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Synthesis of Poly(indene carbonate) from Indene Oxide and Carbon Dioxide—A Polycarbonate with a Rigid Backbone

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Supporting Information

ABSTRACT: The catalytic coupling of carbon dioxide with indene oxide utilizing (salen)Co(III)-2,4-dinitrophenoxide in the presence of an onium salt is presented. X-ray structural data for indene oxide monomer as well as *cis*-indene carbonate display near planarity of the fused cyclopentene and benzene rings. Low temperature (0 °C) is required to selectively afford copolymer vs cyclic carbonate from the coupling reactions of CO_2 and indene oxide. The produced poly(indene carbonate) samples have molecular weights of up to 7100 Da, with corresponding glass transition temperatures of up to 134 °C, the highest yet reported for polycarbonates produced from CO_2/epoxides coupling. Poly(indene carbonate) is thermally stable up to 249 °C. The polymerizations are well controlled, with PDI values ≤1.3.

Polycarbonates are widely used thermoplastic polymers found in nearly every facet of our daily lives. The most common of these, bisphenol-A (BPA) polycarbonate, has numerous useful physical and mechanical properties, including high transparency to visible light and a high glass transition temperature (T_g) of ~150 °C.[1] Despite controversies regarding the safety of the material for foodstuff containers, BPA polycarbonate remains a valuable commodity in today's world. BPA polycarbonate and other polycarbonates are industrially produced through the polycondensation of a diol and phosgene or phosgene derivative in a biphasic medium. More recently, a greener and more sustainable commercial route has been developed by the Asahi Kasei Corp. which involves a phosgene-free production of BPA polycarbonate from bisphenol-A and diphenylcarbonate.[2] Beginning with Inoue's discovery in 1969, the catalytic coupling of oxiranes (epoxides) and carbon dioxide has become a viable alternative for the production of select polycarbonates.[3]

Most investigations of CO_2/epoxide copolymerization processes utilize cyclohexene oxide and propylene oxide monomers.[4] While the production of poly(cyclohexene carbonate) has numerous advantages (i.e., fast reaction time, relatively high T_g of ~115 °C, a variety of catalysts capable of production, typically low conversion to cyclic carbonate), the resulting polymer is brittle in nature and currently without many practical uses. On the other hand, poly(propylene carbonate) is an amorphous polymer with excellent mechanical properties but a rather low T_g (~41 °C) that limits its use to applications as ceramic binders, adhesives, coatings, and packaging materials.[5] Presently, Novomer in the US and SK in Korea have undertaken the industrial production of poly(propylene carbonate) through catalytic CO_2/propylene oxide copolymerization. Companies including Bayer, BASF, and Sumitomo are also conducting research into poly(propylene carbonate) commercialization. These operations represent the current industrial polycarbonate production processes involving CO_2/epoxide coupling utilizing homogeneous metal catalysts.

Still very important though far less numerous are investigations into other epoxide monomers. Monomers such as 1-butene oxide,[6] 1-hexene oxide,[6,7] and [2-(3,4-epoxycyclohexyl)ethyl]-trimethoxysilane[8] have been successfully polymerized with CO_2. Recently, Coates reported the co- and terpolymerization of CO_2 with several different cyclohexene oxides that had been functionalized at the monomer's 4-position.[9] Multiblock copolymers with up to seven distinct cyclohexene oxide-based blocks were formed. Also notable is the copolymerization of CO_2 and styrene oxide or epichlorohydrin to form polycarbonates with T_g = 80 and 31 °C, respectively.[3a,10,11]

Despite the significant progress in this field, the catalytic coupling of CO_2 and epoxides is still lacking in the production of polycarbonates with glass transition temperatures similar to that of BPA polycarbonate. In an effort to expand upon this horizon, our group published a 2004 report investigating the coupling of 2,3-epoxy-1,2,3,4-tetrahydronaphthalene (1,4-dihydronaphthalene oxide) and CO_2.[12] This monomer was chosen so that the bulky benzene rings would hinder molecular rotation of the polymer backbone and therefore increase the T_g. However, 1,4-dihydronaphthalene oxide was found to couple with CO_2 to selectively provide cyclic carbonate. We have recently begun reexamining these bulky epoxide monomers for polycarbonate formation. As in the case of 1,4-dihydronaphthalene oxide, we looked for available bulky olefins that we could convert to the corresponding epoxide. Indene, consisting of fused cyclopentene and benzene rings, is a readily available olefin found in 1 wt % of coal tar.[13] Its primary use is in the indene–coumarone resins (ICRs) found in paints, printing inks, adhesives, rubber, etc. produced globally at about 100 000 tonnes/yr.[13,14] Following epoxidation to indene oxide, this monomer represents a sound choice for CO_2 coupling with a bulky oxirane. In previous studies, indene,[15] indene oxide,[16] *trans*-2-bromo-1-indanol,[16] and *cis*-1,2-indandiol[17] have been employed as starting materials for the production of cyclic indene carbonate. Herein we report both the production of cyclic indene carbonate and the novel production of poly(indene carbonate) through the catalytic coupling of indene oxide and carbon dioxide (Scheme 1). To our knowledge, this marks the first time that an aromatic group has been rigidly incorporated into the polymer backbone utilizing CO_2/epoxides coupling.

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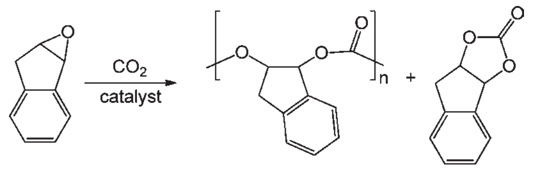
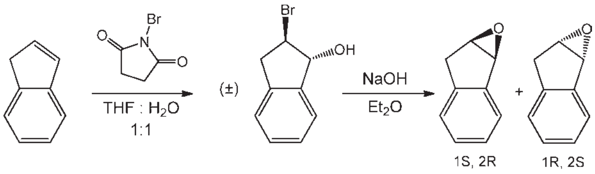
The non-commercially available indene oxide is well known to be both acid-sensitive and labile.[18] On the basis of our own experimental observation of Meinwald rearrangement of indene oxide to 2-indanone when utilizing *m*CPBA as an oxidant[19] (see Supporting Information), the alternate stepwise synthesis through formation of the bromohydrin and ring-closing using NaOH was settled upon (Scheme 2).[20,21] Purification by sublimation afforded pure *rac*-indene oxide capable of coupling with CO_2. It is worth noting that indene oxide is slightly hygroscopic and must be transferred into an inert atmosphere immediately following sublimation.

Indene oxide crystals suitable for X-ray diffraction were obtained via sublimation (Figure 1). The fused benzene and cyclopentene rings are nearly planar, with a C8−C5−C3−C1 torsion angle of 1.591°. This differs from crystals grown of 1,4-dihydronaphthalene oxide, where a distinct pucker is found within the cyclohexane ring.[12]

Scheme 1



Scheme 2



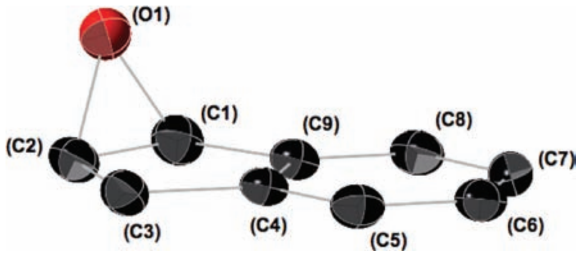


Figure 1. Thermal ellipsoid representation of (1*S*,2*R*)-indene oxide with ellipsoids at 50% probability surfaces. Hydrogen atoms have been omitted for clarity. Bond angles and lengths are identical for the (1*R*,2*S*)-indene oxide enantiomer.

On the basis of its successes with the difficult copolymerization of CO_2 and styrene oxide,[10a] we chose to initially employ *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamino cobalt(III)-2,4-dinitrophenoxide (**1**) as the catalyst along with PPN-2,4-dinitrophenoxide as cocatalyst. Both resolved [(*S*,*S*)- or (*R*,*R*)-] and racemic versions of catalyst **1** were employed in this study.

Indene oxide melts at ~32−33 °C, and thus initial coupling reactions of neat indene oxide and CO_2 were performed at or above 35 °C (Table 1, entries 1 and 2). Ring-opening of the epoxide is typically the rate-limiting step at high pressure of CO_2,[4a] and thus the differences in CO_2 pressures for the two entries can be largely ignored. As expected, the increase in reaction temperature from 35 to 60 °C is mirrored by an increase in both conversion to cyclic carbonate from 11.5% to 71.3% and turnover frequency (TOF) from 0.80 to 5.01 h^{-1}. In the ^1H NMR and FT-IR spectra of the crude reaction products, no polymer formation was observed in either case.

The production of poly(styrene carbonate) from the same catalytic system was enhanced and more selective at lower temperatures.[10a] Thus, we decided to employ cosolvents and study the coupling of CO_2 and indene oxide both at and below room temperature. Despite the potential for HCl poison in dichloromethane, CH_2Cl_2 was chosen as the solvent due to PPNX salts' inability to dissolve in toluene. Similar toluene-soluble $n\mathrm{Bu}_4\mathrm{NX}$ cocatalysts are inherently wet with trace water. As expected, $n\mathrm{Bu}_4\mathrm{NBr}$ with the better leaving group was more active than PPNY, with respective TOF of 19.0 and 11.4 h^{-1} at 25 °C (entries 3 and 4).

Following removal of residual indene oxide *in vacuo*, cyclic indene carbonate was purified by flushing a CH_2Cl_2 solution

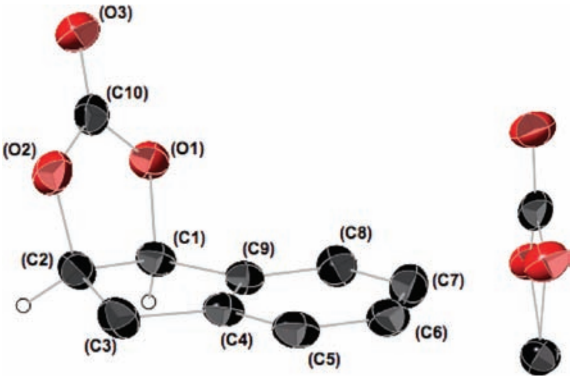


Figure 2. Thermal ellipsoid representation of *cis*-indene carbonate with ellipsoids at 50% probability surfaces. All hydrogens have been omitted for clarity except H1 and H2 to display the *cis* nature of the product. Inset image is looking down the C2−C1 bond angle, displaying the torsion in the five-membered cyclic ring.

Table 1. Production of Indene Carbonate[a]

entry	catalyst	*t*(d)	*T* (°C)	[IO] (g/mL)	pressure (MPa)	conversion (%)[b]	TOF (h^{-1})[c]
1[d]	(*S*,*S*)-**1**/PPNY[e]	3	60	N/A	2.1	71.3	5.0
2[d]	(*S*,*S*)-**1**/PPNY	3	35	N/A	3.4	11.5	0.8
3	(*R*,*R*)-**1**/PPNY	1	25	1.0	2.1	54.6	11.4
4	(*R*,*R*)-**1**/$n\mathrm{Bu}_4\mathrm{NBr}$	1	25	1.0	2.1	91.3	19.0

[a] The coupling reactions were performed with catalyst/cocatalyst/epoxide = 1/1/500 molar ratio with CH_2Cl_2 solvent in a 300 mL stainless steel Parr autoclave. [b] Determined using ^1H NMR spectroscopy. [c] Turnover frequency of indene oxide to indene carbonate as determined by ^1H NMR spectroscopy. [d] Experiment run in neat indene oxide. [e] PPN = bis(triphenylphosphine)iminium, Y = 2,4-dinitrophenoxide anion.

Table 2. Low-Temperature Couplings of Indene Oxide and CO_2[a]

						M_n (Da)					
entry	catalyst	t (d)	conversion (%)[b]	PIC/IC[b]	TOF (h^{-1})[c]	theor[d]	GPC[e]	PDI[e]	T_g (°C)[f]	T_d (°C)[g]	T_{d50} (°C)[h]
1[i]	(*S,S*)-**1**/PPNY	7	16.7	45/55	1.1	14600	4200	1.19	114	245	262
2	(*S,S*)-**1**/PPNY	6	59.0	57/43	2.1	29600	7000	1.09	133	249	264
3	*rac*-**1**/PPNY	6	50.1	59/41	1.7	26000	7100	1.16	134	245	266
4	*rac*-**1**/PPNY	2	16.2	59/41	1.7	8300	3500	1.30	109	236	259
5	*rac*-**1**/$n$$Bu_4NBr$	2	50.6	0/100	4.0						

[a] The coupling reactions were performed with catalyst/cocatalyst/epoxide = 1/1/500 molar ratio in a 300 mL autoclave with indene oxide concentrations of 1.0 g/mL in CH_2Cl_2. Temperature and pressure were held at 0 °C and 3.4 MPa, respectively. Data regarding selectivity for carbonate linkages can be found in the Supporting Information. [b] Determined using ^1H NMR spectroscopy. [c] Turnover frequency of indene oxide to products [poly(indene carbonate) and indene carbonate] as determined by ^1H NMR spectroscopy. [d] Theoretical M_n = (M/I) × (% conversion) × (mol. wt. of indene carbonate). [e] Monomodal molecular weight distribution determined by gel permeation chromatography in THF; calibrated with narrow polystyrene standards. [f] The midpoint temperature of the major T_g during the second heating using DSC. [g] Onset decomposition temperature, as determined by TGA. [h] Temperature at which 50% of the polymer's mass has been lost. [i] 0.2 g/mL indene oxide in CH_2Cl_2.

through both activated carbon and a silica pad. Clear, colorless block crystals suitable for X-ray diffraction were grown from a concentrated CH_2Cl_2 solution. Two unique yet similar molecules of *cis*-indene carbonate are found within the unit cell, one of which is displayed in Figure 2. Rather than displaying near planarity in the five-membered cyclic ring as in the case of propylene carbonate[22] and *cis*-1,4-dihydronaphthalene carbonate,[12] the two *cis*-indene carbonate molecules have an O1−C1−C2−O2 torsion angle of 14.187° and an O4−C11−C12−O5 angle of 8.252°, with the difference in the two molecules likely due to packing effects.

When the reaction temperature was decreased further to 0 °C, the first indications of polymer formation were observed (Table 2, entries 1−3). After 1 week of reaction at 0 °C, we were gratified to find that a 0.2 g/mL solution of indene oxide utilizing the (*S,S*)-**1**/PPNY system formed a mixture of indene carbonate and poly(indene carbonate), the latter identified by its characteristic polycarbonate FT-IR stretch at 1750 cm^{-1} (entry 1). In an effort to suppress cyclization to indene carbonate and induce further polycarbonate production, the concentration of indene oxide was increased to 1.0 g/mL. After 6 days at 0 °C, both (*S,S*)- and *rac*-**1**/PPNY afforded an ∼60/40% mixture of poly(indene carbonate) and cyclic indene carbonate (entries 2 and 3, respectively). The observed low molecular weights are likely due to slow polymer growth combined with rapid, reversible chain transfer with trace water.

When purified, poly(indene carbonate) is slightly off-white in color. Though the color may be due to residual cobalt remaining in the polymer, it appears to be inherent as it remains after multiple purifications. Each of the polymer samples has a slightly different T_g, ranging from 108 to 130 °C. The differences between entries 1 and 2 (114 vs 133 °C) may be attributed to molecular weight discrepancies between the more oligomeric 4200 vs the longer-chained 7000 Da sample. Similar jumps in both T_g (109 vs 134 °C) and molecular weight (3500 vs 7100 Da) are observed between entries 4 and 3. Because the molecular weight of polymers, especially with lower molar masses, has a strong influence on the T_g, it is anticipated that copolymers of molecular weights greater than 10 000 Da will exceed 134 °C.

Distinct differences in the regio- and stereoregularity of the polymer chains can be observed for polymer samples produced from different catalysts (Figure 3). Though the peaks have not been definitively assigned, it can be seen from the carbonate region of the ^{13}C NMR that the resolved (*S,S*)-**1** does display increased selectivity for specific ring-opening patterns of indene oxide over *rac*-**1**. The peaks centered at 154.5 ppm are enhanced over those centered at 154.2 ppm for (*S,S*)-**1** (red) relative to *rac*-**1** (blue). Identical selectivity is observed for the polymer produced from (*S,S*)-**1** in entry 1. Thermogravimetric analyses of the polymer samples indicate that poly(indene carbonate) is thermally stable at up to ∼245 °C, with 50% degradation occurring by ∼264 °C. The polymer's molecular weight appears to play a more significant role in T_d determination as compared to regio- and stereoregularity. A representative TGA decomposition curve can be found in the Supporting Information.

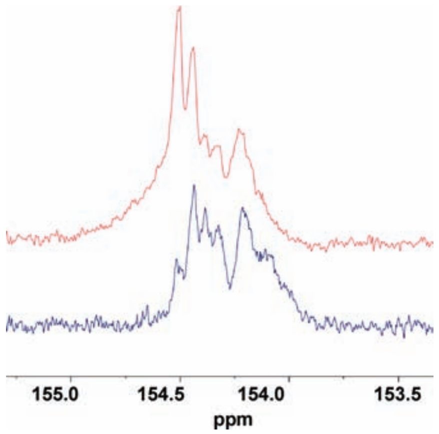


Figure 3. ^{13}C NMR of carbonate [O(C=O)O] stretching region of poly(indene carbonate). Seen from Table 2 are entry 2 (red) and entry 3 (blue). The spectrum of entry 1 is identical to that of entry 2 and is not shown in this figure (see Supporting Information).

To conclude, the first samples of poly(indene carbonate) have been produced via the Co-catalyzed coupling of indene oxide and CO_2. This marks the first time that a benzene ring has been rigidly linked to the backbone of a polycarbonate produced using CO_2/epoxides coupling, and the resulting polymer has the highest T_g yet reported for this process, up to 134 °C. While this is still significantly lower than BPA polycarbonate's T_g of 150 °C, progress is being made in the right direction. Additionally, the molecular weights of these species are still quite low (∼7000 Da), and it can thus be inferred that the T_g will be even higher when larger molecular weight species are obtained. Poly(indene carbonate) is thermally stable at temperatures of up to

249 °C. The appropriate choice of catalyst, cocatalyst, and reaction temperature appears to be very important to induce polymerization. Ongoing efforts involve finding ways to optimize polymer production and increase chain length by increasing reaction time, employing improved catalysts, and reducing the amount of trace water within the system. Additionally, regio- and stereoselective ring-opening studies of optically active indene oxide are planned.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Full experimental details and X-ray structural data. This material is available free of charge via the Internet at http://pubs.acs.org.

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