Macromolecules **2001,** *34,* 8851−8857

A Comparative Study in the Ring-Opening Polymerization of Lactides and Propylene Oxide

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Received July 26, 2001; Revised Manuscript Received October 8, 2001

ABSTRACT: The aluminum chloride complexes $[(O{\sim\sim}O)AlCl]_2$, **I**, $[(O{\sim}CHMe{\sim}O)AlCl]_2$, **II**, and TPPAlCl, **III**, where O∼∼O = 5,5′,6,6′-tetramethyl-3,3′-di-*tert*-butyl-1,1′-biphenoxide, O∼CHMe∼O = 2,2′-ethylidenebis-4,6-di-*tert*-butylphenoxide, and TPP = tetraphenyl porphyrin, are shown to be inactive in initiating the ring-opening polymerization, ROP, of lactides, LA (*L* and *rac*). Upon addition of propylene oxide, PO, they lead to block oligomers/polymers of the form $(PPO)_n(PLA)_m$. The Union Carbide catalyst system known as calcium amide−alkoxide, $[Ca(NH_2)(O^iPr)]$, is active in ROP of lactides at room temperature as well as PO. Block copolymers of PO and LA can be formed by the initial ROP of PO followed by the addition of LA but not from reactions involving the reverse order of the addition of PO/LA. The alkoxide aluminum compounds $[(O{\sim}CHMe{\sim}O)Al(\mu\text{-}O^iPr)]_2$, **IV**, and TPPAlOMe, **V**, are active in PO polymerization at room temperature but will effect lactide ROP only upon heating to 80 °C. The stereoselectivity exhibited in ROP of PO by **III** and **V** and the Union Carbide catalyst system is not observed for ROP of *rac*-LA. These results are discussed in terms of the intimate mechanism of ring opening of PO and lactides, where it is proposed that coordinate catalysts differ in their operation. Single-site catalysis is favored for lactides but coordinate base catalysis for ROP of PO requires the cooperation of two metal sites. Copolymers of PO and LA are thus prepared as block copolymers by consecutive reactions. The copolymers have been characterized by ^1H, ^{13}C NMR spectroscopy, by mass spectrometry (GPC/ESI/MS and LD/FTMS), and by gel permeation chromatography.

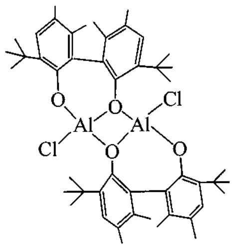
Introduction

One of the major advances in polymer synthesis has been the development of single-site coordination catalysts for the polymerization of α-olefins[1] and their copolymerization with carbon monoxide[2] and in ring-opening metathesis polymerization.[3] Control of polymer microstructure and molecular weight in the area of polyoxygenates is less well-developed but is receiving considerable current attention as exemplified by the recent elegant work from the Coates[4] group in the stereoselective polymerization of lactides, LA, by β-diiminate zinc alkoxide complexes. In our work, we have previously examined the ring-opening polymerization, ROP, of lactides at single-site Mg and Zn alkoxide complexes[5] supported by trispyrazolyl or trisindazolylborate ligands and noted that though epoxides could coordinate they were inert to ring opening. However, at Al^{3+} centers we did observe ROP of propylene oxide, PO, and formation of regioirregular polymers with HH junctions that were formed by inversion of stereochemistry, that is, by backside attack.[6] In comparing the ROP of lactides and PO, we noted that the catalyst systems that were good for one were not good for the other and this prompted us to undertake the work we now disclose. In particular, we investigate the potential use of coordinate catalysts for the copolymerization of PO and LA.

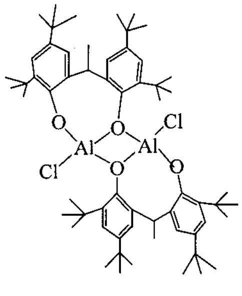
We are not aware of any reports of copolymers involving PO and LA,[7a] though block copolymers of poly(ethylene oxide), PEO, and PLA have been prepared and find use in the biomedical field.[7b−d]

Results and Discussion

The aluminum chloride complexes $[(O{\sim\sim}O)AlCl]_2$, **I**,[6] $[(O{\sim}CHMe{\sim}O)AlCl]_2$, **II**,[6] and TPPAlCl, **III**,[8] where O∼∼O = 5,5′,6,6′-tetramethyl-3,3′-di-*tert*-butyl-1,1′-biphenoxide, O∼CHMe∼O = 2,2′-ethylidenebis-4,6-di-*tert*-



I



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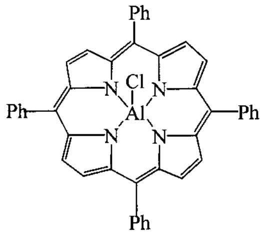
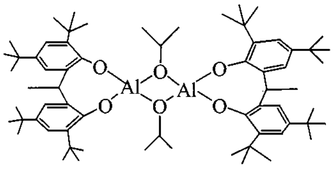


III



IV

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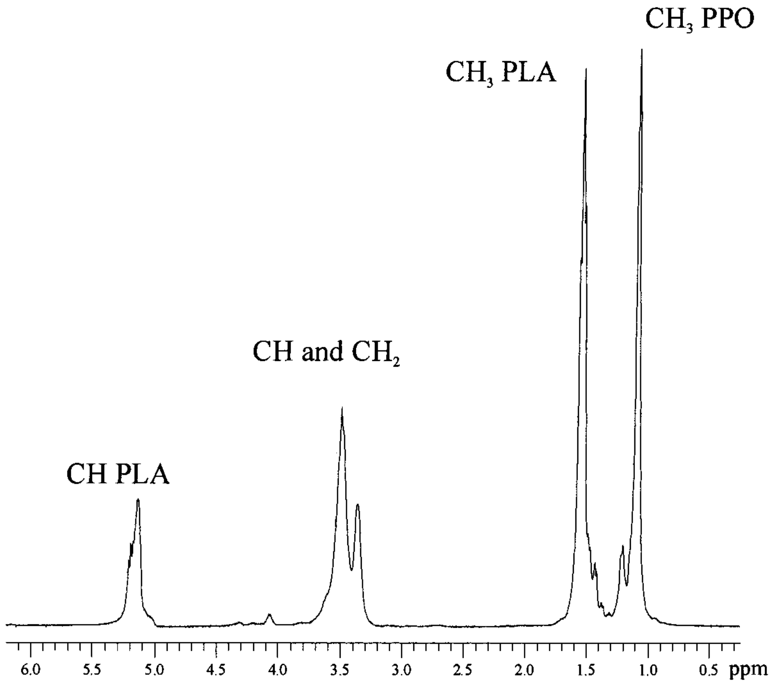
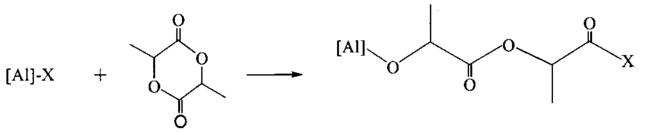


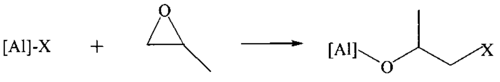
Figure 1. ^{1}H NMR (250 MHz) spectrum of the copolymer obtained from the polymerization of *rac*-LA and *rac*-PO with the initiator TPPAlCl, **III**, in $CDCl_3$.

butylphenoxide, and TPP = tetraphenyl porphyrin, which are known to ring open PO, were totally inactive toward lactides. The biphenoxide complex **I** and the biphenoxide complex **II** are bridged in the solid state and in benzene or toluene solutions as judged by ^{1}H NMR spectroscopy. The bridges are cleaved upon the addition of THF and PO and the active species are believed to be monomeric and akin to the structure seen for (O∼∼CHMe∼∼O)AlCl(THF).[6]

However, LA is apparently not a sufficiently good donor to cleave the bridged structure and no NMR evidence is observed for an adduct of the type (O∼∼CHMe∼∼O)AlCl(LA). However, this alone would not be sufficient to induce ROP if the initiation step, wherein an Al−Cl bond is transformed to AlOCHMeC(O)OCHMeC(O)Cl, is unfavorable. The available evidence indicates that this does not occur. The ring-opening event as represented by eq 1 presumably occurs for X = OR but not for X = Cl, whereas the opposite is true for ring opening of PO (eq 2).



Equation 1.



Equation 2.

From what we saw before, the ROP of LA can readily proceed via a cis-migratory mechanism but for an epoxide this is not the case, though the intimate details of the ROP of epoxides by compounds **I** and **II** are not known.

If, as implied in eq 2, the ROP of PO by an [Al]−Cl species produces a Al−OP growing chain, and as previously documented, then, with the initiation of PO polymerization, a lactide molecule might be expected to enter into the polymerization process as indicated in eq 1. Thereafter, ring opening of either monomers, PO or LA, might occur, giving a random copolymer or a block copolymer, depending upon the relative rates of ring opening and the availability of the monomers.

When LA was dissolved in methylene chloride with PO present, the aluminum chloride complexes **I**, **II**, and **III** did form polymers or oligomers but only in relatively poor yields at room temperature. An examination of the NMR spectra of these polymers/oligomers indicated that these were block polymers. The ^{1}H NMR of the *rac*-LA/PO copolymer formed with TPPAlCl initiator is shown in Figure 1 and the $^{13}C\{H\}$ NMR spectrum is shown in Figure 2. What is significant from these NMR data is that the stereochemistry of the $(PPO)_n$ section is identical to that seen in the reactions between **I**, **II**, and **III** with PO, namely **I** and **II** give regioirregular PPO while **III** gives regioregular $(HT)_n$ with a stereopreference for *ii* triads. The examination of the methine carbon and proton signals of the PLA section formed from *rac*-LA show no stereoselectivity: the tetrad sequence *iii*, *isi*, *iis*, *sii*, and *sis* in the ratio 3:2:1:1:1, respectively.[9]

The low yields of polymers in these reactions can be traced, in part, to the fact that the respective alkoxide derivates of **I**, **II**, and **III** such as [(O∼CHMe∼O)Al(μ-O^{i}Pr)]$_2$, **IV**, and TPPAlOMe, **V**, are very slow in their polymerization of LA, even at 80 °C in benzene. The compound **IV** is known to be dimeric in the solid state and in benzene having isopropoxide bridges. We propose that the μ-OR group is inactive in ROP of LA and that LA is again a poor donor when compared to PO. In the case of the monomeric TPPAlOMe,[8] compound **V**, the cis-migratory ring-opening mechanism for lactide polymerization is sterically not favored at the five-coordinate N_4AlO center. The reaction that leads to PLA at higher temperatures could involve a bimolecular path, as is believed to occur in ROP of PO, but if this is so, then it is noteworthy that it occurs without any stereoselectiv-

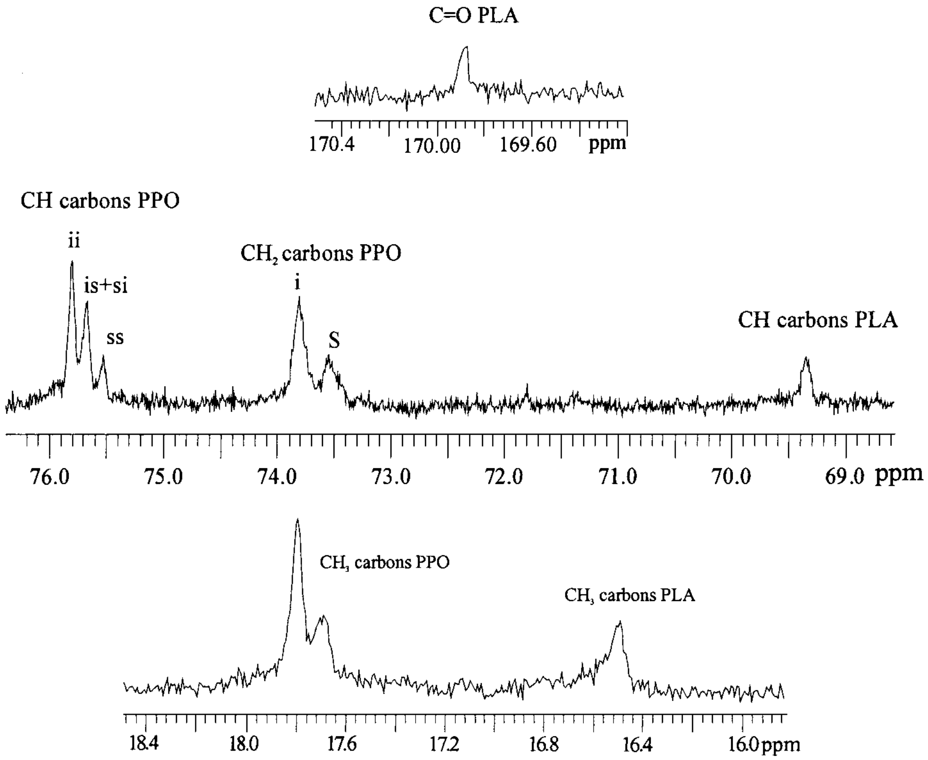


Figure 2. ^{13}C NMR (400 MHz) spectrum of the copolymer obtained from the polymerization of *rac*-LA and *rac*-PO with the initiator TPPAlCl, **III**, in C_6D_6.

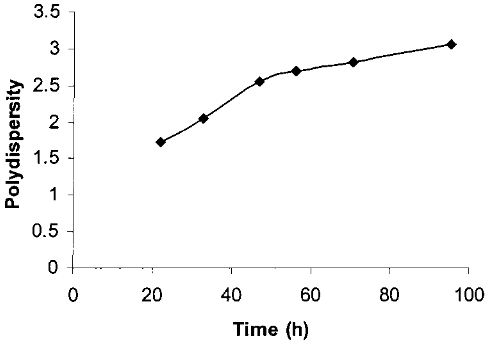


Figure 3. Plot of polydispersity versus time for the polymerization of *rac*-LA with the Union Carbide catalyst system.

ity despite the fact that a chiral alkoxy headgroup TPPAlO*CHMe−OP is present in both PO and LA polymerization.

The block copolymer formation also can be traced to the fact that once lactide polymerization occurs the ROP of PO stops. The activity of the Al−OCHMeX group is therefore greatly dependent on X: the polyether chain is more reactive than the polyester chain.

With the isopropoxide compound **IV**, at 80 °C in benzene, polymerization of *L*-LA and *rac*-LA gives poly(*L*-LA) and amorphous (random) poly(*rac*-LA), respectively. Sequential addition of PO, at room temperature, and LA, at 80 °C, allowed the formation of PPO/PLA copolymers. The same results were observed for TPPAl-OMe, **V**. When the order of polymerization is reversed by initiation with LA and then addition of PO, block oligomers are also formed with these [Al]−OR initiators but the polymerization is not living and is very inefficient. The polyester chain clearly impedes the ROP of PO.

In our studies of the Union Carbide calcium amide−alkoxide catalyst system, reactions were carried in

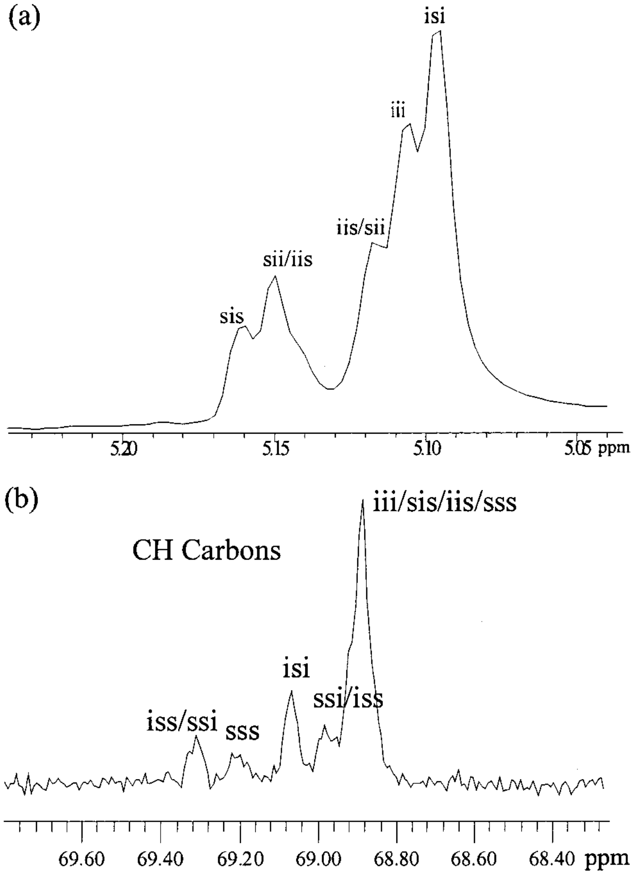


Figure 4. (a) ^{1}H (250 MHz) and (b) ^{13}C (400 MHz) NMR spectra of PLA methine resonances with selective decoupling of PLA methyl resonances from the polymer obtained from polymerization of *rac*-LA with the calcium amide−alkoxide catalyst system in $CDCl_3$.

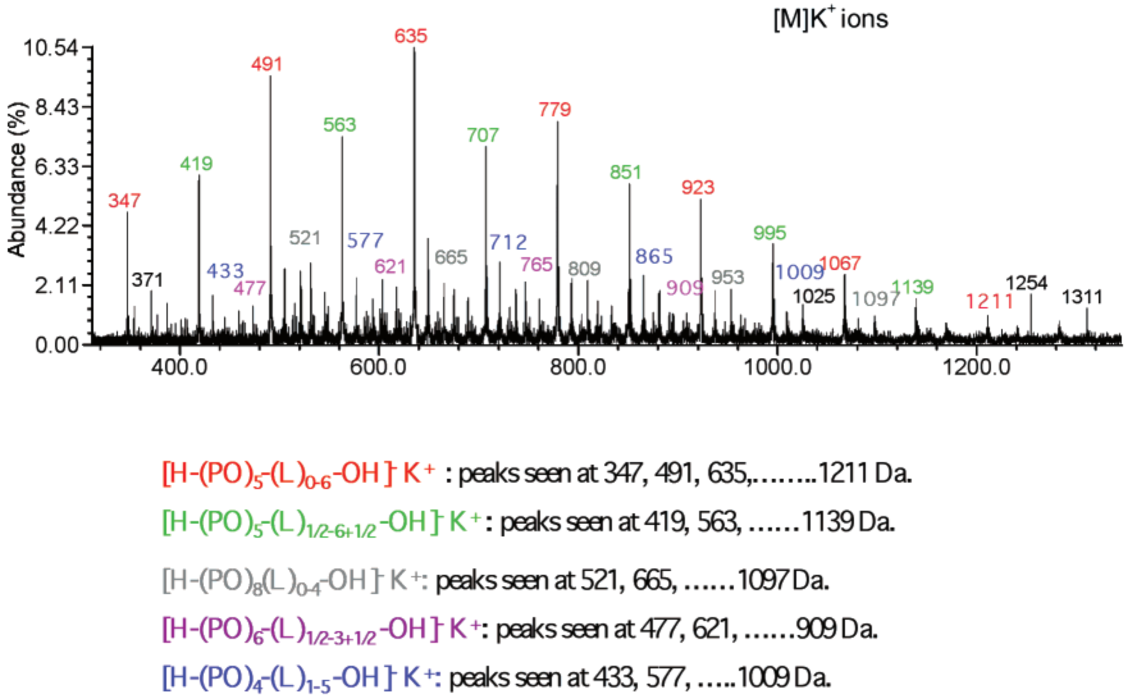


Figure 5. Laser desorption Fourier transform spectrum of the copolymer formed in the reaction with [(O~CHMe~O)AlCl]$_2$, **II**.

benzene or with LA dissolved in PO at room temperature. When LA is present, we observed that selective ROP of LA occurs with no incorporation of PO. Indeed, polymerization of LA deactivates the catalyst system toward PO. The polymerization of LA in benzene has been followed with time by gel permeation chromatography, GPC, and by ^{1}H NMR spectroscopy. With increasing time, the PDI increases from 1 to 3.1 toward 99% conversion, as seen in Figure 3, and for *rac*-LA we observe the growth of an atactic polymer with stereosequences associated with the eight possible tetrads of PLA. This is indicative of extensive trans-esterification. See Figure 4. With *L*-lactide, only poly-*L*-lactide is formed, which indicates that the Union Carbide catalyst system is active in trans-esterification but not in epimerization. (See Supporting Information.)

From elemental analysis of a sample of the Union Carbide catalyst, we estimate an empirical formula to have 13 calcium atoms. Then, from a plot of Mn versus conversion we can estimate the number of active Ca sites to be roughly 1 per formula weight (i.e., 1/13) in the polymerization of LA. (See Supporting Information.)

We attempted to carry out a similar experiment to determine the number of active Ca atoms per formula weight in the polymerization of PO but we were thwarted by the fact that, under similar conditions, the PPO formed has a much higher molecular weight and is very viscous. Also, by following the disappearance of monomer by ^{1}H NMR, we know that the system is much more active in ROP of PO than it is for LA. Under comparable conditions, 60% conversion of PO is achieved within 5 h whereas 60% LA conversion requires 22 h. This leads us to propose that the number of active sites are less for ROP of PO relative to those for LA, though the former are more active in the polymerization of PO than are the total number of active sites for ROP of LA.

Mass Spectral Characterization. Given that the NMR data provide no evidence for the formation of copolymers other than revealing the signals associated with PLA and PPO, we have had to rely on mass spectral data to support the existence of $(PPO)_n(PLA)_m$ units. Consequently, we have used the combined techniques of laser desorption/Fourier transform mass spectrometry (LD/FTMS) and gel permeation chromatography/electrospray/Fourier transform mass spectrometry (GPC/ESI/FTMS) to analyze the oligomers from LA/PO/ [(O~CHMe~O)AlCl]$_2$. The LD data are shown in Figure 5, where all the ions correspond to monopotassiated ion species. Different distributions are observed in the MS spectrum. Some of them show half lactide units, the presence of which could be a consequence of the ionization technique used,[10] as it is known that carbon dioxide laser desorption ruptures the polyester backbone very easily. Furthermore, we do not observe C−Cl-terminated groups. Alternatively, the presence of a half lactide unit can be attributed to intermolecular trans-esterification reactions as was noted by NMR spectroscopy in the polymerization of *rac*-LA by the Union Carbide catalyst system. As shown in Figure 5, the most abundant distribution corresponds to $[H-(PO)_5-(L)_n-OH]\ K^+$, $n = 0-6$, as seen in peaks at $m/z = 347, 495, ..., 1211$. Other distributions are seen at $m/z = 521, 665, ..., 1097$, corresponding to $[H-(PO)_8-(L)_n-OH]\ K^+$, $n = 0-4$, and at $m/z = 433, 577, ..., 1009$, corresponding to $[H-(PO)_4-(L)_n-OH]\ K^+$, $n = 1-5$. The formation of OH-terminated species was described in our previous work.[6] As noted above, LD appears to induce significant fragmentation and consequently only small oligomers are seen when using this technique, while GPC/ESI/FTMS gave distributions corresponding to higher molecular weights. From the GPC trace, the molecular weight distribution was obtained, with $M_n = 1080$ Da, $M_w = 1360$ Da, $M_z = 1680$ Da, and $M_p = 1280$ Da with a polydispersity index for these systems of 1.3. In the ESI spectrum, distributions corresponding to Cl-terminated species were seen. (See Supporting Information.) All the ions shown are monosodiated ions. One of the most abundant distributions corresponds to the species $[H-(PO)_n-(lactide)_3-Cl]\ Na^+$, where $n = 12-17$, which is seen at $m/z = 1188, 1246, ..., 1478$. Another distribution is seen at $m/z = 1100, 1158, ..., 1390$, corresponding to $[H-(PO)_n-(lactide)_4-Cl]\ Na^+$, where $n = 8-13$.

Concluding Remarks

As we noted in the Introduction, ring-opening polymerization of lactides and epoxides by coordinate catalysts differ significantly in the intimate mechanism of the ring-opening event. A consequence of this is seen in this work, namely, that copolymer formation of the type ABAB is not favored. When copolymer formation is observed, we obtain block copolymers and one reaction pathway dominates. In the present work the initiation of ROP of PO by Al–chloride catalyst precursors can be followed by ROP of LA. However, these systems are poor catalysts because ROP of LA is very slow in contrast to the single-site L_nMOR catalysts of Mg and Zn.[4] For catalysts that are active in ROP of PO such as the TPPAlCl and the Union Carbide catalyst system, the ring opening of LA shuts down the activity of the system to further polymerization of PO. This indicates an interesting difference in the reactivity of the M–OCHMeX groups as a function of X. The alkoxy-terminated polyester groups are less effective in ring opening of PO than is the polyether group. From this work, we conclude that it will be very challenging to prepare either an alternating copolymer or a regularly repeating block copolymer from the monomers LA and PO. However, simple block copolymers can be formed in a sequence such as that shown in eq 3 wherein a polyol of known character is allowed to react as an alcohol with a catalyst system that is active in lactide polymerization. In this way we have shown that a commercial sample of poly(propylene glycol) in the presence of the Coates' catalyst[4] will grow a block of PLA.

$$H\text{-}[CH(CH_3)CH_2\text{-}]_n\text{-}OH + rac\text{-}LA \xrightarrow[\text{THF, r.t.}]{(BDI)ZnN(^iPr)_2} H\text{-}(PO)_n(LA)_m\text{-}OH$$

Equation 3.

Entry into alternating block copolymers will require the tandem use of two catalyst systems with chain transfer by alcoholysis.

Experimental Section

All syntheses and solvent manipulations were done under an argon atmosphere using standard Schlenk-line and dry box techniques. Toluene and hexanes were distilled from sodium benzophenone ketyl. Methylene chloride, acetonitrile, methanol, 2-propanol, and propylene oxide were distilled from calcium hydride. Compounds **I**,[6] **II**,[6] **III**,[8] **IV**,[12] and **V**[8] were synthesized according to literature procedures. Synthesis of the calcium amide–alkoxide catalyst, $[(PrO)CaNH_2]_n$, was a modification from a published procedure.[13] Compound $(BDI)Zn\text{-}N(^iPr)_2$ (BDI–H = 2-(2,6-diisopropyl-phenylamino)-4-(2,6-diisopropyl phenyl-imino)-2-pentene) was synthesized according to the literature.[14]

NMR Experiments. ^1H, ^{13}C, and Dept NMR experiments were carried out with ^{UNITY}INOVA, Bruker DPX-400, and Bruker DPX-250 spectrometers, operating at proton Lamor frequencies of 400, 400, and 250 MHz, respectively. Their peak frequencies were referenced against the respective solvents, benzene-d_6 at 7.15 ppm and chloroform-d at 7.24 ppm.

GPC Measurements. GPC analysis was performed on a Waters Breeze system equipped with a Waters 410 Differential Refractometer RI detector using THF (HPLC grade) as an eluent, with a 100-μL loop and a concentration of polymer of 0.1 w/v. Molecular weight and molecular weight distributions were calculated using polystyrene standards. When necessary, the catalyst residue was removed from the solution by filtration or centrifugation.

Mass Spectrometry. The polymers were analyzed by laser desorption/Fourier transform mass spectrometry (LD/FTMS) and gel permeation chromatography coupled with electrospray ionization Fourier transform mass spectroscopy (GPC/ESI/FTMS). The experimental procedure is reported elsewhere.[6]

Polymerization Reactions. Polymerization of LA with the catalyst $TPPAlOCH_3$, **V**, and $[(O{\sim}CHMe{\sim}O)Al(O^iPr)]_2$, **IV**, was done as follows. The monomer was dissolved in benzene and this solution was heated at 110 °C under vacuum for 48 h. The unreacted LA was removed from the mixture by sublimation. Polymerization of PO by **IV** was done in bulk at room temperature. Copolymerization reactions involving PO and LA were done with **I**, **II**, and **III** as follows. The monomers PO and LA were dissolved in methylene chloride or benzene. After the mixture was stirred at room temperature for 72 h, the excess of PO monomer was removed under vacuum and the unreacted LA was sublimed. When the initiator used was TPPAlX (X = Cl, OMe), **III** and **V**, the polymer was separated from the porphyrin–Al residue by the addition of THF and filtration. Polymerization of lactide and PO using the calcium amide–alkoxide catalyst system was done in bulk or using benzene as a solvent at room temperature. After the mixture was stirred for 48 h, the solvent was evaporated under vacuum.

In trying to keep consistent with the existing literature on PLA and PPO, where PLA and PPO NMR spectra are reported in $CDCl_3$ and C_6D_6 respectively, we used the following approach. We report the ^1H spectra and ^1H NMR spectra of PLA methine resonances of the copolymers with selective decoupling of PLA methyl resonances in $CDCl_3$ and the ^{13}C NMR spectra of the copolymers in C_6D_6. (The only differences observed in the ^1H NMR spectrum are a change in the chemical shift of the methyl protons of PPO and PLA; better separation of these two signals is achieved in $CDCl_3$. The resolution of the homodecoupled experiments is much increased when using $CDCl_3$). For the homopolymers, $CDCl_3$ is used for lactide and C_6D_6 is used for PPO.

Conversions and yields for the copolymers formed with compounds **I** and **II** were measured by a weight difference from the initial weight.

PO/L-LA/[(O∼CHMe∼O)AlCl]₂. *L*-LA (0.4 g, 2.8 mmol) was dissolved in methylene chloride. The catalyst (0.014 g, 0.014 mmol) and PO (195 μL, 2.8 mmol) were added to this solution. After the mixture was stirred at room temperature for 72 h, the excess PO was evaporated under vacuum. Unreacted LA was removed by sublimation under vacuum at 100 °C. ^1H NMR ($CDCl_3$, ppm): 1.12 (m, CH_3 of PPO), 1.57, 1.58 (d, CH_3 of PLA), 3.45 (m, CH and CH_2 PPO), 5.14, 5.15, 5.17 (s, CH PLA).^{13}C NMR (C_6D_6, ppm): 16.6 (s, CH_3 PLA), 17.29, 18.40, 18.87 (m, CH_3 PPO), 69.0 (s, CH PLA), 73.40, 73.53, 73.60, 75.30, 75.51, 75.64 (m, CH and CH_2 PPO), 170.0 (s, C=O). Yield: 18%, after 72 h, room temperature GPC/ESI/FTMS, $M_n = 1080$ Da, $M_w = 1360$, $M_z = 1680$ Da, $M_p = 1280$ Da, and PDI = 1.3.

Unless otherwise indicated, the above procedure was used for the following experiments.

PO/*rac*-LA/[(O∼CHMe∼O)AlCl]₂. ^1H NMR ($CDCl_3$, ppm): 1.14, 1.28, 1.37, 1.43, 1.69 (CH_3 of PLA and PPO), 3.24 (m, CH and CH_2 PPO), 5.10 (s, CH PLA).^{13}C NMR (C_6D_6, ppm): 16.61, 16.50 (d, CH_3 PLA), 17.33, 18.45, 18.72 (m, CH_3 PPO), 69.33, 69.51 (d, CH PLA), 73.40, 73.57, 73.60, 75.30, 75.53, 75.72 (m, CH and CH_2 PPO), 169.50, 169.59, 169.90, 169.94 (s, C=O PLA). Yield: 19%, after 72 h, room temperature.

PO/*L*-LA/[(O∼∼O)AlCl]₂. ^1H NMR ($CDCl_3$, ppm): 1.09 (m, CH_3 of PPO), 1.57, 1.58 (m, CH_3 of PLA and PPO), 3.42 (m, CH and CH_2 PPO), 5.13, 5.15 (CH of PLA). ^{13}C NMR (C_6D_6, ppm): 16.6 (s, CH_3 of PLA), 17.5 (m, CH_3 of PPO), 69.0 (s, CH PLA), 73.57, 75.72 (m, CH and CH_2 PPO), 169.6 (s, C=O PLA). Yield: 17% after 72 h, room temperature.

PO/*rac*-LA/[(O∼∼O)AlCl]$_2$. ^{1}H NMR ($\mathrm{CDCl_3}$, ppm): 1.19, 1.23, 1.36, 1.53 ($\mathrm{CH_3}$ of PLA and PPO), 3.24 (CH and $\mathrm{CH_2}$ PPO), 5.06 (s, CH PLA). ^{13}C NMR ($\mathrm{C_6D_6}$, ppm): 16.49, 16.60 (d, $\mathrm{CH_3}$ PLA), 17.33, 18.45, 18.72 ($\mathrm{CH_3}$ PPO), 69.32, 69.51 (d, CH PLA), 73.42, 75.56, 75.74 (CH and $\mathrm{CH_2}$ PPO), 169.40, 169.57, 169.80 ($\mathrm{C{=}O}$ PLA). Yield: 20% after 72 h at room temperature.

PO/*L*-LA/(TPP)AlCl. *L*-LA (0.4 g, 2.8 mmol), the catalyst (0.010 g, 0.014 mmol), and PO (195 μL, 2.8 mmol) were dissolved in methylene chloride. After the mixture was stirred at room temperature for 72 h, the excess PO monomer was evaporated under vacuum. Unreacted LA was removed by sublimation under vacuum at 100 °C. ^{1}H NMR ($\mathrm{CDCl_3}$, ppm): 1.07, 1.10 (m, $\mathrm{CH_3}$ of PPO), 1.54, 1.56 (d, $\mathrm{CH_3}$ of PLA), 3.29, 3.32, 3.38, 3.42, 3.46, 3.48, 3.55 (m, CH and $\mathrm{CH_2}$ of PPO), 5.11, 5.13, 5.15, 5.16 (q, CH PLA). ^{1}H NMR spectrum of PLA methine resonances with selective decoupling of PLA methyl resonances ($\mathrm{CDCl_3}$, ppm): 1.52 (s, $\mathrm{CH_3}$), 5.14 (s, CH). ^{13}C NMR ($\mathrm{C_6D_6}$, ppm): 16.8 (s, $\mathrm{CH_3}$ PLA), 17.7, 17.9 (m, $\mathrm{CH_3}$ PPO), 69.3 (s, CH PLA), 73.5, 73.7, 75.5, 75.7, 75.8 (CH and $\mathrm{CH_2}$ PPO), 169.6 (s, $\mathrm{C{=}O}$ PLA). Yield: 24%, 72 h, room temperature.

Unless otherwise indicated, the above procedure was used for the following experiments.

PO/*rac*-LA/(TPP)AlCl. ^{1}H NMR ($\mathrm{CDCl_3}$, ppm): 1.08 (m, $\mathrm{CH_3}$ of PPO), 1.52, 1.54, 1.56 (m, $\mathrm{CH_3}$ of PLA), 3.36, 3.50, 3.58 (m, CH and $\mathrm{CH_2}$ of PPO), 5.13, 5.15, 5.17, 5.20 (CH of PLA). ^{1}H NMR spectrum of PLA methine resonances with selective decoupling of PLA methyl resonances ($\mathrm{CDCl_3}$, ppm): 1.51 (s, $\mathrm{CH_3}$), 5.12, 5.14, 5.15, 5.18, 5.19 (m, CH). ^{13}C NMR ($\mathrm{C_6D_6}$, ppm): 16.5, 16.7 (d, $\mathrm{CH_3}$ of PLA), 17.8, 17.9 (d, $\mathrm{CH_3}$ of PPO), 68.9, 69.3, 69.5, 69.8 (CH of PLA), 73.6, 73.9, 75.6, 75.7, 75.9 (CH and $\mathrm{CH_2}$ of PPO), 169.9, 169.6, 169.8 ($\mathrm{C{=}O}$ of PLA). Yield: 20%, 72 h, room temperature.

PO/UC Catalyst. $[\mathrm{(PrO)CaNH_2}]_n$ (10 mg) was added to 2 mL of PO. After the mixture was stirred at room temperature for 48 h, the excess of PO monomer was evaporated in vacuo to give a white powder. ^{1}H ($\mathrm{C_6D_6}$, ppm): 1.10, 1.12 (d, $\mathrm{CH_3}$ PPO), 3.25, 3.35, 3.38 (m, CH and $\mathrm{CH_2}$ PPO), 3.47, 3.52, 3.54, 3.59 (m, C*H* and C*H*$_2$ PPO). ^{13}C ($\mathrm{C_6D_6}$, ppm): 17.36, 17.48 ($\mathrm{CH_3}$), 72.9, 73.4 (*C*H$_2$), 75.1, 75.3, 75.5 (*C*H). Yield: 70%, 48 h, room temperature.

***L*-LA/UC Catalyst.** *L*-LA (100 mg, 0.69 mmol) was dissolved in 5 mL of benzene. Then 10 mg of $[\mathrm{(PrO)CaNH_2}]_n$ was added and the solution was left stirring at room temperature for 72 h, after which time, the solvent was evaporated in vacuo to give a white powder. ^{1}H ($\mathrm{CDCl_3}$, ppm): 1.45, 1.47 (d, $\mathrm{CH_3}$), 5.01, 5.02, 5.05, 5.09 (q, CH). ^{13}C ($\mathrm{CDCl_3}$, ppm): 16.6 (*C*H$_3$), 69.0 (*C*H), 169.6 (*C*═O). When PO was used as a solvent instead of benzene, no polymerization of PO occurred. Yield: 98%, 72 h, room temperature.

***rac*-LA/UC System Monitored by GPC.** *rac*-LA (0.3 g, 2.1 mmol) was dissolved in 5 mL of benzene. The catalyst (0.030 g) was added to this solution. Aliquots (0.1 μL) were removed by a syringe from the solution and benzene was evaporated under vacuum. The polymer was dissolved in THF. A cloudy emulsion formed. Filtration through glass wool followed by centrifugation gave a clear solution that was analyzed by GPC and ^{1}H NMR. (See Supporting Information.) ^{1}H ($\mathrm{CDCl_3}$, ppm): 1.48, 1.51, 1.53 ($\mathrm{CH_3}$), 5.15 (m, CH). ^{1}H NMR spectrum of PLA methine resonances with selective decoupling of PLA methyl resonances ($\mathrm{CDCl_3}$, ppm): 1.54 (s, $\mathrm{CH_3}$), 5.10, 5.11, 5.12, 5.15, 5.16 (CH).^{13}C ($\mathrm{CDCl_3}$, ppm): 16.5, 16.6 (*C*H$_3$), 68.9, 69.1, 69.2, 69.4 (*C*H), 169.0, 169.2, 169.05 (*C*═O). As reported in the Supporting Information, conversion is 60% after 22 h.

***L*-LA/TPPAlOMe.** The monomer (0.15 g, 1.04 mmol) and the catalyst (0.010 g, 0.014 mmol) were dissolved in benzene. After the mixture was stirred under vacuum at 100 °C for 72 h, the solvent was evaporated under vacuum and the unreacted monomer was removed by sublimation. Filtration from THF was done to separate the porphyrin residue from the polymer. ^{1}H ($\mathrm{CDCl_3}$, ppm): 1.50 (m, $\mathrm{CH_3}$), 3.7 $(\mathrm{Al(OP)}_n{-}\mathrm{OC}H_3)$, 5.13 (m, CH).^{13}C ($\mathrm{CDCl_3}$, ppm): 16.7 ($\mathrm{CH_3}$), 69.1 (CH), 169.6 ($\mathrm{C{=}O}$). Typical conversions (by ^{1}H NMR) were 10% after 5 days at 80 °C.

PO/TPPAlOMe. PO (0.5 mL, 7.2 mmol) and the catalyst (0.035 g, 0.052 mmol) were mixed together and stirred at room temperature for 48 h, after which time, volatiles were evaporated under vacuum to give PPO. ^{1}H ($\mathrm{C_6D_6}$, ppm): 1.15, 1.17, ($\mathrm{CH_3}$), 3.29, 3.34, 3.42, 3.44, 3.45, 3.48, 3.51, 3.70 (CH and $\mathrm{CH_2}$). Typical conversions (by ^{1}H NMR) were 30% after 5 days at 25 °C.

***L*-LA/[($\mathrm{C_{30}H_{44}O_2}$)AlO^{i}Pr]$_2$.** The monomer (0.2 g, 1.4 mmol) and the catalyst (0.014 g, 0.013 mmol) were dissolved in benzene. After the mixture was stirred under vacuum at 100 °C for 72 h, the solvent was evaporated under vacuum and the unreacted monomer was removed by sublimation. ^{1}H ($\mathrm{CDCl_3}$, ppm): 1.56 (d, $\mathrm{CH_3}$), 5.11, 5.12, 5.13, 5.14 (q, CH). ^{1}H NMR spectrum of PLA methine resonances with selective decoupling of PLA methyl resonances ($\mathrm{CDCl_3}$, ppm): 1.54 (s, $\mathrm{CH_3}$), 5.13 (s, CH). ^{13}C ($\mathrm{CDCl_3}$, ppm): 16.6 ($\mathrm{CH_3}$), 68.9 (CH), 169.6 ($\mathrm{C{=}O}$). GPC data based on polystyrene standards: $M_\mathrm{n} = 21071$, $M_\mathrm{w} = 30917$, $M_\mathrm{p} = 20740$, $M_\mathrm{z} + 1 = 58883$, PDI = 1.46. Typical conversions (by ^{1}H NMR) were 15% after 5 days at 80 °C.

***rac*-LA/[(O∼CHMe∼O)AlO^{i}Pr]$_2$.** ^{1}H ($\mathrm{CDCl_3}$, ppm): 1.52, 1.53 (m, $\mathrm{CH_3}$), 5.11, 5.13, 5.15, 5.17, 5.18 (m, CH). ^{1}H NMR spectrum of PLA methine resonances with selective decoupling of PLA methyl resonances ($\mathrm{CDCl_3}$, ppm): 1.54 (s, $\mathrm{CH_3}$), 5.12, 5.13, 5.14, 5.18 (m, CH). ^{13}C ($\mathrm{CDCl_3}$, ppm): 16.6, 16.7 ($\mathrm{CH_3}$), 69.0, 69.2, 69.5 (CH), 169.1, 169.3, 169.6 ($\mathrm{C{=}O}$). Typical conversions (by ^{1}H NMR) were 14% after 5 days at 80 °C.

PO/[(O∼CHMe∼O)AlO^{i}Pr]$_2$. The catalyst (0.028 g, 0.026 mmol) was added to 0.5 mL of PO (7.2 mmol, ratio catalyst: monomer 1:275). The mixture was left stirring at room temperature for 48 h, after which time, the excess PO monomer was evaporated under vacuum to give a viscous colorless polymer. ^{1}H ($\mathrm{C_6D_6}$, ppm): 1.17, 1.18 ($\mathrm{CH_3}$), 3.28, 3.37, 3.45, 3.47, 3.48, 3.50, 3.56, 3.74 (CH and $\mathrm{CH_2}$). ^{13}C ($\mathrm{C_6D_6}$, ppm): 17.6, 17.7, 18.5, 18.7, 18.8 ($\mathrm{CH_3}$), 73.1, 73.4, 73.5, 73.8, 74.2, 75.3, 75.4, 75.7, 75.8, 76.1, 76.2, 76.4 (CH and $\mathrm{CH_2}$). DEPT NMR ($\mathrm{C_6D_6}$, ppm): 72.6, 72.8, 73.1, 73.2, 73.3 (CH carbons, H−H region), 73.2, 73.3, 73.5, 73.9, 74.1 ($\mathrm{CH_2}$ carbons, H−T region), 75.0, 75.1, 75.3, 75.4, 75.5 (CH carbons, H−T region), 75.5, 75.6, 75.8, 75.9, 76.1, 76.2 ($\mathrm{CH_2}$ carbons, T−T region).[6] Yield: 40%, 48 h, room temperature.

Poly(propylene glycol)/*rac*-LA/(BDI)ZnN(^{i}Pr)$_2$. Poly(propylene glycol), PPG, (0.17 g, 0.086 mmol, $M_\mathrm{n} = 2000$ Da, $\mathrm{H{-}[OCH(CH_3)CH_2]}_n\mathrm{{-}OH}$) was dissolved in THF. The catalyst (0.05 g, 0.086 mmol) was added and the solution was left stirring for 1 h at room temperature. *rac*-LA (0.08 g, 0.55 mmol) was added to the mixture and left stirring for 1 h, after which time, the volatiles were evaporated under vacuum to give a polymer that was analyzed by NMR, GPC, and MS.

^{1}H NMR ($\mathrm{CDCl_3}$): 5.15 (m, CH PLA), 3.52, 3.49 (m, CH PPG), 1.19, 1.17 (m, $\mathrm{CH_3}$ PLA), 1.13, 1.11 (m, $\mathrm{CH_3}$ PPG). GPC trace: $M_\mathrm{n} = 3037$, $M_\mathrm{w} = 3544$, $M_\mathrm{p} = 3037$, PD = 1.18. MS data (electrospray) peaks at $M_\mathrm{z} = 2411.3$, 2555.5, 2699, 2844.6, ... corresponding to spacing of 144 Da, lactide, and 2287, 2345, 2405, 2462.3, ... corresponding to 58 Da, PO.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the ACS, for support of this work.

Supporting Information Available: ^{1}H and ^{13}C NMR and GPC/ESI/FTMS data for copolymers obtained from compound **II**, [(O∼CHMe∼O)AlCl]$_2$. ^{1}H and ^{13}C NMR for PLA from compound **IV**, [(O∼CHMe∼O)Al(O^{i}Pr)]$_2$, and the calcium amide−alkoxide catalyst system as well as the ^{13}C NMR spectrum for PLA/PPO from compound **III**. Plot of number-average molecular weight (M_n) versus conversion for PLA obtained from the UC catalyst system and the calculation of active sites as well as the table of MW distributions, time, and conversion for this system. Conversion data for PO polymerization with the Union Carbide catalyst is also available. Finally, MS data on the poly(propylene glycol)/*rac*-LA/(BDI)-ZnN(^{i}Pr)$_2$ experiment are also available. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA011328V