*Macromolecules* **2006,** *39,* 5679−5685

# Asymmetric Alternating Copolymerization and Terpolymerization of Epoxides with Carbon Dioxide at Mild Conditions

**Lei Shi, Xiao-Bing Lu,* Rong Zhang, Xiao-Jun Peng,* Chun-Qing Zhang,**
**Jian-Feng Li, and Xue-Ming Peng**

*State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012, P. R. China*

*Received February 8, 2006; Revised Manuscript Received June 20, 2006*

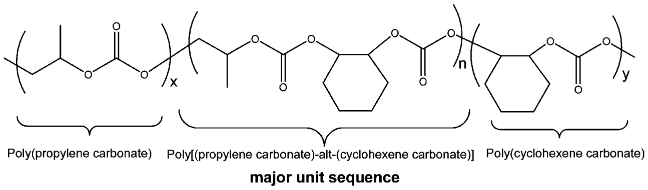
ABSTRACT: Asymmetric alternating copolymerization of $CO_2$ and cyclohexene oxide (CHO) proceeds effectively under mild temperature and pressure for yielding isotactic-enriched poly(cyclohexene carbonate) (PCHC) with a narrow molecular distribution, by using a binary catalyst system of a chiral tetradentate Schiff-base cobalt complex (SalenCoX) in conjunction with a bulky ionic organic ammonium salt such as bis(triphenylphosphine)iminium chloride (PPNCl). An increase in the temperature between 25 and 80 °C results in a dramatic increase in activity and a slight decrease in enantioselectivty, but the variation of temperature does not lead to an observable decrease in selectivity for PCHC formation. The binary catalyst system is also very effective in the terpolymerization of $CO_2$ with CHO and propylene oxide (PO) to selectively provide polycarbonates with a narrow polydispersity ($M_w/M_n$ ratio) of 1.24 and >99% carbonate linkages. The resulting terpolymer has only one glass transition temperature ($T_g$) and one thermolysis peak. The unprecedented results are tentatively assumed that an alternating nature of the two different carbonate units predominantly exists in the resulting polycarbonate. Furthermore, the $T_g$ of the PO/CHO/$CO_2$ terpolymer can be easily adjusted by controlling the proportion of cyclohexene carbonate linkages and propylene carbonate linkages.

## Introduction

Conversion of carbon dioxide ($CO_2$) to desirable, economically competitive products has received much attention because $CO_2$ is naturally abundant, relatively nontoxic, and inexpensive and is also the major greenhouse gas.[1] One of the most promising green reactions in this area is the alternating copolymerization of $CO_2$ and epoxides to generate biodegradable polycarbonates (Scheme 1),[2] which was first reported by Inoue et al. in the late 1960s.[3] This process represents an environmentally benign approach compared to the alternative route of condensation polymerization involving the use of toxic phosgene.[4] In recent decades, numerous catalyst systems, including heterogeneous catalysts mainly based on diethylzinc combined with a modifier having at least two labile hydrogen atoms,[5] and homogeneous catalysts associated with discrete zinc-based complexes,[6] magnesium,[7] aluminum,[8] manganese,[9] cobalt,[10] chromium,[11] and rare-earth metals,[12] have been developed for this transformation. Prominent among these are single-site homogeneous catalysts being the most efficient for $CO_2$/epoxides copolymerization and in some cases approach to the regio- and/or stereoselective polymerization.[10]

Although the advances have been significant, the industrial utilization of the $CO_2$/epoxides copolymers is extremely small, predominately due to their limitations on thermal and mechanical properties. As a result, the adjustment of the glass transition temperature ($T_g$) of the polycarbonates is necessary in order to be suitable as structural materials in various fields. Some scientists attempted to achieve this goal by the terpolymerization of aliphatic epoxides such as propylene oxide (PO) and alicyclic epoxides such as cyclohexene oxide (CHO) and $CO_2$, but only limited success was obtained.[13] The main problem is that the great difference in reactivity of CHO and PO during the terpolymerization of epoxides with $CO_2$ leads to the difficulty in controlling the composition and the alternating nature of the resulting copolymer. Indeed, in sharp contrast to the copolymerization of $CO_2$ with aliphatic epoxides, the copolymerization of $CO_2$ with alicyclic epoxides has great selectivity for polycarbonates formation even at elevated temperature due to alicyclic epoxides to the increased strain in forming the five-membered carbonate ring imposed by the conformation of the alicyclic group.[14] Interestingly, some efficient catalyst systems associated with discrete zinc-based complexes for $CO_2$/CHO copolymerization have been reported that offer significant advantages over traditional heterogeneous catalysts, but they are much less effective when aliphatic epoxides are empolyed as substrates.[6,13a]

**Scheme 1. Alternating Structure of the PO/CHO/$CO_2$ Terpolymer**



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. On the basis of this idea, Nozaki and co-workers first reported the asymmetric synthesis catalyzed by $Et_2Zn$−chiral amino alcohol to produce optically active poly[cyclohexene oxide-*alt*-$CO_2$] of ∼70% ee,[16] and then the Coates group reported the use of a well-defined chiral Zn−imine oxazoline complex as catalyst for this reaction, which showed similar enantioselectivity but higher activity and controlled molecular weight.[17] Recently, our group reported that a chiral SalcyCo(III) complex in conjunction with a quaternary am-

---

* Corresponding author: Fax 0086-411-83633080; e-mail lxb-1999@163.com.

10.1021/ma060290p CCC: \$33.50

monium 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.[10b] Prior to our work, Coates et al. have reported the use of chiral cobalt complexes alone as catalyst for this coupling at high $CO_2$ pressure, and ~80% head-to-tail linkage was observed in the resulted polymer.[10a] Of importance, they further discovered the synthesis of syndio-enriched PPC generated from *rac*-PO/$CO_2$ with catalyst *rac*-SalcyCoBr.[18] These unprecedented results stimulated Coates and our group independently to apply these catalyst systems to the copolymerization of $CO_2$ with alicyclic epoxides such as CHO, with a focus on maximization of catalyst activity and stereochemistry control of polycarbonates.[19]

Herein, we report the asymmetric alternating copolymerization of CHO and $CO_2$ with binary chiral electrophile−nucleophile catalyst system and also further explore the terpolymerization of CHO, PO, and $CO_2$ for synthesizing novel polycarbonates materials with various glass transition temperatures, in which different carbonate units predominantly exhibit alternating structure with each other (Scheme 1).

## Experimental Section

**Materials.** All manipulations involving air- and/or water-sensitive compounds were carried out using standard Schlenk techniques under dry nitrogen. Propylene oxide was refluxed over a mixture of KOH/$CaH_2$ and fractionally distilled under a nitrogen atmosphere prior to use. Cyclohexene oxide was purchased from Acros company and distilled under reduced pressure over $CaH_2$. Carbon dioxide (99.995%) was purchased from Dalian Institute of Speical Gases and used as received. Tetrahydrofuran, toluene, and hexane were distilled under nitrogen from sodium/benzophenone. Methylene chloride and chloroform were distilled from calcium hydride under nitrogen. Bis(triphenylphosphine)iminium chloride (PPNCl) was purchased from Aldrich Chemicals Co. and recrystallized from dichloromethane/ether. $PPNN_3$ was synthesized according to the literature method.[20] Various chiral tetradentate Schiff-base ligands were easily synthesized by the condensation of salicylaldehydes with chiral 1,2-diamines in ethyl alcohol and are in agreement with the literature characterization.[21] The method for synthesizing (1*R*,2*R*)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II) [(1*R*,2*R*)SalcyCo(II)] (reported by Jacobsen's group) was also applied to synthesize other tetradentate Schiff-base cobalt(II) complexes.[22] The characterizations of the chiral cobalt complexes are described in the Supporting Information.

**Analyses.** $^1H$ and $^{13}C$ NMR spectra were recorded on a Varian INOVA-400 MHz type ($^1H$,400 MHz) and a Bruker 500 MHz type ($^{13}C$, 125 MHz) spectrometer, respectively. Their peak frequencies were referenced vs an internal standard (TMS) shift at 0 ppm for $^1H$ NMR and against the solvent, chloroform-*d*, at 77.0 ppm for $^{13}C$ NMR, respectively. Molecular weights and molecular weight distributions of polymers were determined with a PL-GPC 220 high-temperature chromatograph (Polymer Laboratories Ltd.) equipped with the HP 1100 series pump from Agilent Technologies. The GPC columns were eluted with tetrahydrofuran at 35 °C at 1.00 mL/min. The sample concentration was about 0.1%, and the injection volume was 100 $\mu$L. The curve was calibrated using monodisperse polystyrene standards covering the molecular weight range from 580 to 460 000 Da. A Micromass Q-Tof (Micromass, Wythenshawe, UK) mass spectrometer equipped with an orthogonal electrospray source (Z-spray) [electrospray ionization mass spectrometry (ESI-MS)] was operated in positive and negative ion mode. ESI-MS spectra of the cobalt complexes in positive ion mode were referenced against the sample of $(m/z)^+ = 574.3182$ (capillary = 2000 V, sample cone = 20 V), and those in negative ion mode were referenced against the sample of $(m/z)^- = 193.0898$ (capillary = 2000 V, sample cone = 30 V). Differential scanning calorimetry (DSC) analyses of all resulted polymers was performed on a NETZSCH DSC 204, with a heating rate of 10 K/min from 0 to 150 °C. Thermogravimetric analyses (TGA) of all resulted polymers were measured on a Mettler-Toledo TGA/SDTA851$^e$, with a heating rate of 10 K/min from ambient temperature to 450 °C.

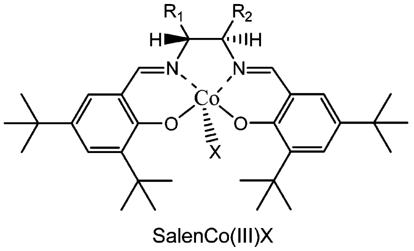
**Representative Procedure for the Copolymerization of $CO_2$ with Cyclohexene Oxide.** To a stirred mixture of complex **1a** (0.0754 g, 0.1 mmol, 1 equiv) was dissolved in cyclohexene oxide (100 mmol, 1000 equiv) to form a red-brown solution, and then PPNCl (0.1 mmol, 1 equiv) was added into it in a nitrogen atmosphere. The mixture solution was stirred about 30 min and then charged into a predried 75 mL autoclave equipped with a magnetic stirrer under a $CO_2$ atmosphere. The autoclave was put into a bath of 25 °C and then pressurized to the appropriate pressure with $CO_2$. After the allotted reaction time, a small amount of the resultant polymerization mixture was removed from the autoclave for $^1H$ NMR analysis to quantitatively give the selectivity of polycarbonates to cyclic carbonate as well as carbonate linkages and also used for GPC analysis. The crude polymer was dissolved in a 10 mL $CHCl_3$/MeOH (5/1, v/v) mixture with 0.5% HCl solution and precipitated from methanol or diethyl ether. This process was repeated 3−5 times to completely remove the catalyst, and white polymer was obtained by vacuum-drying.

**Terpolymerization of $CO_2$ with Propylene Oxide and Cyclohexene Oxide.** To a stirred mixture of complex **1b** (0.0786 g, 0.1 mmol, 1 equiv) was dissolved in the mixture solution composed of 50 mmol of cyclohexene oxide (~50 mol %) and 50 mmol of propylene oxide (~50 mol %) to form a red-brown solution, and then PPNCl (0.1 mmol, 1 equiv) was added into it in a nitrogen atmosphere. The mixture solution was stirred about 30 min and then charged into a predried 75 mL autoclave equipped with a magnetic stirrer under a $CO_2$ atmosphere. The autoclave was put into a bath of 25 °C and then pressurized to the appropriate pressure with $CO_2$. Other procedures are the same as the copolymerization of $CO_2$ with cyclohexene oxide.

**Hydrolysis of Poly(cyclohexene carbonate) and Determination of Enantiomeric Purity of Cyclohexanediol.** The hydrolysis of poly(cyclohexene carbonate) was applied as previously described by Nozaki et al., and an almost quantitative yield was obtained for cyclohexanediol.[16a] The enantiomeric excess of the resulted cyclohexane diol was determind by GC analysis with a chiral column (GC column, 2,6-dibutyl-3-butyryl-$\beta$-Cyclodex, 30 m × 0.25 mm id × 0.25 $\mu$m film; injecton temperature = 250 °C; detection temperature = 250 °C; oven temperature (programmed): 100−125 °C, 1 °C/min, hold 10 min; then 125−140 °C, 10 °C/min, hold 5 min, $t_{[(S,S)-\mathrm{PCHC}]} = 34.6$ min, $t_{[(R,R)-\mathrm{PCHC}]} = 35.0$ min).

## Results and Discussion

**Asymmetric Alternating Copolymerization of Cyclohexene Oxide (CHO) and $CO_2$.** Although the asymmetric alternating copolymerization of CHO and $CO_2$ has been demonstrated first by Nozaki using organozinc−chiral amino alcoholate catalysts for several years, only zinc has been the metal of choice for designing discrete chiral catalysts for this process.[16,17] Stimulated by our success with binary chiral electrophile−nucleophile cobalt-based catalyst systems for the asymmetric alternating copolymerization of aliphatic epoxides and $CO_2$,[10b] we likewise apply these systems to the asymmetric copolymerization of alicyclic CHO and $CO_2$. We were gratified to discover that the binary system of the complex (1*R*,2*R*)-**1a** as an electrophile (Figure 1) in conjunction with bis(triphenylphosphine)iminium chloride (PPNCl) as a nucleophile could operate very efficiently at ambient temperature and 1.5 MPa $CO_2$ pressure for CHO/$CO_2$ copolymerization to provide isotactic (*S*,*S*)-enriched polycarbonates with a narrow polydispersity ($M_w/M_n$ ratio) of 1.23. Indeed, only limited catalysts exhibit certain activities for CHO/$CO_2$ copolymerization at room temperature and relatively low $CO_2$ pressure, probably due to the more sterically hindered, less



**1a**: $R_1$ and $R_2$ = (*1R,2R*)-trans-$(CH_2)_4$-, X = $OOCCCl_3$;
**1b**: $R_1$ and $R_2$ = (*1R,2R*)-trans-$(CH_2)_4$-, X = 2,4-dinitrophenoxy;
**2a**: (*1R,2R*)-trans, $R_1$ = $R_2$ = Ph, X = $OOCCCl_3$;
**3a**: $R_1$ = (*R*)-$CH_3$, $R_2$ = H; X = $OOCCCl_3$;

**Figure 1.** Tetradentate Schiff-base cobalt complexes with varying chiral diamine backbones.

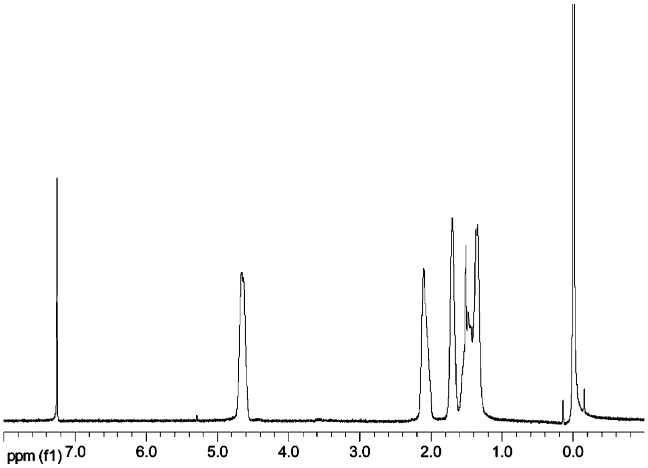


**Figure 2.** $^1H$ NMR spectrum of poly(cyclohexene carbonate).

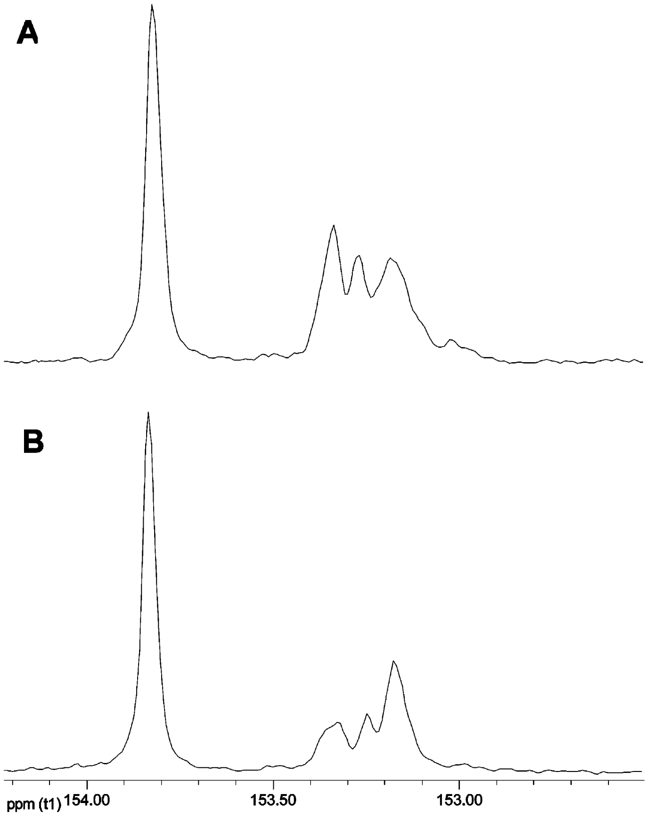
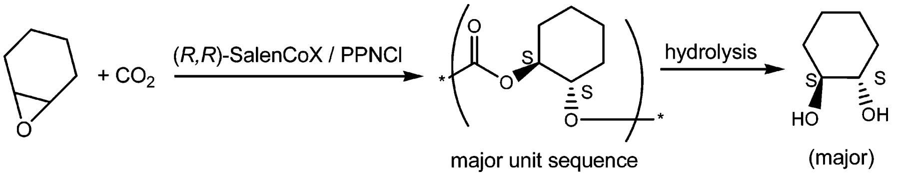


**Figure 3.** Carbonyl region of $^{13}C$ NMR of (A) the copolymer obtained with the binary racemic **1a**/PPNCl catalyst system and (B) the copolymer obtained with the binary (*R*,*R*)-**1a**/PPNCl system.

reactive CHO monomer.[6e,17] The completely alternating nature (>99% carbonate linkages) of the resulting polymer was reflected in the presence of the methane proton peak in cyclohexene carbonate unit at $\delta = 4.65$ ppm and the absence of that in the reparting oxy(1,2-cyclohexene) unit (ether linkage) at $\delta = 3.45$ ppm (Figure 2). Figure 3 shows the carbonyl region of $^{13}C$ NMR spectra of (A) the copolymer obtained with the binary racemic **1a**/PPNCl catalyst system and (B) the copolymer of 38% ee obtained with the binary (*R*,*R*)-**1a**/PPNCl system. As illustrated, the signals are not identical with each other, indicating the difference in tacticity.[23] More recently, the Coates group has reported that racemic or chiral SalenCoX (X = Cl, Br, I, pentafluorobenzoate ($ObzF_5$)) alone as catalysts are active for the copolymerization of CHO and $CO_2$ at a high pressure of up to 54.4 atm (~5.5 MPa), yielding syndiotactic enriched poly(cyclohexene carbonate) (PCHC).[19b] In addition, the copolymerization reaction at low $CO_2$ pressure generally resulted in a loss of syndiospecificity and a significant decrease of catalyst activity, but the use of most sterically bulk chiral SalenCoX complexes surprisingly produced isotactic-enriched PCHC with 65% *m*-centered tetrads. Interestingly, the addition of PPNCl to the SalenCoX complexes catalyzed CHO/$CO_2$ copolymerization also resulted in the loss of syndiospecificity. However, for the (1*R*,2*R*)-(Salen-1)$CoObzF_5$/PPNCl system, the authors did not determine the enantiomeric purity of cyclohexanediol originating from the hydrolysis of PCHC, which is dependent on the tacticity of PCHC. We tentatively assume that SalenCoX complexes alone as catalyst involve a copolymerization mechanism with initiation occurring by a bimetallic process and propagation operating by a monometallic mode, as similar to SalenCrX systems proposed by Darensbourg and coworkers.[11b,c] For binary electrophile−nucleophile systems, such as the (*R*,*R*)-**1a**/PPNCl catalyst system, both initiation and propagation operate only a monometallic process. The difference in the initiation process may significantly influence the tacticity of PCHC. On the other hand, the use of chiral cobalt complexes should benefit for the formation of isotactic-enriched PCHC. However, it is difficult to understand why racemic SalenCoX complexes alone are higher syndiospecifity catalyst than their corresponding chiral complexes.[19b]

The enantioselectivity of the resulting polycarbonates was evaluated by the procedure reported by Nozaki et al.[16] and based on the enantiomeric excess (ee) of the cyclohexane-1,2-diol produced from the hydrolysis of PCHC. After hydrolysis of the PCHC with aqueous NaOH, the enantiomeric excess of the resulting cyclohexane-1,2-diol was measured by chiral GC to be only 38% with an *S*,*S* configuration, which value is much less than that of PCHC (~70%) obtained by the use of the reported organozinc−chiral amino alcoholate or hybrid imine−oxazoline zinc-based catalysts.[16,17] Entries 1−4 in Table 1 show the strong influence of reaction temperature on rate. An increase in the temperature between 25 and 80 °C results in a dramatic increase in activity, but the variation of temperature does not lead to an observable decrease in selectivity for PCHC formation. For example, a change in the reaction temperature from 25 to 80 °C resulted in TOF from 91 $h^{-1}$ rapidly increasing to 925 $h^{-1}$ and polymer enantioselectivity from 38% ee decreasing to 28% ee, respectively. Similar to the $CO_2$/PO copolymerization with the binary catalyst system, a decrease in the $CO_2$ pressure from 1.5 to 0.6 MPa during the $CO_2$/CHO copolymerization does not cause an observable decrease in rate, enantioselectivity, and selectivity for PCHC formation (entry 5). However, increasing the $CO_2$ pressure from 1.5 to 5.2 MPa led to a dramatic loss in catalyst activity. Indeed, in the system of

**Table 1. Asymmetric Alternating Copolymerization of $CO_2$ with Cyclohexene Oxide**[a]



| entry | catal | cocatal | temp (°C) | pressure (MPa) | time (h) | TOF[b] ($h^{-1}$) | $M_n$[c] × $10^{-3}$ | PDI[c] ($M_w/M_n$) | *RR*:*SS*[d] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | **1a** | PPNCl | 25 | 1.5 | 5.0 | 89 | 20.2 | 1.23 | 31:69 |
| 2 | **1a** | PPNCl | 40 | 1.5 | 2.0 | 286 | 21.9 | 1.18 | 33:37 |
| 3 | **1a** | PPNCl | 60 | 2.5 | 0.8 | 687 | 17.9 | 1.29 | 34:66 |
| 4 | **1a** | PPNCl | 80 | 2.5 | 0.5 | 925 | 11.4 | 1.30 | 36:64 |
| 5 | **1a** | PPNCl | 25 | 0.6 | 5.0 | 91 | 20.6 | 1.17 | 31:69 |
| 6 | **1a** | PPNCl | 25 | 5.2 | 5.0 | 59 | 11.3 | 1.22 | 36:64 |
| 7 | **1a** | $PPNN_3$ | 25 | 1.5 | 5.0 | 94 | 18.7 | 1.25 | 31:69 |
| 8 | **1b** | PPNCl | 25 | 1.5 | 5.0 | 83 | 21.2 | 1.22 | 31:69 |
| 9 | **2a** | PPNCl | 25 | 1.5 | 5.0 | 81 | 17.9 | 1.23 | 32:68 |
| 10 | **3a** | PPNCl | 25 | 1.5 | 5.0 | 67 | 11.8 | 1.18 | 43:57 |

[a] The reaction was performed in neat CHO (100 mmol; catalyst/cocatalyst/CHO = 1/1/1000, molar ratio) in 75 mL autoclave. [b] Turnover frequency of CHO to PCHC. [c] Determined by GPC against polystyrene standards. [d] Measured by hydrolyzing the polymer and analyzing the resulting diol by chiral GC.

SalenCrX/PPNCl or tricyclohexylphosphine-catalyzed $CO_2$/CHO copolymerization, Darensboug et al. have observed a similar pressure dependence, which was simply attributed to a dilution effect of excess $CO_2$ into the liquid phase where catalyst and epoxide reside.[24] Surprisingly, the increase in the $CO_2$ pressure also led to an obvious decrease in enantioselectivity of PCHC (Table 1, entry 6, and Supporting Information, Figure 1), which is very different from some SalenCoX complexes alone as catalyst for the synthesis of syndiotactic-enriched PCHC,[19b] but the reason is not clear.

With PPNCl as cocatalyst, several SalenCo(III)X complexes with varying chiral diamine backbones or axial X group (Figure 1) were investigated as catalyst for $CO_2$/CHO copolymerization (entries 8−10). For the same axial X group, changing the Salen ligand framework to noncyclic (1*R*,2*R*)-diphenyldiamine backbone had no observable effect on catalyst activity and polymer enantioselectivity, but changing to (*R*)-propyldiamine backbones resulted in a significant decreases in polymer enantioselectivity. With the (1*R*,2*R*)-cyclohexyl backbone, substitution of dinitrophenoxy for trichloroacetate on the axial X group had little effect on catalyst activity and polymer enantioselectivity (entry 7).

**Terpolymerization of $CO_2$ with Propylene Oxide (PO) and Cyclohexene Oxide (CHO).** In contrast to the brittle behavior of PCHC, PPC has an excellent elongation property, but relatively low glass transition temperature (35−45 °C) of this polymer limits its use as structural materials in various fields. As a result, some attention was paid to the terpolymerization of PO, CHO, and $CO_2$ for adjusting the glass transition temperature ($T_g$) of the polycarbonates.[13] Unfortunately, the great difference in reactivity of CHO and PO during the terpolymerization of epoxides with $CO_2$ in the zinc-based catalyst systems leads to the difficulty in controlling the composition and the alternating nature of the resulting copolymer. For example, bis 2,6-difluorophenoxide dimeric complexes of zinc have been reported as catalyst for the terpolymerization of PO (50 mol %) and CHO (50 mol %) with $CO_2$ at 55 °C and 600−700 psi pressure, but the resulting polymer had 84.76 mol % cyclohexene carbonate linkages, only 11.90% propylene carbonate linkages, and 3.34 mol % propylene ether linkages, with concomitant production of cyclic propylene carbonate.[13a] On the basis of our success in the use of binary electrophile−nucleophile cobalt-based catalyst systems for the alternating copolymerization of both PO and CHO with $CO_2$ at mild conditions, we became interested in the possibility of exploring the binary catalyst system for the terpolymerization of $CO_2$ with PO and CHO. We were delighted to find that the binary system of the complex **1a** and PPNCl could operate very efficiently at 25 °C and 1.5 MPa $CO_2$ pressure for the terpolymerization of $CO_2$ with PO (50 mol %) and CHO (50 mol %) to selectively provide polycarbonates with a narrow polydispersity ($M_w/M_n$ ratio) of 1.24, in the $^1H$ NMR of which one ($\delta = 4.99$ ppm) of the two peaks was attributed from CH in propylene carbonate unit and the other ($\delta = 4.65$ ppm) from CH in cyclohexene carbonate unit (Figure 4). The completely alternating structure (>99% carbonate linkages) was verified by no observable signal assignable to the reparting oxy(1,2-cyclohexene) or oxy(1,2-propylene) unit ($\delta = 3.4{-}3.5$ ppm, ether linkage) in the $^1H$ NMR spectrum of the resulting terpolymer.

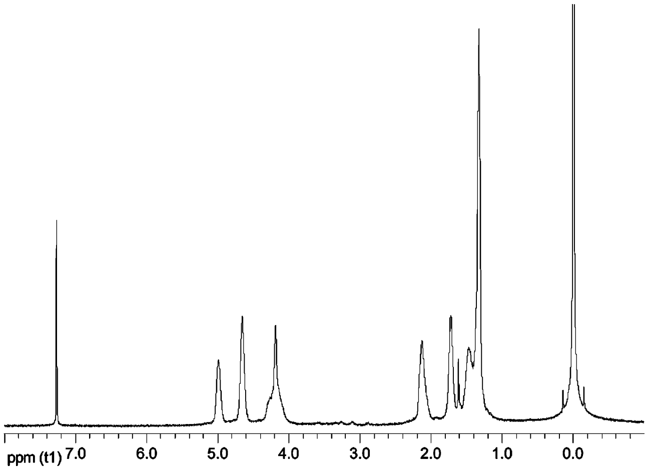


**Figure 4.** $^1H$ NMR spectrum of the PO/CHO/$CO_2$ terpolymer.

Interestingly, the multiple splits of the peak at 4.65 ppm in PCHC and 4.19 ppm in PPC were hardly observed in the $^1H$ NMR of the resulting terpolymer but obviously appeared in the $^1H$ NMR of the blend of PPC and PCHC (Figure 5). Notably, after ~50% conversion of all epoxides, the resulting polycarbonate has about 60 mol % propylene carbonate linkages and 40 mol % cyclohexene carbonate linkages, though the rate of the PO/$CO_2$ copolymerization in the presence of the binary **1b**/PPNCl system is about 6 times that of the CHO/$CO_2$ copolymerization at the same reaction condition (Table 2). The

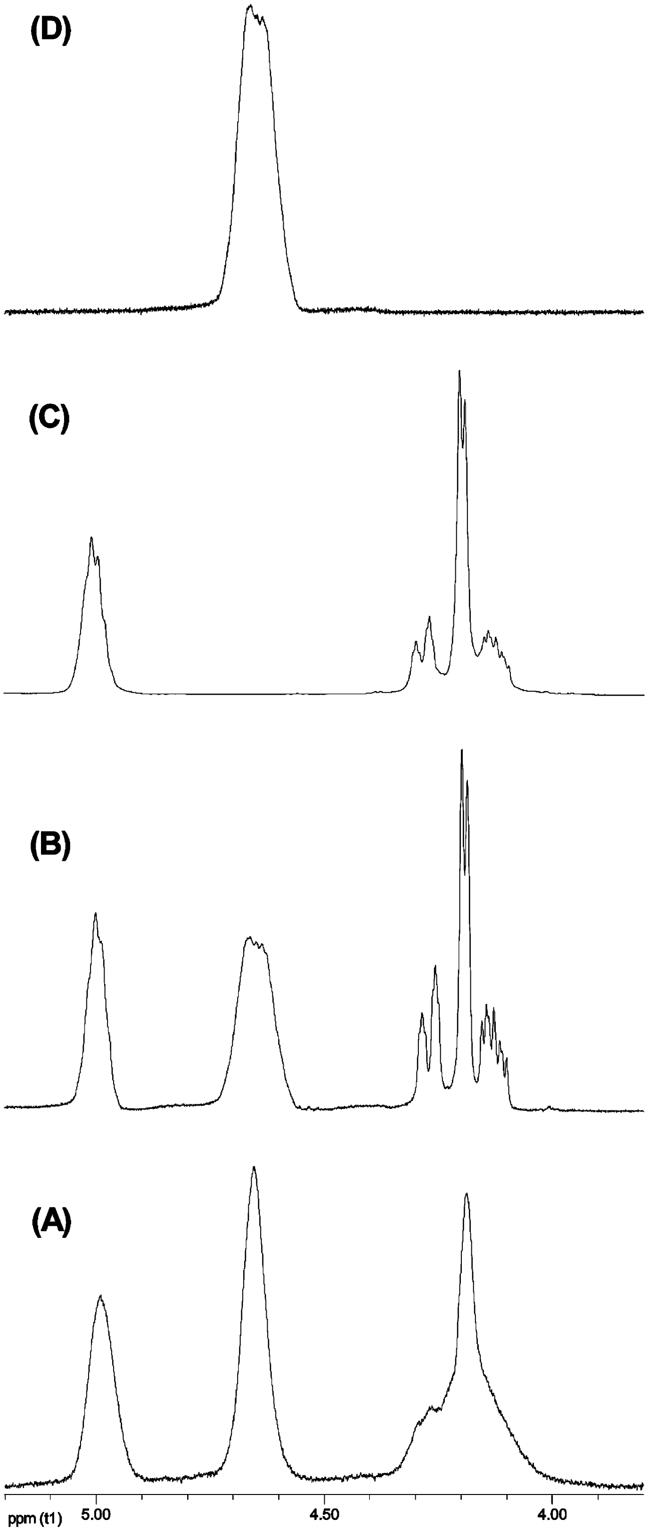


**Figure 5.** $^1$H NMR spectra of (A) the PO/CHO/$CO_2$ terpolymer, (B) the blend of PPC and PCHC, (C) PPC, and (D) PCHC.

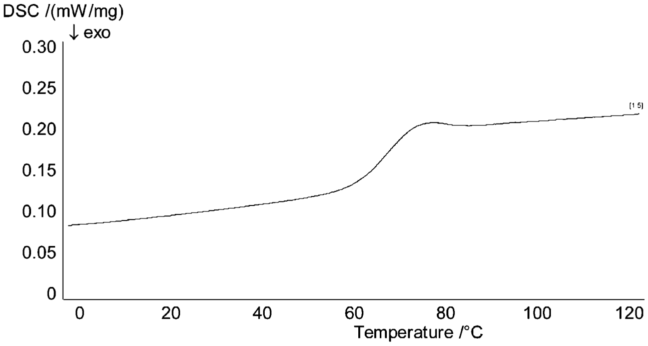


**Figure 6.** DSC thermogram of the PO/CHO/$CO_2$ terpolymer containing 60 mol % propylene carbonate linkages and 40 mol % cyclohexene carbonate linkages.

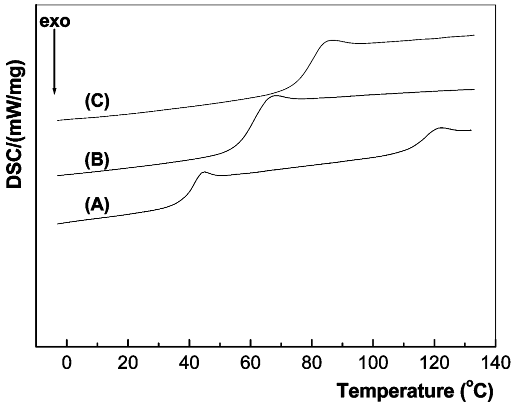


**Figure 7.** DSC thermograms of (A) the blend of PPC and PCHC and the PO/CHO/$CO_2$ terpolymer (B) containing 30 mol % and (C) 60 mol % cyclohexene carbonate linkages, respectively.

unprecedented results have led us to tentatively assume that an alternating nature of the two different carbonate units predominantly exists in the resulting polycarbonate (Scheme 1). This assumption was further supported by differential scanning calorimetry analysis (DSC) and thermogravimetry (TG) analyses of the terpolymer. The DSC thermogram is given in Figure 6. This thermogram clearly shows only one $T_g$ of 68.8 °C. On the contrary, the thermogram of the PCHC/PPC blend shows two baseline shifts (Figure 7), one $T_g$ at 41.6 °C (attributable to the PPC) and the other $T_g$ at 117.1 °C (attributable to the PCHC). The thermolysis curve of the terpolymer indicates a narrow range 276−300 °C of 10%−90% thermal decomposition and only one thermolysis peak at 290 °C, compared to a relatively broad range 262−313 °C, and two thermolysis peaks at 285 and 305 °C for the PCHC/PPC blend (Figures 8 and 9). For confirming the alternating nature of the resulting terpolymer, we also performed electrospray ionization mass spectrometry (ESI-MS) for investigating the mode of polymer chain growth. Unfortunately, no signal concerning polymer chain growth was observed in the mass spectra of the positive or negative mode, predominately because of the very low correspondence of growth polymer with chlorine as end group. Therefore, we have to choose 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD, a sterically hindered strong organic bases) to substitute for PPNCl as a cocatalyst consistent with **1b** for the terpolymerization of CHO/PO/$CO_2$. In the ESI-Q-TOF mass spectra in positive ion mode, we observe the strong signals of 314, 354, 456, 558, 598, and 700, which are attributed to the species of [($H^+$ + MTBD + PO) + PC], [($H^+$ + MTBD + PO) + CHC], [($H^+$ + MTBD + PO) + PC + CHC] or [($H^+$ + MTBD + PO) + CHC + PC], [($H^+$ + MTBD + PO) + 2PC + CHC], [($H^+$ + MTBD + PO) + PC + 2CHC], and [($H^+$ + MTBD + PO) + 2(PC + CHC)], respectively (see Supporting Information, Figure 2). This result clearly indicates that the terpolymer is not poly(PO-*alt*-$CO_2$)-*block*-(CHO-*alt*-$CO_2$). Of course, we also cannot affirm that the two different carbonate units are arranged in an alternating fashion or incorporated in a random fashion. However, if agree with the latter assumption, it is difficult to understand why the rate of the PO/$CO_2$ copolymerization in the presence of the binary **1b**/PPNCl system is about 6 times

**Table 2. Polymerization of $CO_2$ with Various Epoxides Catalyzing by the Binary 1b/PPNCl System[a]**

| entry | epoxide | epoxide/catal (mol/mol) | time (h) | TOF[b] ($h^{-1}$) | $M_n$[c] × $10^{-3}$ | PDI[c] ($M_w/M_n$) | $T_g$[d] (°C) | $T_{50}$[e] (°C) |
|---|---|---|---|---|---|---|---|---|
| 1 | PO | 2000 | 1.5 | 530 | 30.9 | 1.20 | 40.5 | 257 |
| 2 | CHO | 1000 | 4.0 | 85 | 16.6 | 1.25 | 117.3 | 312 |
| 3[f] | PO/CHO | 1000 | 4.0 | 129 | 24.4 | 1.24 | 68.8 | 289 |
| 4[g] | PPC/PCHC | blend | | | | | 41.6, 117.1 | 295 |

[a] The reaction was performed in neat epoxide (**1b** / PPNCl = 1/1, molar ratio) at 25°C and 1.5 MPa $CO_2$ pressure in a 75 mL autoclave. [b] Turnover frequency of epoxides to polycarbonates. [c] Determined by GPC against polystyrene standards. [d] Glass transition temperature determined by DSC. [e] The temperature at polymer decomposition of 50% measured by TGA. [f] **1b**/PPNCl/CHO /PO = 1/1/500/500, molar ratio. [g] The blend of PPC ($M_n$ = 45 000, PDI = 1.30, $T_g$ = 42.1 °C) and PCHC ($M_n$ = 16 600, PDI = 1.25, $T_g$ = 117.3 °C) (propylene carbonate linkages/cyclohexene carbonate linkages = 1/1, molar ratio).

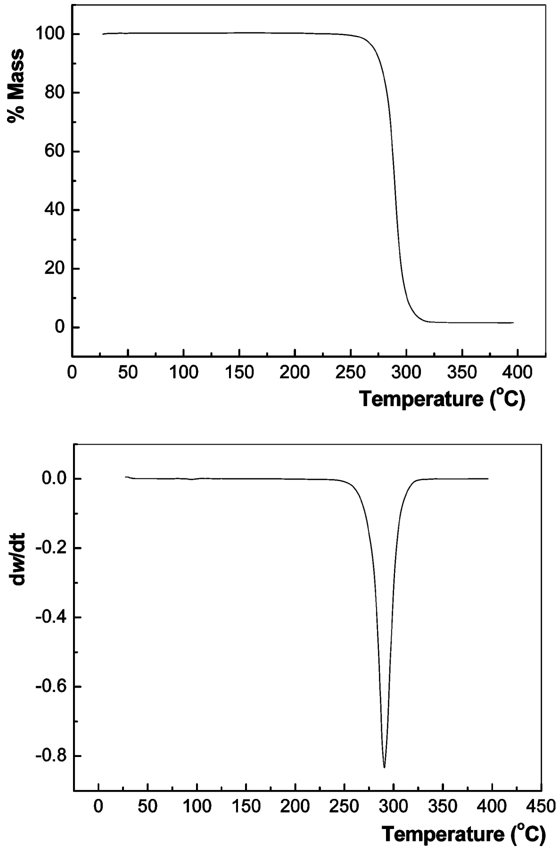


**Figure 8.** Thermolysis curve of the PO/CHO/$CO_2$ terpolymer containing 60 mol % propylene carbonate linkages and 40 mol % cyclohexene carbonate linkages.

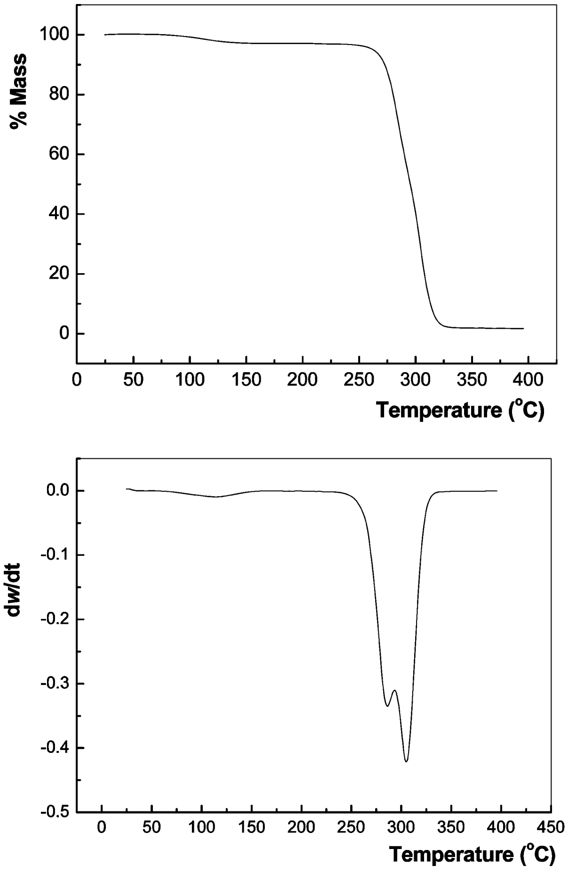


**Figure 9.** Thermolysis curve of the blend of PPC and PCHC (propylene carbonate linkages/cyclohexene carbonate linkages = 1/1, molar ratio).

that of the CHO/$CO_2$ copolymerization at the same reaction condition, while the polycarbonate resulting from the PO/CHO/$CO_2$ terpolymerization (PO/CHO, 1/1 molar ratio) has about 60 mol % propylene carbonate linkages and 40 mol % cyclohexene carbonate linkages, after ~50% conversion of all epoxides in the system (Table 2). Therefore, we tentatively assume that the two units, (PO-*alt*-$CO_2$) and (CHO-*alt*-$CO_2$), are predominately incorporated in alternating mode, but the alternating nature is not perfect. In other words, the content of the (PO-*alt*-$CO_2$)-*alt*-(CHO-*alt*-$CO_2$) unit is significantly higher than that of the dimer of (PO-*alt*-$CO_2$) or (CHO-*alt*-$CO_2$).

The unprecedented alternating nature of cyclohexene carbonate linkages and propylene carbonate linkages in the terpolymer is probably attributed to four factors: (1) The relatively high basicity and coordination ability of CHO inhibit the reactivity of PO during the coordination polymerization. (2) The relatively low reactivity and the steric hindrance of CHO retard the formation of the homopolymerization unit of cyclohexene carbonate linkages. (3) The dissociation of the propagating carboxylate from the metal center is much faster process than propagation, and the free propagating carboxylate can also act as a nucleophile for attacking a cobalt-coordinated epoxide during the terpolymerization. In a previous paper,[19a] we found the number of polycarbonate chains is independent of the initial cobalt complex concentration but is only in consistent with the PPNCl concentration. The result that the narrow molecular weight distribution was observed in the resulting polymer obtained from the catalyst system with high molar ratio of PPNCl to the cobalt complex suggests the reversible chain transfer of the propagating species during the reaction. The further in-situ infrared spectra show that free $CO_2$ in the copolymerization process helps to stabilize the propagating carboxylate against decomposition to $CO_2$ and long-chain alkoxide, which easily degrades into cyclic PC. This assumption is in sharp contrast to the suggestion of the Riger group based on a DFT theoretical calculation, in which they proposed that the formation of cyclic carbonate from the polymer chain in the catalyst system of chromium(III) or aluminum(III) metal−Salen complexes would involve attack of a free propagating carboxylate rather than an alkoxide at the last unit of the growing chain.[11f] (4) More importantly, the dissociation of the propagating carboxylate with propylene carbonate linkage as end unit from the metal center is much easier than that with cyclohexene carbonate linkage as end unit. If not, the homochain CHC sequence rather than the alternating sequence of PC and CHC will predominantly exist in the PO/CHO/$CO_2$ terpolymer.

Of importance, the $T_g$ of the PO/CHO/$CO_2$ terpolymer can be easily adjusted between 50 and 100 °C by controlling the proportion of cyclohexene carbonate linkages and propylene carbonate linkages in the terpolymer. For example, a change in the content of cyclohexene carbonate linkages in the terpolymer from 30 mol % increasing to 60 mol % results in the $T_g$ from 59.6 °C significantly increasing to 80.5 °C (Figure 7).

## Conclusion

We have demonstrated that a chiral tetradentate Schiff-base cobalt complex in conjunction with a bulky ionic organic ammonium salt is a highly efficient catalyst for the asymmetric alternating copolymerization of $CO_2$ with cyclohexene oxide at mild temperature and pressure to afford isotactic-enriched polycarbonates with a narrow molecular distribution. Increasing the $CO_2$ pressure from 1.5 to 5.2 MPa led to a dramatic loss in catalyst activity and an obvious decrease in enantioselectivity of PCHC. Also, the binary catalyst system was proved to be very effective in the terpolymerization of CHO, PO, and $CO_2$. Of importance, the resulting terpolymer has only one glass transition temperature ($T_g$) and one thermolysis peak. We tentatively assume that an alternating nature of the two different carbonate units predominantly exists in the resulting polycarbonate. Further investigations on confirming the alternating nature of the two different carbonate units and how to precisely control the terpolymerization process are in progress. Additionally, the $T_g$ of the PO/CHO/$CO_2$ terpolymer can be easily adjusted between 50 and 100 °C by controlling the proportion of cyclohexene carbonate linkages and propylene carbonate linkages in the terpolymer.

**Acknowledgment.** Gratitude is expressed to the National Natural Science Foundation of China (NSFC) program (Grant 20574008), the Key Project on Science and Technology (Grant 105051, Ministry of Education of China), and the Specialized Research Fund for the Doctoral Program of Higher Education (SREDP) (Grant 20050141017) for financial support.

**Supporting Information Available:** General experimental procedures of the cobalt complexes and ESI-Q-TOF mass spectrum of the PO/CHO/$CO_2$ terpolymer. This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

(1) (a) Behr, A. *Angew. Chem.* **1988**, *100*, 681−698. (b) Leitner, W. *Coord. Chem. Rev.* **1996**, *153*, 257−284. (c) Yin, X. L.; Moss, J. R. *Coord. Chem. Rev.* **1999**, *181*, 27−59. (d) Walther, D.; Ruben, M.; Rau, S. *Coord. Chem. Rev.* **1999**, *182*, 67−100. (e) Beckman, E. J. *Science* **1999**, *283*, 946−947.

(2) For recent reviews on $CO_2$/epoxides copolymerization, see: (a) Coates, G. W.; Moore, D. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6618−6639. (b) Darensbourg, D. J.; Mackiewicz, R. M.; Phelps, A. L.; Billodeaus, D. R. *Acc. Chem. Res.* **2004**, *37*, 836−844. (c) Sugimoto, H.; Inoue, S. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5561−5573. (d) Kuran, W. *Prog. Polym. Sci.* **1998**, *23*, 919−992. (e) Darensbourg, D. J.; Holtcamp, M. W. *Coord. Chem. Rev.* **1996**, *153*, 155−174.

(3) (a) Inoue, S.; Koinuma, H.; Tsuruta, T. *J. Polym. Sci., Polym. Lett.* **1969**, *7*, 287−292. (b) Inoue, S.; Koinuma, H.; Tsuruta, T. *Makromol. Chem.* **1969**, *130*, 210−220.

(4) Wilks, E. S. *Industrial Polymers Handbook*; Wiley-VCH: Weinheim, 2001; pp 291−304.

(5) (a) Chen, X. H.; Shen, Z. Q.; Zhang, Y. F. *Macromolecules* **1991**, *24*, 5305−5308. (b) Darensbourg, D. J.; Holtcamp, M. W. *Macromolecules* **1995**, *28*, 7577−7579. (c) Hsu, T. J.; Tan, C. S. *Macromolecules* **1997**, *30*, 3147−3150. (d) Ree, M.; Bae, J. Y.; Jung, J. H.; Shin, T. J. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 1863−1876. (e) Liu, B. Y.; Zhao, X. J.; Wang, X. H.; Wang, F. S. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2751−2754. (f) Quan, Z.; Wang, X. H.; Zhao, X. J.; Wang, F. S. *Polymer* **2003**, *44*, 5605−5610. (g) Darensbourg, D. J.; Lewis, S. J.; Rodgers, J. L.; Yarbrough, J. C. *Inorg. Chem.* **2003**, *42*, 581−589. (h) Eberhardt, R.; Allmendinger, M.; Zintl, M.; Troll, C.; Luinstra, G. A.; Riger, B. *Macromol. Chem. Phys.* **2004**, *205*, 42−47.

(6) (a) Super, M.; Berluche, E.; Costello, C.; Beckman, E. *Macromolecules* **1997**, *30*, 368−372. (b) Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **1998**, *120*, 11018−11019. (c) Sârbu, T.; Beckman, E. J. *Macromolecules* **1999**, *32*, 6904−6912. (d) Cheng, M.; Moore, D. R.; Reczek, J. J.; Chamberlain, B. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 8738−8749. (e) Moore, D. R.; Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *Angew. Chem., Int. Ed.* **2002**, *41*, 2599−2602. (f) Lee, B. Y.; Kwon, H. Y.; Lee, S. Y.; Na, S. J.; Han, S.-i.; Yun, H.; Lee, H.; Park, Y.-W. *J. Am. Chem. Soc.* **2005**, *127*, 3031−3037. (g) Kröger, M.; Folli, C.; Walter, O.; Döring, M. *Adv. Synth. Catal.* **2005**, *347*, 1325−1328. (h) Xiao, Y.; Wang, Z.; Ding, K. *Chem.—Eur. J.* **2005**, *11*, 3668−3678.

(7) Xiao, Y.; Wang, Z.; Ding, K. *Macromolecules* **2006**, *39*, 128−137.

(8) (a) Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1983**, *105*, 1304−1309. (b) Aida, T.; Ishikawa, M.; Inoue, S. *Macromolecules* **1986**, *19*, 8−13. (c) Aida, T.; Inoue, S. *Acc. Chem. Res.* **1996**, *29*, 39−48. (d) Darensbourg, D. J.; Billodeaux, D. R. *Inorg. Chem.* **2005**, *44*, 1433−1442.

(9) Sugimoto, H.; Ohshima, H.; Inoue, S. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3549−3555.

(10) (a) Qin, Z.; Thomas, C. M.; Lee, S.; Coates, G. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 5484−5487. (b) Lu, X. B.; Wang, Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 3574−3577. (c) Paddock, R. L.; Nguyen, S. T. *Macromolecules* **2005**, *38*, 6251−6253.

(11) (a) Mang, S.; Cooper, A. I.; Colclough, M. E.; Chauhan, N.; Holmes, A. B. *Macromolecules* **2000**, *33*, 303−308. (b) Darensbourg, D. J.; Yarbrough, J. C. *J. Am. Chem. Soc.* **2002**, *124*, 6335−6342. (c) Darensbourg, D. J.; Yarbrough, J. C.; Ortiz, C.; Fang, C. C. *J. Am. Chem. Soc.* **2003**, *125*, 7586−7591. (d) Eberhardt, R.; Allmendinger, M.; Rieger, B. *Macromol. Rapid Commun.* **2003**, *24*, 194−196. (e) Darensbourg, D. J.; Mackiewicz, R. M.; Rodgers, J. L.; Fang, C. C.; Billodeaux, D. R.; Reibenspies, J. H. *Inorg. Chem.* **2004**, *43*, 6024−6034. (f) Luinstra, G. A.; Hass, G. R.; Molnar, F.; Bernhart, V.; Eberhardt, R.; Rieger, B. *Chem.—Eur. J.* **2005**, *11*, 6298−6314. (g) Darensbourg, D. J.; Mackiewicz, R. M. *J. Am. Chem. Soc.* **2005**, *127*, 14026−14038.

(12) Cui, D.; Nishiura, M.; Hou, Z. *Macromolecules* **2005**, *38*, 4089−4095.

(13) (a) Darensbourg, D. J.; Wildeson, J. R.; Yarbrough, J. C.; Reibenspies, J. H. *J. Am. Chem. Soc.* **2000**, *122*, 12487−12496. (b) Quan, Z.; Min, J.; Zhou, Q.; Xie, D.; Liu, J.; Wang, X.; Zhao, X.; Wang, F. *Macromol. Symp.* **2003**, *195*, 281−286.

(14) Darensbourg, D. J.; Phelps, A. L. *Inorg. Chem.* **2005**, *44*, 4622−4629.

(15) Willis, M. C. *J. Chem. Soc., Perkin Trans. 1* **1999**, 1765−1784.

(16) (a) Nozaki, K.; Nakano, K.; Hiyama, T. *J. Am. Chem. Soc.* **1999**, *121*, 11008−11009. (b) Nakano, K.; Nozaki, K.; Hiyama, T. *J. Am. Chem. Soc.* **2003**, *125*, 5501−5510. (c) Nakano, K.; Hiyama, T.; Nozaki, K. *Chem. Commun.* **2005**, 1871−1873.

(17) Cheng, M.; Darling, N. A.; Lobkovsky, E. B.; Coates, G. W. *Chem. Commun.* **2000**, 2007−2008.

(18) Cohen, C. T.; Chu, T.; Coates, G. W. *J. Am. Chem. Soc.* **2005**, *127*, 10869−10878.

(19) (a) Lu, X. B.; Shi, L.; Wang, Y. M.; Zhang, R.; Zhang, Y. J.; Peng, X. J.; Zhang, Z. C.; Li, B. *J. Am. Chem. Soc.* **2006**, *128*, 1664−1674. (b) Cohen, C. T.; Thomas, C. M.; Peretti, K. L.; Lobkovsky, E. B.; Coates, G. W. *Dalton Trans.* **2006**, 237−249.

(20) Demadis, K. D.; Meyer, T. J.; White, P. S. *Inorg. Chem.* **1998**, *37*, 3610−3619.

(21) (a) Zhang, W.; Jacobsen, E. N. *J. Org. Chem.* **1991**, *56*, 2296−2298. (b) Pospisil, P. J.; Carsten, D. H.; Jacobsen, E. N. *Chem.—Eur. J.* **1996**, *2*, 974−980.

(22) Schaus, S. E.; Brandes, B. D.; Larrow, J. F.; Tokunaga, M.; Hansen, K. B.; Gould, A. E.; Furrow, M. E.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2002**, *124*, 1307−1315.

(23) Nakano, K.; Nozaki, K.; Hiyama, T. *Macromolecules* **2001**, *34*, 6325−6332.

(24) Darensbourg, D. J.; Mackiewicz, R. M.; Billodeaux, D. R. *Organometallics* **2005**, *24*, 144−148.

MA060290P