Controlled Synthesis of Polycarbonate Diols and Their Polylactide Block Copolymers using Amino-bis(phenolate) Chromium Hydroxide Complexes†

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† Electronic supplementary information (ESI) available: MALDI-TOF MS, representative ^1H, ^{31}P NMR, DSC, TGA data, DOSY NMR of block copolymer and crystallographic information files (CIF) for ***4****. CCDC 2075754.*

Abstract

A diamine-bis(phenolate) chromium(III) complex, CrOH[L] ([L] = dimethylaminoethylamino-*N,N*-bis(2-methylene-4,6-*tert*-butylphenolate)), **2**, in the presence of tetrabutylammonium hydroxide effectively copolymerizes CO_2 and cyclohexene oxide (CHO) into polycarbonate diol. The resultant low molecular weight (6.3 kg mol^{-1}) diol is used to initiate ring-opening polymerization of *rac*-lactide with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) giving ABA-type block copolymers with good molecular weight control through varying *rac*-LA-to-diol loading, and with narrow dispersities. As the degree of *rac*-LA incorporation increases, the glass transition temperatures (T_g) are found to decrease, whereas decomposition temperatures (T_d) increase. (Diphenylphosphonimido)triphenylphosphorane ($Ph_2P(O)NPPh_3$) was used as a neutral nucleophilic cocatalyst with **2**, giving phosphorus-containing

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polycarbonates with M_n of 28.5 kg mol^{-1}, dispersity of 1.13, T_g of 110 °C and T_d over 300 °C. A related Cr(III) complex (**4**) having a methoxyethyl pendent group rather than a dimethylaminoethyl group was structurally characterized as a hydroxide-bridged dimer.

Introduction

There is a need to find alternatives to petroleum-derived plastics with those that incorporate significant amounts of renewably sourced materials and are also less harmful to the environment and human health. Various biomass-derived polymers are being commercially produced, most notably poly(lactide) (PLA), poly(hydroxyl alkanoates) and cellulosic/starch derivatives. Because PLA is biocompatible, compostable and can be sourced from renewable feedstocks, it has received significant interest in both academic and industrial research.[1-4] Another process that utilizes an abundant, inexpensive and non-toxic carbon source is the production of carbonates from CO_2, such as the coupling or copolymerization of CO_2 with epoxides. Since the discovery of this reaction by Inoue in 1969,[5] many catalyst systems have been developed that yield polycarbonates via routes that avoid hazardous reagents such as phosgene and bis(phenol)-A.[6-11] Although many advances have been achieved in terms of increasing CO_2 incorporation into the carbonate linkages, polymer selectivity, molecular weight control, and detailed mechanistic investigations, further work towards improving the material performance is needed.

The preparation of new materials incorporating CO_2-based copolymers with other monomers to give multi-block polymers is a valuable and challenging goal for future research and development.[12-13] There have been two main strategies reported to date for the synthesis of block co-polymers of polycarbonates obtained from CO_2 and epoxides and other monomers. One involves the use of monomers such as cyclic anhydrides along with epoxides and CO_2. This route relies upon the rate of CO_2 incorporation to be slower than that of anhydride/epoxide copolymerization to give polyester-block-polycarbonate polymers. This has the advantage of being a one-pot terpolymerization of the three monomers and several catalyst systems have demonstrated the ability to perform this reaction.[14-18] Its disadvantage, however, is that it is rather limited in that only cyclic anhydrides are suitable. Other monomers such as lactide,[19] lactone[20] or maleic anhydride[21] give random structures with typically broad molecular weight distributions and ether linkages when copolymerized with epoxides and CO_2. Rieger showed that β-diiminate (BDI) zinc complexes are able to terpolymerize epoxide, CO_2 and butyrolactone to afford polyester-carbonates in both a block and a statistical configuration through changing CO_2 pressure.[22] Williams also demonstrated a one-pot procedure for polymerization of ε-decalactone, cyclohexene oxide, and CO_2 using a heterodinuclear Zn(II)/Mg(II) catalyst to selectively and efficiently yield degradable ABA type block polymers.[23] Pang reported that salenCo(III) combined with zinc glutarate and bis(triphenylphosphine)iminium chloride (PPNCl) can combine ring-opening polymerization of lactide and the ring-opening copolymerization of epoxides and CO_2, to form multiblock copolymers through a unique synergistic effect between cobalt and zinc.[24] Another strategy that has been exploited is the use of a polymer with terminal initiating sites that can be used as chain-transfer agents. By preparing polycarbonates with hydroxyl-functionalized end groups, these diols can be used as macroinitiators for polymerization of a third monomer such as lactide[25-28] or a cyclic phosphate monomer.[29] A further promising application of polycarbonate diols is in the production of polyurethane foams.[30-32] Although polycarbonate diols have been observed by us using MALDI-TOF MS of polymer products obtained by CO_2/epoxide copolymerization by various catalytic systems,[33-36] selective formation of di-hydroxyl end-capped chains has required using hydrolysable sites. Darensbourg and Williams have shown that using trifluoroacetate-containing (TFA) metal complexes leads to TFA-polycarbonate-OH polymers, which upon hydrolysis or in presence of adventitious water yield polycarbonate diols.[25-26] Later, Darensbourg and Williams directly used water as a chain transfer reagent during copolymerization of CO_2 and epoxide to afford polycarbonate diols with relative low molecular weight.[27-28] Recently various polymers with two hydroxyl end groups such as poly-(dimethylsiloxane), polyethylene glycol, polypropylene glycol and polystyrene diol have been used as macro chain transfer agents to synthesize new CO_2-based block copolymers.[37-38]

Herein, we describe the synthesis of two amino-bis(phenolate) chromium(III) hydroxide complexes, with structural characterization by single crystal X-ray diffraction of the compound bearing a methoxyethylamino group. The dimethylaminoethyl-functionalized compound **2** is an efficient polymerization catalyst system for production of polycarbonate diol from cyclohexene oxide and CO_2 independent of using hydrolysable sites. The resultant hydroxyl-terminated polycarbonate serves as macroinitiator for the ring-opening polymerization of *rac*-lactide in the presence of DBU to generate the block copolymer.

Experimental

General Materials

Unless otherwise stated, all manipulations were performed under an atmosphere of dry, oxygen-free nitrogen by means of Schlenk techniques or using an MBraun Labmaster DP glove box. $CrCl_3(THF)_3$ was prepared by the Soxhlet method from anhydrous $CrCl_3$.[39] $H_2[L]$ proligands were prepared by a modified literature procedure by using water instead of methanol as the reaction medium,[40] and dried over sodium sulfate in tetrahydrofuran (THF). Anhydrous THF was distilled from sodium/benzophenone ketyl under nitrogen. Cyclohexene oxide (CHO) was purchased from Aldrich and freshly distilled from CaH_2 under nitrogen. CH_2Cl_2 was purified by an MBraun Manual Solvent Purification System. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was purchased from Aldrich, dried over CaH_2, and distilled under reduced pressure. Bis(triphenylphosphine)iminium chloride (PPNCl) and NaOH were purchased from Alfa Aesar or Caledon, and used without further purification. *rac*-Lactide was purchased from Aldrich or Alfa Aesar and dried over Na_2SO_4 in THF, recrystallized and stored under an inert atmosphere prior to use. Bu_4NOH solution in MeOH was purchased from Alfa Aesar and used without further purification.

Characterization Methods

MALDI-TOF MS was performed using an Applied Biosystems 4800 MALDI TOF/TOF Analyzer equipped with a reflectron, delayed ion extraction and high-performance nitrogen laser (200 Hz operating at 355 nm). Samples of chromium complexes were prepared in the glove box and sealed under nitrogen in a Ziploc© bag for transport to the instrument. Anthracene was used as the matrix for the metal complexes. Anthracene and complex were each dissolved in toluene at concentrations of 10 mg mL^{-1} and combined in a 1:1 ratio. 2,5-Dihydroxybenzoic acid (DHBA) was used as the matrix for the copolymers. DHBA was dissolved in THF at approximately 16 mg mL^{-1} and polymer was dissolved in THF at approximately 10 mg mL^{-1}. The matrix and polymer solutions were combined in a 4:1 ratio. 1 µL aliquots of these samples were spotted on the MALDI plate and left to dry. Images of mass spectra were prepared using mMass™ software (www.mmass.org).

Molecular weight determination of copolymer was performed on an Agilent Infinity HPLC instrument connected to a Wyatt Technologies triple detector system (multi angle light scattering (MALS), viscometry and refractive index) equipped with two Phenogel 10^3 Å 300 × 4.60 mm columns with THF as eluent. Copolymer samples were prepared in THF at a concentration of 4 mg mL^{-1} and filtered through syringe filters (0.2 µm). The sample solution was then eluted at a flow rate of 0.30 mL min^{-1}. The values of dn/dc were calculated online (columns detached) assuming 100% mass recovery using the Astra 6 software package (Wyatt Technologies) giving dn/dc (poly(cyclohexene carbonate) = 0.0701 mL g^{-1} and dn/dc (tri-block copolymer) = 0.0497 mL g^{-1}.

^{1}H and ^{31}P NMR spectra were recorded on a Bruker Avance III NMR spectrometer at 300 MHz and 121 MHz, respectively, in $CDCl_3$. ^{1}H DOSY experiments were carried out on a Bruker Avance 500 MHz spectrometer and samples were equilibrated at the measurement temperature of 298 K for 5 min before data collection. Spinning was deactivated to avoid convection. For polymer analysis the NMR tube was filled with 0.7 mg mL^{-1} of polymer in 1 mL deuterated $CDCl_3$ to reduce the impact of polymer viscosity and molecular interactions. 1D ^{1}H spectra were acquired with the zg30 pulse program from the Bruker library. 2D DOSY spectra were acquired using a double stimulated echo sequence ("dstegp2s") for convection compensation and with monopolar gradient pulses. D1 was set to 5 seconds, collecting 64k data points and 16 scans per gradient level. 32 gradient strengths were used between 2 and 95%. The spectra were multiplied with an exponential window function before Fourier transformation (xf2), and subsequently phase corrected. The diffusion coefficients were obtained on MestReNova processing software by fitting a peak heights fit method to the spectra.

In situ IR experiments were performed with a Mettler Toledo ReactIR 15 reaction analysis system with a SiComp Sentinel probe coupled to a 100 mL Parr stainless steel pressure vessel. The glass transition (T_g) temperatures were measured using a Mettler Toledo DSC 1 STARe System. Samples were weighed into 40 µL aluminum pans and subjected to two heating cycles from 0 to 180 °C at a rate of 10 °C min^{-1}. T_g of copolymers were determined from the second heating. Thermogravimetric analysis measurement was performed with a TA Instruments Q500. Samples were loaded onto a platinum pan and subjected to a dynamic high-resolution scan. Each sample was heated from room temperature to 450 °C at a heating rate of 10 °C min^{-1}.

X-Ray diffraction experimental for **4**: A dark green prism crystal of $C_{66}H_{102}Cr_2N_2O_8$ having approximate dimensions of 0.16×0.14×0.08 mm was mounted on a low temperature diffraction loop. All measurements were made on a Rigaku Saturn70 CCD diffractometer using graphite monochromated MoKa radiation, equipped with a SHINE optic. The crystal was kept at 153(2) K during data collection. Details of refinement are provided in ESI.

Elemental analysis was performed at Saint Mary's University, Halifax, Nova Scotia, Canada.

Preparation of compounds

CrCl(THF)[L] (1) and (3). Synthesis of complexes **1** and **3** followed our previously reported procedures.[34,41] $H_2[L]$ (6.67 mmol) and sodium hydride (0.64 g, 26.67 mmol) were weighed in a Schlenk tube and cooled to –78 °C. THF (50 mL) was added to give a white suspension, which was warmed to room temperature and further stirred for 2 h. This mixture was transferred via filter cannula to a suspension of $CrCl_3(THF)_3$ (2.50 g, 6.67 mmol) in THF (50 mL) cooled to –78 °C to give a pink/pale-purple mixture. The resulting mixture was warmed to room temperature and stirred overnight to give dark purple solutions for both **1** and **3**. The solutions were filtered and evaporated to dryness. The residues were extracted into toluene, filtered through Celite and the solvent removed under vacuum. The residue was washed with pentane and dried resulting in purple (**1**) and green (**3**) powders (yields of >80%). **1**: Anal. Calcd (%) for $C_{38}H_{62}ClCrN_2O_3$: C, 66.89; H, 9.16; N, 4.11. Found: C, 66.77; H, 8.89; N, 3.94. MS (MALDI-TOF) *m/z* (%, ion): 609.3 (100, $[CrCl[L]^+]$), 574.3 (35, $[Cr[L]^+]$). **3**: Anal. Calcd (%) for $C_{33}H_{51}Cl_1Cr_1N_1O_3$: C, 66.37; H, 8.64; N, 2.35. Found (%): C, 66.13; H, 8.42; N, 2.62. MS (MALDI-TOF) *m/z* (%, ion): 596.3 (100, $CrCl[L]^+$), 561.3 (50, $Cr[L]^+$), 1157.5 (9, $[Cr[L]]_2Cl^+$) and 1194.5 (3, $[CrCl[L]]_2^+$).

CrOH[L] (2) and (4). Complex **1** (1.00 g, 1.47 mmol) or **3** (1.00 g, 1.50 mmol) and sodium hydroxide (0.29 g, 7.30 mmol) were weighed into a Schlenk tube under dry nitrogen. THF (20 mL) was added and stirred for 2 days giving a green suspension. Filtration of the mixture via filter cannula gave a green solution, which upon removal of solvent under vacuum gave a green solid. The residue was extracted into toluene, filtered through Celite and the solvent was evaporated to dryness. The products were obtained as green crystalline solids (yields over 65%). Single crystals of **4** suitable for single crystal diffraction were obtained by slow evaporation of a toluene solution. **2**: Anal. Calcd for $C_{34}H_{55}CrN_2O_3 \cdot NaCl$: C, 62.80; H, 8.53; N, 4.31. Found: C, 62.46; H, 9.04; N, 4.07. MS (MALDI-TOF) *m/z* (%, ion): 614.4 (80, $[CrOH[L]Na^+]$), 591.4 (10, $[CrOH[L]^+]$), 574.4 (10, $[Cr[L]^+]$). **4**: Anal. Calcd for $C_{33}H_{52}CrNO_4$: C, 68.48; H, 9.06; N, 2.42 Found: C, 68.06; H, 9.42; N, 1.97. MS (MALDI-TOF) *m/z* (%, ion): 578.3 (10, $[CrOH[L]^+]$), 561.3 (10, $[Cr[L]^+]$).

$Ph_2P(O)NPPh_3$. PPNCl (2.00 g, 3.48 mmol) was dissolved in 1 mL methanol and chilled to below 10 °C in an ice bath. NaOH (0.18 g, 4.50 mmol) was dissolved in 3 mL methanol and the NaOH solution was added dropwise to the stirred PPNCl solution. The mixture was stirred for 3 h, with a precipitate observed after ～20 min. The resulting mixture was filtered and the solvent removed yielding a light-yellow oil. The oil was dissolved in a 50/50 mixture (v/v) of acetonitrile and diethyl ether and slowly crystallized giving a colourless solid. Yield: 0.7 g (42%). ^{31}P NMR (ppm, $CDCl_3$): 13.23, 14.35.

Representative copolymerization conditions. 2 (67 mg, 0.10 mmol) and $Ph_2P(O)NPPh_3$ (47 mg, 0.10 mmol) were first combined in 3 mL of CH_2Cl_2 and stirred for 10 min before removal of solvent in vacuum. CHO (5.0 g, 50 mmol) was added to the residue and stirred for 10 min. The CHO solution was added via syringe to a stainless-steel Parr autoclave, which was pre-dried under vacuum overnight at 80 °C. The autoclave was heated to 60 °C, then charged with 40 bar of CO_2 and stirred for 24 h. The autoclave was cooled in an ice bath and vented. An aliquot for ^1H NMR was taken immediately after opening for the determination of conversion. The copolymer was extracted with CH_2Cl_2 and precipitated using cold methanol. The product was then dried at 80 °C in a vacuum oven overnight. For reactions done in the presence of Bu_4NOH, **2** was first dissolved in CHO followed by addition of the resulting green solution to Bu_4NOH (40% w/w in methanol) and stirring for 5 min. The remaining procedure was followed in the same manner as described above.

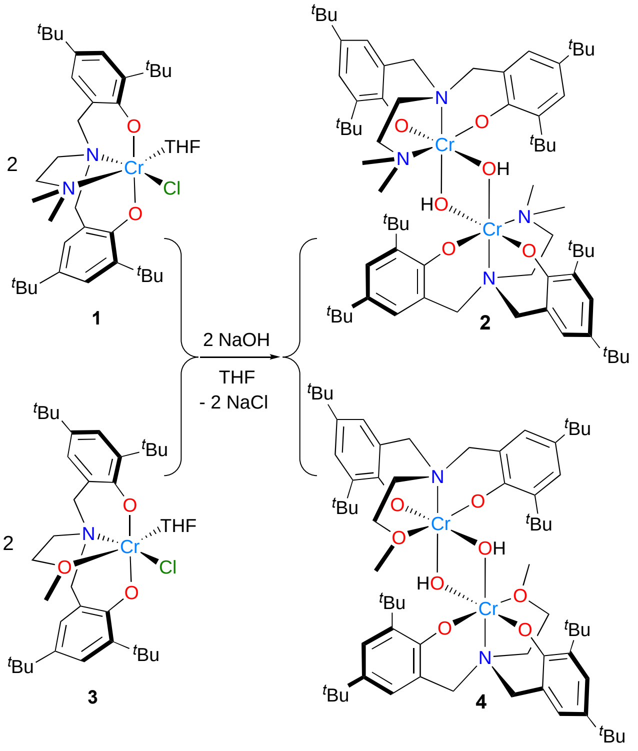
Block copolymerization conditions. Poly(cyclohexene carbonate) diol (PCHC) (0.50 g) and the required amount of *rac*-lactide were dissolved in 4 mL CH_2Cl_2. After 5 min, DBU (0.085 g, 0.56 mmol) dissolved in 1 mL CH_2Cl_2 was added and stirred overnight at 40 °C in an ampule. The solvent was removed under vacuum to give a crude polymer. This polymer was dissolved in CH_2Cl_2 and benzoic acid as per the method of Darensbourg,[25] then precipitated from cold methanol. The purified, colourless polymer was dried at 80 °C in a vacuum oven overnight.

Results and discussions

Synthesis and characterization of chromium complexes

We previously reported a Cr(III) diamine-bis(phenolate) catalyst, **1**, which showed good activity for converting of CHO and CO_2 to polycarbonate in the presence of various cocatalysts.[34] MALDI-TOF

MS of the produced polycarbonates showed the presence of multiple end groups, including poly(carbonate) diols. We speculated whether the presence of hydroxide groups, either added via an external ionic co-catalyst or in the form of a well-defined metal hydroxide complex, could selectively yield polycarbonate diols in a controlled fashion. Complexes **2** and **4** bearing chromium-hydroxide functionalities were prepared from previously reported complexes **1**[34] and **3**[41] via reaction with sodium hydroxide under nitrogen in THF to produce dark green solids in good yield (Scheme 1). Complexes **2** and **4** were characterized by MALDI-TOF MS and combustion analysis. The MALDI-TOF mass spectrum of starting chloride complex **1**, for example, showed peaks at *m/z* 609.3 and 574.3 corresponding to $[CrCl[L]]^+$ and $[Cr[L]]^+$, respectively, whereas **2** showed peaks at *m/z* 614.4 and 591.4 corresponding to $[CrOH[L] + Na]^+$ and $[CrOH[L]]^+$ (Figure S1). The absence of a peak at *m/z* 609.3 in the mass spectrum of **2** indicates replacement of the chloride by a hydroxide. Combustion analysis of **2** consistently showed contamination by NaCl which was the by-product derived from the reaction of **1** and sodium hydroxide.



Scheme 1. Synthesis of chromium hydroxide complexes **2** and **4**.

Crystals suitable for X-ray diffraction were obtained for complex **4**. The structure of **4** is shown in Figure 1 with selected bond lengths and angles. The structure displays a central Cr_2O_2 rhomboid and the two Cr(III) centres exhibit distorted octahedral geometries. A related hydroxide-bridged Cr(III) dimer of an aminopyridyl-bis(phenolate) ligand was previously reported by us as a product obtained upon quenching a polymerization of propylene oxide and CO_2 by a chromium chloride complex of that ligand.[42] Darensbourg and co-workers also isolated related hydroxide-bridged dimeric Cr(III) complexes possessing salen and acacen (N,N'-bis(t-butylacetylacetone)-1,2- ethylenediamine) ligands.[43] The Cr(1)–O(7)–Cr(2) and Cr(1)–O(8)–Cr(2) angles in **4** are 100.85(19)° and 100.09(19)°, respectively. The hydroxides are orientated *cis* to the oxygen on the pendant methoxy group. The Cr–OH bond distances are asymmetric, with Cr(1)–O(7) at 1.995(4) and Cr(1)–O(8) at 2.063(4) Å, whereas Cr(2)–O(7) and Cr(2)-O(8) bond distances are 2.049(4) and 2.003(4) Å, respectively.

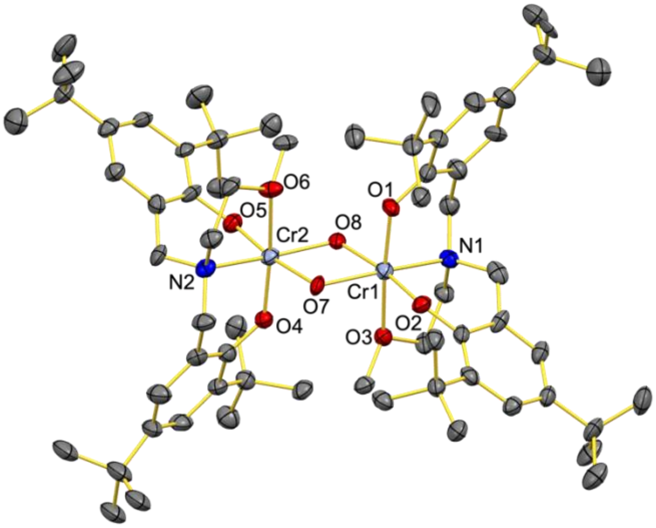


Figure 1. Molecular structure (ORTEP) and partial numbering scheme of complex **4**. Ellipsoid are drawn at 30% probability for visibility. Hydrogen atoms and disordered C-positions in *tert*-butyl groups are omitted for clarity. Selected bond distances (Å) and angles (°): Cr(1)–O(1) 1.901(4), Cr(1)–O(2) 1.918(4), Cr(1)–O(3) 2.078(4), Cr(1)–N(1) 2.076(5), Cr(1)–O(7) 1.995(4), Cr(1)–O(8) 2.063(4), Cr(1)···Cr(2) 3.117(2), O(2)–Cr(1)–O(3) 90.29(2), O(2)–Cr(1)–N(1) 91.98(19), O(2)–Cr(1)–O(1) 91.90(17), O(2)–Cr(1)–O(7) 94.25(17), O(7)–Cr(1)–O(8) 79.46(17), O(7)–Cr(2)–O(8) 79.60(17), N(1)–Cr(1)–O(8) 93.87(18), N(1)–Cr(1)–O(1) 92.35(17), N(1)–Cr(1)–O(3) 81.22(17), O(1)–Cr(1)–O(8) 92.19(16), O(1)–Cr(1)–O(3) 173.28(17).

Copolymerization of CHO and CO_2

Complex **3**, the chromium-chloride precursor to **4**, was previously reported by us and found to be inferior to **1** as a CO_2/cyclohexene oxide copolymerization catalyst.[41] Complex **2** was, therefore, initially used as the catalyst for the copolymerization of CHO and CO_2 under 40 bar CO_2 and 60 °C to produce PCHC. Using **2** in the absence of a cocatalyst resulted in very low epoxide conversion to give a low molecular weight polycarbonate (Table 1, entry 1).) This observation is consistent with our previous results concerning Cr(III) diamine-bis(phenolate) catalysts where copolymerization of epoxides and CO_2 typically requires an additional nucleophilic cocatalyst, such as Cl^- or N_3^- combined with a very bulky cation, such as bis(triphenylphosphine)iminium (PPN^+).[10,33-34] When PPNCl was used as the cocatalyst, complex **2** can efficiently produce polycarbonate with M_n of 27 kg mol^{-1} and a narrow dispersity (Table 1, entry 2). Similar polymerization activity was shown by **4**, but the polymer obtained had a lower molecular weight (Table 1, entry 5). Complex **2** was used for the remaining studies. MALDI-TOF MS analysis of the polymer obtained from entry 2 showed polymers possessing several different end-groups, including (a) di-hydroxyl-group terminated polymer with an ether linkage, (b) chloride and hydroxyl-group terminated polymer with an ether linkage, (c) dichloride terminated polymer with an ether linkage, and (d) chloride and hydroxyl terminated polymer (Figure S2). Series (a) is the expected polymer chain if polymerization is initiated by the hydroxide from complex **2** and terminated by hydrolysis. However, the two hydroxyl end groups could also possibly result from water contamination causing chain transfer,[42,44] which could also lead to the formation of the ether linkage, but contamination by cyclohexene diol or double insertion of two epoxide units without CO_2 incorporation are also possible.[26] The appearance of chloride as one of the end groups in the produced PCHC demonstrates the chloride of PPNCl also initiated the epoxide ring-opening. Therefore, providing hydroxide nucleophiles exclusively could potentially produce strictly polycarbonate diols.

Table 1. Copolymerization of CHO and CO_2 catalyzed by **2** and **4**[a]

Entry	Catalyst	[Cat]:[CHO]: [cocat]	Cocat.	Conv.[b] (%)	TON	M_n[c] (kg mol^{-1})	Đ[c] (M_w/M_n)	T_g (°C)	T_d (°C)
1	**2**	1:500:0	---	6	30	4.80	1.09	ND[d]	ND
2	**2**	1:500:1	PPNCl	89	445	27.0	1.19	104	284
3	**2**	1:500:1	$Ph_2P(O)NPPh_3$	84	420	28.5	1.13	110	302
4	**2**	1:500:1	Bu_4NOH	88	440	6.30	1.10	79	254
5	**4**	1:500:1	PPNCl	87	435	18.4	1.12	ND	ND

[a] Copolymerization reactions were carried out in neat CHO at 60 °C and 40 bar CO_2 for 24 h. [b] Calculated by ^1H NMR. [c] Determined by triple detection GPC in THF using a dn/dc value of 0.0701 mL g^{-1}. [d] ND = not determined.

To prepare a hydroxide-containing co-catalyst, the synthesis of PPNOH was attempted using sodium hydroxide with PPNCl. However, the ^{31}P NMR spectrum of the isolated product showed two phosphorus resonances at 13.23 and 14.35 ppm, identical to the resonances observed for (diphenylphosphonimido)triphenylphosphorane, $Ph_2P(O)NPPh_3$, obtained from the reaction of PPNCl with NaOMe in methanol,[45] and commercially obtained $Ph_2P(O)NPPh_3$ (Figure S3 and S4). Interestingly, the combination of **2** with $Ph_2P(O)NPPh_3$ can also efficiently convert CHO to PCHC with a similar molecular weight and narrow dispersity to that produced using **2** and PPNCl (Table 1, entry 3). The MALDI-TOF MS of this polymer showed multiple series of signals separated by a repeating unit of *m/z* 142 (Figure S5). A closer inspection of these repeating fragments showed the presence of three ions (Figure 2). Series (a) and (c) correspond to polycarbonate diols, likely produced from hydroxide originating from **2**. Series (a) contains one ether linkage, [17 (OH) + 142n (repeating cyclohexene carbonate unit) + 180 ($C_{12}H_{20}O$) + 17 (OH)] possibly occurring from chain transfer by adventitious water. The dominant series (b), however, corresponds to the presence of $Ph_2P(O)NPPh_3$ and hydroxyl end groups, [17 (OH) + 142n (repeating cyclohexene carbonate unit) + 82 (C_6H_{10}) + 477 ($Ph_2P(O)NPPh_3$)].

The ^1H NMR spectrum of the purified polymer also showed the appearance of aromatic hydrogens (Figure S6). The ^{31}P NMR spectrum of the resulting polymer, however, showed no phosphorus resonances. One possible reason for the absence of phosphorus signals is the high molecular weight of the polymer leading to the resulting phosphorus concentration being too low to be detected. Therefore, the copolymerization of CHO and CO_2 by **2** and $Ph_2P(O)NPPh_3$ was run for 2 h to obtain low molecular weight polymer with a higher number of phosphorus-containing groups per mass of polymer. The GPC traces of the resulting polymer vs. the polymer obtained after 24 h clearly demonstrated that the polymer obtained after 2 h had a lower molecular weight (Figure S7). The

^{31}P[^{1}H] NMR spectrum of the resulting purified polymer clearly showed two peaks at 29.71 and 20.57 ppm, which we believe correspond to the $Ph_2P(O)NPPh_3$ end-group in the polymer chain (Figure S8). Unlike the TFA-polycarbonate-OH polymers,[25-26] the $Ph_2P(O)NPPh_3$-polycarbonate-OH polymer did not exhibit hydrolysis in the presence of adventitious water during the reaction or by termination of polymerization in methanol to afford polycarbonate diol.

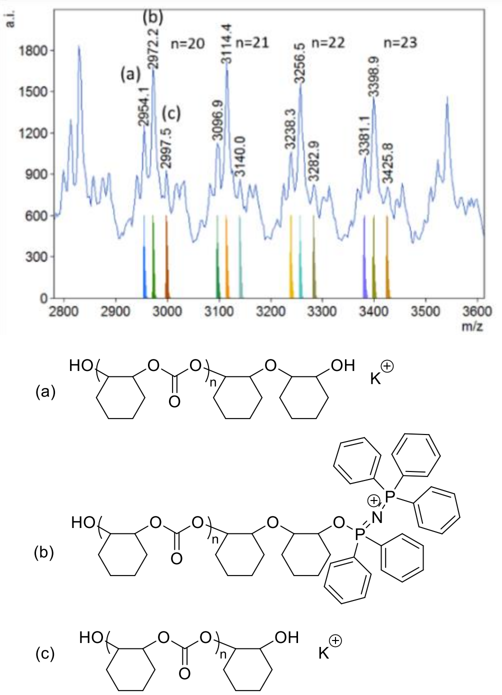


Figure 2. Magnified section of MALDI-TOF mass spectrum for PCHC obtained using **2** with $Ph_2P(O)NPPh_3$ as cocatalyst (Table 1, entry 2). Modeled isotopic masses for polymers (a–c) containing different end groups are shown below the experimental spectrum.

Tetra(*n*-butyl)ammonium hydroxide (Bu_4NOH) with complex **2** was tested for polycarbonate diol production. Because isolation of pure Bu_4NOH can induce a Hofmann elimination forming Bu_3N and 1-butene, a methanol solution of Bu_4NOH was used as cocatalyst for the copolymerization reaction (Table 1, entry 4). The produced PCHC showed a good conversion but a lower number-averaged molecular weight (M_n = 6.3 kg mol^{-1}) than that produced by using PPNCl or $Ph_2P(O)NPPh_3$ as cocatalyst, likely due to chain transfer reactions by the presence of water and methanol.[9,46] The MALDI-TOF MS of this PCHC showed a single series of polymer chains corresponding to the expected polycarbonate diol, but with ether linkages, [17 (OH) + 142n (repeating cyclohexene carbonate unit) + 5 × 98 ($C_6H_{10}O$) + 82 (C_6H_{10}) + 17 (OH)] (Figure 3 and Figure S10), wherein the hydroxide from complex **2** or Bu_4NOH initiate the polymerization and the reaction is terminated by hydrolysis. In addition, the ether linkages can also be observed in the ^{1}H NMR spectrum (Figure S9).

The thermal properties of the produced PCHCs were analyzed using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). The midpoint glass transition temperatures of PCHC with M_n = 27.0 and M_n = 28.5 kg mol^{-1} are 104 °C and 110 °C, respectively (Figures S14 and S15), which are similar to the reported value of 116 °C.[47] For the lower molecular weight polycarbonate diol (M_n = 6.3 kg mol^{-1}), a lower midpoint glass transition temperature of 79 °C was observed, which can be attributed to its lower molecular weight and the presence of multiple ether linkages.[48] The onset of decomposition temperatures of the produced PCHCs were found to be between 254 and 284 °C (Figure S16), which are similar to the values between 253 and 275 °C reported by Darensbourg and co-workers.[49] The polycarbonate prepared in the presence of $Ph_2P(O)NPPh_3$ exhibited a higher decomposition temperature of 302 °C (Figure S17).

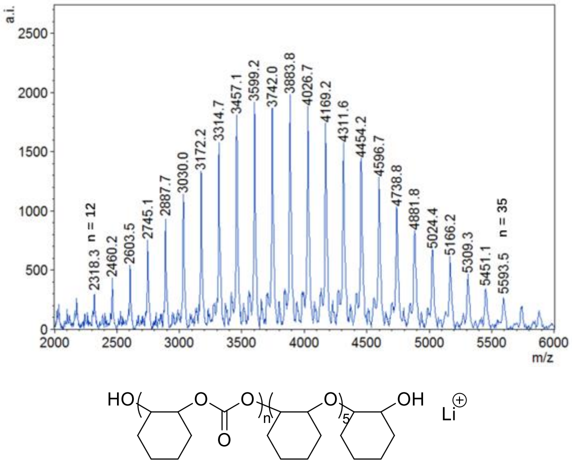
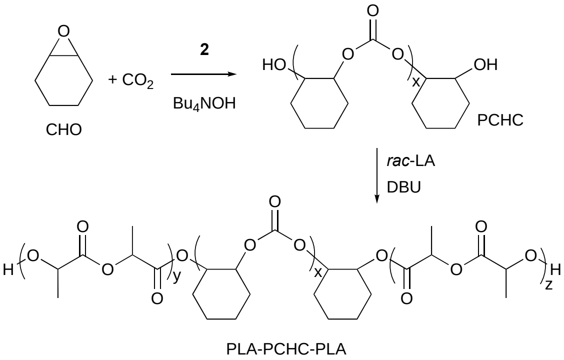


Figure 3. MALDI-TOF mass spectrum of polycarbonate diol produced by using Bu_4NOH as cocatalyst according to the conditions in Table 1, entry 4. The ether linkages are not explicitly implied to be part of block as shown, but instead may be randomly distributed throughout the polycarbonate.

Block copolymerization of PCHC and lactide

The di-hydroxyl terminated PCHC (M_n = 6.3 kg mol^{-1}) obtained by using **2** with Bu_4NOH was used for ring opening polymerization of *rac*-lactide in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to produce a block copolymer (Scheme 2). The molar mass of the resulting PCHC-PLA copolymer was found to grow in proportion to the amount of *rac*-lactide added (Table 2, entries 1 and 2).



Scheme 2. Copolymerization of CHO and CO$_2$ and subsequent block copolymerization with *rac*-lactide.

Table 2. Block copolymerization from PCHC macroinitiator and *rac*-lactide

Entry	**M_n PCHC[a] (kg mol^{-1})**	**T_g (°C)**	**T_d (°C)**	**[PCHC]: [*rac*-LA] (molar ratio)**	**Conv[b] (%)**	**M_n[c] LA-PCHC-LA (kg mol^{-1})**	**Đ[c] (M_w/M_n)**	**M_n[d] LA-PCHC-LA (Calc) kg mol^{-1}**	**T_g (°C)**	**T_d (°C)**
1	6.3	79	254	1:87	98	14.0	1.05	18.0	56	313
2	6.3	79	254	1:44	97	11.0	1.04	12.0	71	311

[a] Determined by triple detection GPC in THF (dn/dc = 0.0701 mL g^{-1}). [b] Conversion determined by ^{1}H NMR. [c] Determined by triple detection GPC in THF (dn/dc = 0.0497 mL g^{-1}). [d] Determined from the sum of experimentally determined M_n (GPC) for PCHC and the expected M_n for the PLA blocks calculated from the conversion of lactide.

The ^{1}H NMR spectrum of the resulting product indicates a block copolymer is obtained (Figures S11 and S12). The resonances at 4.6 ppm and 5.2 ppm (a and b) are assigned to poly(cyclohexene carbonate) and PLA chains, respectively. The resonances assigned to the PCHC methine protons (e) were not observed in the block copolymer, which was attributed to the deshielding by the adjacent ester group leading to them being masked by the PCHC polymer chain resonances (a).[26] Two resonances at 4.3 ppm were observed, which can be assigned to the methine protons within the linking PCHC-lactide unit (c) and the methine protons in the terminal lactide unit (d). Similar resonances were also observed in the ^{1}H NMR spectra for block copolymers (PLA-X-PLA) obtained from using poly(ethylene glycol)s as macroinitiators.[50]

DOSY NMR is a two-dimensional NMR technique that can determine self-diffusion coefficients (D) which are related to the properties of an individual molecule such as size, mass as well as its surrounding environment. Thus, each component in a mixture can be pseudo-separated based on its own diffusion coefficient.[51] The DOSY NMR spectrum with the related ^{1}H NMR spectrum projected above are shown in Figure S13. The signals at 4.6 ppm and 5.2 ppm corresponding to polycarbonate block and polylactide block show the same diffusion coefficient, which confirms the block copolymer formation. The M_n of the resulting block copolymers determined by triple-detection GPC in THF were in reasonable agreement with the values for the calculated M_n based on *rac*-LA and macroinitiator ratios. Although using triple detection and dn/dc values is generally not suitable for GPC of block copolymers, block copolymers with narrow molecular weight dispersity, such as those presented here, can be assumed to be close to the true molar mass, which make them suitable for triple detection.[52] The GPC traces of the PCHC and the resultant PLA-PCHC-PLA block copolymer obtained using the conditions in Table 2 are shown in Figure 4. It is apparent that the resulting copolymer showed an increased molecular weight and is monodisperse, demonstrating successful chain extension from the hydroxyl end groups of the PCHC. In addition, using different loadings of *rac*-LA showed an increase in the molecular weight of the resulting copolymer consistent with the amount of *rac*-lactide used. It is worth noting the GPC trace of the polycarbonate diol (peak a) showed slight bimodality, most likely due to the chain transfer reactions (likely resulting from the presence of cyclohexane diol) causing the presence of ether linkages.

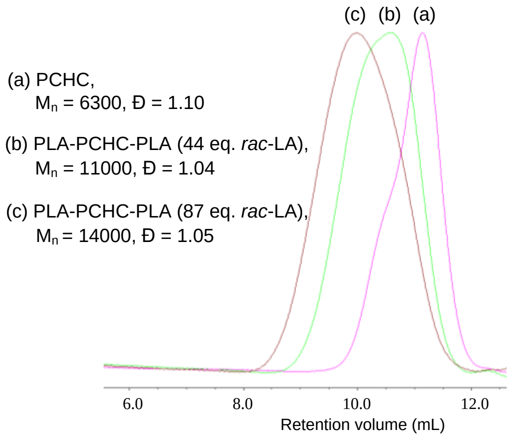


Figure 4. GPC traces of PCHC and PLA-PCHC-PLA from RI detector using THF as eluent (Table 2, entries 2 and 3).

The glass transition temperatures for the resulting block copolymers are expected to decrease because of the presence of PLA blocks,[53] and was evident here (cf. Table 1, entry 4, T_g = 79 °C, Table 2, Entry 2, T_g = 71 °C). More importantly, the decreasing glass transition temperature of the block copolymer could be observed with an increase in *rac*-lactide incorporation (Table 2, entry 1, T_g = 56 °C and entry 2, T_g = 71 °C, Figure S17). The onset decomposition temperatures of the block copolymers (Table 2, entry 2 and 3) were found to increase, ranging between 307 °C and 313 °C (Figure S18) compared with 254 °C for the diol macroinitiator (Table 1, entry 4).

Block copolymerization was also monitored by using in situ infrared spectroscopy. Figure 5 shows the three-dimensional plot of the ring-opening polymerization of *rac*-lactide initiated by PCHC in the presence of DBU. From the infrared spectra, it is apparent that addition of DBU to the solution of lactide and PCHC causes a decrease in the *rac*-lactide carbonyl absorption at 1772 cm^{-1} commensurate with an increase in the carbonyl absorption of block copolymer at 1757 cm^{-1}.

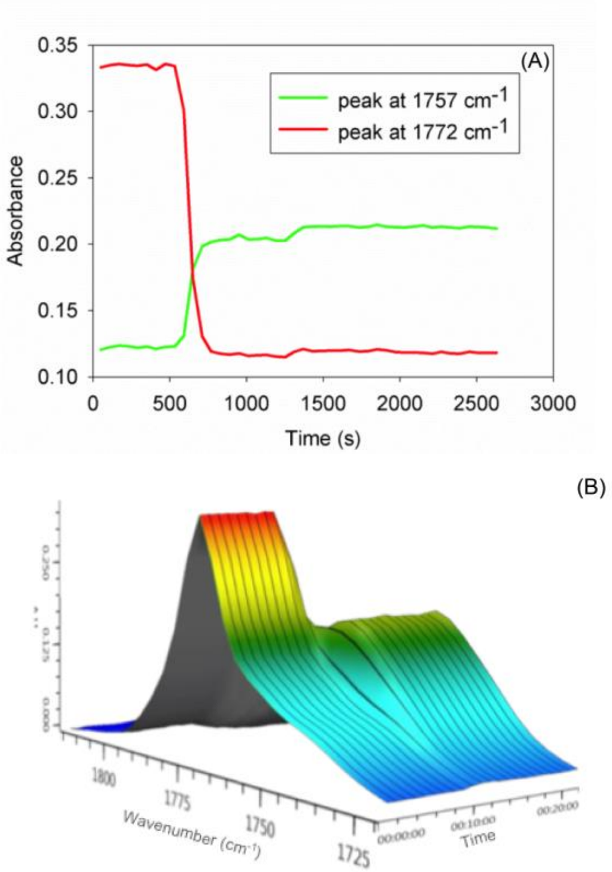


Figure 5. (A) Reaction profile and (B) resulting three-dimensional plot of IR spectra. The absorptions at 1772 and 1757 cm^{-1} arise from the carbonyl groups from *rac*-lactide and the resulting PLA of the block copolymer, respectively. DBU added at *t* = 10 min.

Conclusions

An amino-bis(phenolate) chromium hydroxide complex in combination with different cocatalysts such as PPNCl, $Ph_2P(O)NPPh_3$ or Bu_4NOH can efficiently convert of CHO to PCHC. In the case of hydroxide-containing cocatalyst, Bu_4NOH can copolymerize cyclohexene oxide with CO_2 to give di-hydroxyl terminated PCHC in a controlled and systematic fashion. The PCHC diol can be used as a macroinitiator in the ring-opening polymerization of *rac*-lactide, using DBU as co-initiator. Near-quantitative conversion of *rac*-lactide was achieved to give block copolymers. The new copolymers were characterized by NMR, GPC, DSC and TGA analysis and represent potentially useful materials based on renewable feedstocks.

Author Contributions

Kaijie Ni performed the experiments and drafted the manuscript. Louise N. Dawe and Amy Sarjeant conducted the single crystal X-ray diffraction measurements. Christopher M. Kozak designed and supervised the execution of this project and edited the manuscript.

Conflicts of interest

There are no conflicts to declare.

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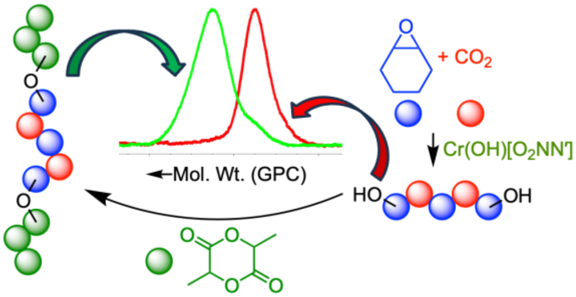
TOC Graphic



Summary text for TOC use

A chromium hydroxide diamino-bis(phenolate) complex copolymerizes cyclohexene oxide and CO_2 to a polycarbonate diol, which can be act as a macroinitiator for polymerization of lactide to give a polycarbonate-block-polyester copolymer.