Chemoselective alternating copolymerization of limonene dioxide and carbon dioxide

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

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

Abstract: The alternating copolymerization of biorenewable limonene dioxide with carbon dioxide (CO₂) catalyzed by a zinc β-diamininate 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 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-diaminate (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 urethane)s. The reaction of this dicyclic carbonate with polyamines 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.[10] Utilizing 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-oxide carbonate) (PLOC). To our best knowledge, this is the first report on the synthesis of such linear, non-gelling epoxide-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).[5b, 5e] The polymerization results are summarized in...
These are not the final page numbers!

Table 1. Effect of experimental conditions on \((\text{LDO})/\text{CO}_2\) copolymerization.

<table>
<thead>
<tr>
<th>Entry</th>
<th>([\text{LDO}]/[\text{Zn}])</th>
<th>(p_{\text{CO}}) [bar]</th>
<th>Time [h]</th>
<th>Conv. (%)</th>
<th>(M_n) [kDa]</th>
<th>(M_w/M_n)</th>
<th>% trans(^\text{c})</th>
</tr>
</thead>
<tbody>
<tr>
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<td>10</td>
<td>6</td>
<td>34</td>
<td>19.4</td>
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<td>98</td>
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<tr>
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<td>10</td>
<td>18</td>
<td>44</td>
<td>22.4</td>
<td>1.44</td>
<td>95</td>
</tr>
<tr>
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<td>40</td>
<td>6</td>
<td>45</td>
<td>23.9</td>
<td>1.41</td>
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<td>12</td>
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<td>12</td>
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<td>1.27</td>
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<td>13</td>
<td>7.5</td>
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<td>100</td>
<td>10</td>
<td>22</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

[a] Reactions were performed in neat LDO (2 mmol) at 25 °C. [b] Conversion of LDO, determined by \(^1\)H NMR spectroscopy. [c] Determined by GPC in THF at 25 °C, calibrated with polystyrene standards. [d] Percentage of the trans monomer unit in the copolymer, determined by \(^1\)H NMR. [e] VCHDO used. [f] amino-trisphenolate aluminium complex (All)/[PPNCI] = 1/1 used, 45 °C. [g] Value not determined due to signal overlap.

of the reaction mixture, yielding an LDO conversion of 44 % after 18 h. Increasing the \(CO_2\) 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 \(^1\)H NMR. Coates reported a similar stereo-selective preference for the LMO/\(CO_2\) copolymerization.\(^{[7a]}\) 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 \(^1\)H NMR monomer conversion and the catalyst concentration, \(M_c\) (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.\(^{[7a]}\) An increase of the \([\text{LDO}] / [\text{Zn}]\) 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 \([\text{LDO}] / [\text{Zn}]\) = 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 \([\text{LDO}] / [\text{Zn}]\) 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 \(CO_2\) (see Figure S10 in the Supporting Information). These results also point to a chemoselective copolymerization.

The \(^1\)H 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 \(\delta = 5.05 \text{ ppm}\), attributed to a head-to-tail linkage.\(^{[7a]}\) A new resonance, appearing after 6 h at \(\delta = 5.12 \text{ ppm}\), 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 chemo-selective copolymerization. The BDI zinc complex employed in our study has been reported to be inactive in the PO/\(CO_2\) reaction for producing PPC or propylene carbonate.\(^{[11]}\) Therefore, a preferred reactivity of (Et-BDI)Zn[N(SiMe$_3$)$_2$] towards the 1,2-epoxide group of LDO is expected due to the even bulkier substituents in the 8,9-epoxide moiety compared with PO. The \(^1\)H 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/\(CO_2\) copolymerization, the origin of cyclic carbonate is attributed to the 8,9-epoxide.\(^{[7c]}\) However, the conversion of the pendent 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 \(/C=C/\) at 1800 cm$^{-1}$.
It is worth mentioning that the Et-BDI zinc complex, which is inactive towards the PO/CO\textsubscript{2} reaction, showed a significant activity for the CHO/CO\textsubscript{2} copolymerization.\cite{7c,13} 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-mediated VCHDO/CO\textsubscript{2} copolymerizations.\cite{14} 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 \(\beta\)-diminate complexes, only the amino-triphenolate aluminum compounds described by Kleij et al. showed, when combined with bis(triphenylphosphoranyl-diene)ammonium chloride (PPNCl) as a co-catalyst (Scheme 1), a remarkable catalytic activity in the LMO/CO\textsubscript{2} copolymerization, even in the presence of protic species like methanol and water.\cite{7b,15} The LDO/CO\textsubscript{2} copolymerization catalyzed by this complex resulted in a viscous mixture without gelation after 22 h of reaction at 42 °C under 10 bar of CO\textsubscript{2}. 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.\cite{7h} 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/CO\textsubscript{2} copolymerization using the same complex showed a high selectivity for the copolymer. The presence of oligomers caused overlapping resonances with the cyclic carbonate species,\cite{7i} so the LDO conversion for Entry 11 (Table 1) could not be determined by \(^1\)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.\cite{7j} 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, even in the presence of protic species like carboxylic acids, amines, and inorganic hydroxide can promote the degradation of the polycarbonates.\cite{16} 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).\cite{19} 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 \(M_n\) 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-mercaptocarboxylic acid (COOH) generated copolymer P3, carrying primary OH functionalities, with an \(M_n\) of 11.8 kDa and a \(T_g\) of 115 °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.\cite{20} The molecular weight increase after the modification was consistent with a stable polycarbonate backbone under acidic conditions. The \(^1\)HNMR 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-epoxy groups was observed for the modification of P1 with 6-hexanoic acid, which led to P4 with an \(M_n\) of 13.9 kDa. The reaction of PLOC and AA yielded polymer P5 with an \(M_n\) of 14.1 kDa. Interestingly, the grafting of the dimer of AA, produced through Michael addition side reactions was revealed by \(^1\)HNMR.\cite{21} 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-dimethylaminopyridine, lithium trifluoromethanesulfonate, and iron(III) perchlorate hydrate.\cite{22} Indeed, at low temper-
atures, no reaction occurred owing to the low reactivity of the 1,1'-disubstituted oxiranes, whereas degradation of the poly-
mer main chain was promoted at high temperatures. The
selection of proper catalysts for this specific modification is
still ongoing. The high reactivity of limonene dicyclic
ketone towards aliphatic amines\(^{[23]}\) prompted us to convert
the pendant oxiranes into cyclic carbonates by CO\(_2\) inser-
tion.\(^{[23]}\) The reaction proceeded quantitatively using NaBr
(5 mol %) as the catalyst, affording a new polymer with a
polycarbonate backbone and a cyclic carbonate side group
(5 mol%) as the catalyst, affording a new polymer with
5.

A preliminary curing experiment has been performed to
explore the potential use of PLOC as a thermoset coating
resin. P1 was mixed with trimethylolpropane tri(3-mercapto-
acetone resistance, high pencil hardness (2H) and high
pendulum hardness.

In conclusion, we report the chemoselective copolymer-
ization of limonene dioxide with CO\(_2\), catalyzed by an Et-BDI
zinc amido complex, to yield new polycarbonates bearing
pendent epoxide groups. The polymers exhibit \(T_g\) values up to
135 °C. Additionally, the poly(limonene-8,9-oxide carbonate)
readily undergoes chemical modifications by catalyzed epox-
ide ring-opening reactions with thiols and carboxylic acids or
CO\(_2\) insertion, without affecting the polycarbonate main
chain. The versatile functionality, the tunable \(T_g\) and the
abundance of the monomer make the fully bio-based
polycarbonates promising materials for many applications
like epoxy resins, drug delivery systems, tissue engineering,
or NIPU precursors. We are currently investigating the use
of this novel class of materials as thermoset coating resins.

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homogeneous catalysis · post-modification ·
renewable resources

\[^{[1]}\] a) M. Werner, S. David, in Advances in Polycarbonates, Vol. 898,
American Chemical Society, Washington, 2005, pp. 244; b) T.
Artham, M. Doble, Macromol. Biosci. 2008, 8, 14; c) J. Feng,
Niaounakis, Biopolymers: Reuse, Recycling, and Disposal,
William Andrew, Elservier, Oxford, 2013; e) J. Xu, E. Feng, J.
Song, J. Appl. Polym. Sci. 2014, 131, 39822; f) K. Fukushima,

\[^{[2]}\] a) M. I. Childers, J. M. Longo, N. J. Van Zee, A. M. LaPointe,
G. W. Coates, Chem. Rev. 2014, 114, 8129; b) D. J. Darenbourg,
Inorg. Chem. 2010, 49, 10765; c) M. Taheirimehr, P. P. Pescar-
2011, 255, 1460; e) H. Sugimoto, S. Inoue, Kobunshi Ronbunshu
2005, 62, 131; f) D. J. Darenbourg, R. M. Mackiewicz, A. L.
Phelps, D. R. Billodeaux, Acc. Chem. Res. 2004, 37, 836; g) C. K.
Williams, G. Trott, P. Saini, Philos. Trans. R. Soc. A 2016, 374,
20150085.

\[^{[3]}\] a) C. A. Simoneau (NOVOMER INC), WO2015154001-A1,
2015; b) S. D. Allen, A. E. Cherian, G. W. Coates, J. J. Farmer,
A. Gründen, R. E. Lapointe, C. A. Simoneau (NOVOMER INC),
WO2010022388-A2, 2010; c) S. D. Allen, A. E. Cherian,
G. W. Coates, J. J. Farmer, A. A. Gründen, C. A. Simoneau

\[^{[4]}\] a) G. A. Linastra, Polym. Rev. 2008, 48, 192; b) G. A. Linastra,
E. Borchartd, in Synthetic Biodegradable Polymers, Vol. 245
(Eds.: B. Rieger, A. Kunkel, G. W. Coates, R. Reichardt,
E. Nijenhuis, W. J. Mijks, Macromol. Chem. Phys. 1982,
183, 2085; c) J. Lukaszczyk, K. Jaszez, W. Kuran, T. Listoń,
Macromol. Biosci. 2001, 1, 282; d) J. C. Jansen, R. Addink,
200, 1473; g) J. C. Jansen, R. Addink, K. T. Nijenhuis,
2005, 4, 571; j) M. Takashashi, Y. Nomura, Y. Yoshida, S. Inoue,
Makromol. Chem. 1982, 183, 2085; c) J. Lukaszczyk, K. Jaszez,
W. Kuran, T. Listoń, Macromol. Biosci. 2001, 1, 282; d) Y. Qin,
X. Wang, X. Zhao, F. Wang, Acta Polym. Sin. 2015, 4, 571; m) D.
1982, 183, 2085; c) J. Lukaszczyk, K. Jaszez, W. Kuran, T. Listoń,
Int. Ed. 2015, 54, 10206; Angew. Chem. 2015, 127, 10344; i) D. J.
Darenbourg, W. Chung, J. A. Christopher, F. T. Tsai, S. J.
Kyran, Macromolecules 2014, 47, 7347; m) D. J. Darenbourg,
W. Yang, Polym. Chem. 2015, 6, 1768.


[7] a) O. Hauenstein, M. Reiter, S. Agarwal, B. Rieger, A. Greiner,
Green Chem. 2016, 18, 760; b) L. Peña Carrodugas, J. Gonzá-
2015, 21, 6115; c) C. M. Byrne, S. D. Allen, E. B. Lobkovsky,
G. W. Coates, J. Am. Chem. Soc. 2004, 126, 11404; d) F.
Auriemma, C. De Rosa, M. R. Di Caprio, R. Di Girolamo,
W. C. Ellis, G. W. Coates, Angew. Chem. Int. Ed. 2015, 54,
1215; Angew. Chem. 2015, 127, 1231; f) F. Auriemma, C.
De Rosa, M. R. Di Caprio, R. Di Girolamo, G. W. Coates,
Macromolecules 2015, 48, 2534; f) O. Hauenstein, S. Agarwal,
A. Greiner, Nat. Commun. 2016, 7, 11862.

GB2461624-B, 2010; b) R. P. Eckberg (General Electric Co),
US4547341-A, 1985; c) R. Akiyama, T. Ushirogochi, Y. Kawa-

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[15] We performed LMO/CO$_2$ 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.


[23] 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.


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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.