

## Highly Selective and Reactive (salan)CrCl Catalyst for the Copolymerization and Block Copolymerization of Epoxides with Carbon Dioxide

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**ABSTRACT:** Chromium(III) derivatives of the tetradentate phenoxyamine ligand H<sub>2</sub>salan, where salan = the *N,N'*-dimethylated bis(aminophenoxide) ligand or the saturated version of the corresponding salen ligand, in the presence of 1 equiv of [PPN]<sup>+</sup>N<sub>3</sub><sup>−</sup> (PPN<sup>+</sup> = Ph<sub>3</sub>P=N<sup>+</sup>=PPh<sub>3</sub>) are shown to effectively catalyze the copolymerization of cyclohexene oxide and carbon dioxide. X-ray crystallographic analysis reveals the structure of the complex to be different from that of its salen analogue, with an all *cis* arrangement of the nitrogen and oxygen atoms. Although these catalysts are selective for copolymerizing propylene oxide and CO<sub>2</sub> at ambient temperature with a high degree of regioselectivity, the copolymerization of cyclohexene oxide and CO<sub>2</sub> requires higher temperatures (e.g., 60 °C). Nevertheless, the random polymerization of cyclohexene oxide and propylene oxide with CO<sub>2</sub> at ambient temperature provides a terpolymer with a nearly statistical distribution of monomer units. In addition, these catalysts have been shown to be efficient at producing diblock copolymers of poly(propylene carbonate) and poly(cyclohexylene carbonate) as well as triblock copolymers of poly(propylene carbonate)/poly(cyclohexylene carbonate)/poly(vinylcyclohexylene carbonate).

### Introduction

There is much current interest in the use of carbon dioxide as both a solvent and a monomer for the production of biodegradable copolymers. In this regard, efforts to develop effective, regio- and stereoselective catalysts for the coupling of carbon dioxide and epoxides to selectively provide polycarbonates with minimal ether linkages are being systematically explored. To this aim, we, along with numerous other researchers, have focused on the use of salen(salicylaldimine) derivatives of chromium(III) and cobalt(III).<sup>1,2</sup> Recently, it has become apparent that ligands with greater donor character than salen, namely, tmtaa(tetramethyl-tetraazaannulene)<sup>3</sup> and salan(*N,N'*-disubstituted bis(aminophenoxide)),<sup>4</sup> provide more active chromium(III) sites for this catalytic process. The latter salan ligand system with its sp<sup>3</sup>-hybridized amino donors represents a saturated version of the pervasive salen ligand. An additional feature of metal complexes of the salan ligand which might dramatically impact catalytic behavior and control polymer stereochemistry is the potential of this ligand system to afford a *cis*-coordination geometry as depicted in the cartoons in Figure 1.<sup>5</sup> Indeed, Lu and co-workers have shown chiral (salan)CrX complexes in the presence of ionic quaternary ammonium salts to catalyze the copolymerization of racemic propylene oxide to afford a copolymer with very high head-to-tail linkages and moderate enantioselectivity.<sup>4</sup>

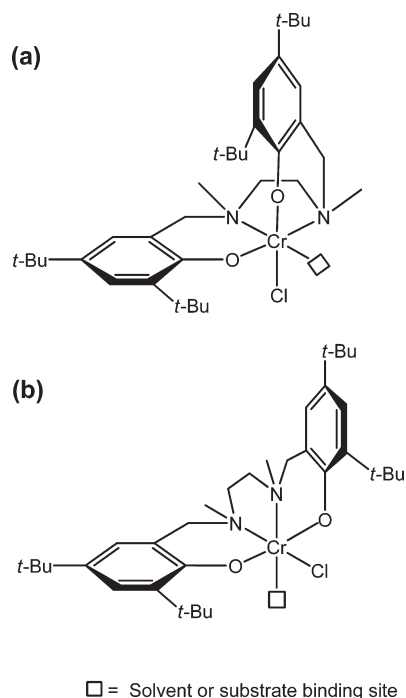
In this correspondence we wish to report our initial investigation of the use of salan metal complexes as catalysts for the production of polycarbonates. These studies will focus on utilizing complex **1** (Figure 1) as a catalyst in the presence of the [PPN]<sup>+</sup>[N<sub>3</sub><sup>−</sup>] salt (PPN<sup>+</sup> = Ph<sub>3</sub>P=N<sup>+</sup>=PPh<sub>3</sub>) as ionic initiator for the copolymerization of propylene oxide, cyclohexene oxide, and

4-vinylcyclohexene oxide with carbon dioxide. The syntheses of di- and triblock polycarbonates of the corresponding copolymers will also be described.

### Experimental Section

**Method and Materials.** Syntheses were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk techniques or in an argon-filled glovebox. Cyclohexene oxide (CHO) and propylene oxide (PO) were purchased from TCI America, and vinylcyclohexene oxide (VCHO) was purchased from Aldrich. All epoxides were freshly distilled from CaH<sub>2</sub> prior to use. The solvents Et<sub>2</sub>O, pentane/hexane, CH<sub>3</sub>CN, THF, and CH<sub>2</sub>Cl<sub>2</sub> were purified by a MBraun Manual Solvent Purification System packed with Alcoa F200 activated alumina desiccant. [PPN]<sup>+</sup>[N<sub>3</sub><sup>−</sup>] was prepared according to the published procedure.<sup>6</sup> Bone-dry CO<sub>2</sub> supplied in a high-pressure cylinder and equipped with a liquid dip tube was purchased from Scott Specialty Gases. All <sup>1</sup>H and <sup>13</sup>C NMR spectra were performed in CDCl<sub>3</sub>. <sup>1</sup>H NMR spectra were recorded at 295 K using an Inova Varian spectrometer at 500 MHz, and <sup>13</sup>C NMR spectra were recorded at 295 K at 125 MHz. Chemical shifts are given in ppm relative to TMS and coupling constants (*J*) in hertz. Infrared spectra were recorded on a Mattson 6021 Fourier transform (FT)IR spectrometer with a MCT detector. Analytical elemental analysis was provided by Canadian Microanalytical Services Ltd. High-pressure reaction kinetic measurements were performed using an ASI ReactIR 1000 reaction analyses system with stainless steel Parr autoclave modified with a permanently mounted ATR crystal (SiComp) at the bottom of the reactor (purchased from Mettler Toledo). The starting 3,5-di-*tert*-butylsalicylaldehyde was prepared from commercially available 2,4-di-*tert*-butylphenol according to the literature procedure.<sup>7</sup> The H<sub>2</sub>salen ligand (salen = *N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-ethylenediimine) was synthesized as previously described.<sup>8</sup>

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**Figure 1.** Proposed structures of complex **1** employed as catalyst in the copolymerization processes.

**Synthesis of Tetrahydrosalen Ligand.** To 0.01 mol of the  $H_2salen$  ligand in 20 mL of glacial acetic acid was added 0.03 mol of  $NaBH_4$  in  $CH_3CN$  over a 2–3 h period, during which time the solution became colorless. 20 mL of water was added to the reaction mixture, and it was neutralized via the addition of 2 N NaOH. The product was extracted with 150 mL of  $CH_2Cl_2$ , dried with  $MgSO_4$ , and isolated as a solid upon solvent removal under vacuum. The ligand was stirred in 5.0 mL of cold methanol for 10 min and isolated by filtration. Crystalline product was obtained in 67% yield upon layering a saturated solution of the product with methanol.  $^1H$  NMR: 1.28 (s, 18H,  $tBu$ ); 1.40 (s, 18H,  $tBu$ ); 2.87 (s, 4H,  $CH_2$ ); 3.96 (s, 4H,  $CH_2$ ); 6.85 (s, 2H, Ar–CH); 7.22 (s, 2H, Ar–CH).

**Synthesis of Salan Ligand.** The salan ligand was synthesized from the tetrahydrosalen ligand according to the published method.<sup>4,5</sup> The product was obtained in 74% yield upon crystallization by layering methanol over a saturated methylene chloride solution of the compound.  $^1H$  NMR: 1.27 (s, 18H,  $tBu$ ); 1.39 (s, 18H,  $tBu$ ); 2.26 (s, 6H,  $CH_3$ ); 2.63 (s, 4H,  $CH_2$ ); 3.66 (s, 4H,  $CH_2$ ); 6.80 (s, 2H, Ar–CH); 7.19 (s, 2H, Ar–CH).

Alternatively, the salan ligand was synthesized according to the route reported in the literature.<sup>9</sup> After washing with cold methanol, the product was dried and analyzed by  $^1H$  NMR,  $^{13}C$  NMR, and elemental analysis. Anal. Calcd (%) for  $C_{34}H_{56}O_2N_2$ : C, 77.86; H, 10.69; N, 5.34. Found: C, 77.68; H, 10.92; N, 5.25.

**Synthesis of (salan)CrCl(I).** 1.0 mmol of salan ligand and chromium(II) chloride (1.1 mmol) were dissolved in 10 mL of THF and stirred under argon at ambient temperature for 24 h. The reaction mixture was exposed to air and stirred an additional 24 h. After pouring the reaction mixture into 100 mL of diethyl ether, the organic layer was separated and washed with aqueous saturated  $NH_4Cl$  (3  $\times$  100 mL) and brine (3  $\times$  100 mL) followed by drying over  $Na_2SO_4$ . After filtration to remove solid impurities and drying agent, solvent was removed in vacuo, yielding a green powder. No further purification was performed. Anal. Calcd (%) for  $C_{34}H_{54}N_2O_2CrCl \cdot H_2O$ : C, 65.00; H, 8.98; N, 4.46. Found (%): C, 64.33; H, 9.29; N, 4.35.

**Synthesis of (salan)CrN<sub>3</sub>(2).** 0.5 mmol of (salan)CrCl complex was dissolved in 10 mL of  $CH_3CN$ . In another Schlenk flask, 0.5 mmol of  $AgClO_4$  was dissolved in an equal volume of  $CH_3CN$ .

The (salan)CrCl solution was then cannulated into the silver perchlorate solution. Immediate precipitation of  $AgCl$  was observed, and the reaction was allowed to stir overnight. 1.5 mmol of  $NaN_3$  was added, keeping exposure to air at a minimum. The reaction was stirred for an additional 24 h. The mixture was diluted with distilled diethyl ether and the organic portion washed with water to remove  $NaClO_4$  and excess  $NaN_3$ , dried with  $Na_2SO_4$  and the solvent removed in vacuo, yielding a dark green powder with a  $\nu_{N_3}$  vibrational mode at  $2062.9\text{ cm}^{-1}$ .

**Copolymerization of Epoxides (CHO or PO) with  $CO_2$ .** Measurements of the copolymerization processes at high pressure were carried out using a stainless steel Parr autoclave modified with a SiComp crystal to allow for attenuated total reflectance spectroscopy using infrared radiation (ASI ReactIR 1000 in situ probe). The (salan)CrCl (50 mg) and PPNN<sub>3</sub> were dissolved in  $CH_2Cl_2$  and stirred for 1 h. The  $CH_2Cl_2$  solvent was evaporated to dryness in vacuo, and epoxide (CHO or PO) was added to the catalyst and stirred for 10 min. The Parr autoclave reactor was dried in vacuo at 80 °C and cooled down to room temperature before the reaction mixture was injected into it. A 128-scan background spectrum was collected and followed by immediate charging with 3.4 MPa  $CO_2$  pressure. With a reaction temperature of 60 °C being maintained, a single 128-scan spectrum was collected every 3 min during the reaction time. Profiles of the absorbance at  $1750\text{ cm}^{-1}$  (polycarbonate) with time were recorded after baseline correction. After cooling and venting the reactor in a fume hood, the polymer was extracted with dichloromethane. The polymer was precipitated with hexane to remove unreacted CHO. The polymer was purified by dissolving it in methylene chloride and precipitating it out with acidified methanol. Molecular weight determinations ( $M_w$  and  $M_n$ ) were carried out in THF solutions using a Viscotek gel permeation chromatograph equipped with refractive index and right-angle and low-angle light scattering detectors.

**Diblock Copolymerization of Epoxides (PO and CHO) with  $CO_2$ .** 50 mg of (salan)CrCl and an equimolar (49 mg) amount of PPNN<sub>3</sub> were dissolved in  $CH_2Cl_2$  and stirred for 1 h at ambient temperature. The  $CH_2Cl_2$  was evaporated to dryness in vacuo, 2.9 mL (1/500, cat./PO) of PO was added to the catalyst, and the solution was stirred for 10 min. The Parr autoclave reactor was dried in vacuo at 80 °C and cooled down to room temperature before the reaction mixture was injected into it. The reactor was maintained at 25 °C for 16 h, followed by venting the excess  $CO_2$ . Immediately 5.0 mL (1/500, cat./CHO) of CHO was injected under an inert atmosphere into the reactor. The reactor was pressurized with  $CO_2$  (3.4 MPa) and heated at 60 °C for 4 h. After cooling and venting the reactor in a fume hood, the diblock copolymer was extracted as a dichloromethane solution. The diblock copolymer was precipitated with hexane and again with acidified methanol. Molecular weight determinations ( $M_w$  and  $M_n$ ) were carried out in THF solutions using gel permeation chromatography.

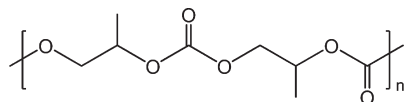
**Triblock Copolymerization of Epoxides (PO, CHO, and VCHO) with  $CO_2$ .** The same procedure for preparing the diblock copolymer (with same catalyst and cocatalyst ratio, also 1.94 mL (1/333, cat./PO) of PO and 3.33 mL (1/333, cat./CHO) of CHO was used as monomers) was carried out followed by immediately venting the  $CO_2$ . 4.2 mL (1/333, cat./VCHO) of VCHO was injected under inert atmosphere into the reactor. The reactor was pressurized with  $CO_2$  (3.4 MPa) and heated at 60 °C for 4 h. The same purification method was performed after cooling the reactor to room temperature and venting the excess  $CO_2$  in a fume hood.

**Differential Scanning Calorimetry Measurements.** Glass transition ( $T_g$ ) temperatures were measured using a Mettler Toledo polymer DSC equipped with a liquid nitrogen cooling system and 50 mL/min purge of dry nitrogen gas. Samples (~6 mg) were weighed into 40  $\mu$ L aluminum pans and subjected to two heating cycles. The first covered the range from 25 to 140 at 5 °C/min and was then cooled back to 25 °C. The second heating cycle covered 25 to 200 at 2 °C/min.

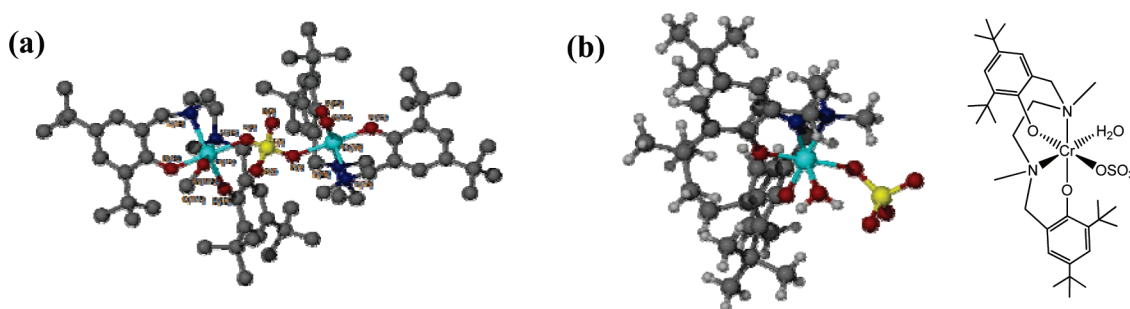
## Results and Discussion

It is well-established that *alicyclic* epoxides (e.g., cyclohexene oxide) in the presence of various metal catalysts react with carbon dioxide to selectively afford copolymers at much harsher reaction conditions than the coupling of *aliphatic* epoxides (e.g., propylene oxide) with CO<sub>2</sub>. We and others have shown that this is due to the difference in activation energies for copolymers vs cyclic carbonate formation,  $E_a$  being much greater in the case of cyclohexene oxide copolymerization with CO<sub>2</sub>.<sup>10</sup> With regard to the copolymerization of propylene oxide and CO<sub>2</sub>, regio- and stereoselectivity for copolymer formation are also important qualities of an effective catalyst system. Relevant to this latter point, Coates and co-workers have demonstrated a chiral (salen)CoX catalyst in the presence of PPNX salts provides high regioregularity (95% head-to-tail) (Figure 2) and good control of polymer tacticity from isotactic to syndiotactic.<sup>11</sup> Reaction conditions were generally 22 °C and 3.4 MPa.

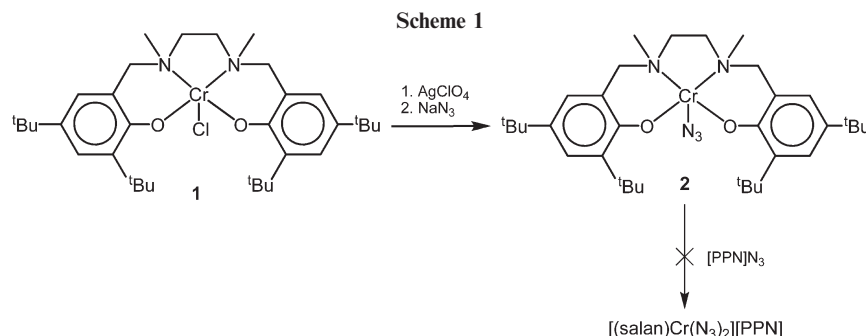
In this report, the *N,N'*-dimethyl-substituted H<sub>2</sub>salan ligand was synthesized following the general procedures in the literature.<sup>4,5,9</sup> The route described in ref 9 is a more facile one-pot preparation achieved by the reaction of 3,5-di-*tert*-butylphenol, paraformal-



**Figure 2.** Head-to-tail (HT) regiochemistry of poly(propylene carbonate).



**Figure 3.** (a) X-ray structure of dimeric complex obtained from crystallization of complex 1. (b) Truncated model of one of the metal fragments containing the H<sub>2</sub>O molecule, with stick drawing for better clarity.



**Table 1.** Copolymerization of Cyclohexene Oxide and Carbon Dioxide by Complex 1<sup>a</sup>

entry	PPNN <sub>3</sub> (equiv)	time (h)	cat./CHO (molar ratio)	TOF <sup>b</sup>	$M_n$ (kg/mol) <sup>c</sup>	PDI ( $M_w/M_n$ ) <sup>c</sup>
1	2	2	1/1250	321	11.9	1.10
2	2	4	1/1250	240	15.8	1.19
3	2	17	1/1250	61	27.2	1.10
4	1	4	1/2500	405	19.5	1.19
5	1	10	1/1250	95	21.7	1.10
6	0	10	1/1250	14	3.92	1.31

<sup>a</sup> All reactions performed at 3.4 MPa CO<sub>2</sub> and 60 °C. <sup>b</sup> The rate is expressed in terms of the turnover frequency (TOF, mol of epoxide consumed/mol catalyst h). <sup>c</sup> Determined by using gel permeation chromatography in THF, calibrated with polystyrene standards.

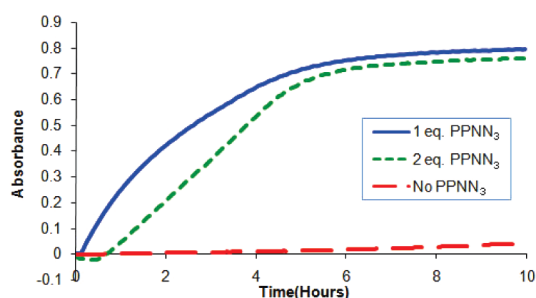
dehyde, and *N,N'*-dimethylethylenediamine in methanol 50 °C. The corresponding (salan)CrCl was prepared from the H<sub>2</sub>salan ligand and anhydrous CrCl<sub>2</sub> following oxidation with air or directly from CrCl<sub>3</sub>(THF)<sub>3</sub>. Replacement of the chloride ligand by azide was achieved via the standard procedure employed for the preparation of the analogous (salen)CrN<sub>3</sub> derivative (Scheme 1).<sup>12</sup> However, strikingly unlike the (salen)CrN<sub>3</sub> complex, addition of excess PPNN<sub>3</sub> (20 equiv) to a solution of (salan)CrN<sub>3</sub> over a prolonged reaction time (2 days) did not afford a stable bis-azide complex, (salan)Cr(N<sub>3</sub>)<sub>2</sub>.<sup>13</sup>

In an attempt to crystallographically characterize complex 1, crystals of a close derivative of complex 1 were isolated from the reaction solution. The crystals obtained were shown by X-ray crystallography to be a dimeric metal complex where the anion is a bridging sulfate group, originating from the drying reagent sodium sulfate, with the sixth coordination sites of the two chromium(III) centers occupied by methanol and water, respectively (Figure 3).<sup>14</sup> Included in Figure 3 is a model of one of the metal centers, illustrating the geometry of the metal–salan framework (Figure 3b). The importance of this structure is that, unlike the salen ligand, the salan ligand adopts a cis-coordination mode with the anion and neutral ligand occupying positions trans to oxygen and nitrogen donors, respectively (Figure 1a). Similarly, the crystal structure of the (salan)AlMe derivative displays a distorted trigonal-bipyramidal coordination geometry with cis arrangements of oxygen atoms and of nitrogen atoms.<sup>15</sup>

We initially examined the copolymerization of cyclohexene oxide and carbon dioxide employing (salan)CrCl (1) with varying



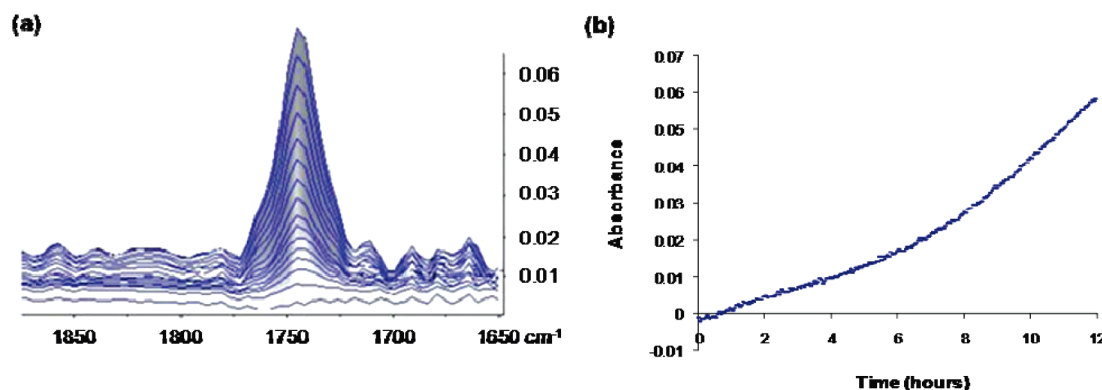
quantities of  $\text{PPNN}_3$  for comparison with our earlier studies involving the corresponding  $(\text{salen})\text{CrCl}$  catalyst systems. Since the quaternary organic salt,  $\text{PPNN}_3$ , is insoluble or very sparingly soluble in epoxides at room temperature, pretreatment of **1** with  $\text{PPNN}_3$  is required to ensure maximum catalytic activity. In a typical copolymerization experiment, complex **1** and the desired equivalents of  $\text{PPNN}_3$  were dissolved in methylene chloride and stirred for 1 h at ambient temperature. Upon removing the methylene chloride under vacuum cyclohexene oxide was added with stirring, and the solution was cannulated into the stainless steel reactor. Following the copolymerization reaction, the polymer was dissolved in methylene chloride and precipitated upon addition of acidified methanol. Table 1 summarizes the results of a series of copolymerization reactions carried out under various reaction conditions for the formation of poly(cyclohexylene carbonate). It is noteworthy that TOFs as reported here and elsewhere in the literature are highly dependent on reaction time. That is, the highest TOFs are obtained during the initial period of high polymer production.



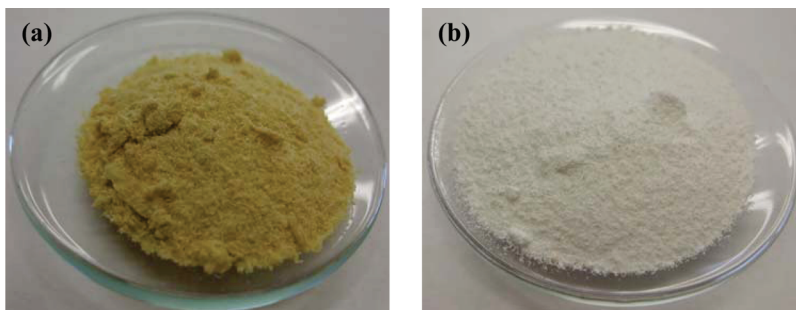
**Figure 4.** In situ infrared monitoring of copolymer production from CHO and  $\text{CO}_2$  as catalyzed by complex **1** in the presence of varying quantities of  $\text{PPNN}_3$ .

As evident from Table 1, complex **1** is a very effective catalyst for the copolymerization of cyclohexene oxide and  $\text{CO}_2$ . In general, reaction of cyclohexene oxide and  $\text{CO}_2$  was carried out at  $60^\circ\text{C}$  and 3.4 MPa  $\text{CO}_2$  pressure to afford poly(cyclohexylene carbonate) in good yield with narrow molecular weight distributions. For example, entry 4 in Table 1 for the process starting with 20 mL of cyclohexene oxide following 10 h of reaction time provided 18.1 g of purified copolymer (60% yield) with a polydispersity of 1.19. Interestingly, an increase in catalytic activity is noted for 1 equiv of quaternary organic salt over 2 equiv (entries 2 and 4 in Table 1). This is in contrast to what is observed in our previous studies utilizing  $(\text{salen})\text{CrX}$  or  $(\text{tmtaa})\text{CrX}$  as catalysts, where 2 equiv of cocatalyst optimizes the rate of copolymer formation. It is however consistent with the *cis*- $(\text{salen})\text{CrN}_3$  complex not undergoing reaction with an additional equivalent of azide, whereas  $(\text{salen})\text{CrN}_3$  readily forms a stable  $(\text{salen})\text{Cr}(\text{N}_3)_2^-$  complex in the presence of added azide ions. In a related observation, Lu and co-workers have recently shown that the  $(\text{salen})\text{Cr}^+$  ion adds one molecule of DMAP,<sup>16</sup> whereas  $(\text{salen})\text{Cr}^+$  coordinates two molecules of the amine.<sup>16</sup> The reaction profiles depicted in Figure 4 illustrate the effect of adding various quantities of  $\text{PPNN}_3$  on the catalytic system. From these profiles it is apparent that the decrease in rate of copolymer production is due to an inhibition process involving the added equivalent of  $\text{PPNN}_3$ . On the other hand, in the absence of any  $\text{PPNN}_3$  the reaction is very slow, similarly exhibiting a profile indicative of rate inhibition during the early stages of the process (Figure 5).

For comparative purposes a catalytic run of the copolymerization of cyclohexene oxide and  $\text{CO}_2$  carried out under identical reaction conditions as entry 1 in Table 1 except utilizing the corresponding  $(\text{salen})\text{CrCl}$  catalyst affords a somewhat lower TOF of  $228\text{ h}^{-1}$ . However, the isolated copolymer possessed a similar molecular weight of 11 600 with a PDI of 1.11. Of notable



**Figure 5.** (a) Three-dimensional stack plots of the infrared spectra collected every 3 min during the coupling reaction of CHO and  $\text{CO}_2$  ( $60^\circ\text{C}$  and 500 psi pressure) in the absence of  $\text{PPNN}_3$ . (b) Reaction profile of this catalytic system.



**Figure 6.** Photographs of the isolated poly(cyclohexylene carbonate) after one methanol precipitation: (a) using  $(\text{salen})\text{CrCl}$  as catalyst and (b) using complex **1** as catalyst.

**Table 2.** Copolymerization of *rac*-Propylene Oxide and Carbon Dioxide Using Complex 1<sup>a</sup>

entry	time (h)	temp (°C)	TOF <sup>b</sup>	head-to-tail linkages (%) <sup>c</sup>	$M_n$ (kg/mol) <sup>d</sup>	PDI ( $M_w/M_n$ ) <sup>d</sup>
1	48	22	6	93	11.8	1.06
2	16	25	21	92	8.0	1.13
3	4	60	220 <sup>e</sup>			
4	4	0	NA	NA	NA	NA

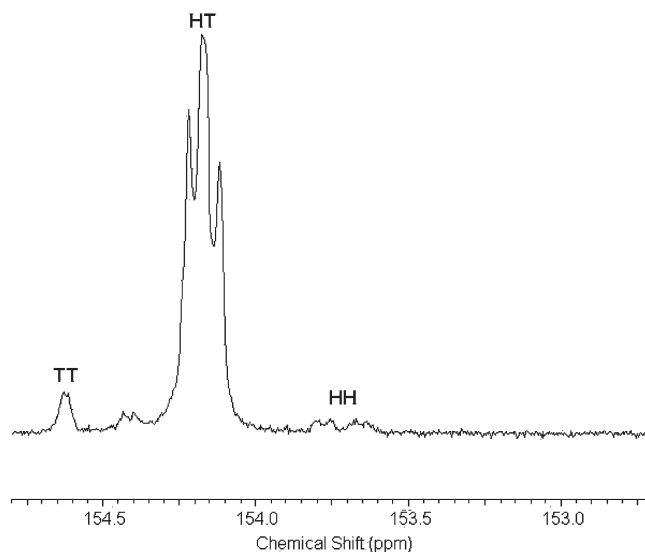
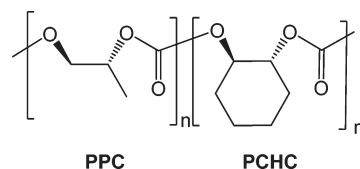
<sup>a</sup> All reactions performed with 1 equiv of PPNN<sub>3</sub> in *rac*-PO and 1.5 MPa CO<sub>2</sub> at included temperatures. <sup>b</sup> The rate is expressed in terms of the turnover frequency (TOF (mol of epoxide consumed (mol of catalyst h)<sup>-1</sup>) = turnovers/h). <sup>c</sup> Determined by using <sup>13</sup>C NMR spectroscopy. <sup>d</sup> Determined by using gel permeation chromatography in THF, calibrated with polystyrene standards. <sup>e</sup> Only propylene carbonate obtained (3.4 MPa of CO<sub>2</sub> used).

interest, because of the increased solubility of the (salen)CrX derivatives, much more of the metal catalyst is removed from the polymer with only one methanol purification step. This is illustrated in Figure 6, where the copolymer isolated from the process catalyzed by complex 1 is white, and the correspondingly obtained copolymer produced in the presence of the (salen)CrCl analogue is colored because of the presence of metal contaminant.

Importantly, unlike its (salen)CrX analogue, complex 1 is an effective catalyst for the selective coupling of propylene oxide and carbon dioxide to poly(propylene carbonate) at ambient temperature. This has recently been reported by Lu and co-workers for other related (salen)CrX derivatives. Table 2 contains a compilation of the copolymerization reaction of propylene oxide and CO<sub>2</sub> catalyzed by complex 1. As indicated in Table 2, upon raising the reaction temperature to 60 °C, the coupled product of propylene oxide and CO<sub>2</sub> is exclusively propylene carbonate. This observation is anticipated based on our earlier studies using (salen)CrX based catalysts, where lower reaction temperature favors the production of copolymer. This result stems from the fact that the activation barrier for copolymer formation was shown to be 33 kJ mol<sup>-1</sup> less than the corresponding value for cyclic carbonate production. In other words, a lowering of the reaction temperature has a much greater effect on the rate of propylene carbonate formation than the rate of poly(propylene carbonate) production. Furthermore, for the reaction catalyzed by complex 1 at ambient temperature the process is highly selective for the production of regioregular head-to-tail linkages (Figure 7).

We further investigate this catalyst system for the synthesis of diblock copolymers of poly(propylene carbonate) and poly(cyclohexylene carbonate). This was achieved by first performing the copolymerization of propylene oxide and CO<sub>2</sub> at ambient temperature and 3.4 MPa CO<sub>2</sub> pressure for 16 h. Following the evacuation of carbon dioxide and unreacted propylene oxide, cyclohexene oxide was cannulated into the reactor under an inert atmosphere. The reactor was repressurized with 3.4 MPa of CO<sub>2</sub> and heated at 60 °C for 4 h. The resulting polymer was dissolved in methylene chloride and precipitated first from hexane, followed by precipitation from acidified methanol to yield a purified sample of diblock terpolymer (Figure 8). From <sup>1</sup>H NMR analysis the diblock polymer's composition was determined to be 53% poly(cyclohexylene carbonate) (Figure 9a). <sup>13</sup>C NMR spectroscopy revealed the poly(cyclohexylene carbonate) to be atactic and the poly(propylene carbonate) to have 94% HT carbonate linkages (Figure 9b). The diblock polymer's molecular weight ( $M_n$ ) as determined by gel permeation chromatography was found to be 16 500 with a PDI of 1.08.

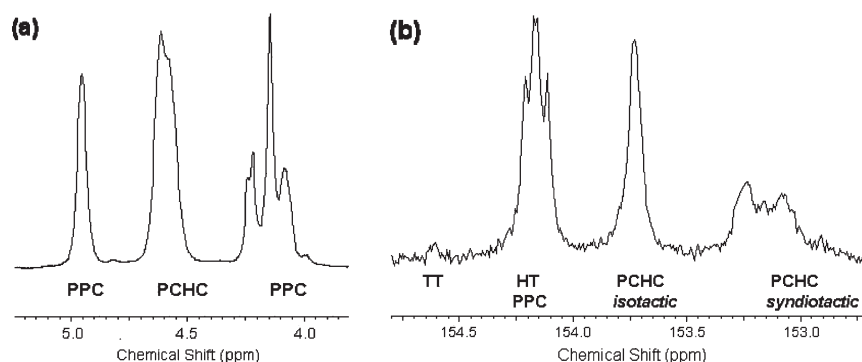
An interesting note that will be the subject of more far-reaching studies is our observation that whereas propylene oxide and CO<sub>2</sub> in the presence of complex 1 and [PPN]N<sub>3</sub> readily copolymerize at ambient temperature where cyclohexene oxide displays no

**Figure 7.** Carbonyl region of the <sup>13</sup>C NMR spectra (125 MHz, CDCl<sub>3</sub>) generated from the copolymerization of *rac*-PO/CO<sub>2</sub> at 22 °C and 1.5 MPa for 16 h: head-to-tail (HT); tail-to-tail (TT); head-to-head (HH).**Figure 8.** Diblock copolymer of poly(propylene carbonate) and poly(cyclohexylene carbonate) where  $n \approx m$ .

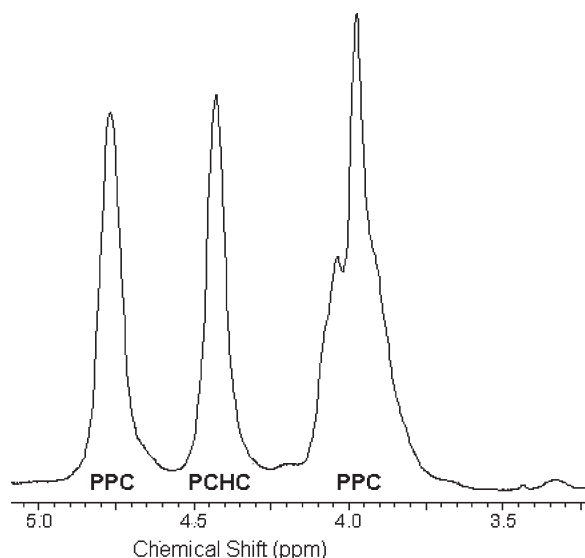
activity, the two epoxide monomers undergo a facile terpolymerization process at ambient temperature. Indeed, the <sup>1</sup>H NMR spectrum of the resulting terpolymer shown in Figure 10 reveals an almost statistical distribution of propylene oxide and cyclohexene oxide monomers in the polymer. Relevant to this point, we have previously demonstrated that the ring-opening of a metal bound propylene oxide monomer is much easier than the corresponding process involving cyclohexene oxide.<sup>13</sup> A similar observation, i.e., the addition of propylene oxide greatly enhances the copolymerization of cyclohexene oxide and CO<sub>2</sub>, was recently noted by Lu and co-workers employing a (salen)Co(III) catalyst system.<sup>17</sup>

In addition, a triblock polymer was synthesized in a similar manner to that utilized for the preparation of the diblock polymer (vide supra). That is, subsequent to preparation of the diblock polymer of poly(propylene carbonate) and poly(cyclohexylene carbonate), vinylcyclohexene oxide (4-vinyl-1-cyclohexene 1,2-epoxide) was cannulated under an inert atmosphere into the reactor. The reactor was repressurized with CO<sub>2</sub> to 3.4 MPa and heated at 60 °C for 4 h. Following the venting of CO<sub>2</sub> the polymeric residue was dissolved in methylene chloride and first precipitated from hexane and then acidified methanol to afford a purified sample of a triblock polymer (Figure 11). Because of the overlap of the proton resonances, it is difficult to be precise in the composition of the triblock polymer; however, its composition is consistent with the equal quantities of the monomers utilized in its synthesis (Figure 12). The triblock polymer's molecular weight ( $M_n$ ) was found to be 22 200 with a polydispersity index of 1.08.

The thermal properties of the copolymers prepared in this report were determined by thermal gravimetric analysis and digital scanning calorimetry measurements. The onset of weight loss for the poly(propylene carbonate) sample was 175 °C with 95% loss occurring at 200 °C, whereas the corresponding values



**Figure 9.** (a)  $^1\text{H}$  NMR spectrum in methine and methylene regions of diblock copolymer of poly(propylene carbonate) and poly(cyclohexylene carbonate). (b)  $^{13}\text{C}$  NMR spectrum in carbonate region of diblock copolymer of poly(propylene carbonate) and poly(cyclohexylene carbonate). The *m*-centered tetrads (*isotactic*) appear at 153.7 ppm and *r*-centered tetrads (*syndiotactic*) appear at 153.1 ppm.

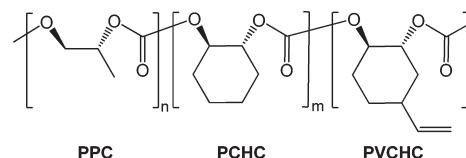


**Figure 10.**  $^1\text{H}$  NMR spectrum in methine and methylene regions of terpolymer prepared from a 1.5 ratio of propylene oxide to cyclohexene oxide. Ratio of corresponding monomers (PO:CHO) in terpolymer is approximately two to one.

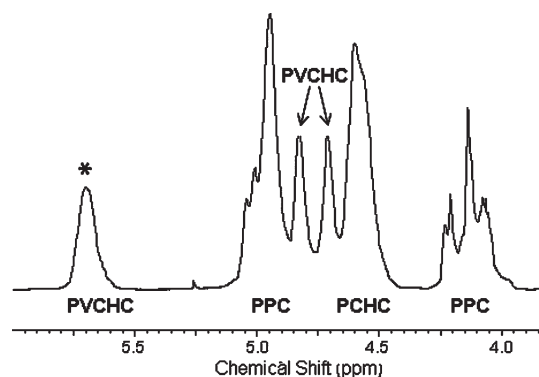
for poly(cyclohexylene carbonate) were found to be 253 and 275 °C. Similar parameters for the onset of weight loss for the diblock and triblock were noted. The glass transition temperatures ( $T_g$ s) of the diblock copolymers of poly(propylene carbonate) and poly(cyclohexylene carbonate), which possess long enough homocopolymer chains, displayed  $T_g$  values similar to the individual copolymers. That is, the midpoint glass transition temperatures in the diblock polymer were determined to be 43.4 and 121.6 °C. Similar parameters for the triblock copolymer sample were found at 40.6 and 102.3 °C. For comparison, the  $T_g$  values of random copolymers lie between the values of the homocopolymers, poly(PPC) and poly(CHC).<sup>18</sup>

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**Supporting Information Available:** X-ray crystallographic files in CIF format for the structural determination of dimeric complex obtained upon crystallization of complex **1**. This



**Figure 11.** Triblock copolymer of poly(propylene carbonate), poly(cyclohexylene carbonate), and poly(vinylcyclohexylene carbonate).



**Figure 12.**  $^1\text{H}$  NMR spectrum in the methine, methylene, and vinyl (\*) regions of triblock copolymer of poly(propylene carbonate), poly(cyclohexylene carbonate), and poly(vinylcyclohexylene carbonate).

material can be found free of charge via the Internet at <http://pubs.acs.org>.

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