

Alternating Copolymerization of Limonene Oxide and Carbon Dioxide

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The discovery and use of abundant naturally occurring compounds for chemical synthesis is an important strategy for reducing our dependence on petroleum-derived raw materials.^{1,2} The use of carbon dioxide as an inexpensive C₁ feedstock is of particular note, especially for the alternating copolymerization with epoxides.³ While the use of CO₂ does carry several benefits, such as low toxicity and general abundance, most epoxide/CO₂ copolymerization systems focus on petroleum derivatives such as propylene oxide or cyclohexene oxide.³ While new substrates have been explored,⁴ the use of epoxides based on biorenewable resources has not been reported. Given our previous work on the copolymerization of epoxides and CO₂ using β -diiminato (BDI) zinc complexes,⁵ we focused on limonene oxide (**1**), derived from the naturally occurring cyclic monoterpene, limonene.

Produced by more than 300 plants, limonene is the most common terpene.⁶ The (*R*)-enantiomer constitutes 90–96% of citrus peel oil,⁷ and its world production is estimated to be between 110 and 165 million pounds per year.⁸ Though the alicyclic epoxide is commercially available as a mixture of the *trans* (**1a**) and *cis* (**1b**) diastereomers (Scheme 1), kinetic resolution successfully affords either **1a** or **1b** in >98% de.⁹ Its abundance, low cost, and structural similarity to cyclohexene oxide make (*R*)-limonene oxide (LO) an excellent choice as a biorenewable epoxide monomer for copolymerization with CO₂. Herein, we describe the alternating copolymerization of LO and CO₂ to give a new biodegradable polycarbonate from biorenewable resources, proceeding with highly selective incorporation of **1a** under mild conditions.

On the basis of the conditions used for the cyclohexene oxide/CO₂ system, we performed initial copolymerizations using 0.4 mol % **2** with commercially available **1** (**1a**:**1b** = 1.2:1) at 50 °C and 100 psi CO₂. Long reaction times (24 h) were required for appreciable conversion (15%) with good selectivity for **1a** (Table 1, entry 1). After 2 h, polymer formation was not observed by ¹H NMR spectroscopy. Lowering the temperature to 35 °C resulted in improved catalytic activity and greater selectivity for **1a** (entry 2). The optimal balance of high catalytic activity and selectivity was achieved at 25 °C, yielding regioregular polycarbonate **11** (entry 3). Overall, copolymerization activities decline drastically at any temperature above 35 °C or below 25 °C (entries 4, 5), while selectivity is compromised beyond 35 °C. At 50 °C, the copolymerization yields **12**, which exhibits a broadened molecular weight distribution (MWD = M_w/M_n = 1.34).

The copolymer regiochemistry can be determined by ¹H NMR spectroscopy. Copolymer **11** exhibits a single resonance in the polycarbonate methine region (δ 4.9 to 5.2 ppm), while **12** displays a pair of resonances, representing head-to-tail and tail-to-tail linkages.¹⁰ Lower temperature copolymerizations give polycarbonate **11** through repeated regio- and stereoregular ring opening of **1a**. Additionally, the regioregular polymers have narrow MWDs and M_n values in agreement with [epoxide]/[Zn] ratios.¹¹ A sample of higher molecular weight polymer (M_n = 25 kg/mol; MWD = 1.16) was readily obtained using a *cis/trans* mixture of (*S*)-LO and 0.2

Scheme 1. Copolymerization of *trans*- (**1a**) and *cis*-(*R*)-Limonene Oxide (**1b**) and CO₂ using β -Diiminato Zinc Acetate Complexes

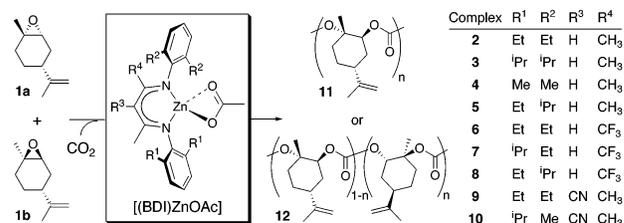


Table 1. Effects of Temperature and Pressure on (*R*)-Limonene Oxide and CO₂ Copolymerization using Complex **2a**

entry	<i>T</i> (°C)	<i>P</i> _{CO₂} (psi)	TOF ^b (h ⁻¹)	<i>M_n</i> ^c (kg/mol)	<i>M_w</i> / <i>M_n</i> ^c	% <i>trans</i> in copolymer ^d
1 ^e	50	100	1	4.5	1.34	86.9
2	35	100	33	6.9	1.24	96.8
3	25	100	32	9.3	1.13	98.3
4	10	100	4	ND ^f	ND ^f	ND ^f
5	0	100	0	ND ^f	ND ^f	ND ^f
6	25	50	17	4.0	1.14	98.4
7	25	250	28	6.2	1.12	98.6
8	25	400	27	6.0	1.12	98.5
9	25	550	21	4.5	1.14	98.7
10	25	700	16	3.7	1.13	99.1

^a Conditions: 0.4 mol % **2**, **1a**:**1b** = 1.2:1, 2 h. ^b TOF (turnover frequency) = mol LO·mol Zn⁻¹·h⁻¹, determined by ¹H NMR spectroscopy. ^c Determined by gel permeation chromatography (GPC). ^d Determined by ¹H NMR spectroscopy; see Supporting Information. ^e Time = 24 h. ^f Not determined; polymer not recoverable.

mol % **2** over 24 h at 25 °C and 100 psi CO₂. The effect of CO₂ pressure was also studied for copolymerizations at 25 °C using complex **2**. Between 100 and 400 psi, the copolymerization is essentially unaffected (entries 3, 7, 8), while pressures above (entries 9, 10) or below (entry 6) this range result in lower TOFs and M_n values.

Using this optimized set of conditions, we sought to identify the most active catalyst for the copolymerization. In previous work, systematic variation of [(BDI)ZnOAc] complexes revealed improved activity with electron-withdrawing groups on the ligand backbone and moderate steric bulk present at the ortho positions of the *N*-aryl rings.^{5c–e} Given that structurally similar catalysts displayed a broad range of activities, we synthesized and screened a collection of [(BDI)ZnOAc] complexes (**2–10**) for the copolymerization of LO and CO₂ (Table 2). Entries 1–3 emphasize the sensitivity of the copolymerization to ligand sterics. Complex **3**, with bulky isopropyl groups in the ortho positions, yields little polymer, most likely due to the inability of the complex to attain the necessary arrangement for epoxide enchainment. Decreasing steric bulk at the R¹ and R² positions to ethyl substituents (complex **2**) increases catalytic activity, while the use of methyl groups (complex **4**) results in no activity.

An electron-withdrawing trifluoromethyl group on the ligand backbone has a varying effect on catalytic activity as well (entries

Table 2. Effect of Ligand Variation on (*R*)-Limonene Oxide and CO₂ Copolymerization^a

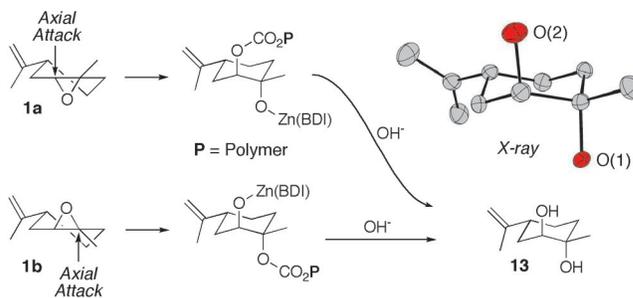
entry	complex	TOF ^{b,c} (h ⁻¹)	M _n ^d (kg/mol)	M _w /M _n ^d	% trans in copolymer ^e
1	2	32	9.3	1.13	98.3
2	3	10	ND ^f	ND ^f	ND ^f
3	4	0	ND ^f	ND ^f	ND ^f
4	5	16	4.8	1.13	99.2
5	6	29	7.8	1.12	99.5
6	7	20	5.5	1.15	99.3
7	8	37	10.8	1.12	98.9
8 ^g	8	19	8.1	1.14	98.5
9 ^g	9	9	ND ^f	ND ^f	ND ^f
10 ^g	10	3	ND ^f	ND ^f	ND ^f

^a Conditions: 0.4 mol % complex, 100 psi CO₂, 25 °C, **1a:1b** = 1.2:1, 2 h. ^b TOF = mol LO·mol Zn⁻¹·h⁻¹. ^c Determined by ¹H NMR spectroscopy. ^d Determined by GPC. ^e Determined by ¹H NMR spectroscopy; see Supporting Information. ^f Not determined; polymer not recoverable. ^g Performed with 1 mL of CH₂Cl₂, 4 h.

6–8). A comparison of complexes **2** and **6** offers essentially identical activities; however, for **5** and **8**, the electron-withdrawing group at the R⁴ position doubles the TOF. The location of the CF₃ group also dictates reactivity: complex **8** shows almost twice the activity of **7**. Substitution of a cyano group at the R³ position of the ligand resulted in complexes that were insoluble in neat epoxide. Copolymerizations with these complexes were run with 1 mL of CH₂Cl₂ and resulted in moderate TOFs after 4 h (entries 9, 10). Under the same conditions, complex **8** still gave superior reactivity. For all catalysts, the polycarbonate produced was **11** (by ¹H and ¹³C NMR analysis), which displayed narrow MWDs.

The selectivity demonstrated by these catalysts was confirmed by the copolymerization of pure **1a** with 0.4 mol % **2** at 100 psi CO₂. The reaction proceeds smoothly at 25 and 50 °C to give regioregular polycarbonate **11**. Attempted copolymerization of **1b** with CO₂ at both 25 and 50 °C after 24 h resulted in no observable reaction. Structural analysis of **11** using one- (¹H, ¹³C) and two-dimensional (HMBC, HSQC) NMR experiments revealed the polymer repeat unit to be consistent with the copolymer **11**; there is no indication of polyether linkages.⁵ Hydrolysis of copolymers **11** and **12** each yielded a single diol product, (1*S*,2*S*,4*R*)-1-methyl-4-(1-methylethenyl)-1,2-cyclohexanediol (**13**), matching an independently synthesized authentic sample and further characterized by single-crystal X-ray diffraction (Scheme 2). Given that copolymer **12** comprises both **1a** and **1b** and that hydrolysis yields a single repeat unit, the regiochemistry of the epoxide ring-opening can be explained. Nucleophilic attack on the epoxides occurs at different sites for each diastereomer, resulting from a preference for axial attack (Scheme 2).¹² The attack on **1a** occurs at the less hindered carbon, while attack on **1b** occurs at the tertiary carbon of the oxirane,¹³ both of which result in the (1*S*,2*S*,4*R*)-1-methyl-4-(1-methylethenyl)-1,2-cyclohexanediol (**13**). Since attack on a tertiary center (as in **1b**) is less favorable than on a secondary center (as in **1a**), **1a** is consumed more readily than **1b** at lower temperature.

In conclusion, we have demonstrated the alternating copolymerization of limonene oxide with CO₂. Complex **8** exhibits the best catalytic activity (TOF = 37 h⁻¹) and maintains superior selectivity for **1a** (% trans in copolymer = 98.9%). The alternating polycarbonate copolymer produced from a cis/trans mixture of epoxide is highly regio- and stereoregular. High molecular weight

Scheme 2. Ring Opening of **1a** and **1b** during Copolymerization and Hydrolytic Cleavage to Give Diaxial Diol **13**

polymer can be produced using longer reaction times and higher [epoxide]/[Zn] ratios.

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Supporting Information Available: General experimental procedures, selectivity data, TGA, DSC, and NMR data for polycarbonate polymers, and X-ray data for **13** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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