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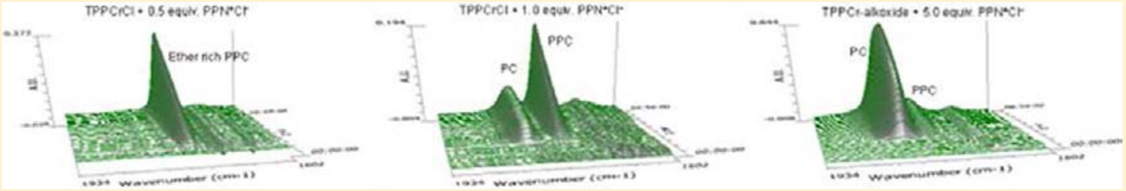
Influence of the Metal (Al, Cr, and Co) and the Substituents of the Porphyrin in Controlling the Reactions Involved in the Copolymerization of Propylene Oxide and Carbon Dioxide by Porphyrin Metal(III) Complexes. 2. Chromium Chemistry

Chandrani Chatterjee and Malcolm H. Chisholm*

Department of Chemistry and Biochemistry, The Ohio State University, Columbus, Ohio 43210, United States

Supporting Information



ABSTRACT: The reactivities of chromium(III) complexes LCrX, 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-octaethylporphyrin (OEP) and X = Cl or OH, 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) or propylene carbonate (PC), respectively, with and without the presence of a cocatalyst, namely, 4-dimethylaminopyridine (DMAP) or PPN^+Cl^- (bis(triphenylphosphine)iminium chloride). The homopolymerization is notably faster (TOF ≈ 2000 h^{-1} at room temperature) than copolymerization, which commonly leads to ether-rich polymers. Studies of kinetics reveal that for TPPCr(OH) with DMAP (1 equiv) the propagation reaction rate is first order in [Cr] with excess PO. With PPN^+Cl^- as a cocatalyst the reaction order in [Cr] and [Cl^-] is complicated by the presence of two growing chains, and the presence of excess [Cl^-] facilitates the formation of PC by two different backbiting mechanisms. The fixation of CO_2 is promoted by [Cl^-] but is not greatly influenced by CO_2 pressure (1−50 bar). The reactions and polymers have been monitored by UV−visible spectroscopy, react-IR, GPC, ESI, and MALDI TOF, and NMR (^{1}H, ^{13}C{^{1}H}) spectroscopy. Notable differences are seen in these reactions when compared with earlier studies by Darensbourg et al. with salen chromium(III) systems and related aluminum(III) porphyrins.

■ INTRODUCTION

The potential use of CO_2 in the production of polycarbonates, as shown in eq 1, in contrast to the use of diphenylcarbonate, phosgene, or its derivative,[1] is an attractive alternative based on atom efficiency, cost, and environmental considerations.

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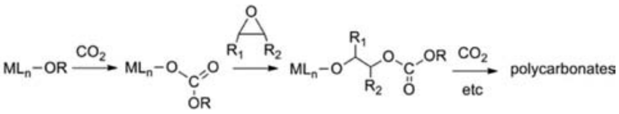

This reaction involves the consecutive insertion of CO_2 into a metal−alkoxide bond followed by the ring-opening or enchainment of the epoxide. There are now many reports in the literature of studies of this reaction involving metal-coordination complexes and cyclohexene oxide (CHO) and propylene oxide (PO).[2−9] As was nicely established by Darensbourg and co-workers, there are three competing reactions: polyether formation, C, polycarbonate formation, A, and cyclic carbonate formation, B.[10] These are shown in Scheme 1. Clearly for the formation of polycarbonates the metal−alkylcarbonate must ring-open the epoxide more rapidly than the metal−alkoxide bond, and thus the equilibrium reaction involving the M−OR bond and CO_2 is particularly important. Also it is known that the cyclic carbonate is thermodynamically favored with respect to the polycarbonate.[10] Thus polycarbonates must be formed under kinetic control, and this provides a challenge for the synthetic chemist who wishes to design an active catalyst system for polycarbonate formation based on eq 1.

Currently among the most active catalyst systems are the Schiff base complexes of chromium(III) and cobalt(III) where for PPC formation TOFs (h^{-1}) on the order of 10^2 and 10^3 have been reported at high temperature with 50 bar of CO_2 pressure.[11−18] Both mononuclear and dinuclear systems with independent or covalently bound cocatalysts have been employed. These divalent Schiff bases offer a multitude of substituents that can vary steric and electronic effects,[5,7,19] but a mechanistic understanding of what promotes high reactivity is often inferred on product formation with time rather than a knowledge of the specific individual reactions involved. It is

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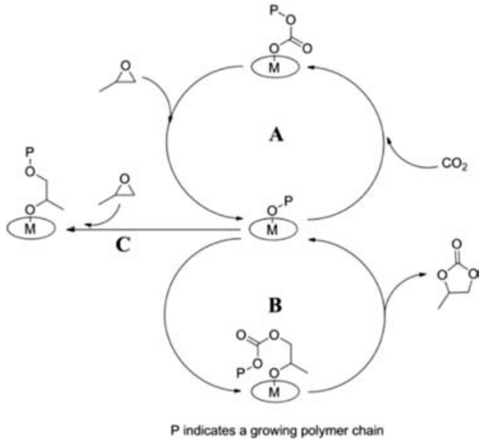
Scheme 1. Competing Reactions, A, B, and C, Involved in the PO/CO_2 Copolymerization Processes



P indicates a growing polymer chain

desirable to know how a given metal with a specific ligand set influences the individual reactions and equilibria shown in Scheme 1. In this series of papers we are comparing the metals aluminum, chromium, and cobalt in their +3 oxidation states with the porphyrin ligands 5,10,15,20-tetraphenylporphyrin (TPP), 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (TFPP), and 2,3,7,8,12,13,17,18-octaethylporphyrin (OEP).

The metals all have a similar ionic radius in the +3 oxidation states and allow a comparison of d^0, d^3, and d^6 effects. For cobalt the spin state is also a variable. The choice of porphyrin allows the substituents to influence electronic factors without having any significant steric influence at the metal centers. Also, in contrast to Schiff bases, which may accommodate both *cis*- and *trans*-pseudo-octahedral geometries,[19] the porphyrin restricts the other ligands to the *trans* geometry. The metal can move in and out of the plane of the porphyrin, and in contrast to the Schiff base, dissociation of a metal−ligand bond is unfeasible. In this paper we describe our studies of the reactivities of chromium porphyrin complexes and compare these with earlier studies of aluminum complexes,[20−25] which date back to the original work of Inoue,[26,27] and also with the related studies of Schiff base chromium complexes that were pioneered by Darensbourg.[5,19]

■ RESULTS AND DISCUSSION

Homopolymerization of PO. The reactions of the (porphyrin)CrCl complexes (porphyrin = TPP, TFPP, OEP) with neat PO have been studied and shown to have little activity toward homopolymerization with the formation of PPO. There is, however, a problem for the complex TFPPCrCl, which is essentially insoluble in neat PO. Furthermore, this compound yields regioirregular PPO akin to its aluminum analogue.[25] See Figure S1 in the Supporting Information. By ESI mass spectrometry only low molecular weight oligomers were observed. The complex TPPCrCl was more active than OEPCrCl and had a TOF ≈ 10 h^{-1} (see Table 1) yielding regioregular PPO.

The kinetics of the reaction between TPPCrCl and PO was studied in CH_2Cl_2 under pseudo-first-order conditions with an excess of PO. As shown in Figure 1 the rate increased with TPPCrCl concentration but not with a simple first order dependence. The order in [Cr] was determined to be ∼1.5 which implicates the involvement of a binuclear process. This has been previously seen for the reactions of salenCrCl in the initial ring-opening of PO by both Jacobsen and Darensbourg.[10,28,29]

Table 1. Homopolymerization of PO by (porphyrin)CrCl Catalysts with or without Added Cocatalysts (0.5 equiv)[a]

entry	catalysts	cocatalyst	TOF[b] (h^{-1})
1	TPPCrCl		10
2	TPPCrCl	DMAP	230
3	TPPCrCl	PPN^+Cl^-	2000
4	TPPCrCl(py)		126
5	OEPCrCl		5
6	OEPCrCl	DMAP	12
7	OEPCrCl	PPN^+Cl^-	21
8	OEPCrCl(py)		
9	TFPPCrCl(py)		4

[a] Reaction conditions: 0.85 mL of PO (12 mmol), catalyst 0.02 mmol, additives 0.01 mmol when used, reaction time 2.5 h, at 25 °C. [b] Calculated from ^1H NMR analysis of reaction aliquots, TOFs calculated as (mmol of PO consumed)/(mmol of catalyst × reaction time).

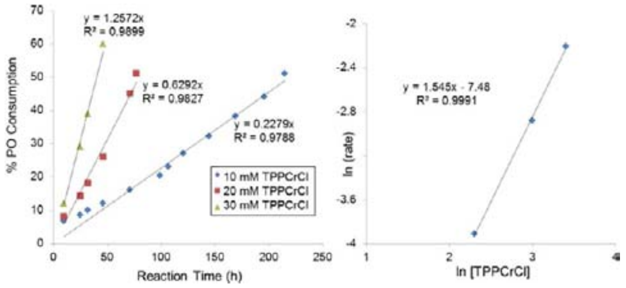


Figure 1. Kinetics of PO homopolymerization by TPPCrCl under pseudo-first-order conditions with an excess of PO (6.25 M).

The ring-opening of PO by the (porphyrin)CrCl catalysts is greatly enhanced with the addition of the cocatalysts 4-dimethylaminopyridine (DMAP) and bis(triphenylphosphine)-iminium chloride (PPN^+Cl^-). Now all catalyst systems yielded regioregular PPO, and for TPPCrCl the TOF was ∼2000 h^{-1}. See Table 1.

For the TFPP complex there is still some problem of solubility, which can be overcome only if a solvent such as THF is present or if the cocatalyst is present in excess in CH_2Cl_2. Chromium(III) complexes are well known to have a high preference for six-coordination, and it is likely that this is the case for all the complexes formulated as (porphyrin)CrCl. Indeed, we know of no such five-coordinate structure, but TPPCrCl(H_2O) is known and is likely present in this study. Alternatively a chloride-bridged polymeric structure is possible that could be responsible for the relative insolubility of TFPPCrCl. The porphyrin chromium complexes with one pyridine (py) ligand, namely, OEPCrCl(py), TPPCrCl(py), and TFPPCrCl(py), are all soluble in CH_2Cl_2.

In neat PO the relative rates of homopolymerization in the presence of PPN^+Cl^- (0.5 equiv) follow the order TPP > OEP > TFPP. By $^{13}C\{^1H\}$ NMR spectroscopy the PPO was seen to be regioregular with an enhancement of the *ii* triads[30,31] over the *ss* by a factor of ∼4:1. See Figure S2 in the Supporting Information. The reaction involving *R*-PO gave regioregular isotactic PPO, as evidenced by $^{13}C\{^1H\}$ NMR spectroscopy (Figure S2). This is similar to that found for the related aluminum complexes, although OEPAlCl in the presence of PPN^+Cl^- or DMAP did not yield any PPO.[25] The reactivity order is thus clearly seen to be Cr(III) > Al(III), and the relative reactivity of the TPPCr(III) system is quite remarkable when compared to the OEP and TFPP analogues. GPC analyses of the polymers were carried out monitoring the refractive index of the polymer samples. The polystyrene equivalent molecular weights are summarized in Table 2.

Table 2. GPC Analysis of PO Homopolymerization Reactions

catalyst	equiv PPN^+Cl^-	M_n[a] (kDa)	M_w[a] (kDa)	PDI[a]	M_{calc}[b] (kDa)
TPPCrCl	0.5	13.1	14.3	1.10	34.8
		5.1	5.8	1.10	
TPPCrCl	0.5	40	49	1.22	81.2
TPPCrCl[c]	0.5	22	36	1.60	34.8
TPPCrCl[c]	1.0	18	31	1.60	34.8
TPPCrCl (py)		21	29	1.41	22.0
TFPPCrCl (Py)		3.7	4.7	1.26	16.4
OEPCrCl	0.5	7.6	9.2	1.20	34.8

[a] GPC analysis of pure polymers after 100% PO consumption, using polystyrene standard. [b] Calculated maximum molecular weight for 1 polymer chain growing per metal center. [c] Used 0.5 mL of CH_2Cl_2 solvent during polymerization. The other polymers were prepared using neat PO.

Studies of the homopolymerization reaction involving both TPPCrCl and PPN^+Cl^- in CH_2Cl_2 were undertaken in order to determine the rate expression. From reactions involving [Cr] to [PPN^+Cl^-] ratios of 1.0:0.25, 1.0:0.5, and 1.0:1.0 we observed a rate acceleration with increasing [Cl^-], but with the ratio of [Cr] to [PPN^+Cl^-] equal to 1.0:2.0, the rate of consumption of PO was not significantly different from that seen for the ratio 1.0:1.0. See Figure S3 in the Supporting Information. By GPC we observed a broad molecular weight distribution, and by mass spectrometry the polymers were based on $H(PO)_n$-Cl and $H(PO)_n$-OH end groups. The latter may arise from the presence of H_2O initially present in the catalyst system.

Studies of the reaction between (TPP)Cr(OH) and PO in the presence of 1.0 equiv of DMAP showed that the rate of propagation was first order in [Cr]. See Figure 2.

We also studied the influence of DMAP concentration on the homopolymerization of PO. With the ratio of [(TPP)Cr(OH)] to [DMAP] of 1.0:0.25, 1.0:0.5, and 1.0:1.0 we observed an induction period that increased with DMAP concentration. However $k_{propagation}$ was greater for the 1.0:1.0 ratio. See Figure S4 in the Supporting Information. Although it is possible to explain this induction period as a result of DMAP suppressing the initial ring-opening of PO by a bimolecular reaction involving two Cr^{3+} centers, it is also possible that the DMAP deprotonates the Cr−OH bond in a reversible manner and that the $[(TPP)Cr{=}O]^-$ anion is not active in the ring-opening of PO. Some support of the latter hypothesis is seen in the observation that TPPCrOH and PO show very little activity in the presence of proton sponge (1,8-bis(dimethylamino)-naphthalene) and DMAP.

In the reaction involving TPPCrCl and PO, the presence of DMAP can both accelerate and retard the reaction. Indeed, greater than 2.0 equiv of DMAP effectively shuts down the reaction when the TPPCrCl and DMAP are initially dissolved in CH_2Cl_2 and the PO then added. We attribute this to the formation of $(TPP)Cr(DMAP)_2{}^+Cl^-$. If the reaction is initiated prior to the addition of DMAP, then homopolymerization proceeds. This is understandable because DMAP, like the azide ion, may displace the chloride ligand but not the alkoxide, which is the ligand of the growing chain bound to chromium. Plots of the consumption of PO with time and varying ratios of [TPPCrCl]:[DMAP] are shown in Figure S5 in the Supporting Information.

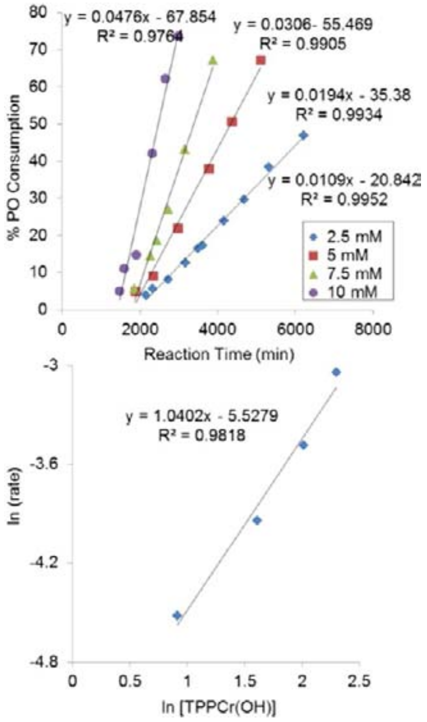


Figure 2. Kinetics of PO homopolymerization by TPPCr(OH) and 1.0 equiv of DMAP in the presence of an excess of PO (7.1 M).

We also examined briefly the *meso*-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin CrCl system, which as a result of the introduction of the two *meta* ${}^tBu$ groups suppresses both a binuclear mechanism[10,28,29] involving two Cr(III) units and access to the Cr(III) center. This was found to be notably slower in the homopolymerization of PO with and without a cocatalyst and was even less active than the OEP derivative.

We have found evidence of the ability of chromium to support two growing polymer chains.

(1) The strongest evidence comes from the reaction involving TPPCr(OH) and PO, which gives a monodispersed polymer with hydroxyl end groups as seen in the MALDI-TOF spectrum. Upon addition of PPN^+Cl^- (1.0 equiv) to this living system, a bimodal mass distribution was seen in the GPC and the presence of both series of ions with OH and Cl end groups in the mass spectrum. See Figure 3.

(2) A comparison of the molecular weights of the polymers formed in the reactions involving TPPCrCl and PO (270 equiv) in the presence of PPN^+Cl^-, 0.5 equiv vs 1.0 equiv, indicated a proportionate decrease with the higher [Cl^-] concentration, M_n 10 070 vs 6990 Da as determined by GPC, where the theoretical maximum value of molecular weight was ∼15 500 Da for just one growing chain.

(3) The ESI mass spectra of PPO formed from the reaction between TPPCrCl and PO in the presence of a cocatalyst, i.e., ${}^nBu_4N^+Br^-$ or $PPN^+N_3{}^-$, showed end groups of both Cl^- and Br^- or Cl^- and $N_3{}^-$ in addition to those with OH^-. The latter are typically present due to adventitious water, which acts as an effective chain transfer agent. Because Br^- might displace Cr−

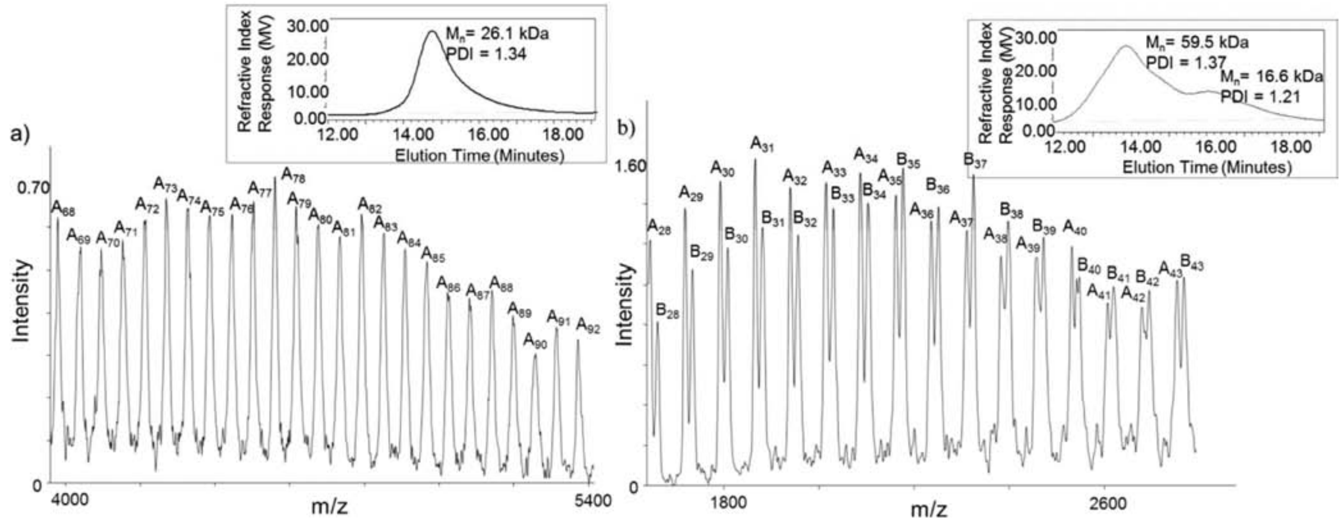


Figure 3. ESI-MS of the polypropylene oxide obtained (a) from the TPPCr(OH) catalyst and (b) after adding PPN^+Cl^- to the already living system containing (TPP)Cr(OP). The polypropylene oxide series observed are A_n = H-[(C_3H_6O)$_n$]-OH.Na^+; B_n = H-(C_3H_6O)$_n$-Cl·Na^+. Inset shows the unimodal and bimodal GPC profiles observed.

Cl bonds, this reaction was also carried out after initiating the ring-opening of PO by TPPCrCl with subsequent addition of $^nBu_4N^+Br^-$. The presence of Br^- in the polymer chains was again seen by ESI mass spectrometry. As a control experiment, the admixture of a PPO-Cl-terminated chain was allowed to be mixed with $^nBu_4N^+Br^-$, and no bromide incorporation into the PPO was seen by ESI-MS. Representative mass spectra are shown in Figure S6 in the Supporting Information.

(4) When $TPPCrO_2CMe$ is employed as a catalyst initiator, we observed IR evidence of the acetate end group at 1740 cm^{-1}, ν(C=O). When $PPN^+O_2CMe^-$ was added to a chloride-initiated polymer, the subsequent polymer was found to contain O_2CMe end groups by IR spectroscopy, as shown in Figure S7. We also observed a bimodal polymer mass distribution by GPC.

The ability of the TPPCr(III) system to support two growing chains is in marked contrast to that of the related aluminum(III) systems[24,25] and also contrasts with the results of Darensbourg for salen chromium(III) systems.[32]

Copolymerization of PO and CO_2. In the absence of a cocatalyst the (porphyrin)CrCl initiators produced only ether-rich polymers, as evidenced by $^{13}C\{^1H\}$ NMR spectroscopy. See Figure S8 in the Supporting Information. However, with the addition of PPN^+Cl^- the incorporation of CO_2 was greatly enhanced, as can be seen from the $^{13}C\{^1H\}$ NMR spectra of the polypropylene carbonates in Figure 4.

The spectrum of the polymer produced in the reaction catalyzed by the OEPCrCl initiator with neat PO and CO_2 (50 bar) with 0.5 equiv of PPN^+Cl^- reveals the presence of the predominant $(HT)_n$ sequences[22,25] (~90%) relative to the irregularities of HH and TT (~10%) and the minor amount of HT′ due to ether-rich sections. An examination of the HT region shows no evidence of stereoselectivity in the ring-opening of *rac*-PO, indicating that the carbonate methine nearest the Cr(III) center is not influential in the PO enchainment process. See Figure 4.

The influence of CO_2 pressure was also investigated, and for the OEPCr(III) system there was no apparent difference in the carbonate region for 10, 30, and 50 bar, as shown in Figure 4. The TFPPCr(III) system with neat PO and CO_2 gave similar results in the presence of PPN^+Cl^- (0.5 equiv) but with a slower turnover frequency; see Table 3.

The TPPCr(III) system under analogous conditions yielded only ether-rich PPC, as shown in Figure 5. It was also clear that the rate of enchainment of PO was notably slower with the applied CO_2 pressure: TOF ~1600 h^{-1} at 50 bar CO_2. Thus, for TPPCr(III) the ring-opening of PO by a [Cr]−OR bond is faster than that by [Cr]−O_2COR, which is the inverse of what is seen for the related TPPAl(III) system.

The reactions involving TPPCrCl and PO/CO_2 were also examined in CH_2Cl_2 solutions at various concentrations. Under these conditions (see Experimental Section) the dilution of PO slows the rate of PO enchainment but allows for the formation of PPC with fewer ether-rich segments, in the presence of 1 equiv of PPN^+Cl^-. See Figure S9. Increasing the Cl^- concentration up to 1 equiv enhances CO_2 incorporation. In comparing the rates of PO enchainment with 0.5, 0.75, and 1.0 equiv of PPN^+Cl^- the enchainment is seen to decrease beyond 0.5 equiv, although the CO_2 incorporation is enhanced. Increasing the concentration of PPN^+Cl^- beyond 1 equiv changes the product distribution in favor of the thermodynamic product PC. The decrease in enchainment of PO with increasing concentration of Cl^- is consistent with the ring-opening order [Cr]−OR > [Cr]−O_2COR since [Cl^-] favors CO_2 insertion. Furthermore, as we show later, the addition of an excess of Cl^- causes displacement of the alkylcarbonate growing chain with subsequent backbiting, which thus favors the formation of PC relative to PPC. GPC analysis of PPC samples is shown in Table 4.

Comments on Microstructure of Stereosequences. As shown in Figure 4 the formation of PPC occurs with predominantly $(HT)_n$ junctions.[22,25] In principle a $(HT)_n$ polymer could be formed by ring-opening at either the methine or methylene carbon in a persistent manner, but we can be confident that $(HT)_n$ units in PPC are in fact formed by the consecutive attack and opening at the methylene carbon based on the following. Use of either *R*- or *S*-PO produces essentially one triad HT sequence, and degradation of the polymer by $LiO^tBu/^tBuOH$ yields the cyclic carbonate, PC, with retention of stereochemistry at the methine carbon; also the backbiting mechanism occurs with retention of stereo-

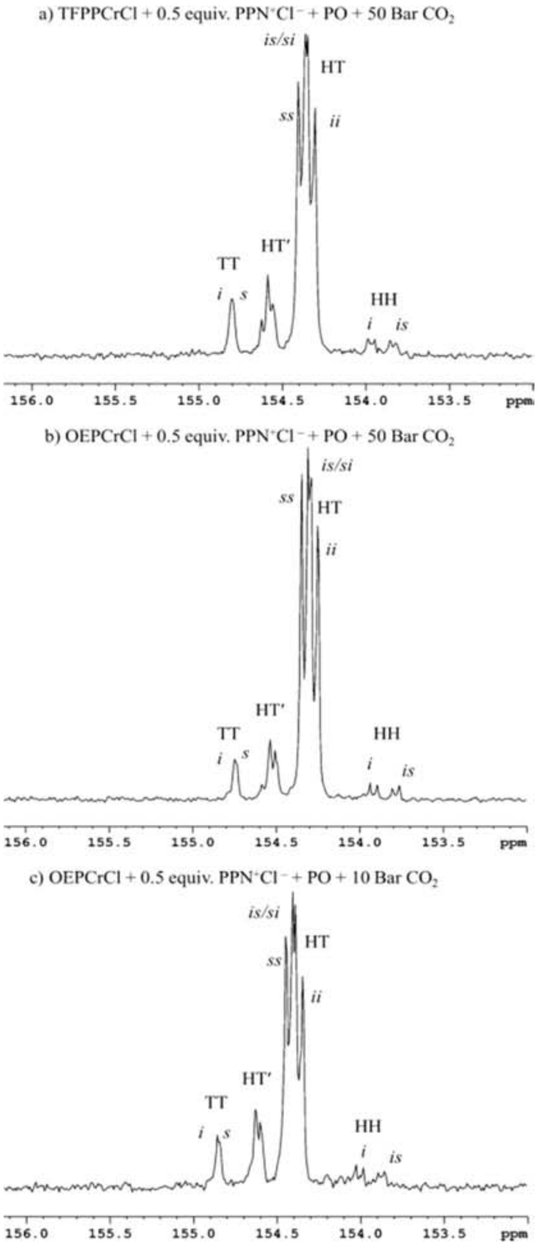


Figure 4. $^{13}C\{^1H\}$ (125.73 MHz, $CDCl_3$) NMR spectra of the carbonate region in polypropylene carbonates prepared using (porphyrin)Cr(III) catalysts, showing 80−90% HT junctions. HT′ represents an ether-rich carbonate signal.

chemistry.[25] The carbonate carbon signal of the $(HT)_n$ junction shows only triad sensitivity, and this is similarly seen for the HH junctions but not for the TT junction. We can account for this based on the bond distances from the carbonate carbon in the diads. So for the HH junctions the carbonate carbon to methine carbon involves just two bonds, whereas for the TT junctions there are three bonds and for the HT two and three bonds, as shown in Figure 6. With triad sensitivity we can reasonably speculate that the secondary stereocenter of magnetic significance is that closest to the carbonate carbon. Given that the predominant ring-opening of PO occurs via attack at the methylene carbon, when *R*-PO is employed in the formation of PC, we expect to see the dominance of the HT *ii* triad, and at diad sensitivity the HH and TT junctions will be *s* if the ring-opening occurs via an inversion of stereochemistry at the methine center.

Table 3. PO and CO_2 Polymerization by (Porphyrin)CrCl Catalysts with or without Added Cocatalysts (0.5 equiv)[a]

entry	catalyst	additive	TOF[b] (h^{-1})	%HT[c]
1	TPPCrCl		12.5[d]	
2	TPPCrCl	DMAP	178[d]	
3	TPPCrCl	PPN^+Cl^-	1600[d]	
4	TPPCrCl	PPN^+Cl^-	1270[d]	
5	TPPCrCl (py)		94	50
6	OEPCrCl		10[d]	
7	OEPCrCl	DMAP	43	85
8	OEPCrCl	PPN^+Cl^-	72	87
9	OEPCrCl (py)		30	84
10	TFPPCrCl	PPN^+Cl^-	9	83
11	TFPPCrCl (py)		43	59

[a] Reaction conditions: 0.85 mL of PO (12 mmol), catalyst 0.02 mmol, additives 0.01 mmol when used, 2.5 h, at 25°C. [b] Calculated from ^1H NMR analysis of reaction aliquots, TOFs calculated as (mmol of PO consumed)/(mmol of catalyst × reaction time). [c] Calculated from ^{13}C NMR spectra of pure polymers. [d] Ether-rich copolymers obtained.

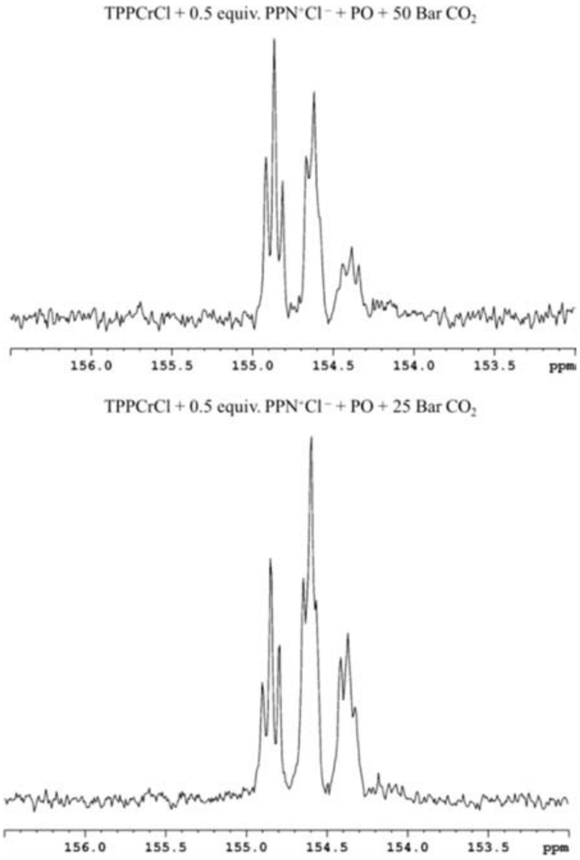


Figure 5. $^{13}C\{^1H\}$ (125.73 MHz, $CDCl_3$) NMR spectra of the carbonate region in ether-rich polypropylene carbonates prepared using the combination of TPPCrCl and 0.5 equiv of PPN^+Cl^- at various CO_2 pressures.

We have previously established for zinc glutarate that the downfield HH and TT signals correspond to *s* diads and furthermore that for TPPAlCl the *s* diad was predominant.[22] In the present work we also see that the *s* diad is predominant for the HH and TT junctions and furthermore that the HH signals that have triad sensitivity revealed the preference for the more

Table 4. GPC Analysis of Copolymers Prepared at 50 bar CO_2 Pressure

entry	catalyst	equiv PPN^+Cl^-	M_n,[a] kDa	M_w,[a] kDa	PDI[a]	M_{calc},[b] kDa
1	TPPCrCl	0.5	22	23	1.1	35
			8.1	9.6	1.2	
2	TPPCrCl	1.0	13	16	1.3	35
3	TPPCrCl	0.5	32	54	1.6	81
4	TPPCrCl(py)		61	72	1.2	22
5	OEPCrCl	0.5	8.6	10	1.2	35
6	OEPCrCl	0.5	24	66	2.8	81
7	TFPPCrCl[c]	0.5	8.7	98	1.1	35
8	TFPPCrCl(py)		5.2	7.1	1.2	22

[a] GPC analysis of pure copolymers after 100% PO consumption, using polystyrene standard. [b] Calculated maximum molecular weight for 1 polymer chain growing per metal center. For entries 1, 2 and 7, reactions were run using 0.5 mL of CH_2Cl_2 solvent; other reactions were run in neat PO. [c] Catalyst was partially soluble.

downfield signal of the *s* diads. Since the preferential ring-opening of PO is at the methylene carbon, the previous methine carbon will have retained its stereochemistry. Thus for the HH triads shown in Figure 6 the downfield signal can be assigned as *is* with the chain growing from right to left. It can be noted from the reaction involving a 50:50 mixture of *rac* and *R*-PO that the other triad sequences, namely, *ss*, *si*, and *ii*, are of equal intensity, as predicted by statistics. See Figure S10.

React IR Studies. The reaction between TPPCrCl and PO is, as noted before, very slow in the absence of a cocatalyst or promoter but does proceed slowly to form the active Cr—alkoxide bond.

To such a solution in CH_2Cl_2, after any excess PO had been removed, we added CO_2 (1 bar) and observed the formation of a new IR-active band at 1680 cm^{-1} that we assign to the formation of the $TPPCrO_2COR$ moiety, namely, the alkylcarbonate group bound to Cr. This IR band is not present during the homopolymerization of PO. See Supporting Information Figure S11.

When PO is added and the CO_2 atmosphere maintained, we observe the slow growth of an IR band at ~1750 cm^{-1}, which we can assign to the carbonate group in an ether-rich polymer. The latter is readily apparent from the $^{13}C\{^1H\}$ NMR signal of the carbonate carbon, which is quite different from that of the alternating copolymer PPC.

The above reactions are very slow compared to those carried out in the presence of a cocatalyst such as PPN^+Cl^- or DMAP. The addition of PPN^+Cl^- or DMAP accelerates the reaction and promotes the enchainment of CO_2. A similar observation was noted in the reaction of TPPAl(III) alkoxides, where DMAP promoted CO_2 insertion into the Al—alkoxide bond. The IR band at 1750 cm^{-1} attributable to the carbonate moiety is not sensitive to the CO_2:PO ratio (which can be determined by NMR spectroscopy), and so this IR band cannot be used alone to distinguish between an ether-rich polymer or PPC.

Studies of the copolymerization of PO and CO_2 in CH_2Cl_2 were carried out with varying [TPPCrCl]:[PPN^+Cl^-] ratios, namely, 1.0:0.5; 1.0:1.0, 1.0:1.2, and 1.0:5.0. However, with the increase of Cl^- addition we observed an increase in the formation of PC, as indicated by the IR band at 1805 cm^{-1}. See Figure 7. From this we can see that the rate of formation of PC is initially faster than that of PPC, but with time the formation of PC effectively stops while the formation of PPC continues. With a [Cr] to [PPN^+Cl^-] ratio of 1.0:5.0, the formation of PC dominates. This is quite striking, and although it is known that PPC can be degraded to the thermodynamically more stable PC, we have found that in the presence of an atmosphere of CO_2 the polymer attached to the chromium catalyst does not degrade to any significant extent at room temperature. From this we must conclude that the initial formation of PC involves a different mechanism in these reactions.

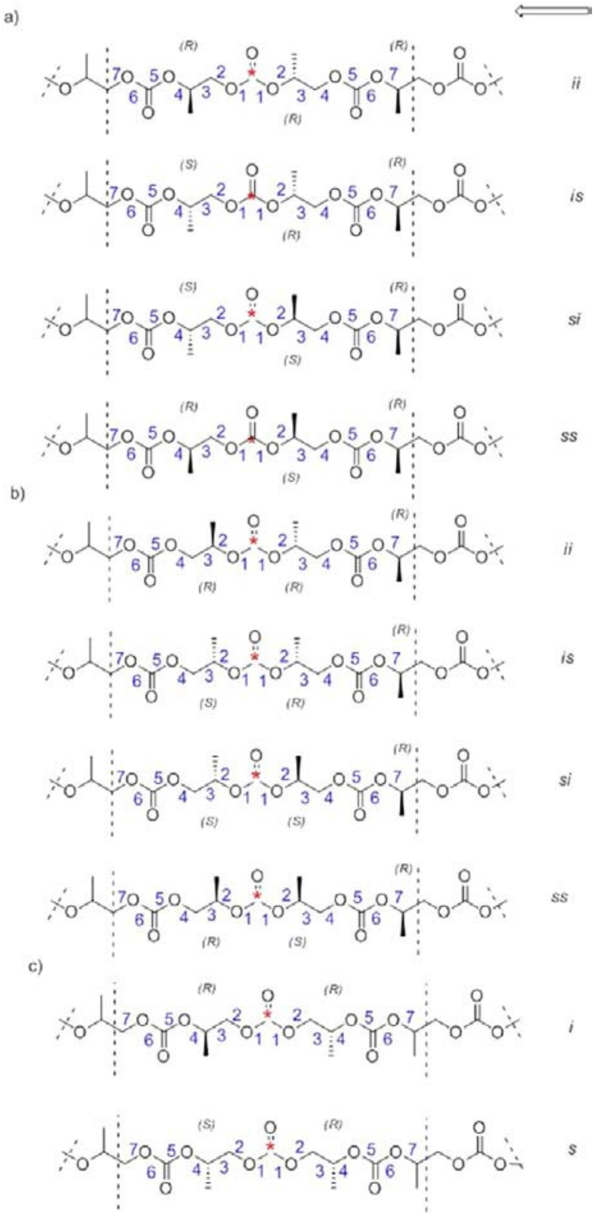


Figure 6. Microstructure of PPC showing triad level sensitivity for (a) HT and (b) HH and diad level for (c) TT junctions. Arrow indicates the direction of polymer growth.

When the related reactions were carried out with 1.0 equiv of $^nBu_4N^+Br^-$ and TPPCr-alkoxide with excess PO and CO_2, we observed an even greater enhancement of PC relative to polymer. When TPPCr(OH) is employed as the initiator with DMAP as a cocatalyst, no PC is formed and only the growth of the IR band associated with the carbonate in the polymer is seen. However when PPN^+Cl^- (1.0 equiv) is added to this living system, we see the formation of PC, which again ceases with time as the polymer carbonate IR band continues to grow.

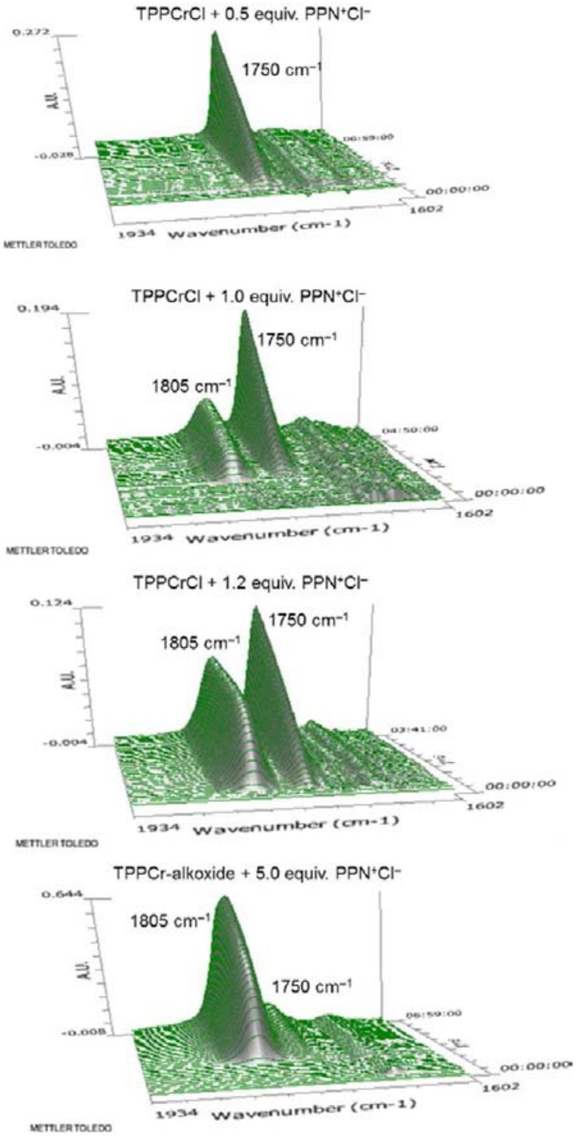


Figure 7. Three-dimensional stack plots of PO/CO_2 copolymerization reactions carried out using TPPCr(III) initiator with varying amounts of PPN^+Cl^- at 1 atm pressure of CO_2.

See Figure 8. We can attribute this to the initiation of the second chain upon Cl^- addition.

At this point we can propose a mechanism for the formation of PC based on the reaction of the Cl^- ion to enchain one PO molecule followed by CO_2 insertion and a backbiting reaction involving the displacement of the Cl^- and the re-formation of the Cr−Cl bond. This process is apparently more rapid than the enchainment of a PO molecule by the Cr−O_2CO(PO)Cl moiety, but when the latter enchainment occurs, the backbiting ceases and the polymer chain grows. This reaction pathway is summarized in Scheme 2.

In the presence of an excess of Cl^-, it is also likely that Cl^- displaces an alkylcarbonate anion, $[O_2CO(PO)Cl]^-$, which rapidly undergoes cyclization with the elimination of Cl^-, and in this way PC is formed catalytically with the enchainment of PO by Cr−O_2CO(PO)Cl being suppressed. Reactions involving *R*-PO under these conditions yield >99% *R*-PC, as determined by chiral GC. This is consistent with ring-opening of PO at the methylene carbon. If there is a minor pathway involving attack at the methine carbon, this must go with

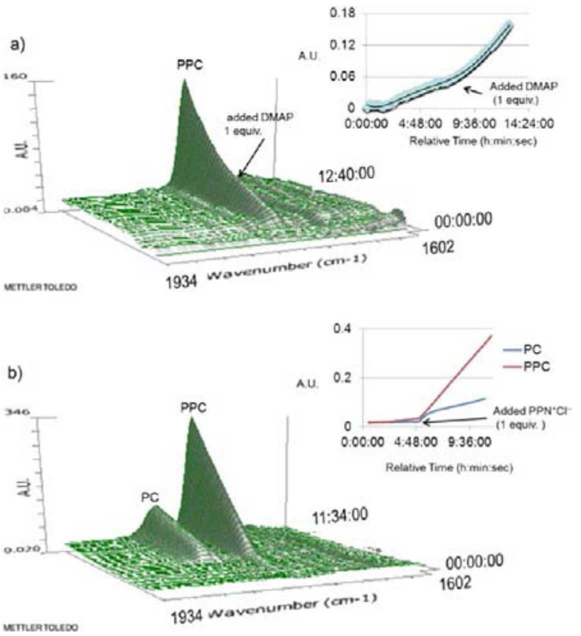
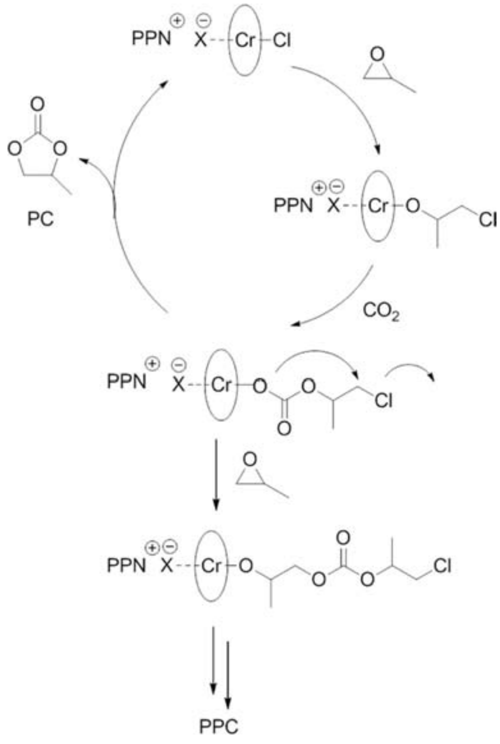


Figure 8. Three-dimensional stack plots of PO/CO_2 (1 atm) copolymerization reactions carried out using (a) TPPCrOH + 1 equiv of DMAP; (b) TPPCrOH + 1 equiv of PPN^+Cl^-.

Scheme 2. Proposed "Backbiting" Reaction That Produces PC during PO/CO_2 Copolymerizations[a]



[a]X is initially Cl^- but with time becomes active in the formation of PC and PPC.

inversion, as seen for the HH junctions in the formation of PPC. The ring closure to form PC by backbiting is an S_N2 Cl^- displacement recation, and so the effect of double inversion is retention.

When the reaction between TPPCrCl and excess PO is carried out at room temperature in the presence of either 0.75

or 1.0 equiv of PPN$^+$Cl$^-$, the system grows just PPO. When CO$_2$ is now added along with more PO, we observe the formation of PPC with little if any production of PC. This is shown in the react-IR plots in Figure 9.

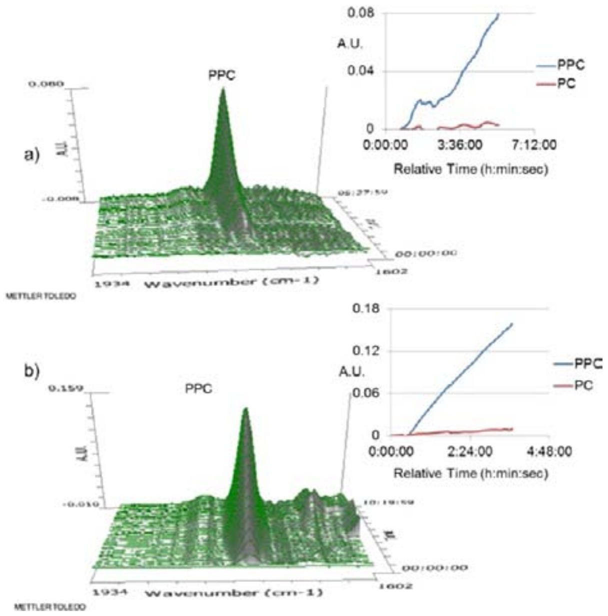


Figure 9. Three-dimensional stack plots of PO/CO$_2$ (1 atm) copolymerization reactions carried out after preparing the PPO block with (a) TPPCrCl + 0.75 equiv of PPN$^+$Cl$^-$ and (b) TPPCrCl + 1.0 equiv of PPN$^+$Cl$^-$ and excess PO in either case. Inset shows almost exclusive PPC formation during the course of reaction.

The addition of PPN$^+$Cl$^-$ (5.0 equiv) to this living system initiates the formation of PC and effectively halts production of PPC, as shown in Figure 10.

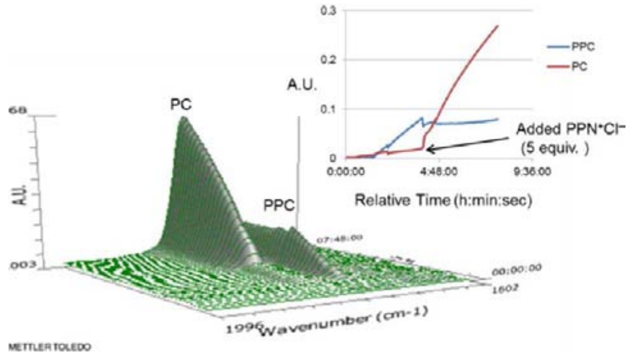


Figure 10. Three-dimensional stack plots of PO/CO$_2$ (1 atm) copolymerization reactions showing the effect of adding PPN$^+$Cl$^-$ (5.0 equiv) to a living polymerization system. The immediate rise in PC formation and the decrease in PPC IR stretch are shown in the inset.

We propose that this arises from the ability of Cl$^-$ to reversibly displace the growing carbonate chain. Indeed, upon addition of PPN$^+$Cl$^-$, there is an initial rapid decrease in the IR signal due to PPC and the simultaneous rapid formation of PC with subsequent steady growth. We propose that this arises from the backbiting of a displaced carbonate chain, which can occur until an ether-rich unit attaches to the chromium center. This is shown in Scheme 3, where we emphasize the ability of Cl$^-$ to displace a carbonate moiety but not an alkoxide. The ether-rich content of PPC obtained at atmospheric CO$_2$ presure using TPPCrCl and 1.0 equiv of PPN$^+$Cl$^-$ is manifested in the ^{13}C{^{1}H} NMR shown in Figure S12. Note that in the homopolymerization of PO the addition of PPN$^+$Cl$^-$ greater than 1 equiv has no effect: Cl$^-$ does not lead to chain transfer involving polyether chains.

The addition of DMAP to a living system producing PPC also leads to some formation of PC but nothing of the order seen upon the addition of PPN$^+$Cl$^-$. DMAP is apparently less effective in displacing the alkylcarbonate chain than is Cl$^-$.

UV−Visible Studies. Since all the chromium(III) complexes are paramagnetic, NMR spectroscopy is not a useful tool in investigating the nature of the groups bound to the metal center due to extensive line broadening. However, all the Cr(III) complexes are highly colored materials (TPPCrCl and TFPPCrCl are green, OEPCrCl is red) and form intensely colored solutions in CH$_2$Cl$_2$ and THF. The color arises from the Q bands of porphyrins,[33,34] which we have found to be useful in the following way. The absorption bands in the region 650−450 nm of the TPPCrCl complex in CH$_2$Cl$_2$ with and without added PPN$^+$Cl$^-$ are shown in Figure S13 in the Supporting Information. The spectrum with 10 equiv of PPN$^+$Cl$^-$ is essentially identical to that with 1.0 equiv, which in both cases we take to be due to the [TPPCr(Cl)$_2$]$^-$ anion. The spectrum with 0.5 equiv of PPN$^+$Cl$^-$ is the sum of the spectrum with no PPN$^+$Cl$^-$ and that with 1.0 equiv, indicating that both species are present.

The visible spectrum of TPPCrCl upon reaction with PO in CH$_2$Cl$_2$ solution, where one growing polyether chain is present, is notably different from that of TPPCrCl and moreover is different from the spectrum observed for the reaction involving TPPCrCl, excess PO, and PPN$^+$Cl$^-$ (1.0 equiv), where we have proposed there are two growing chains. These three spectra are compared in Figure 11.

■ CONCLUDING REMARKS

There are now several important results that contrast with the earlier studies involving aluminum and chromium catalysts in their reactions with PO and CO$_2$.

(1) With TPPCrCl the homopolymerization by chromium is 2 orders of magnitude faster than for aluminum.

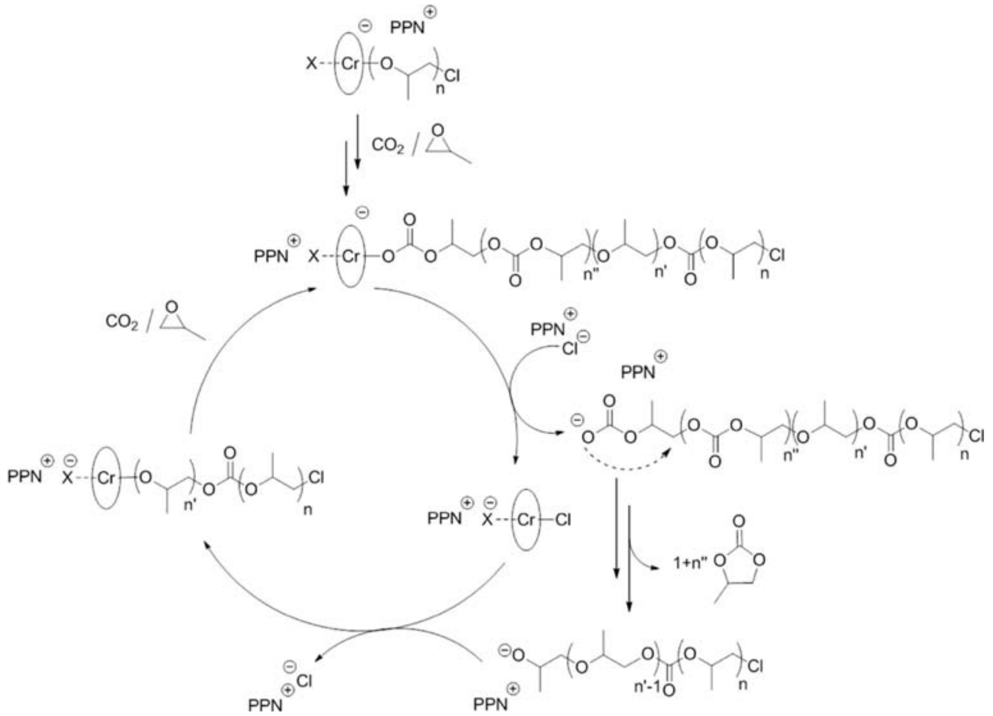
(2) The relative rate of enchainment of PO is faster by the Cr−alkoxide bond than the Cr−alkylcarbonate bond, which is also the opposite of that seen for aluminum.

(3) In the presence of PPN$^+$Cl$^-$ as a cocatalyst, the chromium porphyrin system grows two chains per metal; this again contrasts with the single-chain growth per metal for aluminum and that for the (salen)CrCl systems examined by Darensbourg et al.[32] However, with TPPCr(OH) as an initiator and DMAP as a coctalyst only one chain grows and the kinetics supports the unimolecular nature of the reaction on [Cr] as was first seen by Darensbourg and is akin to that of TPPAlCl-initiated reactions.

(4) The formation of PC in these studies can be clearly traced to the presence of Cl$^-$ and a backbiting reaction involving [Cr]-O$_2$COCH(Me)CH$_2$Cl. This is most likely the reason that Kruper et al. reported that TPPCrCl with PO and CO$_2$ yielded only PC.[35] As we have shown with TPPCrOH and DMAP, PO and CO$_2$ yield ether-rich PPC.

(5) We have also presented evidence that the addition of Cl$^-$ may displace a growing [Cr]-O$_2$COP chain, which induces backbiting involving the carbonate anion. If this is indeed correct, then it challenges belief in proposed mechanisms

Scheme 3. Dissociation of a Growing Polycarbonate Chain upon the Addition of Excess (5.0 equiv) PPN$^+$Cl$^-$[a]



[a]This halts chain growth and promotes PC formation via backbiting reaction involving the anionic carbonate end group. X is initially Cl$^-$ but with time becomes active in the formation of copolymer and PC.

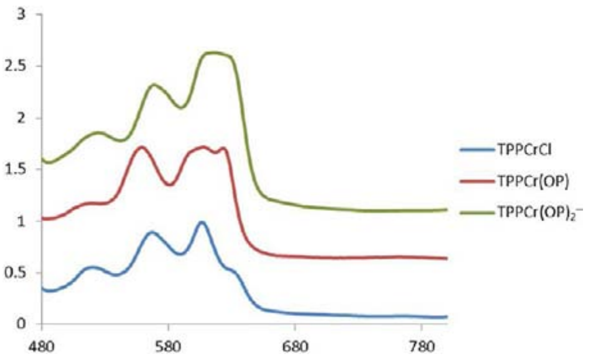


Figure 11. UV–visible spectra of TPPCrCl before and after reaction with PO and PPN$^+$Cl$^-$ cocatalyst in CH$_2$Cl$_2$ solution.

involving carbonate dissociation during the copolymerization of PO and CO$_2$.[36] In the absence of an excess of Cl$^-$ or DMAP this reaction does not occur in the presence of a CO$_2$ atmosphere. This implies that backbiting does not occur by a bound carbonate ligand.

(6) The formation of PPC by TPP chromium catalysts is relatively insensitive to the CO$_2$ pressure. This again contrasts what is seen for aluminum and other chromium and cobalt catalysts, although Williams has reported some cobalt systems that are active at 1 bar CO$_2$.[37,38] This observation suggests that the equilibrium involving the Cr-alkoxide and Cr-alkylcarbonate favors the latter.

We may speculate that many of the differences between aluminum(III) and chromium(III) systems arise from the greater affinity of the latter toward six-coordination in an octahedral or pseudo-octahedral environment. This was seen in gas-phase studies of the binding of PO to the TPPCr$^+$ and TPPAl$^+$ cations.[39] Also for the heavier element in the +3 oxidation state its metal—oxygen bonds may be expected to be more polar, thus favoring CO$_2$ insertion. The presence of a good donor ligand in the *trans* position also facilitates this. Thus with two growing chains the active site is six-coordinate and carries a formal negative charge, which further assists in promoting CO$_2$ insertion into the metal alkoxide bond.

In a pseudo-octahedral coordination the d^3 metal has three unpaired electrons, one in each of d$_{xy}$, d$_{xz}$, and d$_{yz}$ orbitals. The mechanism of PO enchainment involves what is akin to an interchange associative mechanism in ligand substitution reactions.[40] The activated complex can thus be considered a seven-coordinate chromium(III) center where the PO and the growing chain, either an alkoxide or an alkylcarbonate, attacks the PO molecule, which is activated by the coordination to the electrophilic metal center.

It is interesting to note that in these porphyrin-ligated systems the formation of PPO occurs in a rigorous HT manner via the selective ring-opening by attack at the methylene carbon, and furthermore with *rac*-PO this favors the formation of isotactic junctions. The same degree of regio and stereoselectivity is not seen in the formation of PPC, and this presumably reflects the greater steric constraints in the ring-opening event by an alkoxide ligand in the case of the porphyrin ligands. Others have observed both regio- and stereoselectivity in the formation of PPC employing chiral ligands.[8,16] However, with the planar porphyrin the inherent nature of the ring-opening event can be seen in the formation of HH junctions. These reveal the effect of PO coordination to the electrophilic metal center, which transfers positive charge to the methine carbon. In the extreme this can lead to the effective cationic polymerization with the formation of low molecular weight polymers and rings with complete regio-randomness. This is observed for TFPP chromium and aluminum[25] chloride complexes in the absence of a donor ligand as cocatalyst. The same is seen for $AlCl_3$. Thus the mechanism of polymerization by this modified Lewis acidic metal center rests on a careful balance where PO is activated and the neighboring ligand acts as a nucleophile. In the present case we see that the HH junction is formed stereoselectively, namely, with inversion of stereochemistry in the attack on the methine carbon. As we have shown before, this is akin to that seen for catalysis by zinc glutarate but not for other chromium salen complexes.[22] This copolymerization reaction involving coordinate catalysis thus remains an intriguing variation of what is seen in typical organic reactions of PO.

Further work on the ether-rich polypropylene carbonates and the porphyrin cobalt catalyzed polymerizations is under way.

■ EXPERIMENTAL SECTION

Reagents and Methods. All syntheses and solvent manipulations were carried out under a dry nitrogen atmosphere using standard Schlenk-line and drybox techniques unless otherwise mentioned. All solvents (CH_2Cl_2, hexanes, dimethylformamide) 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 over calcium hydride. The porphyrins 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine ($TPPH_2$), 5,10,15,20-tetrakis(pentafluorophenyl)-21*H*,23*H*-porphine ($TFPPH_2$), 2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphine ($OEPH_2$), and *meso*-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphine (Frontier Scientific), chromium(II) chloride (>99% pure, Sigma Aldrich), 99% CO_2 (OSU gas stores), and silica gel (Fisher Scientific, 60 Å particle size) were used as received. Bis(triphenylphosphine)iminium chloride ($(Ph_3P)_2N^+Cl^-$) (Sigma Aldrich) was dried under vacuum at 50 °C and stored inside a drybox before use. 4-Dimethylaminopyridine (Aldrich) was sublimed twice and stored inside a drybox before use. $^nBu_4N^+Br^-$ (Acros) was dried under vacuum, recrystallized twice from a mixture of dry CH_2Cl_2/diethyl ether, and stored inside the glovebox before use. Other PPN^+ salts were prepared from PPN^+Cl^- following literature procedures.[41,42]

NMR Spectroscopy. ^1H and $^{13}C\{^1H\}$ NMR experiments were carried out using 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 ppm relative to the solvent chloroform-*d* at 7.24 ppm for ^1H NMR and 77.23 ppm for $^{13}C\{^1H\}$ 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 2414 refractive index detector and a set of two columns, Waters Styragel HR-2 and HR-4 (7.8 × 300 mm). THF 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 Da.

Gas Chromatography. Gas chromatographic (GC) analysis was carried out at 60 °C using an Agilent Technologies 7820A GC system equipped with a Cyclosil column. A flow rate of 21 mL/min and head pressure of 17 psi were used to separate the enantiomers.

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 was 28 kV. Sodium iodide (Sigma Aldrich ≥99%) was used to aid ionization of polymer samples. Dithranol, the matrix, was dissolved in THF to yield a concentration of 25 mg mL^{-1}. The typical concentrations of sodium iodide solution and polymer solutions were 5 and 20 mg mL^{-1}, respectively. Measured volumes of dithranol, sodium chloride, and polymer sample were premixed in a ratio of 2:1:1. A small amount of this solution was spotted on a stainless steel target plate and allowed to dry at room temperature before use. High-resolution 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. In a typical analysis of polymer samples 0.025 vol % of 0.1% formic acid solution was used to aid ionization of polymer samples.

IR Spectroscopy. FT-IR spectra were recorded using a Perkin-Elmer Spectrum GX spectrometer at room temperature. For polymer samples films were prepared by slow evaporation of a CH_2Cl_2 solution of the polymer on a circular NaCl plate of 2 mm thickness and 25 mm diameter. An ASI react-IR 1000 Reaction Analysis System was used to monitor the PO and CO_2 copolymerization reactions at atmospheric pressure of CO_2.

UV−Visible Spectroscopy. Electronic spectra at room temperature were recorded using a Perkin-Elmer Lambda 900 spectrometer. In a typical experiment a CH_2Cl_2 solution of the Cr(III) complex was run using a 10.00 mm IR quartz cell.

Synthesis of Catalysts. TPPCrCl, TFPPCrCl, and OEPCrCl complexes were prepared according to a slight modification of literature procedures.[34,35,43−45] Instead of column chromatography the crude products were purified by washing with hexanes to remove unreacted porphyrin, if present in trace amounts, followed by crystallization. In a typical crystallization process a concentrated chloroform solution of the crude compound was layered with hexane and slowly cooled to −10 °C inside a freezer for a period of several days. The solids obtained were filtered and washed with cold chloroform. (TPP)chromium hydroxide compound ($TPPCr(OH)\cdot 2H_2O$) was prepared following reported procedures[46,47] and dried under high vacuum for 5 h at 70 °C. The pyridine-coordinated complexes, namely, OEPCrCl(py), TPPCrCl(py), and TFPPCrCl(py), were prepared following reported procedures.[33,48−50] Distilled pyridine (5 equiv) was added to a CH_2Cl_2 solution of the chloride catalyst and stirred for 2 h. The volatile fractions were then removed in vacuo at 50 °C. UV−vis spectroscopy and ESI-MS were used to confirm the formation of the compounds. ESI-MS data: found m/z = 664.3 for $(TPP)Cr^+$, found m/z = 1024.6 for $(TFPP)Cr^+$, found m/z = 584.4 for $(OEP)Cr^+$.

Reactions between (Porphyrin)CrCl and PO. These reactions were carried out in both the presence and absence of Lewis base additives. In a typical reaction, 0.02 mmol of (porphyrin)CrCl and 0.01 mmol of DMAP or PPN^+Cl^- (when used as additives) were dissolved in 0.85 mL (12.00 mmol) of PO in a vial. The above solution was sealed with a Teflon cap and left under a dry N_2 atmosphere at room temperature for 2.5 or 10 h to obtain the TOFs. The later studies with TPPCrCl were done in a mixture of 6.0 mL of CH_2Cl_2 and 0.85 mL (12.00 mmol) of PO to avoid an excessively exothermic reaction. An aliquot was taken from each reaction mixture for ^1H NMR analysis. The polymerization process was quenched by the addition of 1 N HCl/methanol. The unreacted PO and solvents were then removed in vacuo. The polymers were further purified by filtering over a bed of silica gel using 25:75 by volume mixture of ethyl acetate and hexanes solvents. The isolated polymer was further analyzed by ^{13}C NMR, ESI-mass spectroscopy, and GPC.

Kinetics of PO Ring-Opening Polymerizations. In the absence of cocatalysts the order of polymerization reaction was determined with respect to [Cr]. For this purpose TPPCrCl solutions were prepared in three different concentrations (10, 20, and 30 mM) using CH_2Cl_2 solvent. In each case the measured amount of TPPCrCl was completely dissolved in 1.8 mL of CH_2Cl_2, and 1.4 mL of *rac*-PO (20.0 mmol) was added to make a total volume of 3.2 mL. The progress of the reactions was monitored at 25 °C by ^1H NMR spectroscopic analysis of reaction aliquots. The appearance of signals for the methyl group in PPO (chemical shift: 1.1 ppm) and the disappearance of the methyl group signal for PO (chemical shift: 1.3 ppm) were measured. The percent consumption of PO thus obtained was plotted against time to calculate the change in rate of polymerization with the change in [Cr].

Effect of TPPCrOH Concentration. In the absence of cocatalysts the order of polymerization reaction was determined with respect to

[TPPCr(OH)]. For this purpose TPPCrCl solutions containing 1 equiv of DMAP were prepared in four different concentrations (2.5, 5, 7.5, and 10 mM) using CH_2Cl_2 solvent. In each case a measured amount of the 27.3 mM stock solution was mixed with 2.4 mL of *rac*-PO (34.3 mmol), and a measured amount of CH_2Cl_2 was added to make a total volume of 4.8 mL. The progress of the reactions was monitored at 25 °C by ^1H NMR spectroscopic analysis of reaction aliquots. The observed percent consumption of PO was plotted against time to calculate the change in rate of polymerization with the change in [Cr].

Effect of PPN^+Cl^- Concentration. For this purpose [Cr] was left constant at 4.5 mM, and $[Cl^-]$ was varied to obtain 0.25, 0.5, 1.0, and 2.0 equiv in $[Cl^-]$, respectively. To prepare the reaction sets, stock solutions of 27 mM TPPCr(III) and 27 mM PPN^+Cl^- were separately prepared in CH_2Cl_2 solvent. In a typical reaction, 0.8 mL of TPPCrCl solution and a measured amount of PPN^+Cl^- stock solution were mixed followed by the addition of CH_2Cl_2 to make a total volume of 2.4 mL. After stirring this solution for 15 min, 2.4 mL of *rac*-PO (34.3 mmol) was added. The progress of the reactions was monitored at 25 °C by ^1H NMR spectroscopic analysis of reaction aliquots. The observed percent consumption of PO was plotted against time to calculate the change in rate of polymerization with the change in $[Cl^-]$.

Effect of DMAP Concentration. For this purpose [Cr] was left constant at 4.5 mM and [DMAP] was varied to obtain 0.25, 0.5, 1.0, and 2.0 equiv in [DMAP], respectively. To prepare the reaction sets, stock solutions of 27.3 mM TPPCrCl or TPPCrOH and 27.3 mM DMAP were separately prepared in CH_2Cl_2 solvent. In a typical reaction, 0.8 mL of TPPCrCl solution and a measured amount of DMAP stock solution were mixed followed by the addition of CH_2Cl_2 to make a total volume of 2.4 mL. After stirring this solution for 15 min, 2.4 mL of *rac*-PO (34.3 mmol) was added. The observed percent consumption of PO was plotted against time to calculate the change in rate of polymerization with the change in [DMAP].

Copolymerization Reactions of PO/CO_2. These reactions were carried out in both the presence and absence of Lewis base additives. In a typical reaction, 0.02 mmol of (porphyrin)CrCl, 0.01 or 0.02 mmol of DMAP, and PPN^+Cl^- or $^nBu_4N^+Br^-$ (when used as additives) were dissolved in 0.85 mL (12.00 mmol) of PO in a vial. The above solution was allowed to react under CO_2 pressure (10, 25, or 50 bar) in a stainless steel reaction vessel (Parr) at room temperature for a definite time (2.5, 10, or 48 h). The reactions were run for shorter times (1, 2.5, 3 h) to obtain TOFs. The later studies of TPPCrCl and PPN^+Cl^- were done in 0.85 mL (12.00 mmol) of PO diluted with 0.6 mL of CH_2Cl_2 to avoid rapid homopolymerization of PO. The PO/CO_2 copolymerization reactions were also monitored at 1 atm CO_2 pressure in an ASI react-IR system, typically using 0.04 mmol of TPPCr(III) catalyst, 0.5, 0.75, or 1.0 equiv of cocatalyst (DMAP or PPN^+Cl^-), and 2.8 mL of PO (40.00 mmol) in 2.8 mL of CH_2Cl_2 solvent. After releasing the CO_2 pressure an aliquot was taken from each reaction mixture for ^1H NMR analysis. After removing excess PO, the product obtained was dissolved in a minimum amount of CH_2Cl_2. For copolymerizations using PPN^+Cl^- salts as Lewis bases, the polymers were precipitated twice by the addition of 1 N HCl/methanol to the CH_2Cl_2 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 1 N HCl/H_2O. The resulting polymers were isolated by drying the organic phase under vacuum. The PPC samples for GPC and $^{13}C\{^1H\}$ NMR analysis were further purified by precipitation from a concentrated CH_2Cl_2 solution with excess methanol. The ether-rich copolymers were purified by filtering over a bed of silica gel using 40:60 by volume mixtures of ethyl acetate and hexane solvents.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Kinetic profiles of the homopolymerizations of PO, $^{13}C\{^1H\}$ NMR, MALDI TOF, and FT-IR spectra of polymers, and react-IR data for the Cr-carbonate intermediate. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: Chisholm@chemistry.ohio-state.edu.

Notes

The authors declare no competing financial interest.

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