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Concerning the Mechanism of the Ring Opening of Propylene Oxide in the Copolymerization of Propylene Oxide and Carbon Dioxide To Give Poly(propylene carbonate)

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Abstract: The reactions between (TPP)AlX, where TPP = tetraphenylporphyrin and X = Cl, $O(CH_2)_9CH_3$, and $O_2C(CH_2)_6CH_3$, and propylene oxide, PO, have been studied in $CDCl_3$ and have been shown to give (TPP)AlOCHMeCH_2X and (TPP)AlOCH_2CHMeX compounds. The relative rates of ring opening of PO follow the order Cl > OR > O_2CR, but in the presence of added 4-(dimethylamino)pyridine, DMAP (1 equiv), the order is changed to O_2CR > OR. From studies of kinetics, the ring opening of PO is shown to be first order in [Al]. Carbon dioxide inserts reversibly into the Al−OR bond to give the compound (TPP)AlO_2COR, and this reaction is promoted by the addition of DMAP. The coordination of DMAP to (TPP)AlX is favored in the order $O_2C(CH_2)_6CH_3$ > $O_2CO(CH_2)_9CH_3$ ≫ $O(CH_2)_9CH_3$. The microstructure of the poly(propylene carbonate), PPC, formed in the reactions between (TPP)AlCl/DMAP and (*R*,*R*-salen)CrCl and *rac*-PO/*S*-PO/*R*-PO and CO_2, has been investigated by $^{13}C\{^1H\}$ NMR spectroscopy. The ring opening of PO is shown to proceed via competitive attack on the methine and methylene carbon atoms, and furthermore attack at the methine carbon occurs with both retention and inversion of stereochemistry. On the basis of these results, the reaction pathway leading to ring opening of PO can be traced to an interchange associative mechanism, wherein coordination of PO to the electrophilic aluminum atom occurs within the vicinity of the Al−X bond (X = Cl, OR, O_2CR, or O_2COR). The role of DMAP is two-fold: (i) to labilize the trans Al−X bond toward heterolytic behavior, and (ii) to promote the insertion of CO_2 into the Al−OR bond.

Introduction

Developments in polymer chemistry can be described in terms of a continuing series of revolutions and evolutions.[1−6] A revolution represents a major discovery which initiates a change in thinking and practice. This is followed by an evolutionary period during which an understanding and refinement of the chemistry emerges. The latter relies on an elucidation of mechanism and catalyst design and modification, while the former is often ascribed to serendipitous discovery. However, it cannot be denied that the detailed logical study during the evolutionary period provides the setting upon which revolution becomes inevitable. Such is surely the case in the development of polyolefins,[7−11] and it seems the same will hold true for polycarbonates.[12−16]

The discovery of the heterogeneous-catalyzed copolymerization of propylene oxide (PO) and carbon dioxide to give poly(propylene carbonate) (PPC) by Inoue[17,18] in 1969 was followed by extensive studies of heterogeneous systems, although none was sufficiently efficient to bring PPC to the market place.[19−52]

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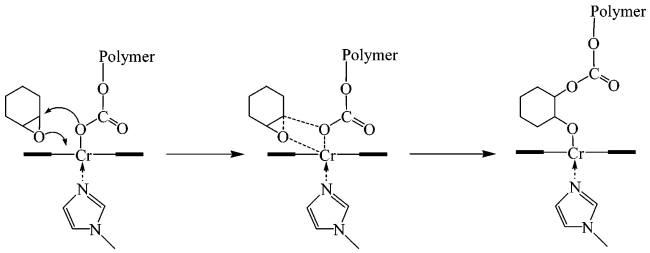
More recently, homogeneous systems have been developed,[53−58] and, as a result of the creative and insightful independent work of Darensbourg and Coates, a basic understanding of the catalytic cycle has emerged.[54−56,58−67] Studies of the related copolymerization of cyclohexene oxide (CHO) and CO_2 have evolved further.[31,46,54,56,61,62,65,66,68−90] For CHO formation of cyclic carbonate does not compete significantly with chain growth, whereas in reactions involving PO and CO_2 the formation of propylene carbonate (PC) often competes with and is favored over PPC formation, particularly at higher temperatures.[32,54,56,57,62,72,91−93] The key steps in the formation of PPC are (i) insertion of CO_2 into a metal−alkoxide bond to form an alkyl carbonate group: M−OR + CO_2 → M−O_2COR, and (ii) ring opening of PO with addition of the alkyl carbonate to regenerate the metal−alkoxide bond: M−O_2COR + PO → M−OCHMeCH_2OR′ or M−OCH_2CHMeOR′. Detailed mechanistic studies of reactions of model compounds and the kinetics of the CHO + CO_2 copolymerization reaction by the Darensbourg and Coates groups have provided considerable insight into these reactions.[54−56,72,78,85] It is, however, the step involving the ring opening of the epoxide (the oxirane), the enchainment step, that is the least well understood. In the case of dimeric zinc complexes, Coates has provided kinetic evidence that implicates a bimetallic pathway,[72] while in the case of salen chromium(III) complexes, Darensbourg has provided evidence for a monometallic single-site pathway (Scheme 1).[54]

Scheme 1. The Monometallic Mechanism Proposed for the CHO/CO_2 Copolymerization Reaction by Darensbourg [Reproduced with Permission from Ref 54. Copyright 2002 American Chemical Society]



Certain catalysts, be they homogeneous or heterogeneous, are capable of both homopolymerizing PO and copolymerizing PO/CO_2. Some, however, are selective in one over the other as shown in Table 1. In the homopolymerization of *rac*-PO, these catalysts yield highly regioregular polymers $(HTHT)_n$ with significant stereoselectivity in the preferential formation of

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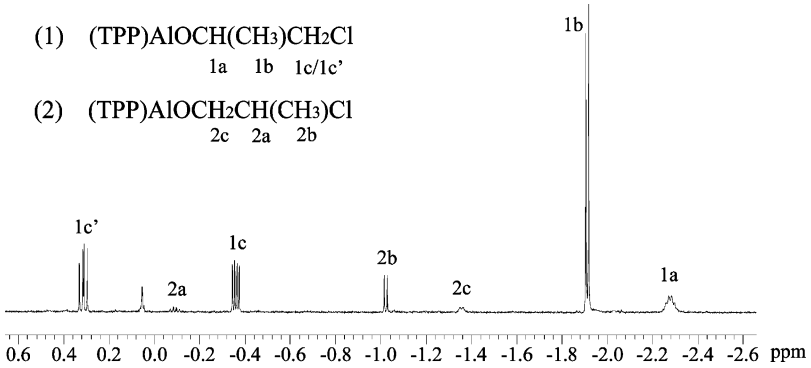

Figure 1. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of PO ring-opened product by (TPP)AlCl, showing two regioisomers.

Table 1. Catalyst Systems Showing Differing Capabilities in PO Homopolymerization and PO/CO_2 Copolymerization Reactions, as Well as CO_2 Incorporation

catalysts[a]	cocatalysts[b]	temp (°C)	PO homopolymerization[c]	CO_2 incorporation in PO/CO_2 copolymerization[d]
(TPP)AlCl		25	yes	0.13
(TPP)AlCl	$EtPh_3PBr$	25	yes	0.43
(TPP)AlCl	DMAP	25	yes	0.48
(TPP)CrCl		25	yes	0.07
(TPP)CrCl	DMAP	25	yes	0.40
(salen)CrCl		25	no[e]	0.49
(salen)CrCl	DMAP	25	no	0.49
zinc glutarate		60	yes	0.50
Union Carbide		25	yes	no

[a] The polymerization reactions were carried out in neat PO (2 mL), 1:1500 molar ratio used for (TPP) and (salen) metal catalyst systems, and 0.1 g of catalysts used for zinc glutarate and Union Carbide systems.[105] [b] One equivalent of cocatalyst was added in the reactions. [c] The reactions were carried out in the absence of CO_2. [d] The reactions were carried out at 49 atm of CO_2 pressure. The molar fractions of CO_2 in the resulting polymers were used to evaluate the CO_2 incorporation, based on the ^{1}H NMR spectra of the products. [e] No polymer formed under the condition described in footnote a. At elevated temperatures and high catalyst concentrations, poly(propylene oxide) can be obtained.

isotactic junctions.[91,94−100] In contrast, the copolymerization of PO/CO_2 yields regioirregular PPC with a ratio of HT:HH+TT junctions that is catalyst dependent.[55,58,91,101] Moreover, the addition of Lewis bases, such as Br^-, 1-methylimidazole, or 4-(dimethylamino)pyridine (DMAP), greatly enhance PPC production at the expense of PPO.[53,54,57,102−104] With porphyrin and salen complexes of Al(III) and Cr(III), this begs the question of how the alkyl carbonate and PO react within the same face of the metal center.

In an attempt to clarify this matter, we have examined the stereochemistry and kinetics of the initial ring-opening event of PO by various aluminum porphyrin and salen initiators. We also examined the influence of the promoter DMAP on this event and on the insertion of carbon dioxide into the Al−OR bond. We describe herein these findings.

Results and Discussion

Studies of the Initial Ring Opening of Propylene Oxide. The reactions between (TPP)AlX initiators, where TPP = tetraphenylporphyrin and X = Cl, $O(CH_2)_9CH_3$, and $O_2C(CH_2)_6CH_3$, and PO give the ring-opened products (TPP)AlOCHMeCH_2X as the major products at short reaction times (Experimental Section in Supporting Information). Because of the large magnetic anisotropy of the porphyrin ring,[104,106−108] the proton resonances of signals of CH, CH_2, and Me groups within ca. 5 Å of the Al center appear notably shifted upfield relative to Me_4Si. Consequently, it is relatively easy to monitor these reactions in solution by ^{1}H NMR spectroscopy. Furthermore, one can unequivocally distinguish between the regioisomers of ring opening, (TPP)AlOCH_2CHMeX versus (TPP)AlOCHMeCH_2X.

A careful examination of the spectrum in this region reveals that both regioisomers are formed but that the major regioisomer (TPP)AlOCHMeCH_2X predominates by ca. 9:1, when X = Cl. The ^{1}H NMR spectrum revealing the presence of the (TPP)AlOCHMeCH_2Cl and (TPP)AlOCH_2CHMeCl isomers is shown in Figure 1. The minor regioisomer was prepared independently from the reaction between (TPP)$AlCH_3$ and the chloro alcohol *S*-ClCHMeCH_2OH (Experimental Section in Supporting Information). The ring opening of PO by (TPP)AlCl is extremely rapid, but the very low solubility of (TPP)AlCl in $CDCl_3$ and C_6D_6 precludes the study of the kinetics of this reaction by NMR methods.

The introduction of the long alkyl chains when X = $O(CH_2)_9CH_3$ and $O_2C(CH_2)_6CH_3$ rendered these derivatives soluble in $CDCl_3$ and to some extent in C_6D_6. The choice of the *n*-octanoate ligand is intended to model for the ring opening of PO by an alkyl carbonate ligand, vide infra.

The ring opening of PO by these two compounds was followed by ^{1}H NMR spectroscopy under pseudo first-order conditions, where [PO]:[Al] was on the order 100:1. The

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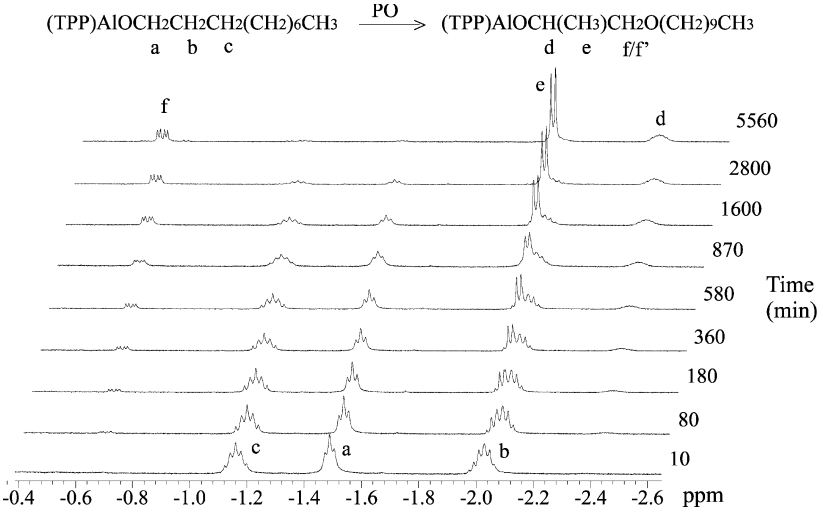


Figure 2. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of the reaction between (TPP)AlO$(CH_2)_9CH_3$ and PO, showing the disappearance of initiator and appearance of product with time.

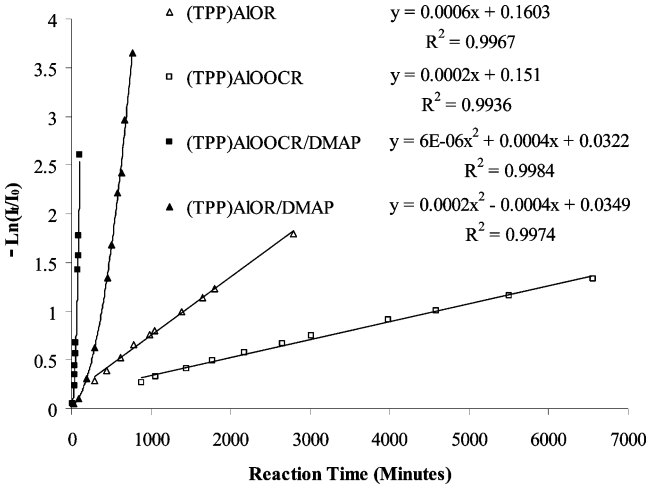


Figure 3. Plots of $-\ln(I_t/I_0)$ versus reaction time for the ring-opening reaction of the first PO molecule by initiators, in the absence and in the presence of 1 equiv of DMAP. I_0 is the initial initiator concentration, and I_t is the initiator concentration at time t. (TPP)AlOR = (TPP)AlO$(CH_2)_9CH_3$, (TPP)AlOOCR = (TPP)Al$O_2C(CH_2)_6CH_3$. In all of the reactions, [Al] = 15 mM, [PO] = 720 mM.

reactions were followed at 25 °C in $CDCl_3$ by the disappearance of the Al−X proton signals (Figure 2). For the reaction involving X = O$(CH_2)_9CH_3$, the product of ring opening was almost exclusively the (TPP)AlOCHMe$CH_2O(CH_2)_9CH_3$ isomer with the other regioisomer being barely detectable. However, for the *n*-octanoate initiator, both regioisomers were formed in an approximate ratio of 4:1, where the major isomer once again represents the formation of the secondary alkoxide by ring opening of PO at the methylene carbon. However, with time this ratio changes as the primary alkoxide, the product of ring opening of PO at the methine carbon, reacts faster with PO than does the *n*-octanoate. The secondary alkoxide also reacts with PO but at a significantly slower rate than the primary. Thus, we can state that in the initiation step the reactivity order for (TPP)AlX compounds is X = Cl > O$(CH_2)_9CH_3$ > $O_2C(CH_2)_6CH_3$ (Figure 3). We also determined, by varying the concentration of (TPP)AlO$(CH_2)_9CH_3$ from 5 to 15 mM in four different experiments, that the rate of ring opening of PO was first order in (TPP)AlO$(CH_2)_9CH_3$ (Figure S1 in Supporting Information). The straight-line plots shown in Figure 3 also confirm this.

The influence of added 4-(dimethylamino)pyridine (DMAP) was examined in the following manner. In a NMR experiment, 1 equiv of DMAP was added to a $CDCl_3$ solution of (TPP)AlX, where X = O$(CH_2)_9CH_3$ or $O_2C(CH_2)_6CH_3$. In each case, the signals associated with the aromatic protons of DMAP were shifted upfield and were significantly broadened relative to signals of DMAP in neat $CDCl_3$ (Figure S3 in Supporting Information). At 25 °C, DMAP is reversibly coordinating to the aluminum porphyrin center, and there is a significant concentration of the 1:1 adduct. Upon cooling to −50 °C, this equilibrium becomes frozen out on the NMR time scale for X = $O_2C(CH_2)_6CH_3$ and $O_2CO(CH_2)_9CH_3$ (see later). The 2,6-protons of the aromatic ring in DMAP appear at δ 0.56 ppm upon complexation to the Al center, which contrasts with δ 8.2 ppm for the free molecule in $CDCl_3$. The 3,5-aromatic protons shift similarly from δ 6.5 ppm to 4.0 ppm on complexation, and the NMe resonances shift from δ 3.0 ppm to 2.0 ppm. In the case of X = O$(CH_2)_9CH_3$, the equilibrium could not be frozen out on the NMR time scale because the equilibrium constant for binding of DMAP was much smaller. At ambient temperature, the ^{1}H signals of DMAP represent a time average between [free] and [complexed], which allows for the estimation of K_{eq} for binding. At 25 °C in $CDCl_3$, we estimate K_{eq} to be 5.8×10^{-3} mM^{-1} for X = O$(CH_2)_9CH_3$, 1.7 mM^{-1} for X = $O_2C(CH_2)_6CH_3$, and 0.51 mM^{-1} for X = $O_2CO(CH_2)_9CH_3$, which reveals that DMAP binds in the order $O_2CR > O_2COR \gg OR$. This order follows roughly the inverse order of the basicity of the oxygen donor ligands.

The kinetics of the ring opening of PO by the (TPP)Al−X compounds in the presence of 1 equiv of DMAP was also determined by NMR studies at 25 °C by monitoring the disappearance of the α-CH_2 protons of the alkoxide or carboxylate group signal. As shown in Figure 3, the influence of added DMAP was very dramatic in enhancing the rate. Now, the ring-opening event is much faster by the carboxylate than the alkoxide, although even the alkoxide is accelerated by an order of magnitude. We also noticed that the kinetic profiles of these two initiators in the presence of DMAP were polynomial rather than linear (Figure S4 in Supporting Information). This is because the secondary alkoxide products are less strongly coordinated by DMAP than the initiators, and the

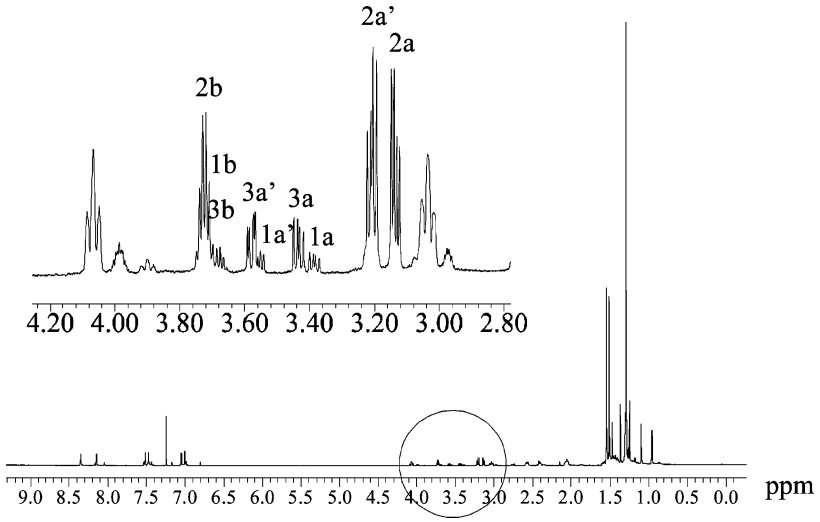


Figure 4. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of *R*-PO ring-opened products by (*R*,*R*-salen)AlCl, showing three isomers. (1) (*R*,*R*-salen)AlOCH$_2$C(*S*)-HMeCl; (2) (*R*,*R*-salen)AlOC(*R*)HMeCH$_2$Cl; (3) (*R*,*R*-salen)AlOCH$_2$C(*R*)HMeCl. (a and a′ represent CH_2 signals, and b represents CH signals derived from PO units, respectively.)

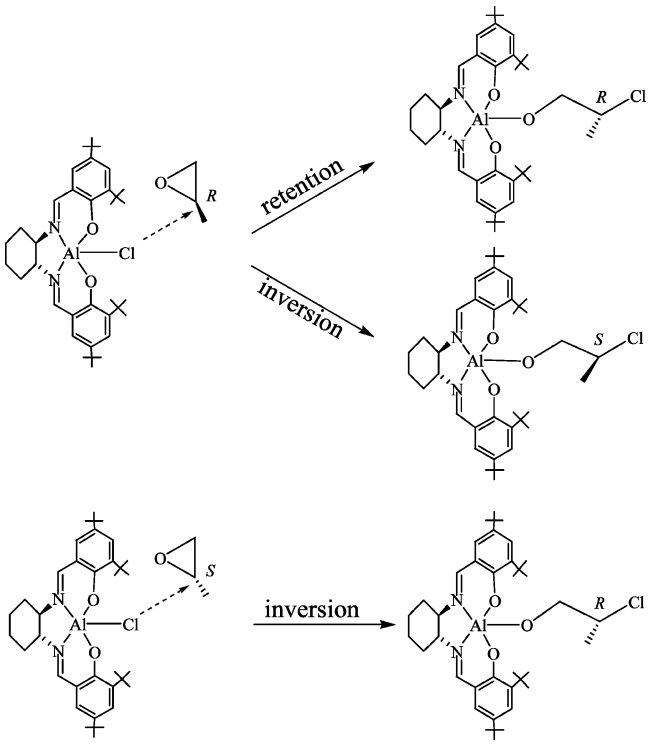
effective [DMAP]:[initiator] ratio increases with time. Thus, the apparent rate constants increase with time in these two reaction systems.

Salen aluminum chloride is not capable of polymerizing PO under the conditions comparable to those of the porphyrin analogue, nor will it act in copolymerizing PO and CO_2. However, it will ring open PO to generate a chloroalkoxide. Because of this, we have studied the ring opening of *S*-PO and *R*-PO by the compound containing Jacobsen's chiral ligand bound to aluminum, (*R*,*R*)-*N*,*N*′-bis(3,5-di-*tert*-butyl-salicylidene)-1,2-cyclohexenediaminoaluminum chloride, (*R*,*R*-salen)AlCl.[109−111] The ring opening of *R*-PO yields a 2.3:1 mixture of (*R*,*R*-salen)-AlOC(*R*)HMeCH$_2$Cl and (*R*,*R*-salen)AlOCH$_2$CHMeCl. The latter compound exists as a mixture of *R*- and *S*-OCH$_2$CHMeCl isomers in the ratio of 2:1, respectively. The related reaction between *S*-PO and (*R*,*R*-salen)AlCl gave (*R*,*R*-salen)AlOC(*S*)-HMeCH$_2$Cl, and apparently only (*R*,*R*-salen)AlOCH$_2$C(*R*)-HMeCl in the ratio of 5:1. The ^{1}H NMR spectrum revealing the products derived from the ring opening of *R*-PO is shown in Figure 4, and other related spectra are given in Figure S5 in the Supporting Information.

The compound (*R*,*R*-salen)AlOC(*S*)HMeCH$_2$Cl was crystallographically characterized (Figure S6), and the aluminum was shown to be in a square pyramidal coordination environment with the β-chloroalkoxy ligand of *S* stereo configuration in the apical site. The molecular structure is unexceptional,[110,111] and details will be reported fully elsewhere. The formation of (*R*,*R*-salen)AlOCH$_2$C(*S*)HMeCl was confirmed by its independent synthesis from the reaction between (*R*,*R*-salen)AlMe and the chiral alcohol HOCH$_2$C(*S*)HMeCl as described in the Experimental Section in the Supporting Information. This compound was also crystallographically characterized and is shown in Figure S6 in the Supporting Information.

These studies of (*R*,*R*-salen)AlCl clearly parallel those of the porphyrin analogue in revealing the ring opening of PO occurs by competitive pathways where the methylene carbon is preferentially but not exclusively attacked in the ring-opening event. Moreover, the use of the chiral salen aluminum template shows that there is a preference in the ring opening of *R*-PO for the formation of the OCH$_2$C(*R*)HMeCl alkoxide when attack occurs at the methine carbon. The ring opening of *S*-PO by attack at the methine carbon also preferentially forms the OCH$_2$C(*R*)-HMeCl ligand. The preferential formation of the β-chloroalkoxy ligand with the *R*-stereocenter is clearly a result of the *R*,*R*-salen template, but its formation in the reaction with *R*-PO occurs with retention of stereochemistry at the methine carbon, whereas for *S*-PO it is formed by inversion (Scheme 2).

Scheme 2. The Stereochemistry in the PO Ring-Opening Event Involving Attack at Methine Carbons by (*R*,*R*-Salen)AlCl



The Carbon Dioxide Insertion Reaction. Carbon dioxide reacts reversibly with (TPP)AlOR compounds to give (TPP)-

(109) Brandes, B. D.; Jacobsen, E. N. *Synlett* **2001**, 1013−1015.
(110) Jacobsen, E. N. *Acc. Chem. Res.* **2000**, *33*, 421−431.
(111) Hansen, K. B.; Leighton, J. L.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1996**, *118*, 10924−10925.

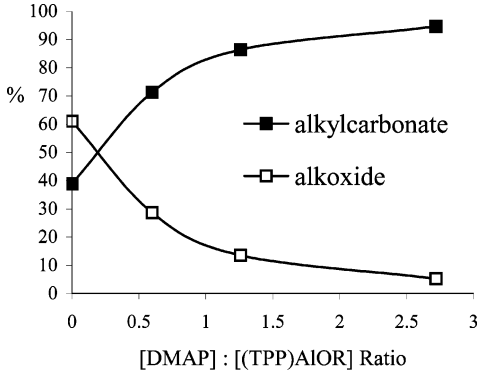


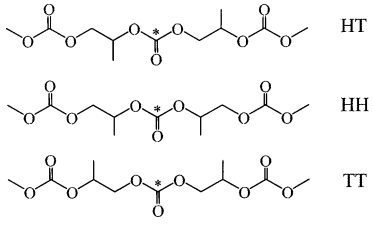
Figure 5. The percentages of alkyl carbonate and alkoxide versus the [DMAP]:[(TPP)AlO$(CH_2)_9CH_3$] ratio for the $^{13}CO_2$ insertion with (TPP)-AlO$(CH_2)_9CH_3$.

AlO_2COR compounds.[104,112] This equilibrium is both temperature and CO_2 pressure dependent, that is, dependent of $[CO_2]$ in solution, and when the CO_2 atmosphere is removed only the alkoxide is recovered. In our studies, we have examined the equilibrium shown in **1** in $CDCl_3$ at 25 °C under 4 atm of $^{13}CO_2$ by ^1H and ^{13}C NMR spectroscopy. The concentration of aluminum complex was 11 mM.

$$(TPP)Al{-}O(CH_2)_9CH_3 + {}^{13}CO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (TPP)Al{-}O_2{}^{13}CO(CH_2)_9CH_3 \quad (1)$$

At 25 °C, under these conditions, the equilibrium favors the alkoxide. Upon the introduction of DMAP, however, the equilibrium shown in **1** is shifted markedly to the right, as shown in Figure 5. At a high concentration of DMAP (5 equiv), the alkoxide was completely converted to carbonate. When CO_2 pressure was released under N_2 atmosphere, ~95% of the Al complexes existed as carbonate in solution. However, if the solvent and CO_2 pressure were removed and the products were dried under vacuum, the alkoxide was recovered. We note in this system that CO_2 insertion/deinsertion is kinetically rapid with respect to the ring opening of PO.

Polymer Microstructure of Polypropylene Carbonate, PPC. We have previously examined the polymer microstructure of PPC formed in the zinc glutarate-catalyzed copolymerization of PO and CO_2 by use of proton decoupled ^{13}C NMR ($^{13}C\{^1H\}$) spectroscopy.[91] Specifically, we used *rac*-PO, *S*-PO, and a 50:50 mixture of *rac* + *S*-PO, and we were thereby able to make assignments for the stereosequences *i* and *s* for the TT, HT, and HH carbonate junctions as defined below.



Zinc glutarate was thus shown to be stereoselective as a catalyst in forming HH and TT junctions. In an earlier publication, we assumed that the ring-opening event at the methine carbon occurred by backside attack, that is, with inversion, and that the observed carbonate signals corresponded to syndiotactic junctions for both HH and TT when *S*-PO was used. We have now prepared a polyether carbonate with a HH carbonate junction of both random stereosequence and one where the HH carbonate is isotactic (Figure 6). From this, we conclude that the syndiotactic HH carbonate carbon-13 signal is upfield in PPC, and this is consistent with the previously suggested assignment for the PPC derived from *S*-PO/CO_2 and a zinc glutarate catalyst.

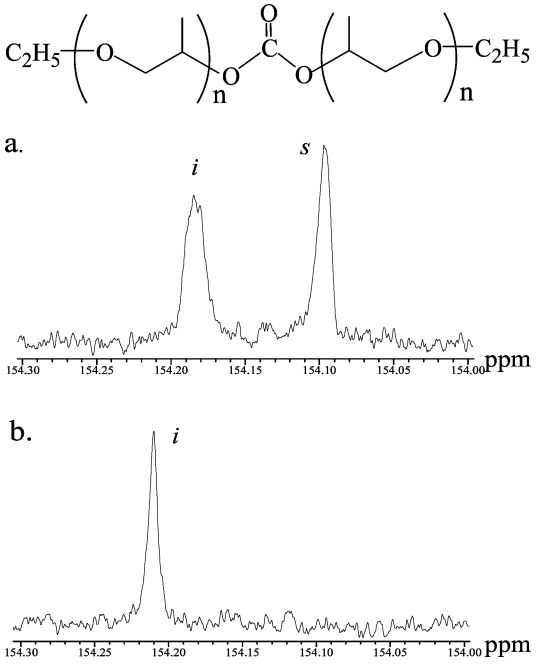


Figure 6. $^{13}C\{^1H\}$ (150 MHz, $CDCl_3$) NMR spectra of the carbonate carbon region of regioregular oligoether carbonate compounds ($n \approx 10$), having a HH carbonate junction. Carbonate compounds in (a) have random stereosequences, while those in (b) have all isotactic sequences.

We have now examined the carbonate ^{13}C signals of PPC prepared by (TPP)AlCl/DMAP and (*R*,*R*-salen)CrCl catalyst systems. As shown in Figure 7, the regio- and stereo-sequences differ quite significantly with the catalyst system employed. The PPC derived from (TPP)AlCl/DMAP has fewer TT and HH junctions, and Coates recently reported that (salen) cobalt(III) acetate produces approximately 80% HT regiosequences, while (BDI) zinc acetate produces almost random TT:HT:HH ≈ 1:2:1.[55,58]

We can reasonably assume that HT carbonate junctions normally retain the stereochemistry at the methine carbon as a consequence of the preferential ring opening at the methylene carbon. However, when ring opening at the methine carbon is relatively competitive, HT junctions may also be formed with either double inversion (backside attack) or with randomization of stereochemistry as shown in Scheme 3.

The maximum information concerning the stereochemistry of the ring-opening event can be gleaned from an examination of the HH carbonate ^{13}C signals of PPC derived from enantiomerically pure PO. As shown in Figure 8, the (TPP)AlCl/DMAP system yields PPC derived from *S*-PO with both *i* and *s* HH (and TT) junctions, although the syndiotactic junctions are preferred by approximately a 2:1 ratio. Rather interestingly, the PPC derived from *S*-PO and (*R*,*R*-salen)CrCl has both *i* and *s* HH (and TT) carbonate junctions, but the ratio is now in the inverse order, $i > s$ (Figure 8).

(112) Takeda, N.; Inoue, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3564−3567.

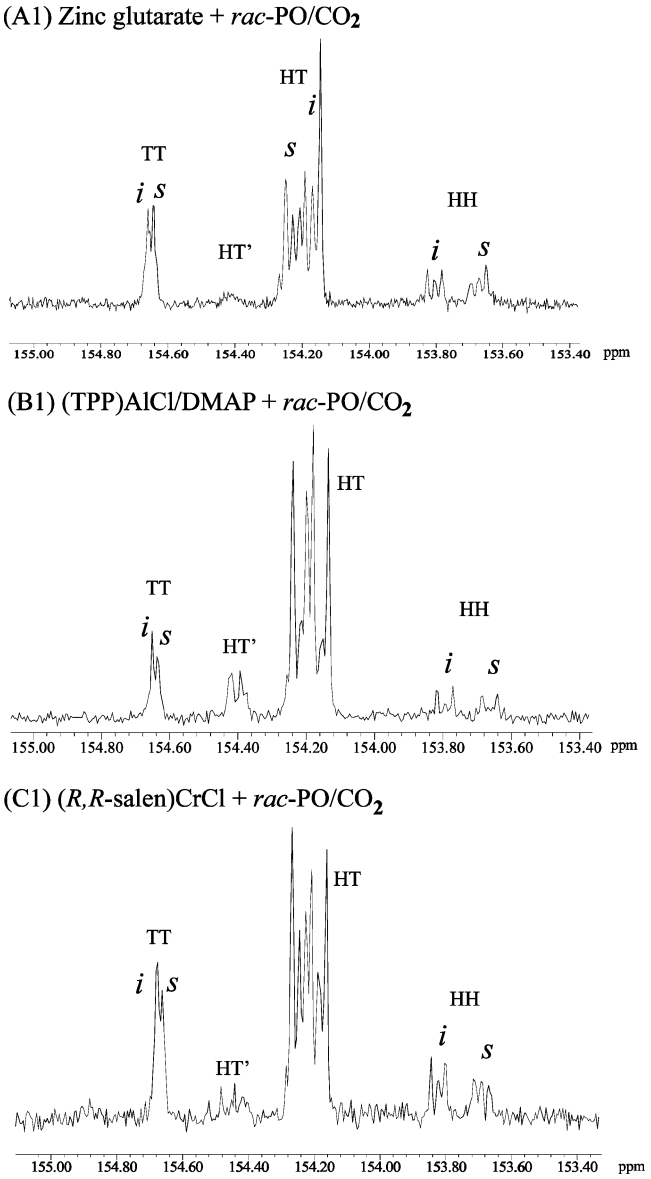
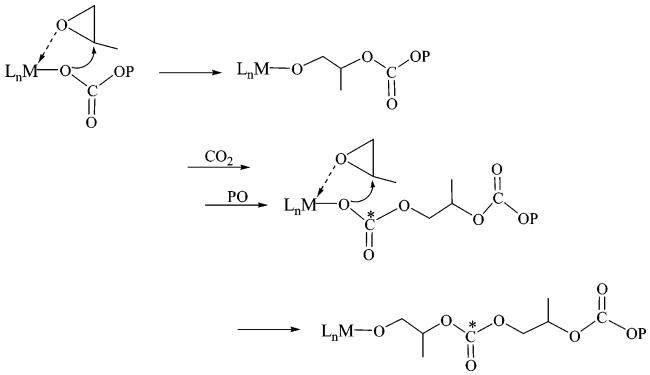


Figure 7. $^{13}C\{^1H\}$ (150 MHz, $CDCl_3$) NMR spectra of the carbonate carbon region of PPC made from (A1) zinc glutarate and *rac*-PO, (B1) (TPP)AlCl/DMAP and *rac*-PO, and (C1) (*R*,*R*-salen)CrCl and *rac*-PO. (HH′ and HT′ are ether-rich carbonate signals.)

When *R*-PO is employed with the chiral salen CrCl catalyst, the ratio of *i*:*s* junctions again changes and is now in favor of *s*. From this, we can conclude that the salenCr catalyst prefers to open the PO molecule to generate the primary alkoxide of *S* stereochemistry by attack at the methine carbon (Scheme 4).

A Proposed Mechanism for the (TPP)AlCl/DMAP Copolymerization of PO and CO_2. Our studies have shown that the ring opening of PO by (TPP)AlX compounds occurs by competitive attack on the methylene and methine carbons. When $X = O(CH_2)_9CH_3$, the reaction is first order in [Al], giving predominately the secondary alkoxide by attack at the methylene carbon. When $X = O_2C(CH_2)_6CH_3$, the regiochemistry of ring opening is less selective, and the ring opening is notably slower than that for $X = O(CH_2)_9CH_3$. However, upon addition of DMAP, we note that the rate of ring opening of PO is accelerated greatly, and now the carboxylate group is much more active in ring-opening PO relative to the alkoxide. This is particularly important as (TPP)AlCl alone in the presence of

Scheme 3. The Chain Growing Pathway Showing HT Carbonate Junction (*) Formation Involving Double Attack at Methine Carbons in the PO/CO_2 Copolymerization (No Mechanistic Information Is Implied by This Scheme, Which Merely Outlines the Regiochemical Consequence of Attack on the Methine Carbon)



PO and CO_2 yields PPO in preference to PPC (Table 1). Furthermore, we note that CO_2 insertion into the Al−OR bond is promoted by the addition of DMAP. Both of these factors assist in producing a regular alternating copolymer and serve to minimize the number of ether-rich linkages as denoted by HT′ and HH′ signals in the carbonate $^{13}C\{^1H\}$ spectra (Figure 7). The CO_2 incorporation into the polymer formed in the PO/CO_2 copolymerization with $(TPP)AlO(CH_2)_9CH_3$ can be increased from 0.20 to 0.50 (molar fraction determined by ^1H NMR) by the addition of 1 equiv of DMAP, yielding a perfectly alternating copolymer as shown by mass spectrometry (Figure 9).

We propose that the role of DMAP is to labilize the ligand trans to it, either the alkoxide or the alkyl carbonate. The fact that HH and TT junctions can be formed with retention of stereochemistry clearly implies that an incipient carbonium ion is captured by a neighboring nucleophile. The PO and the alkyl carbonate must be cis to one another. We pictorially represent this DMAP-promoted PO interchange associative process by the sequence shown in Scheme 5. The PO is activated by coordination to the aluminum center as the $Al-O_2COR$ bond is weakened by the trans-effect of the DMAP ligand. Which oxygen of the carboxylate group is involved in attacking the PO carbon (Schemes 3 and 4) is unknown.

We can now envisage the (TPP)AlX-catalyzed reactions on the basis of the equilibria and cycles shown in Scheme 6. In the absence of DMAP, the ring opening of PO by alkoxide dominates even in the presence of CO_2, such that very little carbonate is incorporated into what is essentially poly(propylene oxide) (Table 1). The addition of DMAP serves to (1) increase the equilibrium concentration of the aluminum alkyl carbonate at the expense of the aluminum alkoxide, and (2) vastly increase the rate of ring-opening PO by the alkyl carbonate ligand (relative to the alkoxide), such that alternating copolymerization of PO and CO_2 to yield PPC now dominates. As shown in Figures 7 and 8, there are few ether linkages in the PPC, and this can be contrasted with the carbonate incorporation into PPO in the absence of DMAP as shown in Table 1 and the spectra (Figure S7) presented in the Supporting Information.

Concluding Remarks

The observation that the ring opening of PO by $(TPP)AlO(CH_2)_9CH_3$ is first order in aluminum complex supports the

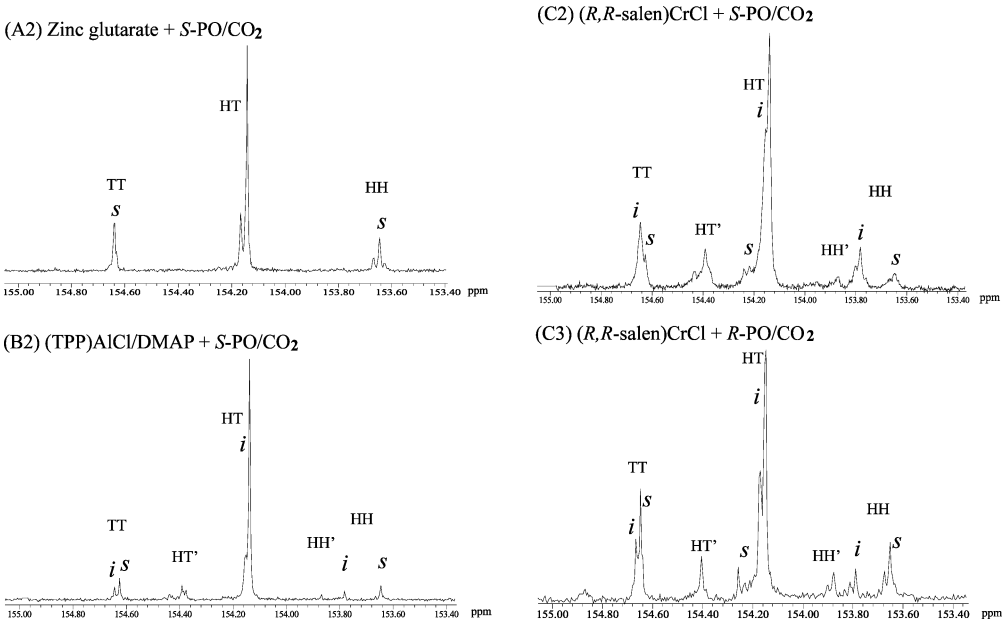
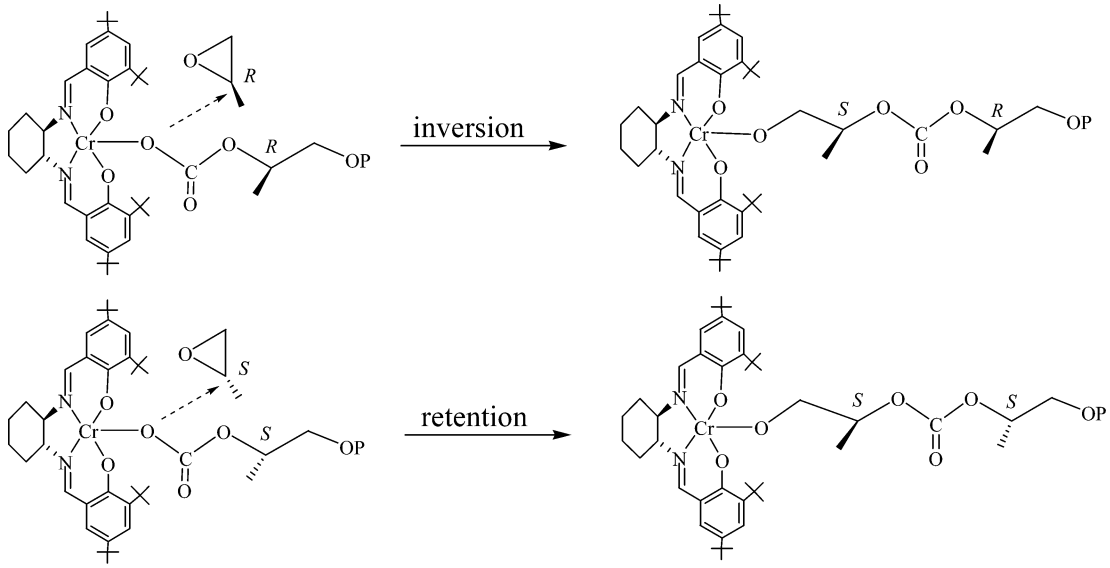


Figure 8. $^{13}C\{^1H\}$ (150 MHz, $CDCl_3$) NMR spectra of the carbonate carbon region of PPCs made from (A2) zinc glutarate and *S*-PO, (B2) (TPP)AlCl/DMAP and *S*-PO, (C2) (*R*,*R*-salen)CrCl and *S*-PO, and (C3) (*R*,*R*-salen)CrCl and *R*-PO. (HH′ and HT′ are ether-rich carbonate signals.)

Scheme 4. The Preferential Stereochemistry Involved in the Formation of HH Carbonate Junctions during the Formation of PPC by the Catalyst Derived from (*R*,*R*-Salen)CrCl



earlier study on the kinetics of PPO formation employing (TPP)-AlCl as initiator. These workers determined that the rate of PPO formation was first order in [Al] and first order in [PO].[113−116] Others have shown that (TPP)AlCl immobilized on a support will also ring open PO to give PPO.[117] The mechanism is thus unequivocally mononuclear and different from that described by Jacobsen for (*R*,*R*-salen)CrN_3.[110,111,118]

We have shown that added DMAP serves to accelerate two principal reactions. (1) It promotes the insertion of CO_2 into the Al-alkoxide, and (2) it labilizes the carboxylate ligand, and by inference the alkyl carbonate ligand, toward ring opening of PO. In the latter reaction, it is evident the DMAP binds more strongly to (TPP)AlO_2CX species (X = R or OR) than it does to the parent alkoxide complex. Thus, whereas in the absence of added DMAP the (TPP)Al system is only effective in the homopolymerization of PO, when DMAP is added, alternating copolymerization of PO and CO_2 is kinetically favored.

The stereochemical studies of the ring opening of PO in these systems reveal that attack occurs at both the methine and the methylene carbons, and furthermore when attack occurs at the methine carbon the ring-opening event can occur with retention or inversion of stereochemistry.[119,120] Collectively, these findings

(113) Yoo, Y.; McGrath, J. E. *Pollimo* **1994**, *18*, 892−894.
(114) Yoo, Y.; McGrath, J. E. *Pollimo* **1994**, *18*, 1063−1070.
(115) Nuytens, F.; Lopitaux, G.; Faven, C.; Coqueret, X. *Macromol. Symp.* **2000**, *153*, 17−25.
(116) Lopitaux, G.; Ricart, G.; Faven, C.; Coqueret, X. *Macromol. Chem. Phys.* **2002**, *203*, 2560−2569.
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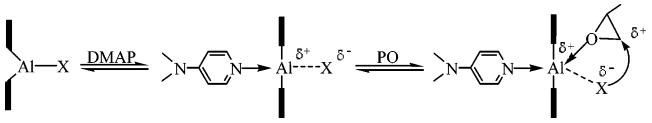
(118) Konsler, R. G.; Karl, J.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1998**, *120*, 10780−10781.
(119) March, J. *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 4th ed.; Wiley: New York, 1992.
(120) Parker, R. E.; Isaacs, N. S. *Chem. Rev.* **1959**, *59*, 737−799.

Scheme 5. Proposed Interchange Associative Pathway for PO Ring Opening by (TPP)AlX/DMAP



serve to support a reaction pathway wherein PO and the growing chain are on the same side of the porphyrin ring. The coordination of DMAP in the trans position serves to labilize the Al−OR or AlO_2CX (X = R or OR) bonds toward dissociation and uptake of PO in an interchange substitution process. Upon coordination to the electrophilic aluminum center, the PO is activated toward carbonium ion-like behavior, and the attack by the nucleophilic growing chain leads to its enchainment in the polymerization reaction in a relatively nonregio- and nonstereoselective manner.

We propose that the use of added ligands, such as 1-methylimidazole and Br^- in related reactions, parallels the effects noted here for DMAP, but to a different degree. Many parallels appear to exist with the findings of Darensbourg in the copolymerization of CHO/CO_2 and PO/CO_2 at the salen chromium(III) center,[54,56] but contrast with the bimetallic mechanism of Jacobsen for ring opening of cyclopentene oxide[110,111,118] and that of Coates for the bimetallic zinc-catalyzed copolymerization of CHO and CO_2.[72] Clearly, more needs to be known about the details of these reaction profiles. An understanding of the factors controlling the reactions shown in Scheme 6 should allow for the development of highly active systems for the catalytic production of PPC and related polycarbonates.

Further work is in progress.

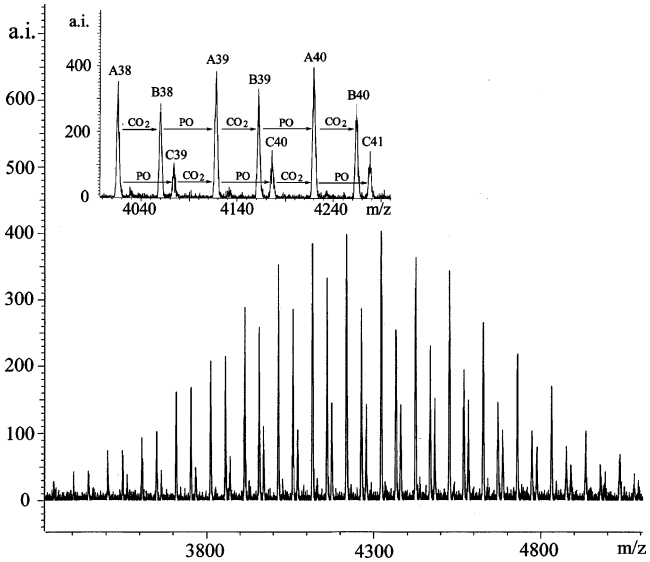
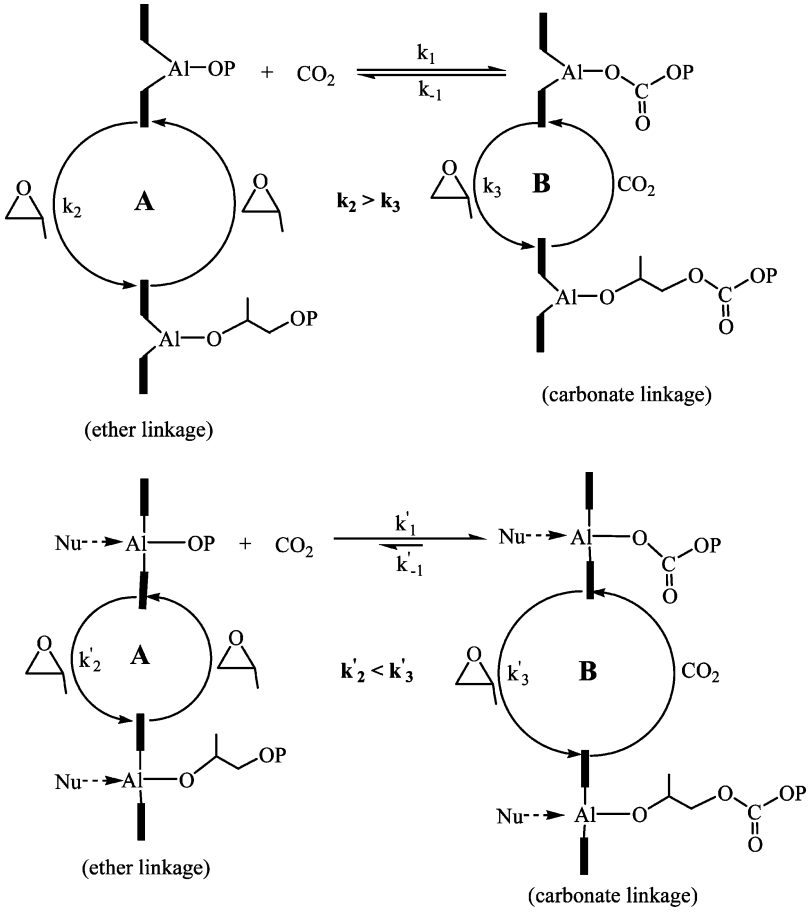


Figure 9. MALDI-TOF mass spectrum of PPC prepared with the (TPP)-$AlO(CH_2)_9CH_3$/DMAP catalyst system. An = H−[$(C_3H_6O)_n$-*alt*-$(CO_2)_{n-1}$]−$O(CH_2)_9CH_3{\cdot}Na^+$; Bn = H−[$(C_3H_6O)_n$-*alt*-$(CO_2)_n$]−$O(CH_2)_9CH_3{\cdot}Na^+$; Cn = H−[$(C_3H_6O)_n$-*alt*-$(CO_2)_{n-2}$]−$O(CH_2)_9CH_3{\cdot}Na^+$. Peaks (*m*/*z*): A38 (4014), A39 (4116), A40 (4218), B38 (4058), B39 (4160), B40 (4262), C39 (4072), C40 (4174), C41 (4276).

Scheme 6. Proposed Mechanism for PO/CO_2 Copolymerization by (TPP)AlX Systems, Where Nu Represents the Added Lewis Base Promoter



Acknowledgment. We thank the Department of Energy, Office of Basic Sciences, Chemistry Division for financial support of this work, Drs. J. C. Gallucci and N. J. Patmore at The Ohio State University for X-ray experiments, and Professor C. M. Hadad at The Ohio State University and Dr. E. M. Dexheimer at BASF for valuable discussions. This paper is dedicated to Ian P. Rothwell in memorium.

Supporting Information Available: Experimental Section. Graphs pertaining to the kinetics for ring opening of PO by varying concentrations of (TPP)AlO(CH_2)$_9$$CH_3$. Kinetic plots of I_0/I_t versus reaction time for ring opening of PO by (TPP)-AlX. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of (TPP)AlX/DMAP mixtures at 25 and −50 °C. Kinetic plots of $-\ln(I_t/I_0)$ versus reaction time for ring opening of PO by (TPP)AlX/DMAP. ^{1}H NMR spectra revealing the products in the reactions between (*R*,*R*-salen)AlCl and *S* (and *R*)-POs. ORTEP drawings of the (*R*,*R*-salen)AlOC(*S*)HMeCH_2Cl and (*R*,*R*-salen)AlOCH_2C(*S*)-HMeCl molecules. ^{1}H and ^{13}C NMR spectra of the polymer prepared in the PO/CO_2 polymerization reaction catalyzed by (TPP)AlCl alone. This material is available free of charge via the Internet at http://pubs.acs.org.

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