Articles

Stereochemistry Control of the Alternating Copolymerization of CO_2 and Propylene Oxide Catalyzed by SalenCrX Complexes

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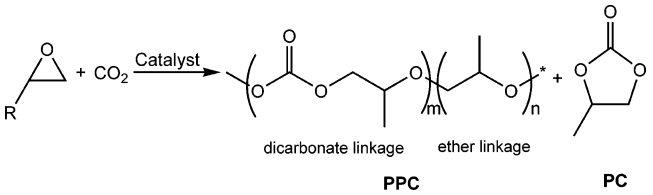
Received November 29, 2006; Revised Manuscript Received February 9, 2007

ABSTRACT: Various poly(propylene carbonate)s (PPC)s with different head-to-tail linkages (from ∼60% to 93%) could be synthesized by the copolymerization of racemic propylene oxide (*rac*-PO) and CO_2 with chromium Salen complexes as catalyst. The axial X group and the Salen ligand framework of the chromium complexes and the properties of cocatalyst significantly affect stereochemistry of the resulting polymer. Continuous determination of a polymer chain end group (initiating and chain growth species) at various times was achieved by in situ electrospray ionization mass spectrometry (ESI-MS), which in combination with the terpolymerization of CO_2 with *R*-PO and cyclohexene oxide (CHO) gave us an insight into the mechanistic understanding of CO_2/PO copolymerization and polycarbonates stereochemistry control. Apart from the effect of the ligand set of the chromium Salen complexes on polymer stereochemistry, a "polymer chain-end control" mechanism also significantly affects the stereochemistry of the resulting polycarbonates.

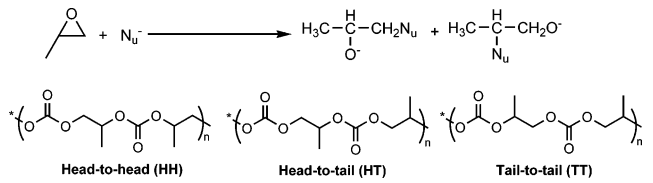
Introduction

The physical properties of a polymer are determined mainly by the relative stereochemistry (the spatial arrangement of atoms or groups in a polymeric unit) of adjacent locations in the polymeric chains. As a result, the control of polymer microstructure is one of the most important goals in the area of stereoselective polymerization catalysis.[1] For CO_2/aliphatic epoxides (such as propylene oxide) copolymerization, there exists much interesting information, such as polymeric/cyclic product selectivity, ether and dicarbonate linkages (Scheme 1), regiochemistry of epoxide ring-opening, and stereochemistry of carbonate unit sequence in a polymer (Scheme 2), which bears a memory of the reaction pathway leading to its formation.[2] Aliphatic epoxide ring-opening is seemed to be typically favored at the least hindered C−O bond, but indeed cleavage is normally observed at both C−O bonds, giving regioirregular polymers with ∼60% head-to-tail linkage.[3,4] Recently, our group reported that a chiral SalenCo(III) complex in conjunction with a quaternary ammonium halide exhibited unprecedented activity for the asymmetric alternating copolymerization of CO_2 with racemic PO (*rac*-PO) and increased stereochemistry control (∼95% head-to-tail linkage) of the product poly(propylene carbonate) (PPC), even at 0.2 MPa CO_2 pressure,[5] while the use of chiral cobalt complexes alone as catalyst, only ∼80% head-to-tail linkage was observed in the resulting polymer.[6] Notably, Coates et al. further discovered the synthesis of syndio-enriched PPC generated from *rac*-PO/CO_2 with catalyst *rac*-SalenCoBr.[6b] On the contrary, although chromium Salen derivatives were also proved to be an effective catalyst for the coupling of propylene oxide and CO_2 to afford poly(propylene carbonate) (PPC), the polycarbonte produced is regioirregular with head-to-head, head-to-tail, and tail-to-tail linkages.[4b,7] The difference only in the central metal ion in the two similar catalyst systems resulting in contrary tendency stimulate us to explore what factor to play significant role in stereoregulation and how to precisely control polymer stereochemistry during the alternating copolymerization of CO_2 and epoxides.

Scheme 1. Reaction of Propylene Oxide and CO_2 To Afford Poly(propylene carbonate) (PPC) and Cyclic Propylene Carbonate (PC)



Scheme 2. Nucleophilic Ring-Opening of Propylene Oxide and Stereochemistry of Poly(propylene carbonate)



On the basis of our success in mechanistic understanding of stereoselective alternating copolymerization of CO_2 and aliphatic epoxides in the presence of a chiral SalenCo(III) complex in conjunction with a sterically hindered strong organic base (7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene, MTBD),[5b] we attempt to adjust the SalenCrX complexes into stereoselective catalyst for CO_2/epoxides copolymerization.

Herein, we report the synthesis of various PPCs with different head-to-tail linkages generated from *rac*-PO/CO_2 with chromium

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10.1021/ma062735f CCC: $37.00 © 2007 American Chemical Society
Published on Web 03/08/2007

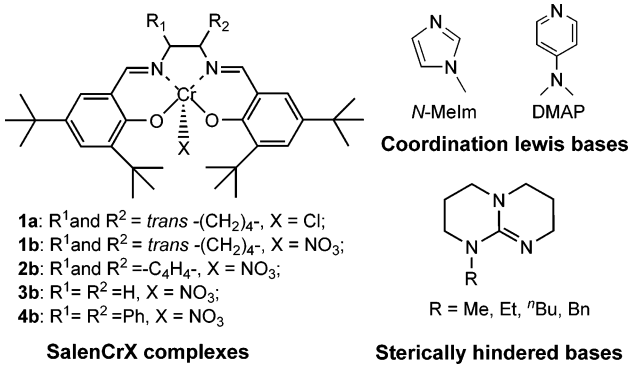


Figure 1. General structure of SalenCr(III) complexes and organic bases utilized for CO_2/PO copolymerization.

Salen complexes (Figure 1) as catalyst, in which the axial X group and the Salen ligand framework of the chromium complexes, and the properties of cocatalyst significantly affect stereochemistry of the resulted polymer. Continuous determination of a polymer chain end group (initiating and chain growth species) at various times was achieved by in situ electrospray ionization mass spectrometry (ESI-MS), which in combination with some control experiments gave us an insight into the mechanistic understanding of CO_2/PO copolymerization and polycarbonates stereochemistry control.

Results and Discussion

Under the experimental conditions (25 °C and 2.0 MPa CO_2 pressure), the chromium complex **1a** alone could catalyze the copolymerization of CO_2 and PO to afford PPC with a head-to-tail connectivity of 64% (Figure 2A), which is close to the statistical calculation date (∼60%) of regioirregular PPC.[8] Simple changes in the axial X group of SalenCr(III)X from Cl^- to NO_3^- (a low nucleophilic anion) drastically resulted in polymer head-to-tail connectivity increasing from 64% to 73% (Figure 2B). Interestingly, in the presence of a coordination organic base such as *N*-methylimidazole (*N*-MeIm) or 4-(*N*,*N*-dimethylamino)pyridine (DMAP), the chromium complex **1b** can effectively catalyze the CO_2/PO copolymerization to form PPC with 78−80% head-to-tail linkages, which value is close to the microstructure of the PPC generated from the binary system of **1b** in conjunction with a bulky ionic ammonium salt such as PPNCl {PPN = bis(triphenylphosphine)iminium} as catalyst (Table 1, entries 3−5). Substituted sterically hindered strong organic bases such as 7-benzyl-1,5,7-triazabicyclo[4.4.0]-dec-5-ene (BnTBD) for coordination organic base with the complex **1b** further results in PPC head-to-tail connectivity increasing to 85−86% (Table 1, entries 6−9, and Figure 2C).

Table 1. Effects of the Structure of SalenCr(III)X and the Properties of Cocatalyst on Stereochemistry of the Resulted Polymer from CO_2/PO Copolymerization[a]

entry	catalyst	cocatalyst	PPC selectivity (%)[b]	HT linkages (%)[c]
1	**1a**		70	64
2	**1b**		>99	73
3	**1b**	*N*-MeIm	80	78
4	**1b**	DMAP	95	80
5	**1b**	PPNCl	97	81
6	**1b**	MTBD	>99	85
7	**1b**	EtTBD	>99	85
8	**1b**	^{n}BuTBD	>99	85
9	**1b**	BnTBD	>99	86
10	**2b**	MTBD	>99	92
11	**2b**	BnTBD	>99	93
12	**3b**	BnTBD	>99	75
13	**4b**	BnTBD	>99	78

[a] The reaction was performed in neat *rac*-PO (3.5 mL, 50 mmol; SalenCr(III)X/PO = 1/500, molar ratio) in an autoclave at 25 °C and 2.0 MPa, cocatalyst/SalenCr(III)X = 0.5/1 (molar ratio). Carbonate linkages of the resulted PPCs are ≥97% based on ^{1}H NMR spectroscopy. [b] Determined by using ^{1}H NMR spectroscopy. [c] Determined by using ^{13}C NMR spectroscopy.

With BnTBD as cocatalyst, several SalenCr(III)NO_3 complexes with varying diamine backbones (Figure 1) were investigated as catalyst for CO_2/PO copolymerization (Table 1, entries 10−13). For the same axial X group, changing the Salen ligand framework to noncyclic diamine backbone had no observable effect on polymer selectivity but resulted in significant decreases in polymer microstructure regularity. To our surprise, changing to conjugated cyclic diamine fragment in the backbone, the resulting PPC has an unprecendented head-to-tail content of up to 93% (Figure 2d). The difference in stereochemistry of PPC generated from various catalyst systems is tentatively assumed to originate from different reaction pathways during CO_2/PO copolymerization (Scheme 3). These

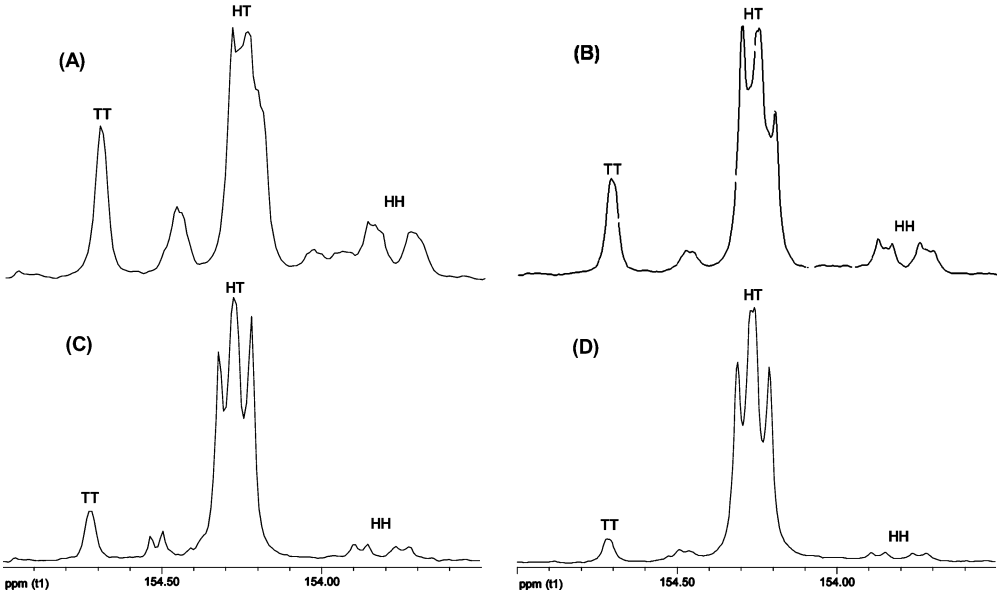
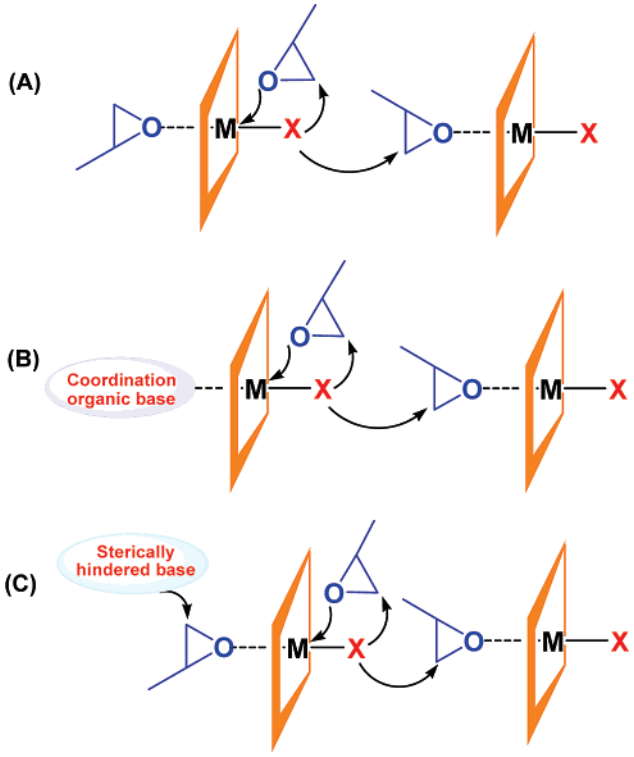


Figure 2. Carbonyl region of the ^{13}C NMR spectra of PPC obtained at 25 °C and 2.0 MPa, with various catalyst systems: (A) **1a**, (B) **1b**, (C) **1b**/BnTBD, and (D) **2b**/BnTBD.

Scheme 3. Possible Initiation Pathways of CO_2/PO Copolymerization



pathways all involve monometallic and bimetallic initiation processes, but probably only one predominantly plays a significant role in the reaction. With metal−Salen complexes (SalenMX) alone as catalyst (Scheme 3A), the epoxide is activated by its simple coordination to an electrophilic metal center from either side of the Salen plane, thereby leading to its ring-opening attacked by the axial X anion of either the SalenMX complex (monometallic initiation mechanism) or a neighboring catalyst molecule (bimetallic initiation mechanism).[7,9] A similar situation also occurs in the presence of a coordination organic base such as *N*-MeIM (Scheme 3B). Binding of the *N*-MeIM ligand at the vacant axial site of SalenMX increases the nucleophilicity about the metal center, thereby enhancing the regioselectivity of epoxide ring-opening by the nucleophilic axial X anion as well as the rate of the subsequent CO_2 insertion process.[7] With the use of a sterically hindered strong organic base as cocatalyst (Scheme 3C), a change in the initiation process certainly takes place because the sterically hindered base as nucleophile also attacks the epoxide coordinated in the vacant axial site of SalenMX.[5b,c]

Recently, an elegant mechanistic study on the stereochemistry of the initial ring-opening event of PO has been conducted in the copolymerization of CO_2 and PO catalyzed by porphyrin and salen complexes of Al(III) and Cr(III) alone or in the presence of a Lewis base cocatalyst, in which a monometallic initiation mechanism was proposed.[2] Prior to this study, Darensbourg and co-workers have performed elegant kinetics studies on the copolymerization of CO_2 and epoxides catalyzed by binary SalenCr(III)X (X = Cl^-, N_3^-)/Lewis base (such as *N*-MeIm) systems and proposed a copolymerization mechanism where initiation occurred by a bimetallic process and propagation operated by monometallic enchainment of epoxides.[7a,10] These studies all have suggested that Lewis base coordinates to the active metal center trans to the propagating metal−polymer chain, thereby labilizing the propagating alkoxide or carboxylate ligand and promoting the insertion of CO_2 into the metal−alkoxide bond. It should be noted that there exists a long induction period in the system of the chromium−Salen complexes alone or in junction with a coordination organic base; while utilizing anionic ammonium salts with non- or low-coordination ability as cocatalyst, no or very short initiation period was observed.[11]

In previous paper, we have reported that in the binary catalyst systems of SalenCo(III) complexes and 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD, a sterically hindered strong organic base) MTBD plays an initiator of polymer-chain growth demonstrated by means of electrospray ionization mass spectrometry (ESI/MS). Indeed, the initiator role of BnTBD in the binary SalenCr(III)/BnTBD systems was also confirmed by this method. In the ESI-Q-TOF mass spectra in positive ion mode (Figure 3), we observed the species [BnTBD + PO + H^+] and [$OCH(CH_3)CH_2$-(CO_2-*alt*-PO)*n*-Bn-TBD + H^+], but with time the former species gradually decreases and the latter species moves to the high *m*/*z* region. As anticipated, we did not observe the species of [BnTBD + (salen)Cr^+] and [2BnTBD + (salen)Cr^+] (corresponding to the coordination of BnTBD to chromium ion) due to the steric repulsion. In contrast, replacing BnTBD with *N*-MeIm (a nonsterically hindered strong organic base), it is clearly seen the coordination of *N*-MeIm to chromium ion even via collision-induced dissociation (CID) experiments of up to 30 V (Figure 4). These results indicate that with the binary catalyst system composed of an chromium−Salen complex and a sterically hindered strong organic base with non- or low-coordination ability, the CO_2/epoxides copolymerization process may operate via a different reaction pathway. Since the nucleophilic axial X group of the chromium complex is also capable of initiation, polymer-chain propagation probably occurs simultaneously on either side of the SalenCr(III) plane, which is similar to that proposed by Inoue et al. using aluminum porphyrins combined with an ionic ammonium or phosphonium salt.[12] Of course, the initiation rate of the cocatalyst and the nucleophilic axial X group of SalenCr(III)X should be different. For the binary **1b**/BnTBD system, a change in the molar ratio of BnTBD to **1b** from 0.5 to 2 leads to an unexpected change in molecular weight distribution of the resulting PPC from bimodal to monomodal distribution (Figure 5). This result suggests that BnTBD has higher initiation ability than the NO_3^- anion. In contrast to that of the binary SalenCo(III)X/MTBD system,[5b] further increasing the molar ratio of BnTBD to **1b**, we did not observe an obvious increase in reaction rate. The fact indicates that the dissociation of the propagating carboxylate from the metal center is very difficult at ambient temperature, although Rieger's group have reported the mechanism understanding of the formation of aliphatic polycarbonates from aliphatic epoxides and CO_2 copolymerization with chromium(III) and aluminum(III) metal−Salen complexes at a relatively high temperature of 75 °C by a DFT theoretical calculation method, in which they proposed the propagating polymer chains easily dissociating from the metal center during the copolymerization.[13] We also performed this reaction at 75 °C with the binary catalyst system and found that an increase in cocatalyst content resulted in an obvious increase in rate but had a negative effect on polymer selectivity (see the Supporting Information, Table 1), which is agreement with Rieger's results.[7c,13]

It is generally known that both the ligand set of a single-site catalyst and the propagating polymer chain influence the stereochemistry of the polymerization reaction.[14] Similarly to stereoselective transformations of small molecules, coordination polymerization also concerns substrates activation and stereochemistry control of key bond-forming steps, which correlate

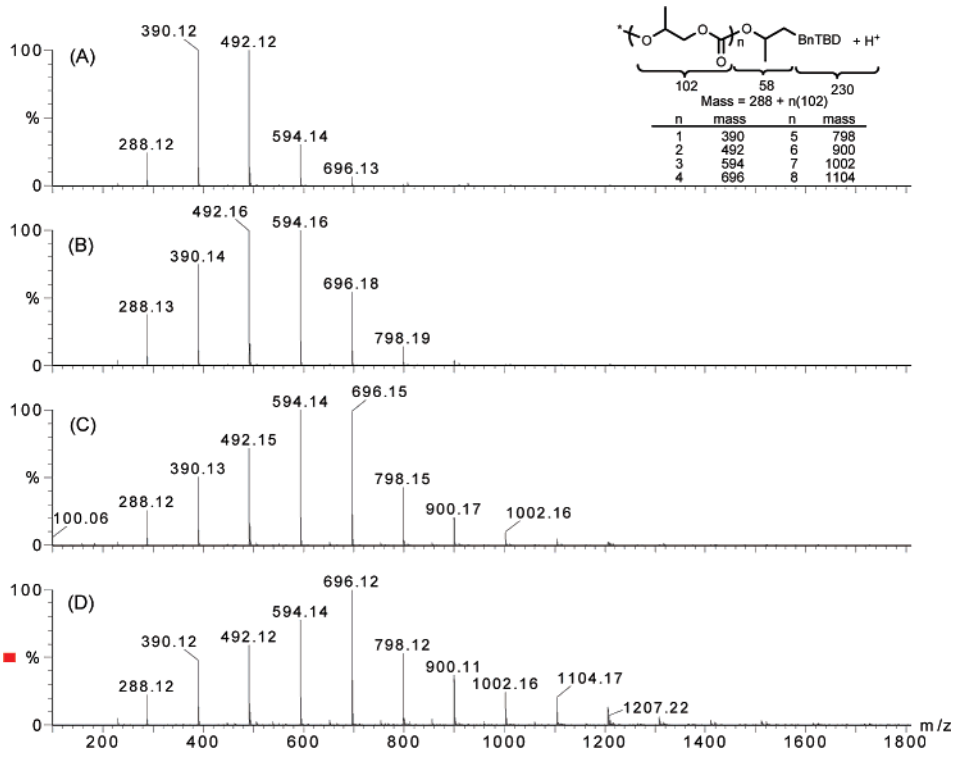


Figure 3. ESI-Q-TOF mass spectra of the reaction mixture resulting from the system of BnTBD/**1b** (0.5:1, molar ratio) at 15 °C and a 1.0 MPa CO_2 pressure with various times: (A) 1, (B) 2, (C) 3, and (D) 4 h.

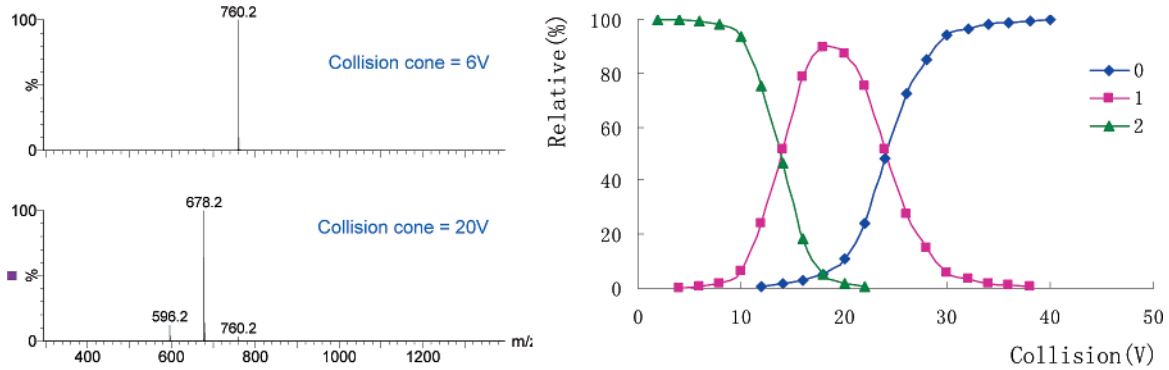


Figure 4. ESI-Q-TOF mass spectra of the mixture resulted from the system of *N*-MeIm/**1b** with different collsion cone voltage (left), and relative strength of M/*Z* = 760.2 = [SalenCr(III) + 2 *N*-MeIm]$^+$ (green line), 678.2 = [SalenCr(III) + *N*-MeIm]$^+$ (pink line) and 596.2 = [SalenCr(III)]$^+$ (blue line) at various collsion cone voltage (right).

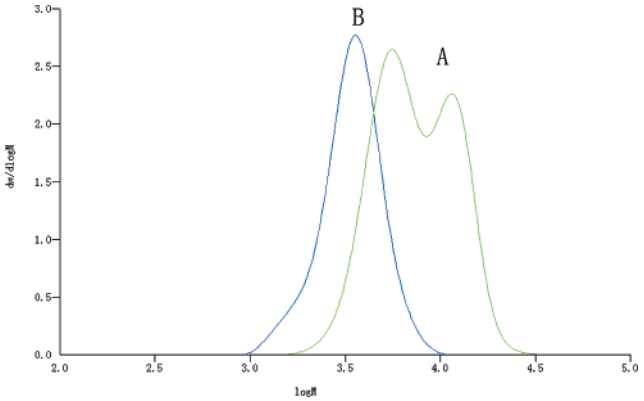


Figure 5. GPC data for CO_2/PO copolymerization by the complex **1b**/BnTBD with various ratio at 25 °C and 2.0 MPa: (A) **1b**/BnTBD = 1/0.5, M*n* = 4726, PDI = 1.23; (B) **1b**/BnTBD = 1/2, M*n* = 3169, PDI = 1.14.

with the ligand structure of a single-site catalyst. However, unlike the catalytic synthesis of small molecules, during a chain-growth polymerization reaction a polymer chain remains bound to the active metal center during monomer enchainment. Thus, the stereogenic center from the last enchained monomer unit will have an influence on the stereochemistry of fresh monomer addition.

For confirming the influence of the "polymer chain-end control" mechanism on polycarbonates stereochemistry control, we also performed some control experiments. The desymmetrization of *meso*-molecules with chiral catalysts or reagents is regarded as valuable strategy for the synthesis of enantiomerically enriched products.[15] Because the ring-opening of a *meso*-epoxide proceeds with inversion at one of the two chiral centers, a successful asymmetric ring-opening by a chiral catalyst can give optically active polycarbonates with an (*R*,*R*)- or (*S*,*S*)-*trans*-1,2-diol unit.[16] We were gratified to discover that the binary system of the complex (*1S*,*2S*)-**1b** in conjunction with MTBD could operate efficiently at ambient temperature and 2.0 MPa CO_2 pressure for CHO/CO_2 copolymerization to selectively provide the corresponding polycarbonates, but the enantiomeric excess (*ee*) of the cyclohexane-1,2-diol produced from the hydrolysis of the resulting poly(cyclohexene carbonate) (PCHC)

Table 2. Terpolymerization of CHO and Chiral PO with CO_2 Catalyzed by SalenCr(III)X and MTBD[a]

entry	catalyst	epoxide (molar ratio)	conversion of CHO (%)[b]	PC linkages/CHC linkages (molar ratio)[b]	ee (%)[c]
1	(*1S,2S*)-**1b**	CHO	23		14.5
2	(*1S,2S*)-**1b**	CHO/(*R*)-PO (1/1)	42	1/2.3	26.6
3	(*1S,2S*)-**1b**	CHO/(*R*)-PO (1/4)	67	1/0.6	37.1
4[d]	(*1S,2S*)-**1b**	CHO/(*S*)-PO (1/4)	28	1/5.8	14.2
5	*rac*-**1b**	CHO/(*R*)-PO (1/4)	79	1/0.7	7.9
6	*rac*-**1b**	CHO/(*S*)-PO (1/4)	73	1/0.7	8.2
7	**3b**	CHO/(*R*)-PO (1/4)	70	1/0.7	7.3

[a] The reaction was performed in an autoclave at 25 °C and 2.0 MPa CO_2 pressure for 24 h, SalenCr(III)X/MTBD/epoxide (CHO + PO) = 1/0.5/500 (molar ratio). [b] Determined by using ^{1}H NMR spectroscopy. [c] Measured by hydrolyzing the polymer and analyzing the resulting diol by chiral GC. [d] The resulted polymers are very difficult to be isolated due to their low molecular weight.

is only 14.5% with an *R,R* configuration (Table 2, entry 1). Notably, a mixture epoxide of CHO and (*R*)-PO (1/1, molar ratio) was used for copolymerization with CO_2; the *ee* of the cyclohexane-1,2-diol produced from the hydrolysis of the resulting terpolymer increased to 26.6%. Further increasing the molar ratio of (*R*)-PO to CHO from 1:1 to 4:1 resulted in the *ee* increasing to 37.1%. Substituting (*S*)-PO for (*R*)-PO with the complex (*1S,2S*)-**1b** led to significant decreases in rate and propylene carbonate linkages in the resulted polymers (entry 4). Interestingly, the *ee* of the corresponding cyclic propylene carbonate produced from the degradation of the resulted terpolymers by ^{t}BuOLi is only 72.5% with an *S* configuration, indicating a stereochemistry inversion occurring in ring-opening of (*S*)-PO during the polymerization. Furthermore, racemic SalenCr(III)X complexes in conjunction with MTBD were performed for terpolymerization of CHO and chiral PO with CO_2, and the resulting polymers show certain enantioselectivity (entries 5−7). The results clearly indicate that a "polymer chain-end control" mechanism originating from the chiral propylene carbonate unit significantly affects the stereoselective opening of freshly inserted CHO and thus further controls the stereochemistry of the resulting polycarbonates to a certain extent.

Conclusion

Various poly(propylene carbonate)s (PPC)s with different head-to-tail linkages (from ∼60% to 93%) could be synthesized by the copolymerization of *rac*-PO and CO_2 with chromium Salen complexes as catalyst. Altering the axial X group and Salen ligand framework of the chromium complexes or/and the addition of cocatalyst significantly affect stereochemistry of the resulting polymers. A SalenCrX complex with a low nucleophilic axial X anion and a conjugated cyclic diamine backbone in the Salen ligand, combined with a sterically hindered strong organic base, is an ideal binary catalyst system for the copolymerization of CO_2 and *rac*-PO to produce polycarbonate with relative high head-to-tail connectivity and >99% carbonate linkages. Continuous determination of a polymer chain end group (initiating and chain growth species) at various times by electrospray ionization mass spectrometry (ESI-MS) indicates that the sterically hindered strong organic base predominately plays an initiator of polymer-chain growth in the copolymerization process. Apart from the effect of the ligand set of the chromium Salen complexes on polymer stereochemistry, a "polymer chain-end control" mechanism also significantly affects the stereochemistry of the resulting polycarbonates.

Acknowledgment. Gratitude is expressed to the National Natural Science Foundation of China (NSFC) program (Grants 20634040 and 20574008) and the Outstanding Young Scientist Foundation of NSFC (Grant 20625414) for financial support.

Supporting Information Available: Synthesis of chromium Salen complexes and sterically hindered strong organic bases, general experimental procedure including CO_2/PO copolymerization and CO_2/chiral PO/CHO terpolymerization, and representative ^{1}H NMR and ^{13}C NMR spectra of the polycarbonates. This materials is available free of charge via the Internet at http://pubs.acs.org.

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MA062735F