the single methine resonance at $\delta = 5.05$ ppm, attributed to a head-to-tail linkage. A new resonance, appearing after 6 h at $\delta = 5.12$ ppm, was assigned to tail-to-tail linkages, whose content in the copolymer increased gradually to 7–9 mole %, as a result of the incorporation of cis-1,2-epoxides with a prolonged reaction time (>48 h). As the zinc catalyst shows a superior selectivity for trans-1,2-epoxides, the content of the cis-isomers in the monomers increases along with the consumption of the former. Thus, the latter have a higher chance of being incorporated into the polymer, especially in the late stages of the reaction. Additionally, no evidence for polyether formation was observed. NMR revealed the presence of one pendent oxirane, namely, the 8,9-epoxide, per monomer unit, indicating chemoselective copolymerization. The BDI zinc complex employed in our study has been reported to be inactive in the PO/CO₂ reaction for producing PPC or propylene carbonate.[13] Therefore, a preferred reactivity of (Et-BDI)Zn[N(SiMe₃)₂] towards the 1,2-epoxide group of LDO is expected due to the even bulkier substituent in the 8,9-epoxy moiety compared with PO. The ¹H NMR spectra of the PLOCs from Table 1 revealed low intensity signals in the cyclic carbonate methylene region ($\delta = 4.0$ and 4.2 ppm). Considering the absence of cyclic carbonate formation during the LMO/CO₂ copolymerization, the origin of cyclic carbonate is attributed to the 8,9-epoxide.[7b] However, the conversion of the pendant epoxides into cyclic carbonate remained limited (below 5%), even after reaction times up to 48 h at high catalyst loadings (Table 1, Entry 4). The presence of small amounts of cyclic carbonate groups in the polymer was confirmed by IR as the absorption band of $\nu_{\text{C=O}}$ at 1800 cm⁻¹.[9]
It is worth mentioning that the Et-BDI zinc complex, which is inactive towards the PO/CO₂ reaction, showed a significant activity for the CHO/CO₂ copolymerization. However, the copolymerization of vinyl cyclohexene dioxide (VCHDO), which bears a mono-substituted oxirane similar to PO, catalyzed by the same Zn species led to gelation (Entry 10 in Table 1). Soluble aliphatic polycarbonates with a tunable number of cyclic carbonate and epoxide pendant groups have been synthesized through (ONSO)CrCl medi- vated VCHDO/CO₂ copolymerizations. However the broad molecular weight distributions of these polycarbonates, even for relatively low monomer conversions, indicate a limited chemoselectivity. These results suggest that the presence of the methyl vicinal to the oxygen atom in the 8,9-epoxy group could be crucial to high chemoselectivity. To our best knowledge, other than the zinc β-diminate complex, only the amino-trisphenolene aluminum compounds described by Kleij et al. showed, when combined with bis(triphenylphospho- phorylily-dene)ammonium chloride (PPNCl) as a co-catalyst (Scheme 1), a remarkable catalytic activity in the LMO/CO₂ copolymerization, even in the presence of protic species like methanol and water. The LDO/CO₂ copolymerization catalyzed by this complex resulted in a viscous mixture without gelation after 22 h of reaction at 42 °C under 10 bar of CO₂. GPC analysis revealed that the mixture contained low molecular weight polymers and oligomers (see Entry 11, Table 1). Kleij and co-workers found that the stirring technique had a significant effect on the molecular weight of the resultant copolymer. The observation was most likely due to the weak stirring during the reaction. IR spectroscopy verified the formation of cyclic carbonate, probably issued from the 8,9-epoxy group since LMO/CO₂ copolymerization using the same complex showed a high selectivity for the copolymer. The presence of oligomers caused overlapping resonances with the cyclic carbonate species, so the LDO conversion for Entry 11 (Table 1) could not be determined by 'H NMR spectroscopy.

In comparison with the known PLCs, PLOC offers a more universal platform to develop new materials with specific functional properties in view of the high versatility of the epoxy groups. The pendant oxirane groups of PLOC underwent ring opening reactions using several nucleophiles, including 2-mercaptoethanol and acrylic acid (AA, see Scheme 2), as model reactions for (bio)functionalization, crosslinking, or grafting of other polymers. The stability of the polycarbonate backbone was verified after modification, such as crosslinking or grafting of other polymers. The stability of the polycarbonate backbone was verified after modification, such as crosslinking or grafting of other polymers.

The results are summarized in Table 2. The parent polymer P1 with a $T_g$ of 135 °C was obtained from Entry 7 in Table 1. The pendant oxiranes reacted almost quantitatively with thiol compounds in the presence of lithium hydroxide as the catalyst (5 mol relative to the oxirane groups), generating thioether species without breakdown of the main chain (see Supporting Information). The molecular weights of the polymers increased with the size of the pendant groups after the modification reactions. The reaction with 1-dodecanethiol resulted in polymer P2 with an $M_w$ of 16.2 kDa and a $T_g$ of 13 °C, indicating a significant $T_g$ lowering effect of the dodecylsulfide group. The reaction of P1 with 2-mercaptoglycidyl generated copolymer P3, carrying primary OH functionalities, with an $M_w$ of 11.8 kDa and a $T_g$ of 118 °C. The coupling reactions of carboxylic acids with the pendant oxiranes were also very efficient at 115 °C, using tetrabutylphosphonium bromide (1 mol%) as the catalyst. The molecular weight increase after the modification was consistent with a stable polycarbonate backbone under acidic conditions. The $T_g$ NMR spectra of the resulting materials were in agreement with the formation of a tertiary alcohol issued from an $S_N2$ reaction following an attack on the least hindered end of the 8,9-epoxide. A conversion of 80% of pendant 8,9-epoxide groups was observed for the modification of P1 with 6-hexanoic acid, which led to P4 with an $M_w$ of 13.9 kDa. The reaction of PLOC and AA yielded polymer P5 with an $M_w$ of 14.1 kDa. Interestingly, the grafting of the dimer of AA, produced through Michael addition side reactions was revealed by $T_g$ NMR. The grafting of the AA dimer and 6-hexanoic group decreased the $T_g$ to 39 °C and 46 °C, respectively.

The modification with aliphatic amines was moderately successful, even in the presence of efficient catalysts for the monosubstituted epoxy-amine reaction like triethylamine, 4-dimethyaminoptyridine, lithium trifluoromethanesulfonate, and iron(III) perchlorate hydrate. Indeed, at low temper-
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Cyclic carbonates are often used in oxyalkylation reactions of −OH, −SH, or aromatic amine groups in place of oxiranes, which can be more difficult to handle.


[15] We performed LMO/CO₂ copolymerizations using the amino trisphenolate aluminum complex as the catalyst. The molecular weight of the resulting polymers could be controlled by adding water as a chain transfer agent.
Chemoselective Alternating Copolymerization of Limonene Dioxide and Carbon Dioxide: A New Highly Functional Aliphatic Epoxy Polycarbonate

Von biobasiertem Diepoxid zu linearen Epoxy-PCs: Ein nachhaltiges Poly(limonen-8,9-oxidcarbonat) wurde durch chemoselektive Copolymerisation von Limonendioxid und CO₂ hergestellt. Die 2-Methyloxiranyl-Gruppen entlang der Polymerkette ermöglichen die leichte Postmodifikation und Insertion von CO₂ zur Bildung cyclischer Carbonate als funktionelle Seitengruppen.