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

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Abstract: *The alternating copolymerization of biorenewable limonene dioxide with carbon dioxide (CO_2) catalyzed by a zinc β-diiminate complex is reported. The chemoselective reaction results in linear amorphous polycarbonates that carry pendent 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 pendent cyclic carbonates can be quantitatively prepared by CO_2 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 alkenyl, 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 CO_2 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.[5j,7]

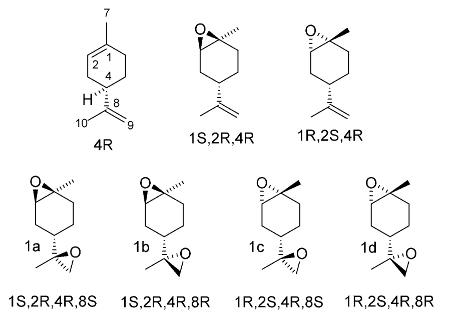

Figure 1. (*R*)-limonene and the corresponding 1,2-mono- and 1,2:8,9-diepoxides.

Limonene dioxide (LDO), the diepoxide counterpart of LMO, normally exists as a mixture of four isomers (see Figure 1 a–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 CO_2, 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 CO_2.[11]

Based on the conditions used for the LMO/CO_2 system, initial copolymerizations with commercially available LDO were performed in bulk at 25°C under 10 bar of CO_2 using 1.0 mol% of the zinc catalyst (Et-BDI)Zn[N(SiMe$_3$)$_2$] (see Scheme 1).[5j,7c] The polymerization results are summarized in

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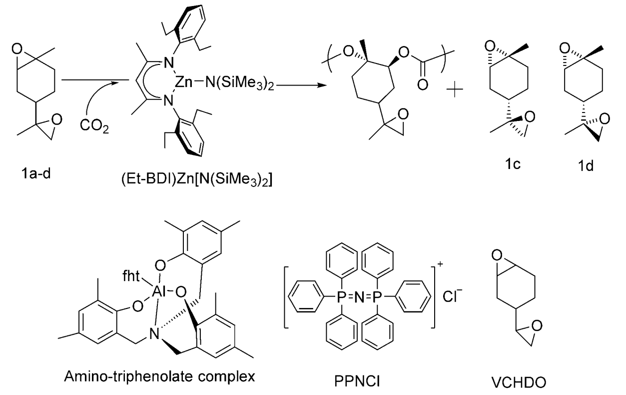


Scheme 1. Copolymerization of limonene dioxide with CO$_2$.

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 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 1 c,d) remained unreacted as indicated by ^{1}H NMR. Coates reported a similar stereo-selective preference for the LMO/CO$_2$ 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 ^{1}H 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 CO$_2$ (see Figure S10 in the Supporting Information). These results also point to a chemoselective copolymerization.

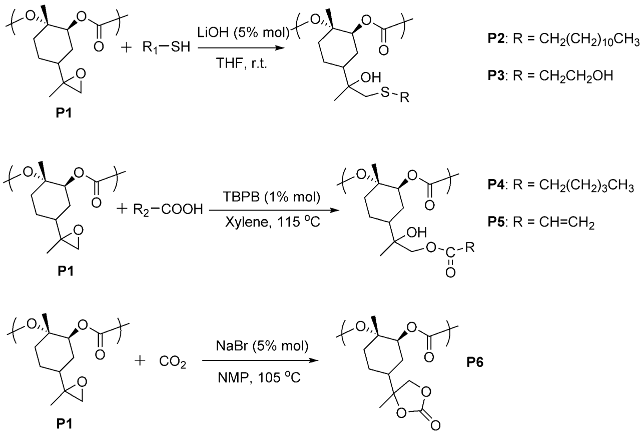
Table 1: Effect of experimental conditions on (*R*)-LDO/CO$_2$ copolymerization using (Et-BDI)Zn[N(SiMe$_3$)$_2$] as the catalyst.[a]

Entry	[LDO]/[Zn]	P_{CO2} [bar]	Time [h]	Conv. %[b]	M_n [kDa][c]	M_w/M_n[c]	% *trans*[d]
1	100	10	6	34	19.4	1.34	98
2	100	10	18	44	22.4	1.44	95
3	100	40	6	45	23.9	1.41	98
4	100	40	48	53	28.5	1.57	91
5	250	10	12	36	24.9	1.27	96
6	250	40	3	13	7.5	1.27	99
7	250	40	5	20	11.4	1.29	98
8	250	40	12	44	29.8	1.29	95
9	250	40	48	50	30.7	1.33	93
10[e]	100	10	22	ND	ND	ND	ND
11[f]	100	10	16	ND	2.6	1.95	ND[g]

[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 (Al]/[PPNCl] = 1/1) used, 45 °C. [g] Value not determined due to signal overlap.

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 $\delta = 5.05$ ppm, attributed to a head-to-tail linkage.[7c] 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/CO$_2$ reaction for producing PPC or propylene carbonate.[13] 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 $\nu_{C=O}$ at 1800 cm^{-1}.[9]

It is worth mentioning that the Et-BDI zinc complex, which is inactive towards the PO/CO_2 reaction, showed a significant activity for the CHO/CO_2 copolymerization.[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 pendent groups have been synthesized through (ONSO)CrCl-mediated VCHDO/CO_2 copolymerizations.[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 β-diiminate complexes, only the amino-trisphenolate aluminum compounds described by Kleij et al. showed, when combined with bis(triphenylphosphoranyli-dene)ammonium chloride (PPNCl) as a co-catalyst (Scheme 1), a remarkable catalytic activity in the LMO/CO_2 copolymerization, even in the presence of protic species like methanol and water.[7b,15] The LDO/CO_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_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.[7b] 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_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,[16] so the LDO conversion for Entry 11 (Table 1) could not be determined by ^{1}H NMR spectroscopy.



Scheme 2. Post-modification of PLOC with different functional compounds.

Table 2: Post-modification of PLOC.[a]

Entry	Reactant	Conv. %[b]	M_n [kDa][c]	M_w/M_n[c]	T_g [°C]
P1[d]	–	–	11.4	1.29	135
P2	$CH_3(CH_2)_{10}CH_2$−SH	98	16.2	1.35	13
P3	$HOCH_2CH_2$−SH	99	11.8	1.47	118
P4	$CH_3(CH_2)_3CH_2$−COOH	80	13.9	1.31	39
P5[e]	CH_2=CH−COOH	90	14.1	1.45	46
P6[f]	CO_2	99	11.2	1.35	146

[a] Reactions conditions: 12 h. [epoxy]:[R-XH] = 1:1.1. [b] Conversion of pendent 8,9-epoxide group, determined by ^{1}H NMR. [c] Determined by GPC in THF at 25 °C, calibrated with polystyrene standards. [d] Polymer from Entry 7, Table 1. [e] [epoxy]:[AA] = 1:2. [f] CO_2 insertion.

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.[17] The pendent 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, since carboxylic acids, amines, and inorganic hydroxide can promote the degradation of the polycarbonates.[18] 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 pendent 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).[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-mercaptoethanol generated copolymer **P3,** carrying primary OH functionalities, with an M_n of 11.8 kDa and a T_g of 118 °C. The coupling reactions of carboxylic acids with the pendent oxiranes were also very efficient at 115 °C, using tetrabutylphosphonium bromide (1 % mol) as the catalyst.[20] The molecular weight increase after the modification was consistent with a stable polycarbonate backbone under acidic conditions. The ^{1}H 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 pendent 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}H NMR.[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.[22] Indeed, at low temperatures, no reaction occurred owing to the low reactivity of the 1,1′-disubstituted oxiranes, whereas degradation of the polymer 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 carbonate towards aliphatic amines[9] prompted us to convert the pendent oxiranes into cyclic carbonates by CO_2 insertion.[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 on each repeating unit (Scheme 2), as indicated by ^{1}H NMR. This was confirmed by the appearance of new signals at 4.0 and 4.2 ppm and the disappearance of the oxirane protons at 2.5–2.7 ppm.[24] The resulting polymer **P6** showed a minor decrease in M_n with respect to the base polymer **P1**, possibly due to the difference in hydrodynamic volume between them, and exhibited a T_g of 146 °C.

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-mercaptopropionate) (TMPMP) in an epoxy/thiol molar ratio of 2 and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as the catalyst. The mixture was cured at 160 °C and a highly transparent film F1 with a T_g of circa 150 °C, as determined by dynamic mechanical thermal analysis (DMTA, see Figure S13 in the Supporting Information) was obtained. The coating based on the mixture showed promising properties such as good acetone resistance, high pencil hardness (2H) and high pendulum hardness.

In conclusion, we report the chemoselective copolymerization 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 epoxide 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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