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The Influence of the Metal (Al, Cr, and Co) and the Substituents of the Porphyrin in Controlling the Reactions Involved in the Copolymerization of Propylene Oxide and Carbon Dioxide by Porphyrin Metal(III) Complexes. 1. Aluminum Chemistry

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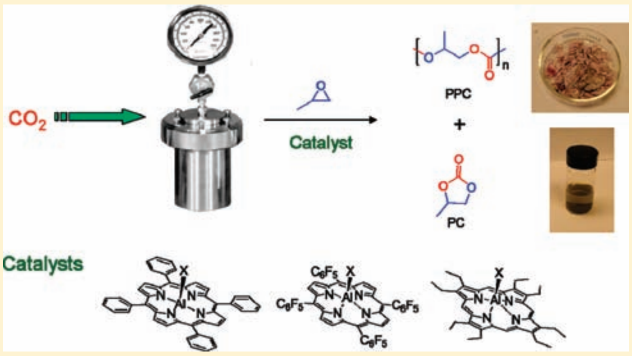
Supporting Information

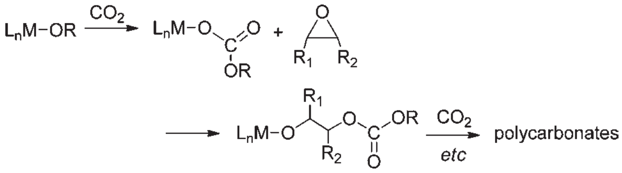
ABSTRACT: The reactivities of aluminum(III) complexes LAlX, where L = 5,10,15,20-tetraphenylporphyrin (TPP), 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (TFPP), and 2,3,7,8,12,13,17,18-octaethylporphyirn (OEP) and X = Cl or OEt, have been studied with respect to their ability to homopolymerize propylene oxide (PO) and copolymerize PO and CO_2 to yield polypropylene oxide (PPO) and polypropylene carbonate (PPC), respectively, with and without the presence of a cocatalyst, namely, 4-dimethylaminopyridine (DMAP) or a PPN^+ salt where the anion is Cl^- or N_3^-. In the presence of a cocatalyst (0.5 equiv), the TFPP complex is the most active in copolymerization to yield PPC, with the latter being effective even at 10 bar CO_2. An increase in the $PPN^+X^-/[Al]$ ratio decreases the rate of PPC formation and favors the formation of propylene carbonate, (PC). Studies of the polymers formed in reactions involving Al-alkoxide initiators and PPN^+ salts by mass spectrometry indicate that one chain is grown per Al center. These results are compared with earlier studies where the reactions display first order kinetics in the metal complex.



INTRODUCTION

Of the four major commercial polymers, namely, polyolefins, polyesters, polyurethanes, and polycarbonates, only polyolefins and polyurethanes are made in what can be considered an atom efficient process,[1,2] and with the exception of polyolefins, they are formed by condensation reactions in step growth polymerizations.[3,4] Polycarbonates are formed by the condensation of a diol and phosgene or its derivative under basic conditions.[5] A more attractive chemical process, which replaces the use of phosgene or a derivative of phosgene and is both atom efficient and a living process, involves the copolymerization of an epoxide and carbon dioxide, providing that the physical properties are equivalent or superior. This can be achieved by metal coordinate catalysis wherein metal−alkoxide and metal−alkylcarbonate bonds are the key reactive intermediates, as shown in eq 1.

1.



Following the initial work of Inoue et al.,[6,7] there has in the past decade been an explosion of interest in this reaction based on well-defined molecular catalyst systems, and excellent recent reviews document this transition from the discovery and early work with ill-defined catalyst systems to the more recent detailed mechanistic studies at single metal centers.[8−16] Although zinc(II) systems have been the focus of considerable attention,[8,17−23] the M(III) centers of Al, Cr, and Co offer some of the most active catalyst systems reported to date[9,24−51] and afford a unique opportunity to study the influence of electronic configurations d^0, d^3, and d^6 on the reactions involved. The M^{3+} ions are of a very similar size with ionic radii of ∼0.6 Å, though for Co^{3+} this depends significantly on its spin state, e.g., for an octahedral complex, whether it is low spin $t_{2g}{}^6$, high spin $t_{2g}{}^4e_g{}^2$, or of intermediate spin in a lower symmetry field.

Of all of the ligand systems employed in the reactions involving Cr^{3+} and Co^{3+} ions, the quadradentate N_2O_2−Schiff base ligands have proved the most popular and effective in the copolymerizations of epoxides and CO_2.[10,9,24−33,52−56] These lend themselves to a vast possibility of substituents present in the backbone, N∼N, and on the aromatic ring to affect chirality and stereoelectronic effects. Darensbourg showed very clearly in his studies of the reactions of salen Cr(III) catalysis that there were three competing reactions, (i) polyether formation, (ii) polycarbonate

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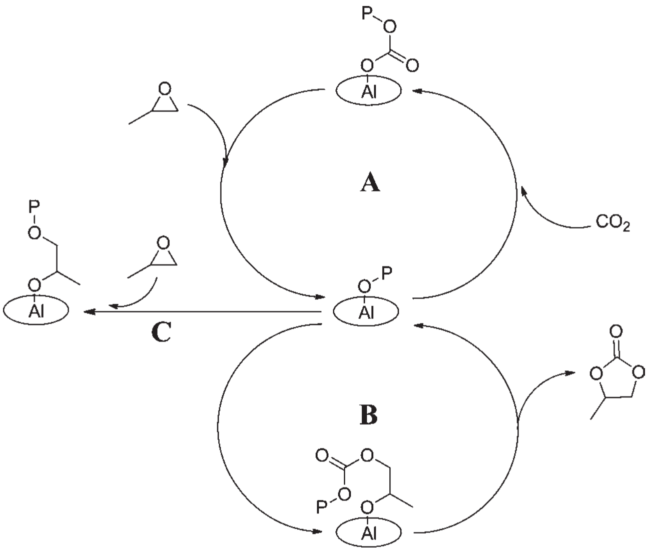
Scheme 1. The Competing Reactions, B and C, Involved in the PO/CO_2 Copolymerization Processes, A



formation, and (iii) cyclic carbonate formation, and moreover, the formation of the cyclic carbonate was thermodynamically favored over the formation of the polycarbonate.[52,57] Furthermore, the difference in the energy of activation for the two latter processes was larger for the alicyclic epoxides than for the aliphatic epoxides. For example, in the reactions involving cyclohexeneoxide (CHO) and CO_2, the $\Delta H^{\ddagger}$ for the formation of polycyclohexenecarbonate was 47 kJ mol^{-1} and that for cyclohexenecarbonate was 133 kJ mol^{-1}, whereas for the reaction involving propylene oxide, PO, and CO_2, the formation of polypropylene carbonate, PPC, was 68 kJ mol^{-1} and that for propylene carbonate, PC, was 101 kJ mol^{-1}.[57] Because of the $\Delta\Delta H^{\ddagger}$ of these two reactions, the polymer, the polycarbonate, is the kinetic product and is favored at lower temperatures. The three competing reactions are shown in Scheme 1, where it also becomes obvious that polycarbonate formation is favored when the rate of ring-opening of the epoxide is favored by the alkylcarbonate over the alkoxides. Thus, matters pertaining to the equilibrium involving the insertion of CO_2 into the alkoxide bond become important.

Although we recognize that there are significant advantages to the development of libraries of Schiff base ligands to exploit steric and electronic effects in studies of these reactions, we have been attracted to the simplicity in the use of porphyrin ligands to study electronic effects on these reactions. For the M(III) ions of Al, Cr, and Co, the metal can basically only move in and out of the plane of the porphyrin. Dissociation of an arm or adoption of a *cis* octahedral LM(X)(Y) geometry is impossible. The porphyrin ligand requires the *trans*-LM(X)(Y) geometry. Any changes in the substituents on the porphyrin occur at a significant distance from the active metal center. Furthermore, in studying mechanisms of reactions, those that are slow are often the most revealing, as are those that offer the greater number of potential products. With this in mind, we will present in this series of papers our studies of the activation of propylene oxide (PO) and CO_2 by (porphyrin)M(III) complexes (Figure 1). This follows from the original work of Inoue and Takeda, who noted the ability of (tetraphenylporphyrin)AlCl to act as an initiator in the homopolymerization of PO and in the presence of additives/cocatalysts such as methylimidizole or various soluble halide salts to copolymerize PO and CO_2, albeit with extremely low turnover frequencies, TOFs, ~1 h^{-1}.[58] This contrasts with TOFs ranging from 10^2 h^{-1} to 10^3 h^{-1} reported by Darensbourg et al. and Coates et al. in their studies of Schiff base catalyst systems of Cr(III) and Co(III), respectively.[29,30,52,55,59] The Al(III) system does, however, offer one advantage in being diamagnetic, and this allows the application of NMR techniques to the elucidation of the nature of species bound to the metal center.[60] This is also greatly enhanced by the large magnetic influence of the porphyrin ligand that shifts the signals [^{13}C, ^{1}H] of axial groups bound to the metal center to higher field by several parts per million.

EXPERIMENTAL SECTION

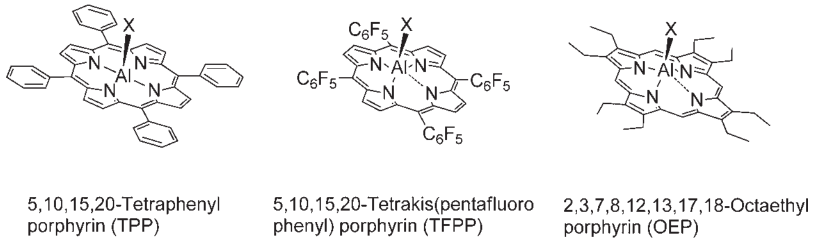
Reagents and Methods. All syntheses and solvent manipulations were carried out under a dry nitrogen atmosphere using standard Schlenck-line and drybox techniques. Ethanol was dried and distilled over magnesium freshly activated with iodine and degassed before use. All other solvents were dried and degassed by standard methods. The deuterated solvents were stored over 4 Å molecular sieves for 24 h prior to use. Propylene oxide (Sigma Aldrich) was distilled from calcium hydride. All three porphyrins, 5,10,15,20-tetraphenyl-21H,23H-porphine ($TPPH_2$), 5,10,15,20-tetrakis(pentafluorophenyl)-21H,23H-porphine ($TFPPH_2$), and 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine ($OEPH_2$) (Frontier Scientific); diethylaluminum chloride (1.0 M solution in hexane, Sigma Aldrich); trimethylaluminum (2.0 M solution in hexane, Sigama Aldrich); 1,8-octanediol (Sigma Aldrich); 99 atom % ^{13}C labeled carbon dioxide (Sigma Aldrich); and 99% CO_2 (OSU gas stores) were used as received. Bis(triphenylphosphine)iminium chloride ($(Ph_3P)_2N^+Cl^-$ (PPN^+Cl^-); Sigma Aldrich) was dried under vacuum and stored inside a drybox before use. 4-Dimethylaminopyridine (DMAP; Aldrich) was sublimed and stored inside a drybox before use. $PPN^+N_3^-$ was prepared from PPN^+Cl^- following a literature procedure.[61]

NMR Spectroscopy. ^{1}H and ^{13}C{^{1}H} NMR experiments were carried out with a Bruker DPX-400 (5 mm broad band probe) and a Bruker DRX-500 (5 mm broad band probe) spectrometer. All chemical shifts are in parts per million relative to the solvent chloroform-*d* at 7.24 ppm for ^{1}H NMR and 77.23 ppm for ^{13}C{^{1}H} NMR spectroscopy.

Gel Permeation Chromatography. Gel permeation chromatographic (GPC) analyses were carried out at 40 °C using a Waters Breeze system equipped with a Waters 2415 Refractive index detector and a set of two columns, Waters Styragel HR-2 and HR-4 (7.8 × 300 mm). $CHCl_3$ was used as the mobile phase at 1.0 mL/min. The samples were filtered before analysis. The sample concentration was approximately 1.0%, and the injection volume was 100 μL. The calibration curve was made with six polystyrene standards covering the molecular weight range from 1320 to 3.15×10^6 Daltons.

Gas Chromatography. Gas chromatograms were obtained on a Hewlett-Packard 6890 series gas chromatograph using a Chiraldex B capillary column (25 m × 0.25 mm, 0.12 mm film thickness), a flame ionization detector, and He carrier gas. The chromatograms were recorded at 90 °C isothermal and a head pressure of 130 psi.

Mass Spectrometry. Matrix assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI−TOF MS) was performed on a Bruker Microflex mass spectrometer provided by a grant from the Ohio BioProducts Innovation Center. The spectrometer was operated in a linear, positive ion mode with a N_2 laser. Laser power was used at a threshold level required to generate a signal. The accelerating voltage



5,10,15,20-Tetraphenyl porphyrin (TPP)

5,10,15,20-Tetrakis(pentafluoro phenyl) porphyrin (TFPP)

2,3,7,8,12,13,17,18-Octaethyl porphyrin (OEP)

Figure 1. Structures of (porphyrin)AlX catalyst precursors employed in this study.

was 28 kV. Equal amounts of the dithranol matrix and sample were dissolved in dichloromethane (approximately 2 mg/0.5 mL). A small amount of this solution was spotted on the target plate and allowed to dry at room temperature before use. Electrospray ionization mass spectroscopy (ESI MS) was carried out in positive ion mode on a Bruker MicrOTOF mass spectrometer provided by a grant from the Ohio BioProducts Innovation Center.

FTIR Spectroscopy. IR spectra were recorded in dichloromethane solution using a Perkin-Elmer Spectrum GX spectrometer at room temperature. A 10.0 mm × 0.2 mm liquid IR cell equipped with CsF windows was used.

Microanalysis was performed by Atlantic Microlab Inc.

Synthesis of Catalysts. (TPP)aluminum chloride,[62] (TFPP)-aluminum chloride,[63] and (TPP)aluminum ethoxide[64] complexes were prepared according to literature procedures. (OEP)aluminum chloride[65] was prepared following a procedure similar to that for the previous (porphyrin)aluminum chlorides and was characterized by ^1H NMR and $^{13}C\{^1H\}$ NMR spectroscopy. ^1H NMR ($CDCl_3$, δ, ppm): 1.99 (t, CH_2CH_3), 4.19 (m, CH_2CH_3), 10.37 (aromatic). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 18.67 (CH_2CH_3), 20.20 (CH_2CH_3), 98.06, 143.05, 146.15 (aromatic), see Figures S7 and S8, Supporting Information.

Synthesis of (TFPP)Aluminum Methyl. The starting material (TFPP)aluminum methyl was prepared according to slight modification of a previously reported procedure.[63] The free $(TFPP)H_2$ (500 mg, 0.51 mmol) was dissolved in 15 mL of dry benzene, and to it was slowly added a hexane solution of trimethylaluminum ($AlMe_3$ 2.0 M solution in hexane, 0.31 mL, 0.62 mmol) at room temperature. The resulting red solution was left stirring for 5 h at 45 °C, after which the volatile fractions were removed under vacuum conditions. After drying in vacuo at 55 °C for 5 h, the product was isolated as a red powder in 93% yield. ^1H NMR ($CDCl_3$, δ, ppm): −6.99 (s, CH_3), 9.08 (aromatic), see Figure S9, Supporting Information.

Synthesis of (TFPP)Aluminum Ethoxide. (TFPP)AlMe (500 mg, 0.49 mmol) was dissolved in 15 mL of dry benzene, and dry ethanol (30 μL, 0.51 mmol) was added to the reaction mixture at room temperature. The resulting purple solution was left stirring for 5 h at 50 °C. The volatile fractions were then removed under vacuum conditions at 50 °C to give a reddish purple powder. After washing with a small amount of benzene and drying under vacuum conditions, the pure product was obtained in 81% yield. ^1H NMR ($CDCl_3$, δ, ppm): −1.37 (q, OCH_2CH_3), −2.03 (t, OCH_2CH_3), 9.15 (s, aromatic). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 16.35 (OCH_2CH_3), 52.05 (OCH_2CH_3) 104.57, 115.38, 127.91, 130.75, 132.66, 136.73, 139.24, 141.36, 143.91, 145.32, 145.60, 147.73, 148.18, 148.88 (aromatic), see Figures S10 and S11, Supporting Information. Elemental analysis found: C, 51.44; H, 1.36; N, 5.30%. Calculated for $C_{46}H_{13}AlF_{20}N_4O$: C, 52.89; H, 1.25; N, 5.36%. MALDI TOF, Calculated MW: 1044.58 for (TFPP)-AlOEt. Found: 999.4 for $(TFPP)Al^+$.

Synthesis of (OEP)Aluminum Methyl. (OEP)AlMe[65] was prepared following a procedure similar to that for (TFPP)AlMe. The free $(OEP)H_2$ (500 mg, 0.93 mmol) was dissolved in 15 mL of dry benzene, and to it was slowly added a hexane solution of trimethylaluminum ($AlMe_3$ 2.0 M solution in hexane, 0.56 mL, 1.12 mmol) at room temperature. The resulting dark red solution was left stirring for 5 h at 45 °C, after which the volatile fractions were removed under vacuum conditions. After drying in vacuo at 55 °C for 5 h, the product was isolated as a red powder in 90% yield. ^1H NMR ($CDCl_3$, δ, ppm): −7.44 (s, CH_3), 1.92 (t, CH_2CH_3), 4.14 (m, CH_2CH_3), 10.21 (aromatic), see Figure S12, Supporting Information.

Synthesis of (OEP)Aluminum Ethoxide. A suspension of (OEP)AlMe (500 mg, 0.87 mmol) in 10 mL of neat dry ethanol was stirred overnight at 50 °C for 5 h. The volatile fractions were then removed under vacuum conditions. After crystallizing from a saturated toluene solution, the red solid was isolated by filtration in 71% yield. ^1H NMR ($CDCl_3$, δ, ppm): −2.49 (t, OCH_2CH_3), −1.72 (q, OCH_2CH_3), 1.88 (t, CH_2CH_3), 4.15 (m, CH_2CH_3), 10.29 (aromatic). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 15.91 ($-OCH_2CH_3$), 51.60 ($-OCH_2CH_3$), 18.49 (CH_2CH_3), 19.95 (CH_2CH_3), 97.72, 142.33, 146.30 (aromatic), see Figures S13 and S14, Supporting Information. Elemental analysis found: C, 73.77; H, 7.81; N, 9.22%. Calculated for $C_{38}H_{49}N_4AlO$: C, 75.46; H, 8.17; N, 9.26%. MALDI TOF Calculated MW: 604.8 for (OEP)AlOEt. Found: 559.8 for $(OEP)Al^+$.

Synthesis of (TPP)Aluminum $O(CH_2)_8O$ Aluminum (TPP). (TPP)AlMe[66] (400 mg, 0.61 mmol) and 1,8-octanediol (45 mg, 0.31 mmol) were dissolved in 15 mL of dry toluene and refluxed overnight at 140 °C. The volatile fractions were removed at 60 °C under vacuum conditions. After being washed twice with small amounts of pentane, the product was obtained as a dark purple powder in 77% yield. ^1H NMR ($CDCl_3$, δ, ppm): −2.22, −1.56, −1.44, 0.59 ($(CH_2)_8$), 7.65, 7.72, 8.06, 8.16, 8.94, 8.99, 9.07 (aromatic). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 24.10, 28.86, 31.28, 57.34 ($(CH_2)_8$), 120.50, 120.72, 127.08, 128.03, 132.26, 134.46, 141.79, 142.01, 148.75, 148.95 (aromatic), see Figures S15 and S16, Supporting Information. Elemental analysis found: C, 78.18; H, 5.32; N, 7.19%. Calculated for $C_{96}H_{72}N_8Al_2O_2$: C, 80.99; H, 5.10; N, 7.87%.

The Binding of $PPN^+N_3^-$ to (porphyrin)AlX Compounds. Ten millimolar stock solutions of (porphyrin)aluminum chloride catalysts and the $PPN^+N_3^-$ additive were separately prepared in a dichloromethane solvent. The required volumes of the catalysts and $PPN^+N_3^-$ were thoroughly mixed, and the resultant solution was transferred into a liquid IR cell which was sealed and taken out of the drybox to record the spectrum. Twenty millimolar stock solutions were used in the cases of (porphyrin)aluminum ethoxide and $(TPP)AlO_2C(CH_2)_6CH_3$[60] catalysts. To investigate the binding of N_3^- ions to the aluminum center in $(TPP)AlO_2C(CH_2)_6CH_3$, the catalyst and $PPN^+N_3^-$ solutions were mixed in the following molar ratios: 1:0.75, 1:1, and 1:2. In each case, free and bound azide IR bands were observed (at 2005 cm^{-1} and 2073 cm^{-1}, respectively), suggesting <1 equiv of N_3^- coordinating to the aluminum center, which remains bound to the carboxylate ligand, even in the presence of excess azide.

Reactions between (porphyrin)AlX and Propylene Oxide-(PO). These reactions were carried out both in the presence and in the absence of Lewis base additives. In a typical reaction, 0.04 mmol of (porphyrin)AlX and 0.02 mmol of DMAP or PPN^+X^- ($X = Cl^-$, N_3^-

wherever used as additives) was dissolved in a combination of 0.42 mL (6.00 mmol) of PO and 0.6 mL of a deuterated chloroform solvent in a vial. The above solution was sealed with Teflon caps and left under a dry N_2 atmosphere at room temperature for 48 h. The later studies were done in 24.0 mmol of neat PO and at shorter reaction times (5 h, 3 h) to obtain relative TOFs. An aliquot was taken from each reaction mixture for ^{1}HNMR analysis. The polymerization process was quenched by the addition of 1N HCl/MeOH. The unreacted PO and solvents were then removed in vacuo. The isolated polymer was further analyzed by ^{13}CNMR and mass spectroscopy.

The Determination of the Order of the Reaction. Stock solutions containing TPPAlOEt and PPN^+Cl^- in a 1:1 ratio were prepared in $CDCl_3$ for the reaction. In a typical reaction, 0.4 mL of *rac*-PO (5.72 mmol) was added to a certain amount of stock solution to make a total volume of 1 mL, and the resulting initiator concentration was 20 mM. A total of four sets of reactions were run with initiator concentrations: 5 mM, 10 mM, 15 mM, and 20 mM. The reactions were monitored at 25 °C by ^{1}H NMR, measuring the disappearance of initiator OCH_2CH_3 signals in the chemical shift region upfield of TMS.

Carbon Dioxide Insertion Experiments with (Porphyrin)-aluminum Ethoxide Catalysts. Twenty millimolar stock solutions of catalysts and DMAP were prepared for these reactions. The 0.2 mL catalyst solutions or a 1:1 mixture of catalyst and DMAP solutions were transferred to a high pressure Wilmad NMR tube. Five atmospheres of $^{13}CO_2$ pressure were then introduced into the NMR tube using standard gas transfer techniques. The formation of an ethoxycarbonate moiety at room temperature was monitored by ^{1}H, ^{13}C {^{1}H} and COSY NMR spectroscopy.

Copolymerization Reactions of PO/CO_2. These reactions were carried out both in the presence and in the absence of Lewis base additives. In a typical reaction, 0.04 mmol of (porphyrin)AlX and 0.02 mmol of DMAP or PPN^+X^- (wherever used as additives) were dissolved in a combination of 0.42 mL (6.00 mmol) of PO and 0.6 mL of deuterated chloroform solvent in a vial. The above solution was reacted under 50 bar of CO_2 pressure in a stainless steel reaction vessel (Parr) at room temperature for 48 h. The later studies were done in 24.0 mmol of neat PO and at shorter reaction times (5 h, 3 h) to obtain TOFs. After releasing the CO_2 pressure, an aliquot was taken from each reaction mixture for ^{1}HNMR analysis. After removing excess PO, the product obtained was dissolved in a minimum amount of dichloromethane. For copolymerizations using PPN^+X^- salts as Lewis bases, the polymers were precipitated by the addition of 1N HCl/methanol to the dichloromethane solution. Faintly colored polymers were then filtered and dried in vacuo. In the case of copolymerizations using DMAP as Lewis bases, excess DMAP was removed by extraction with 1N HCl/H_2O. The resulting polymers were isolated by drying the organic phase under vacuum conditions. The polymer samples for GPC and ^{13}CNMR analysis were further purified by precipitation from a concentrated dichloromethane solution with excess methanol.

■ RESULTS AND DISCUSSION

Lewis Base Bindings to Porphyrin AlX Compounds. The affinity of the five coordinate Al(III) center toward Lewis bases that are commonly employed in the polymerizations involving PO are greatly influenced by both the nature of the porphyrin and the *trans* ligand X. In order to quantify these effects, we have studied the binding of DMAP to TPPAlX, where X = $O(CH_2)_9CH_3$, $O_2CO(CH_2)_9CH_3$, and $O_2C(CH_2)_6CH_3$, using NMR spectroscopy.[60] At 25 °C, the binding of DMAP was found to vary inversely with the trans influence of the X group such that for the reaction shown in eq 2, the K_{eq} (mM^{-1}) values followed the order 5.8×10^{-3}(OR), 0.51(O_2COR), and 1.7(O_2CR). This shows that the alkylcarbonate is more similar to the carboxylate than the alkoxide.

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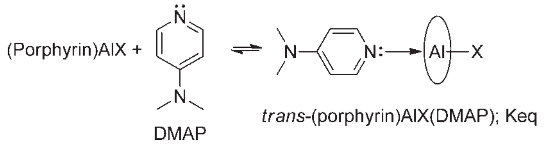

We have also examined the binding of the azide ion to the three porphyrin aluminum complexes, where X = Cl and OEt, which allows a measure of the Lewis acidity of the Al(III) center, as determined by an IR study of reaction 3.

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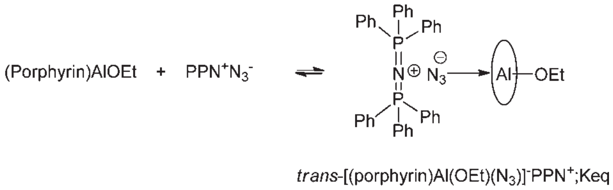


At room temperature in dichloromethane solution, we observed the presence of free and bound azide ions with the former at 2005 cm^{-1},[41,53] see Figure S1 in the Supporting Information. On the basis of this study, we estimate $K_{eq} = 1.6 \times 10^2$ M^{-1} for TFPP, 9.3 M^{-1} for TPP, and 6.6 M^{-1} for OEP on the basis of the integral areas of the IR bands for $\nu(N_3)$. This again reflects the nature of the porphyrin and reveals that the Al(III) center is more Lewis acidic with the fluorinated porphyrin.

The binding of the azide ligand to the (porphyrin)AlCl complexes is different in two respects. The addition of <1 equiv of $PPN^+N_3^-$ always shows the IR band of the bound azide ligand, indicating the fact that the AlCl center is more electrophilic than the AlOEt center. Upon the addition of >1 equiv of $PPN^+N_3^-$, no free azide IR band was observed until >2 equiv of $PPN^+N_3^-$ was added, see Figure S2 in the Supporting Information. This indicates that the azide ligand displaces the chloride to form the anion: *trans*-porphyrinAl$(N_3)_2^-$. This is a similar finding to that of Darensbourg and Fitch in their studies of the binding of azide to (tmtaa)CrCl, where tmtaa is tetramethyltetraazaannulene.[41,42] There is no evidence that N_3^- can displace alkoxide ligands in this manner, nor can N_3^- displace the carboxylic ligand in (porphyrin)$AlO_2C(CH_2)_6CH_3$ in $CHCl_3$ solutions.

Homopolymerization of PO by (Porphyrin)AlX Compounds. *a. Without Additives.* In order to investigate the specific influence of these porphyrin ligands on the ring-opening polymerization of PO, we have examined their reactivity with and without Lewis base additives. In the absence of the additives, the reactions are very slow but follow the order OEP > TPP > TFPP with TOFs (h^{-1}) of 21 > 9 > 3, respectively. However, despite the comparable reactivity of the TFPP and TPP in TOFs, the nature of the polymer is very different. Both OEP and TPP give regio regular PPOs with enhanced isotactic junctions[67,68] due to end-group control in the ring-opening event. The PPO produced by the TFPPAl complexes is regio irregular, see Figure 2. In addition, the ESI-mass spectra revealed that the TFPP ligated complex gives low molecular weight oligomers with an abundance of cycles. The PPOs derived from the TPP and OEP complexes were found to be linear chains with Cl or OEt end groups. A minor series with OH end groups was always present and arises from chain-transfer due to adventitious water.

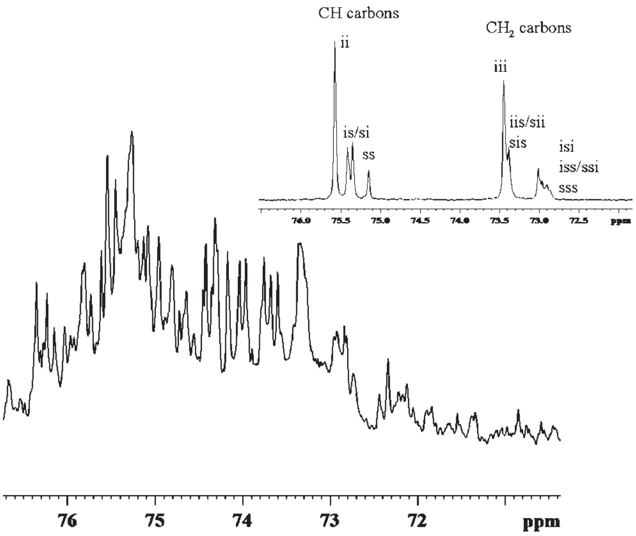
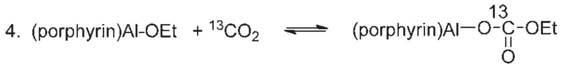


Figure 2. $^{13}C\{^1H\}$ (125.73 MHz, $CDCl_3$) NMR spectrum of regio irregular PPO produced by the TFPPAlX complexes (X = Cl, OEt). Inset shows $^{13}C\{^1H\}$ (125.73 MHz, $CDCl_3$) NMR spectrum of regio regular PPO produced by OEPAlCl catalyst.

The formation of cycles and low molecular weight PPO is characteristic of an acid catalyzed reaction,[10,69,70] and we were for some time suspicious that a trace of acid such as HCl derived from hydrolysis of an Al−Cl bond might have been responsible for the ring-opening of the PO. In order to check for this, we carried out reactions involving a mixture of TFPPAlOEt and TFPPAlMe where the alkoxide derivative was obtained by partial alcoholysis of the methyl complex. The resultant PPO had the same characteristics of a mixture of cycles and chains as determined by MALDI and ESI mass spectrometry and by NMR spectroscopy was regio irregular.

b. With Lewis Base Additives. The influence of added DMAP or PPN^+Cl^- (0.5 and 1.0 equiv) was quite dramatic in yielding higher TOFs, and the order of reactivity of the porphyrin was significantly changed, TPP > TFPP ≫ OEP, with the latter being effectively unreactive. The TFPPAlX generated polymer was now regio regular, as shown in Figure S3, Supporting Information. The TOFs (h^{-1}) for the reactions in the presence of 0.5 equiv of PPN^+Cl^- were 27 and 25 for TPP and TFPP, respectively. The addition of >1 equiv of PPN^+Cl^- was noted to retard the reaction. Previously, we showed[60] DMAP > 2 equiv suppressed the formation of PPO in similar reactions involving TPP complexes of Al(III). Mass spectrometry showed that the PPO had end groups of Cl or OEt depending on the initiator: Al−Cl or Al−OEt, see Figure S4, Supporting Information. TOFs for the series of homopolymerization reactions carried out at room temperature are given in Table 1.

Insertion of Carbon Dioxide into Metal−Ethoxide Bonds. We have followed the reversible insertion of $^{13}CO_2$ into the AlOEt bond of the three porphyrin complexes using $^{13}C\{^1H\}$ NMR and ^1H NMR spectroscopy in $CDCl_3$, eq 4:



$$4.\ (\text{porphyrin})\text{Al-OEt} + {}^{13}CO_2 \rightleftharpoons (\text{porphyrin})\text{Al}{-}\text{O}{-}\underset{\|\atop \text{O}}{\overset{13}{\text{C}}}{-}\text{OEt}$$

In our typical experiments, these reactions were carried out at 5 atm of $^{13}CO_2$ with Willmad high pressure tubes. The reactions are easy to follow using ^1H NMR as the magnetic influence of the porphyrin ring shifts the ethoxy proton signals to high field above δ = 0, see Figure 3. In the $^{13}C\{^1H\}$ NMR spectrum, the free $^{13}CO_2$ and the $O_2{}^{13}COEt$ signals are also readily detected employing 99% $^{13}CO_2$.

Table 1. Turnover Frequencies (TOFs) for the Homopolymerization of Propylene Oxide (PO)[a]

entry	catalysts	additives (0.5 equiv)	TOF (h^{-1})[b]
1	TPPAlCl		9
2	TPPAlCl	DMAP	24
3	TPPAlCl	PPN^+Cl^-	27
4	TFPPAlCl		3
5	TFPPAlCl	DMAP	24
6	TFPPAlCl	PPN^+Cl^-	25
7	OEPAlCl		21
8	OEPAlCl	DMAP	
9	OEPAlCl	PPN^+Cl^-	

[a] Homopolymerization reactions carried out with [catalyst]/[PO] = 1:600, at room temperature for 6 h. [b] TOFs calculated as (mols of PO consumed)(mols of catalyst)$^{-1}$(h)$^{-1}$, from ^1H NMR spectroscopy of reaction aliquots. Entries 8 and 9: TOFs not calculated due to poor reaction yield.

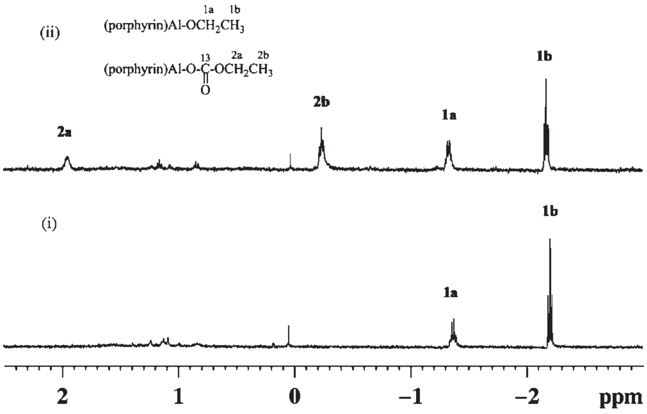


Figure 3. ^1H NMR (400 MHz, $CDCl_3$) spectra of $^{13}CO_2$ insertion studies with the TPPAlOEt catalyst (i) before $^{13}CO_2$ insertion and (ii) after $^{13}CO_2$ insertion. The signal at 0.03 ppm is due to grease, and the signals between 0.8 and 1.2 ppm arise from hexane impurities in the NMR solvent.

The position of the equilibrium in eq 4 that favored the insertion product followed the order OEP (71%) > TPP (69%) > TFPP (52%). This effectively reflects the electron donating power of the respective porphyrins and the resultant polarity of the Al−OR bond.

Upon the addition of 1 equiv of DMAP, this order was reversed such that TFPP (93%) > TPP (89%) > OEP (81%). Clearly, the addition of the Lewis base promotes the insertion of CO_2, and the positions of equilibria for the various porphyrins parallel the Lewis binding affinities (K_{eq}) seen in eq 2.

Copolymerization of PO and CO_2. In the absence of any Lewis base additive, the (porphyrin)AlX compounds are relatively poor catalysts for either the homopolymerization of PO or its copolymerization with CO_2. In our studies of the copolymerization, we have employed reactions at 50 bar CO_2 with PO in $CDCl_3$ over a period of various times. In order to make some easy comparisons of reactivity, product analysis and percent conversions were taken at 48 h in the absence of additives. The results of these studies are shown in Table 2, where it is seen that the percent consumption of PO follows the order TPP > OEP > TFPP. These reactions were carried out in $CDCl_3$ to ensure that the aluminum complexes were completely dissolved and also so that an immediate estimation of the relative amounts of the three products, PPC, PPO, and PC, could be determined using ^1H NMR spectroscopy. It should be noted here that in the absence of Lewis base additives an alternating copolymer of CO_2 and PO is not formed but rather an ether-rich polymer having carbonate junctions. This is readily seen from the $^{13}C\{^1H\}$ signals of the carbonate groups, as shown in Figure 4. Thus, from ^1H NMR, the relative percentage of PPC to PPO is not accurate but can be taken as a crude measure of carbonate incorporation into the polymer. So, in the absence of additives, we see that CO_2 incorporation is favored for TFPP > TPP > OEP even though the consumption of PO is in the order TPP > OEP > TFPP.

Upon the addition of DMAP or PPN^+Cl^-, the consumption of PO is greatly increased, and the incorporation of CO_2 is enhanced in all cases.[34,36,53,60] The reactivity order is PPN^+Cl^- > DMAP and TFPP > TPP > OEP. The reaction now involving TFPP yields an essentially alternating copolymer of PO and CO_2 with only detectible traces of PC and ether rich linkages. The MALDI-TOF mass spectrum in Figure 5 shows an extensive series of sodiated ions $H-(PO)_n(CO_2)_n-Cl$ and a minor series $H-(PO)_n(CO_2)_{n-1}-Cl$. The OEP complex is notably less reactive and also produces a sizable amount of PC.

Table 2. Results Obtained from the Copolymerization Reactions of PO and CO_2[a]

entry	catalyst	additive (0.5 equiv)	% conversion[b]	% PPC[b]	% HT[c]
1	TPPAlCl		61.5	22.1[d]	
2	TPPAlCl	DMAP	87.6	67.9	66.9
3	TPPAlCl	PPN^+Cl^-	98.4	74.9	50.8
4	TFPPAlCl		14.1	6.48[d]	
5	TFPPAlCl	DMAP	99.4	97.9	64.1
6	TFPPAlCl	PPN^+Cl^-	100.0	97.4	66.2
7	OEPAlCl		27.5	4.2[d]	
8	OEPAlCl	DMAP	46.8	25.1	65.8
9	OEPAlCl	PPN^+Cl^-	87.6	30.7	62.5

[a] Entries 1−9 at 50 bar of CO_2, [catalyst]/[PO] = 1:150, at room temperature for 48 h using 0.6 mL of $CDCl_3$ as a solvent. [b] Calculated from ^1H NMR analysis of reaction aliquots. [c] Calculated from ^{13}C NMR spectroscopy of polymer. [d] Ether-rich polymers.

We have also followed these reactions involving PO and CO_2 (50 bar) in neat PO at shorter reaction times, at room temperature, and to partial completion where the PPC is still soluble in the PO, and PPC degradation (discussed later) has not occurred significantly. The reactions are thus not considered to be limited by viscosity or diffusion, which can arise when the PPC solidifies. In this way, we have obtained an estimate of the TOFs for the various porphyrins which follow the order TFPP (120 h^{-1}) > TPP (73 h^{-1}) > OEP (~20 h^{-1}). We also investigated the influence of PPN^+Cl^- concentration and noted that the TOFs were depressed with >1 equiv, and furthermore PC became the major product.

In Figure 6, we show a comparison of the carbonate ^{13}C signals of the products produced in the reactions involving the three porphyrin aluminum complexes and *rac*-PO and CO_2 under the same conditions. The striking feature of the TFPP catalyst system is the lack of PC and the very small amount of ether-rich units where the latter are denoted by HT′. The assignments of HH, HT, TT, and HT′ are based on earlier work.[60,71] The relative concentrations of the HH/TT/HT are, within experimental error, the same for all catalyst systems, indicating a preference for regioregular HT ring-opening of PO being 3:1. In the case of OEP, the amount of ether-rich HT′ is comparable to that for TFPP and less than TPP, but notably the presence of PC is much more significant. When the $[PPN^+Cl^-]/[Al]$ ratio is

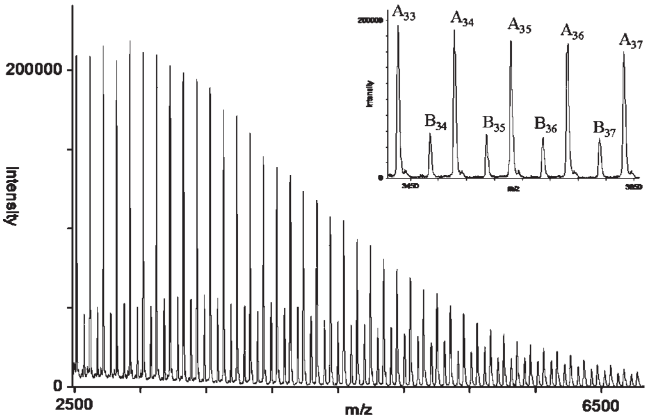
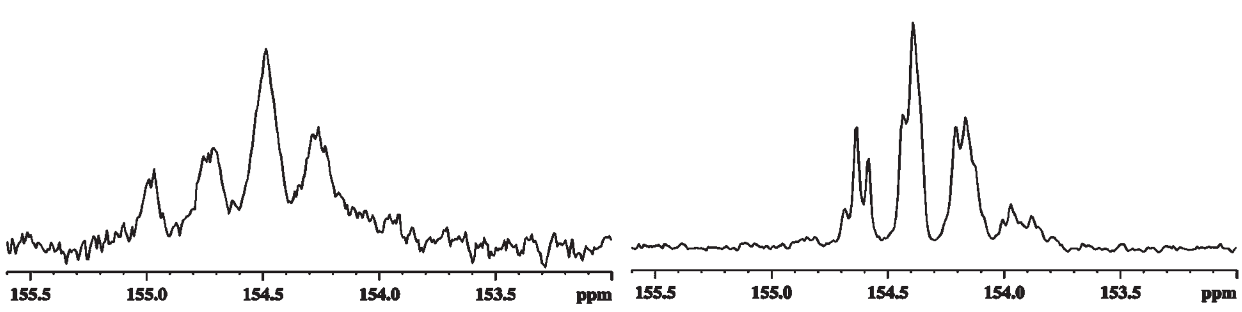


Figure 5. MALDI-TOF mass spectrum of the alternating PPC polymer obtained by the combination of TFPPAlCl as the catalyst and DMAP as the additive. The major series $A_n = H-[(C_3H_6O)_n-alt-(CO_2)_n]-Cl\cdot Na^+$; the minor series $B_n = H-[(C_3H_6O)_n-alt-(CO_2)_{n-1}]-Cl\cdot Na^+$. Inset shows peaks for n = 33−37.


a) TFPPAlCl + *rac*-PO/CO_2

b) TPPAlCl + *rac*-PO/CO_2

Figure 4. $^{13}C\{^1H\}$ (100.61 MHz, $CDCl_3$) NMR spectra of ether-rich PPC formed in the absence of Lewis base additives (a) by (TFPP)AlCl and (b) by (TPP)AlCl complexes.

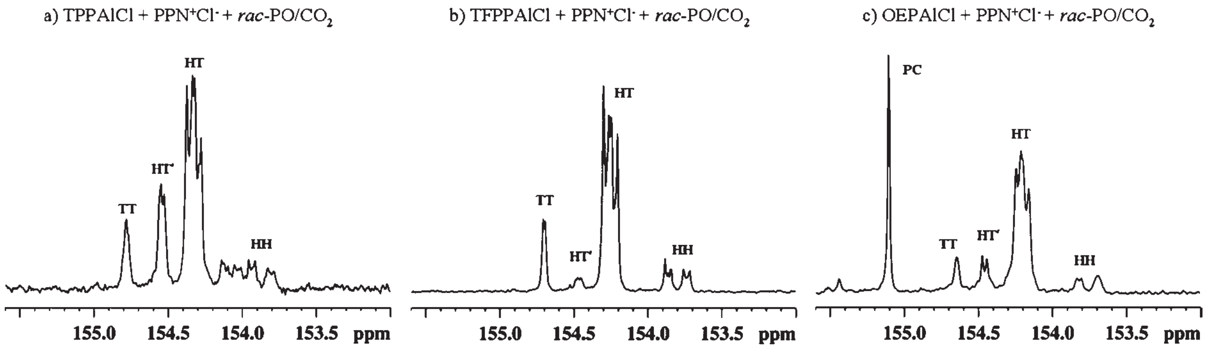


Figure 6. Comparison of the carbonate region of $^{13}C\{^1H\}$ (125.73 MHz, $CDCl_3$) NMR spectra of the products produced in the copolymerizations of *rac*-PO and CO_2 under the same conditions using three porphyrin aluminum complexes and PPN^+Cl^- as an additive.

Table 3. GPC Analysis of Copolymerization Reactions Carried out under Rigorously Dry Conditions[a]

entry	catalyst	additive (0.5 equiv)	M_n[b] (Da)	M_w[b] (Da)	PDI[b] (M_w/M_n)
1	TPPAlCl	DMAP	9600	16100	1.68
2	TPPAlCl	PPN^+Cl^-	11500	14800	1.29
3	TPPAlOEt	DMAP	9200	12500	1.36
4	TPPAlOEt	PPN^+Cl^-	12000	16600	1.39
5	TFPPAlOEt	DMAP	19100	23600	1.23
6	TFPPAlOEt	PPN^+Cl^-	29700	37100	1.24

[a] Entries 1−6 at 50 bar CO_2, [catalyst]/[PO] = 1:600, at room temperature for 6 h. [b] Obtained from GPC studies using polystyrene standard.

increased beyond 1:1, then the formation of PC becomes more competitive with PPC production. It also should be noted that PC will be the dominant product in all reactions left for long periods of time due to backbiting of the polymer chain by the active Al−O bond. More of this is stated later.

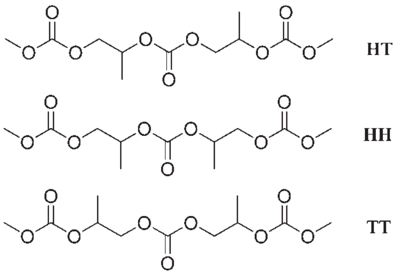
Gel Permeation Chromatography (GPC) of Polymers. We have also examined the refractive index monitored GPC of the polymers produced in the copolymerization reaction. The polypropylene carbonates produced under rigorously dry conditions showed unimodal GPC chromatograms with relatively narrow polydispersity (Table 3), indicating a well controlled polymerization process.

However, when the commercially available PO monomer was used without distillation, the resulting polypropylene carbonates clearly showed bimodal distributions in the GPC analysis, where each peak corresponded to a narrow PDI value. Moreover, the integral area of the higher molecular weight peak observed in each case was approximately twice as large as that of the lower molecular weight peak. We also noticed that upon running the copolymerization reactions for longer time, e.g., a period of two days, the relative intensity of the bimodal GPC traces was reversed: only a small amount of the high molecular weight polymer was now produced (Table 4). Most significant is the fact that the observed M_n and M_w values for the high molecular weight polycarbonate were above the calculated molecular weight values (considering one polymer chain growing per metal center). Other researchers have reported bimodal GPC profiles which were attributed to ongoing chain transfer in the copolymerization process by adventitious water contamination.[30,72,73] However, our interpretation of the bimodal distribution is that hydrolysis kills some of the active catalyst and yields a less active species. The more active species thus yields the high molecular weight fraction and the less active species the lower. According to mass spectrometry, the lower molecular weight fraction has hydroxyl end groups and not Cl.

The starting material TPPAlMe was allowed to react with wet (undried) ethereal solvent. This is expected to hydrolyze the Al−Me bond, presumably producing Al−OH bonds or oxo bridged aggregated species. The partially hydrolyzed material indeed showed poor catalytic activity, producing only low molecular weight polymers both in the copolymerization and the PO homopolymerization processes. The low molecular weight PPO thus obtained had, according to mass spectrometry, hydroxyl end groups.

CO_2 Pressure Effects. We also have examined the influence of CO_2 pressure on the product distribution in these systems. Most significant is the fact that the TFPP catalyst system produces almost exclusively PPC even at 10 bar CO_2 pressure in comparison to the TPP system, which produces an ether-rich carbonate product, see Figure 7. The MALDI-TOF spectrum of the ether-rich carbonate polymer produced by the TPPAlCl catalyst and DMAP at 10 bar was extremely complex in comparison to the copolymer derived from TFPPAlCl and DMAP. However, with TPPAlOEt as the initiator, we were able to identify distinct series of sodiated ions corresponding to $H(PO)_n$−*alt*−$(CO_2)_{n-x}$−OEt·Na^+ where $x = 0-6$, see Figure S5, Supporting Information. In contrast, the MALDI-TOF MS for the polymer produced at 10 bar CO_2 with TFPPAlOEt showed the major series corresponding to H−$(PO)_n$−*alt*−$(CO_2)_n$−OEt·Na^+ with a minor series having a $(CO_2)_{n-1}$ sequence, see Figure S6, Supporting Information.

Polymer Microstructure of Polypropylene Carbonate. We also analyzed the microstucture of the polypropylene carbonate obtained by TFPPAlCl catalysts with a PPN^+Cl^- cocatalyst. The carbonate junctions in PPC can have the following regiosequences:



On the basis of the previously discussed mechanisms[60,67] established for (TPP) aluminum catalysts, we can reasonably assume that regioregular HT junctions are formed by preferential

Table 4. GPC Analysis of Copolymerization Reactions Carried out with under Regular Conditions[a]

entry	catalyst	additive (0.5 equiv)	M_n[b] (Da)	M_w[b] (Da)	PDI[b] (M_w/M_n)	M_c[c] for 100% conversion
1	TPPAlCl	DMAP	2140[br]	2290	1.07	15400
2	TPPAlCl	PPN^+Cl^-	29300	30500	1.04	15400
			10500	11200	1.07	
3	TFPPAlCl	DMAP	33500	35000	1.05	15400
			11200	11700	1.05	
4	TFPPAlCl	PPN^+Cl^-	41400	43000	1.04	15400
			16100	16800	1.05	

[a] Entries 1−4 at 50 bar CO_2, using 0.6 mL $CDCl_3$ as a solvent, and a [catalyst]/[PO] ratio of 1:150 at room temperature. Reaction time was 48 h. [b] From GPC studies using polystyrene standard; [br] broad shoulder observed at high molecular weight region. [c] Theoretical maxima of molecular weight calculated for 100% conversion, considering one polymer chain growth per metal.

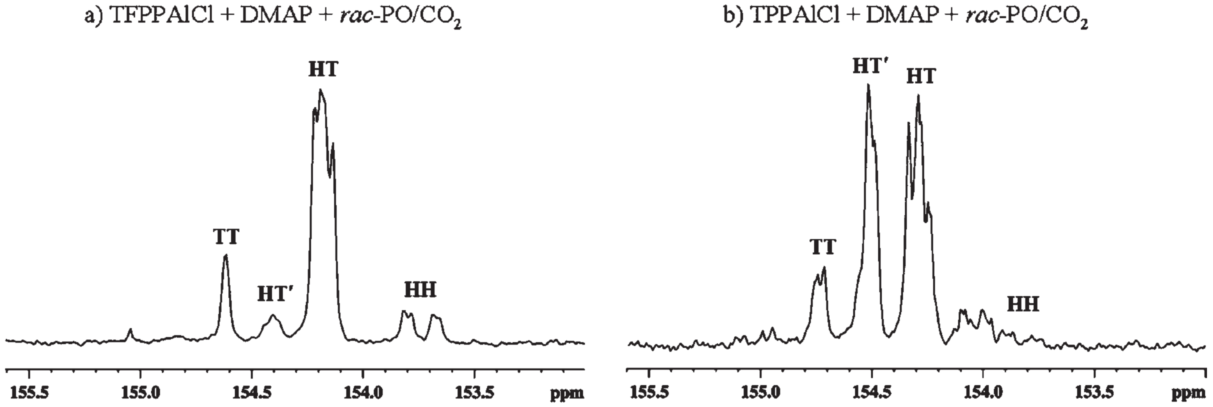


Figure 7. $^{13}C\{^1H\}$ (125.73 MHz, $CDCl_3$)NMR spectra of PPC formed by the (porphyrin)AlCl catalysts and DMAP at 10 bar CO_2 pressure: (a) TFPPAlCl + DMAP; (b) TPPAlCl + DMAP.

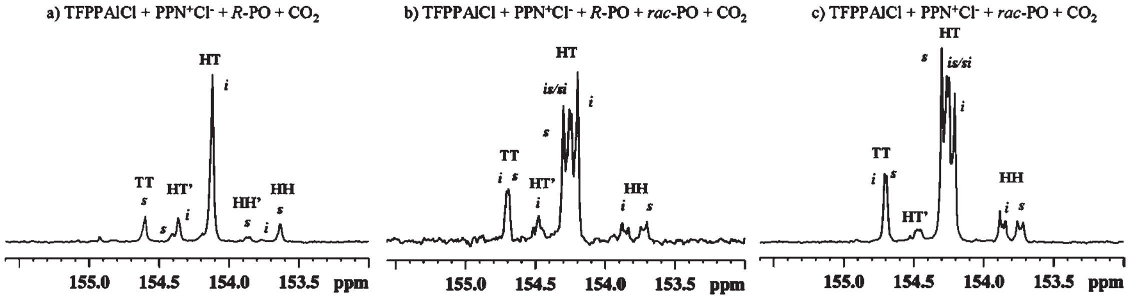
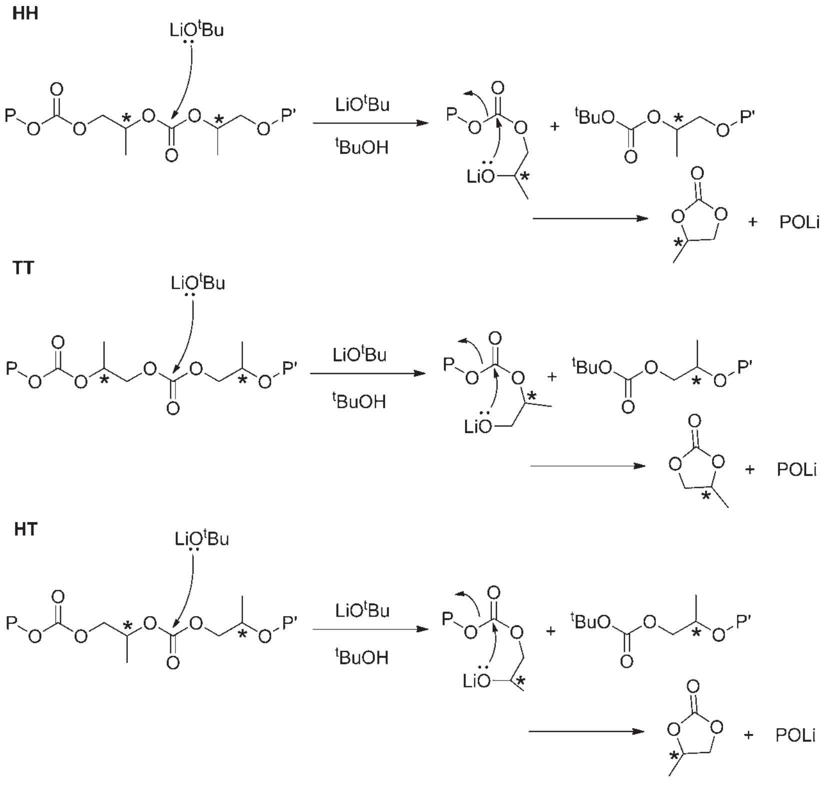


Figure 8. The carbonate region of $^{13}C\{^1H\}$ (125.73 MHz, $CDCl_3$) NMR spectra of the products produced in the copolymerizations of (a) *R*-PO, (b) a 50:50 mixture of *rac*-PO and R-PO, and (c) *rac*-PO, with CO_2 under identical reaction conditions using the TFPPAlCl complex as a catalyst and PPN^+Cl^- as an additive.

ring-opening of PO at the methylene carbon, which retains the stereochemistry at the methine carbon. In contrast, the HH or TT junctions are formed by ring-opening of PO at the methine carbon, resulting in a possible inversion of stereochemistry. It should be noted that the formation of a HT junction generates an isotactic diad, whereas formation of either HH or TT may yield either an isotactic or syndiotactic junction.

We have now compared the regio and stereo sequences observed in the carbonate region of ^{13}C $\{^1H\}$ NMR signals of PPC produced by *rac*-PO, *R*-PO, and a 50:50 mixture of *rac*-PO and *R*-PO (Figure 8). With *R*-PO, the HT carbonate ^{13}C signal of this polymer is expected to be isotactic (*i*). However, the assignment of iso or syndiotactic (*s*) stereocenters to the ^{13}C NMR signals observed in the HH and TT carbonate regions previously involved the investigation of model carbonate compounds.[60] To further clarify this assignment, we did the following experiments. The polymer was degraded into PC by reaction with LiO^{t}Bu in THF in the presence of ^{t}BuOH.[71] The mechanism of the reaction involves an attack of the $^tBuO^-$ ion on the carbonate carbon, resulting in chain fragmentation. The alkoxide anion thus formed attacks an adjacent carbonate carbon, producing the cyclic propylene carbonate product. This "backbiting" reaction degrades the polymer chain, leaving the stereocenters on the methine carbon intact, see Scheme 2. The ratio of (*R*) PC to (*S*) PC was 88:12 according to chiral gas chromatoghaphic (GC) analysis. The calculated ratio of (*R*) to

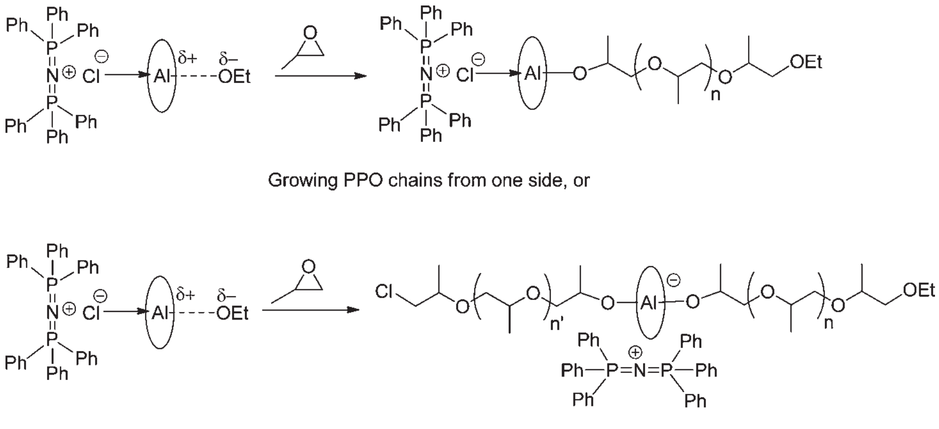
Scheme 2. Degradation of Polypropylene Carbonate into Propylene Carbonate while Conserving the Sterocenters



P and P' indicate growing polymer chains

* indicates stereocenters

Scheme 3. Possible Pathways for Growing One or Two Polymer Chains Per Metal Center, Schematically Shown for PPO



Growing PPO chains from one side, or

Growing PPO chains from both sides

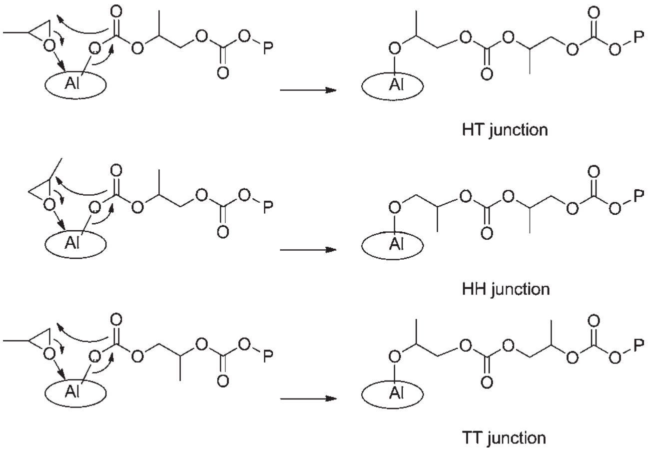
(*S*) stereocenters in the polymer is 89:11 (based on the relative intensity of ^{13}C NMR signals), which provides unequivocal evidence in favor of the current assignment of the HH and TT junctions. Similar observations were obtained with the PPC prepared from a 50:50 mixture of *rac*-PO and *R*-PO. In this case, the ratio of (*R*) PC to (*S*) PC obtained by polymer degradation was 65:35, and the calculated ratio of (*R*) PC to (*S*) PC was 63:37, again supporting the current assignment of *i* and *s* tacticity. We note here that our assignments for the HH and TT junctions differ from those of Coates et al. with respect to *i* and *s* junctions, though we agree with the assignments of HT junctions.[30]

One or Two Growing Chains per Al Center? A question that has often arisen in the literature[30,34,51,72,73] where the metal catalyst employs an ionic cocatalyst, as in PPN$^+$Cl$^-$, is whether there are two growing chains or just one, as shown in Scheme 3. Indeed it has even been questioned whether or not DMAP may be involved as an initiator. This would presumably lead to cyclic

PPC, but this has not been established. In this work, we have examined the polymers produced in the homopolymerization of PO by TPPAlOEt and PPN^+Cl^-. By ESI MS, only polymers with OEt or OH end groups were observed. No evidence of Cl end groups was found, in contrast to PPO grown by a TPPAlCl initiator. We also examined the reactivity of the dinuclear complex $(TPP)AlO(CH_2)_8OAl(TPP)$, formed by the reaction between the diol $HO(CH_2)_8OH$ and TPPAlMe (2 equiv), with PO in the presence of DMAP or PPN^+Cl^-. In both cases, the polymers produced were of the form: $H(PO)_nO(CH_2)_8O(PO)_mH$ or $H(PO)_nO(CH_2)_8OH$ and $H(PO)_nOH$ as judged by ESI MS. The series arising with −OH end groups presumably arises by chain transfer due to adventitious water. Again, no evidence for Cl end groups was found by mass spectrometry, which is in direct contrast to the PPO grown from the TPPAlCl initiator.

Similarly in the reaction between TPPAlOEt, CO_2, and PO in the presence of $PPN^+N_3^-$ as a cocatalyst, the PPC that was formed showed no IR evidence of the characteristic IR active $\nu(N_3^-)$ stretch, which occurs in the region of 2000−2150 cm^{-1}.[74] Furthermore, in reactions involving TPPAlOEt, PPN^+Cl^-, CO_2, and PO, the PPC that was formed had no detectable Cl concentration, as determined by elemental analysis. We note here that Darensbourg and Fitch[72] came to a similar conclusion in a chromium(III) catalyzed copolymerization of PO and CO_2 employing a "strapped" Schiff base ligand that allowed the growth of only one chain per metal.

Scheme 4. Regioconsequences of PO Ring-Opening in the Formation of HT, HH, and TT Junctions



COMPARISON OF THE INFLUENCE OF THE METAL IN TPPMCL INITIATORS

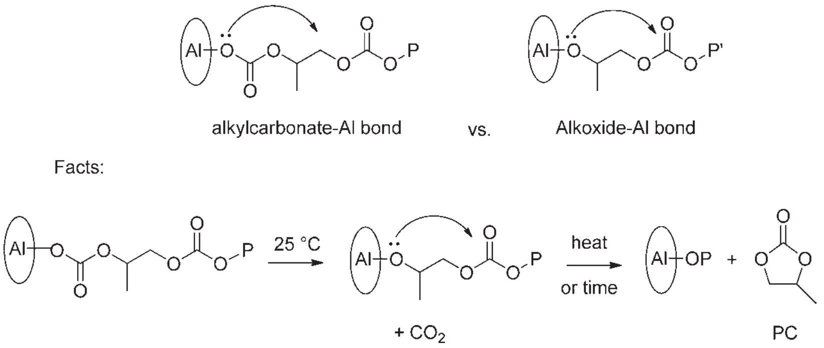
We previously examined by ICR-MS the binding of PO to the cations $TPPM^+$, which revealed the preference for the six-coordinate $TPPCr(PO)_2^+$ over the related ions where M = Al or Co.[75] Furthermore, while the $TPPAl^+$ ion had a high affinity for the binding of one PO, the related Co(III) center had the least affinity for PO complexation. We have now compared the relative activity of PO in reactions with the complexes TPPMCl. Under ambient conditions, the cobalt complex is inert with respect to the homopolymerization of PO, even in the presence of Lewis base additives such as PPN^+Cl^- or DMAP. In contrast, the chromium complex is highly active, and in the comparison with TPPAlCl in the presence of PPN^+Cl^- (0.5 equiv), the chromium catalyst system is 2 orders of magnitude more active. The more detailed studies of the copolymerzation of epoxides and CO_2 with these other metals is, however, the subject of ongoing studies, which will be reported subsequently.

CONCLUDING REMARKS

In this study of the activity of porphyrinaluminum catalysts systems, we have shown the remarkable influence of the porphyrin in the homopolymerization of PO, in the binding of Lewis bases, and in the position of the equilibrium involving the insertion of CO_2 into the Al−OR bond. Collectively, these equilibria lead to relative rates of the copolymerization of PO and CO_2 in the order TFPP > TPP > OEP and, for TFPP in the presence of PPN^+Cl^- (0.5 equiv), a rate enhancement of >2 orders of magnitude compared to that originally observed by Inoue employing TPPAlCl as an initiator. In all of these reactions, the order of the reaction is first order in metal, akin to that originally noted by Darensbourg[9] in his pioneering study of salen CrX catalysis. Thus, the PO and the alkylcarbonate are on the same face of the porphyrin Al center. The mechanism leading PO ring-opening has clearly some incipient carbonium ion character, but the C−O bond forming reaction has typical nucleophilic characteristics, as evidenced by the preponderance of HT junction. It is also evident that in the formation of HH junctions the majority of reactions proceed with inversion, as might be expected for nucleophilic attack. These reactions are depicted in Scheme 4.

In the presence of CO_2 pressure, the polycarbonate chains bound to the Al center do not undergo degradation to form propylene carbonate. However, if the CO_2 pressure is removed, the polycarbonate is readily converted to PC. This we take as evidence that the backbiting reaction to form PC proceeds via an

Scheme 5. The Mechanism of Backbiting to Form Cyclic Carbonates, Which Readily Occurs upon Removal of the CO_2 Atmosphere



alkoxide−Al bond (formed by loss of CO_2/CO_2 deinsertion) and not an alkylcarbonate−Al bond, see Scheme 5.

Finally, we note that the relative rates of ring-opening of PO by Al−X bonds follows the order X = $O_2CR > O_2COR >$ OR. This allows for the copolymerization of PO and organic anhydrides such as succinic anhydride with the formation of polyesters, e.g., polypropylene succinate.[76,77] These and other reactions involving the catalytic ring-opening of epoxides by (porphyrin)MX complexes are currently being explored.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Listings of FT-IR spectra of azide binding, NMR and MS data of polymers, and NMR spectra of catalyst precursors used. This material is available free of charge via the Internet at http://pubs.acs.org.

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