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NOTE

Highly Selective Synthesis of CO_2 Copolymer from Styrene Oxide

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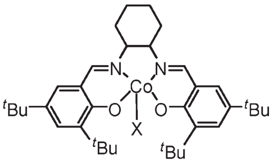
Introduction

The catalytic transformation of carbon dioxide into degradable polycarbonates via the alternating copolymerization with epoxides has received considerable attention during the past decades.[1] Numerous catalyst systems have been developed for this reaction.[2−8] Much progress has been made in the formation of polycarbonates from aliphatic terminal epoxides or cyclohexene oxide derivatives, but the selective synthesis of polycarbonates from epoxides with electron-withdrawing groups such as styrene oxide still remains a challenge. Although some zinc-based catalyst systems were applied to the coupling of CO_2 and styrene oxide, they generally suffered from low activity, poor polymer selectivity, and the concomitant production of ether linkage units.[9] Well-defined β-diiminate−zinc complexes proved to be efficient in catalyzing this reaction at ambient temperature and 2.0 MPa, but the selectivity for copolymer was only 35%.[10] Increasing the CO_2 pressure did not improve the selectivity for copolymer.

Being distinct from the terminal epoxides with electron-donating groups such as propylene oxide, the nucleophilic ring-opening of styrene oxide predominantly occurs at the methine C_α−O bond rather than the methylene C_β−O bond (Scheme 1).[11] As a result, it is very difficult to avoid the formation of styrene carbonate by intramolecularly cyclic elimination via two concurrent backbite mechanisms, one aided by the central metal ion and one taking place on the free anionic polymer chain. The latter process is believed to have a lower activation barrier and to be assisted in the presence of an excess of nucleophilic cocatalyst or adventurous water, which serves to displace the growing polymer chain from the metal center.[8,12] Because of the electron-withdrawing nature of the aromatic ring, it is possible that cyclic styrene carbonate is predominantly produced via backbiting of the propagating polycarbonate anion to the benzyl carbon of the adjacent carbonate unit (Scheme 2, paths B and D). In addition, the isomerization of styrene oxide into hyacinthin easily occurs at enhanced temperatures.[13] Compared with the low glass-transition temperatures (T_g) associated with aliphatic polycarbonates, the polymer from the alternating copolymerization of CO_2 and styrene oxide should exhibit an enhanced T_g value.[14] Therefore, selective synthesis of the corresponding polycarbonate from styrene oxide is highly desirable. The purpose of the present work is to explore selective routes for the preparation of poly(styrene carbonate) using cobalt(III) complexes containing Schiff base ligands as catalysts.

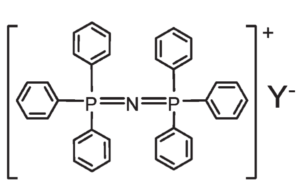
Results and Discussion

Stimulated by our success with binary catalyst systems of a metal−salen complex in conjunction with a bulky onium salt or sterically hindered organic base for the alternating copolymerization of aliphatic epoxides and CO_2,[5,7] we have tested these systems for the coupling reaction of styrene oxide with CO_2. Previously, few catalyst systems based on the salenCo(III)X complex have shown activity for this coupling reaction at ambient temperature with moderate to good selectivity for polymer formation. Most systems predominately afforded cyclic styrene carbonate at various temperatures. However, the judicious choice of axial X anions on salenCo(III)X and Y anions of PPNY [PPN^+ = bis(triphenylphosphine)iminium] significantly impacts the catalytic activity and selectivity for copolymer formation (Table 1, runs 1−4). The screening revealed that salenCo(III) complex **1a** in conjunction with 1 equiv of PPNY [Y = 2,4-dinitrophenoxy] was the most effective binary catalyst to provide polycarbonate with a narrow polydispersity (M_w/M_n ratio) in 99% selectivity. This is a rare example of the selective synthesis of a copolymer from CO_2 and an epoxide with an electron-withdrawing group.

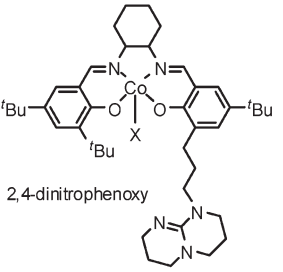


1a: X = 2,4-dinitrophenoxy
1b: X = Cl
1c: X = Br

1



PPNY
Y = Cl, 2,4-dinitrophenoxy



X = 2,4-dinitrophenoxy

2

The isolated polymers have narrow molecular weight distributions less than 1.1 and exhibit monomodal distributions, which is very different from the bimodal distributions generally found in the copolymerization of CO_2 and propylene oxide using these same binary catalyst systems. Notably, the M_n values are close to the expected values and also exhibit a linear relationship with the % conversion (Figure 1). This is consistent with a living polymerization process.

During the optimization of the catalyst systems, we were gratified to discover that a novel cobalt-based catalyst **2** with 1,5,7-triabicyclo[4,4,0]dec-5-ene (designated as TBD, a sterically

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Scheme 1. Difference in Nucleophilic Ring-Opening between Styrene Oxide and Propylene Oxide

Scheme 2. Formation of Styrene Carbonate by Intramolecular Cyclic Elimination of the Propagating Polymer Chains Involving the Carbonate Unit Associated with Ring Opening of Styrene Oxide at the Methine C_α−O Bond

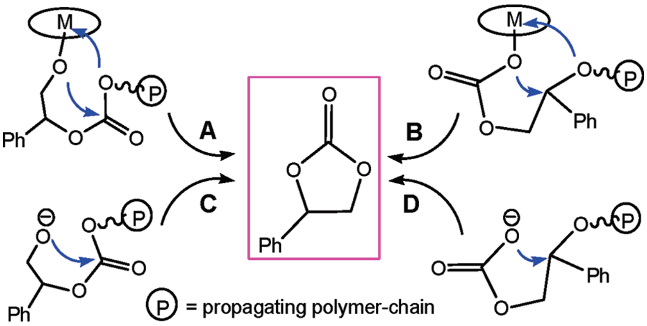
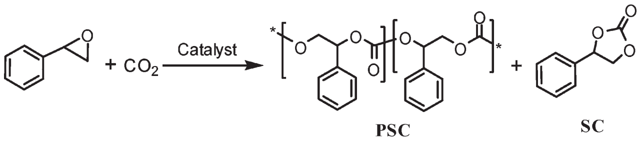


Table 1. Coupling Reaction of Styrene Oxide with CO_2[a]



run	catalyst	*T* (°C)	*t* (h)	TOF[b] (h^{-1})	PSC/SC[c]	M_n[d] (kg/mol)	PDI[d]
1	**1a**/PPNCl[e]	25	3	62	90/10	12.9	1.04
2	**1b**/PPNCl	25	3	61	58/42	7.4	1.12
3	**1c**/PPNCl	25	3	94	5/95		
4	**1a**/PPNY[f]	25	3	75	99/1	15.7	1.05
5	**1a**/PPNY[f]	50	2	160	91/9	20.4	1.05
6[g]	**2**	25	12	60	100/0	76.4	1.03
7[g]	**2**	50	6	134	99/1	86.0	1.10
8[h]	**2**	25	12	13	99/1	16.2	1.07

[a] The coupling reactions were performed in neat styrene oxide (100 mmol) in 50 mL autoclave at 2.0 MPa CO_2 pressure. Catalyst/cocatalyst/epoxide = 1/1/500 (molar ratio). Epoxide/catalyst carbonate linkages of the resulted polymers are >99% based on ^1H NMR spectroscopy. [b] Turnover frequency of styrene oxide to products [poly(styrene carbonate) and cyclic styrene carbonate]. [c] Determined by using ^1H NMR spectroscopy. [d] Determined by gel permeation chromatography in THF, calibrated with polystyrene. [e] PPN = bis(triphenylphosphine)iminium. [f] Y = 2,4-dinitrophenoxy anion. [g] Catalyst/epoxide = 1/3000 (molar ratio). [h] The reaction was performed at 0.1 MPa CO_2 pressure.

hindered organic base) anchored on the ligand framework was highly active for catalyzing CO_2/styrene oxide copolymerization to selectively give the corresponding polycarbonates with more than 99% carbonate linkages even at a low catalyst loading (run 6). However, the activity for CO_2/styrene oxide coupling is less than one-tenth that of CO_2/propylene oxide copolymerization under the same reaction conditions.[8c] Of importance, the catalyst proved to be effective at 0.1 MPa CO_2 pressure and at enhanced temperature of 50 °C with 99% polymer selectivity (runs 7 and 8).

As expected, the resulting polymer exhibits excellent thermal stability with a thermolysis temperature up to 300 °C, which is about 60 °C higher than that of the copolymer obtained with zinc glutarate as catalyst reported by Lee et al.,[9b] and has a relatively high glass-transition temperature of 80 °C (see Supporting Information, Figures S1 and S2).[14]

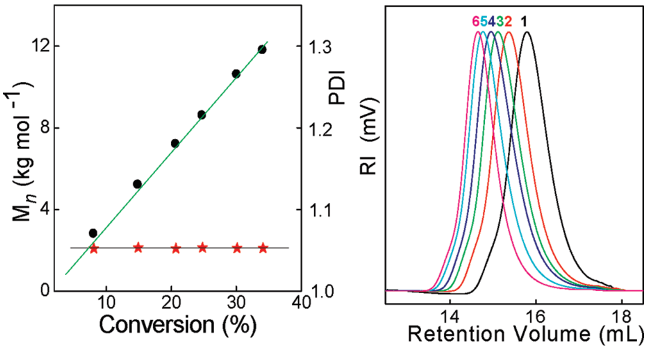


Figure 1. Plots of M_n (●) and PDI (∗) vs % conversion (left) and GPC traces of poly(styrene carbonate)s obtained at various conversions (right). Reaction conditions: epoxide/**1a**/PPNY (Y=2,4-dinitrophenoxy) catalyst = 500/1/1; 25 °C; 2.0 MPa CO_2 pressure.

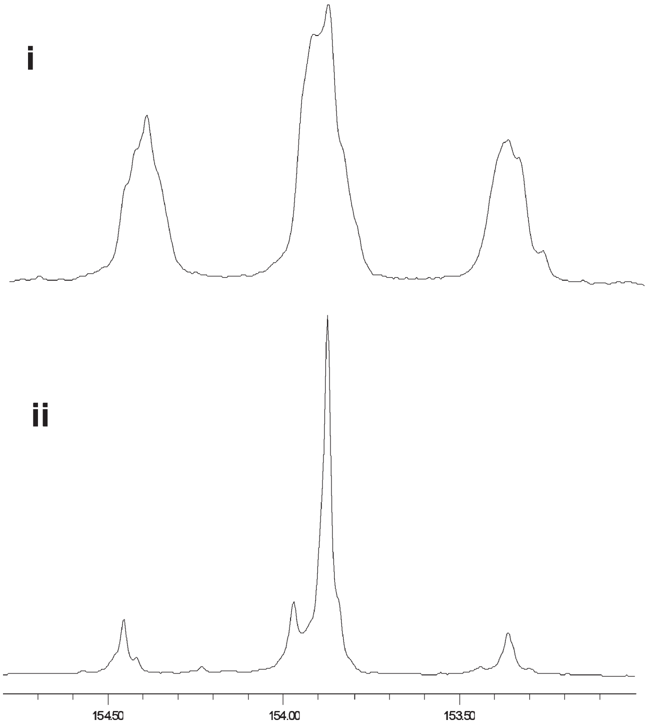


Figure 2. Carbonyl region of ^{13}C NMR spectra of poly(styrene carbonate)s obtained with catalyst system: (i) racemic **1a**/PPNY (Y = 2,4-dinitrophenoxy)/racemic styrene oxide (1/1/500, molar ratio); (ii) (1*R*,2*R*)-**1a**/PPNY (Y = 2,4-dinitrophenoxy)/(*S*)-styrene oxide (1/1/500, molar ratio).

The main-chain sequence of the resulting polycarbonate was confirmed by ^1H and ^{13}C NMR spectroscopy as well as MALDI-TOF (see Supporting Information, Figures S3−S5). In the ^1H NMR spectrum of the resulting copolymer in $CDCl_3$, the resonance of methine CH in styrene carbonate unit is found at 5.87 ppm due to the electron-withdrawing effect of the aromatic ring. No signal at δ = 3.3−3.6 ppm assignable to ether linkage units was observed in this spectrum,[15] demonstrating that the copolymer has >99% carbonate linkages. MALDI-TOF spectroscopy also confirmed the highly alternating nature of the resulting polymer. The ^{13}C NMR spectrum suggests that the resulting copolymer has a head-to-tail content of 51% (Figure 2), indicating that ring-opening of styrene oxide during the copolymerization with CO_2 occurs almost equally at both C_α−O and C_β−O bonds. Even for the copolymerization (*S*)-styrene oxide (98% *ee*) with CO_2 using the binary catalyst system of 1*R*,2*R*-**1a** and PPNY (Y = 2,4-dinitrophenoxy), the resulting copolymer has a head-to-tail content of 82% and its hydrolysis product has a enantioselectivity of 87% with a (*S*)-configuration, suggesting that this reaction proceeds with 11% inversion at the benzyl carbon. The result is in sharp contrast with the copolymerization of optically active styrene oxide and CO_2 using a diethylzinc/water system as catalyst, in which the ring opening predominantly takes place at the methine−oxygen bond cleavage accompanying 96% inversion at the benzyl carbon.[16]

In summary, the alternating copolymerization of CO_2 and styrene oxide to afford the corresponding polycarbonate with more than 99% carbonate linkages was achieved with the use of cobalt-based catalyst systems. The completely alternating polycarbonate exhibits excellent thermal stability and has a relatively high glass-transition temperature of 80 °C. Further investigations aimed at achieving higher catalytic activity and controlling the copolymer's microstructure are underway.

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Supporting Information Available: General experimental procedures and characterization of polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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