Chelation Effect in Polymerization of Cyclic Esters by Metal Alkoxides: Structure Characterization of the Intermediate Formed by Primary Insertion of Lactide into the Al−OR Bond of an Organometallic Initiator

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Well-defined dialkylaluminum alkoxides derived from 2-methoxyethanol $[R_2Al(\mu\text{-OCH}_2\text{CH}_2\text{OMe})]_2$ [where R = Me (**1a**) and ^tBu (**1b**)] and *rac*-ethyl lactate $[Me_2Al(\mu\text{-OCH(Me)CO}_2\text{-Et})]_2$ (**2**) were used as model complexes mimicking intermediate species in the initiation and propagation steps in the ring-opening polymerization of cyclic esters with metal alkoxides. Particularly, the effect of Lewis base termini of both the supporting ligand and the first polymer chain repeating unit on the aluminum alkoxides activity in the polymerization of ϵ-caprolactone (ϵ-CL) and *rac*-lactide (LA) were explored. It revealed that the initiation process is affected by the extent of chelation to a similar degree for ϵ-CL and LA as the character of the donor-functionalized alkoxide ligand determines the access of an incoming cyclic ester molecule to the effective coordinate site. On the other hand, a significant chelation effect on the propagation step was observed only in the polymerization of LA. The difference in the reactivity is rationalized on the basis of the first structurally authenticated intermediate $[Me_2Al(\mu\text{-OCH(Me)C(O))}_2\text{O(CH}_2)_2\text{OMe}]_2$ (**1-LA**) resulting from primary insertion of a lactide molecule into the aluminum−alkoxide bonds of the $[Me_2Al(\mu\text{-OCH}_2\text{CH}_2\text{OMe})]_2$ initiator. The direct relationship between the extent of intramolecular coordination and initiation and propagation steps of polymerization is also presented.

Introduction

The ring-opening polymerization (ROP) of cyclic esters mediated by metal alkoxide initiators, including aluminum alkoxides, constitutes the most convenient method of polymerization allowing stereochemistry control and polymers of low molecular weight distribution.[1] In principle, the process is thought to occur via a coordination−insertion mechanism, whereby the metal center serves to activate the carbonyl group toward attack by the metal alkoxide initiator, and the initiation proceeds by insertion of a monomer unit into the metal−alkoxide bond with cleavage of the acyl−oxygen bond of the monomer. Despite notable advances in the development of well-defined single-site and multinuclear catalytic systems as well as extensive structure/activity studies,[1,2] the mechanism of polymerization still lacks thorough explanation. For instance, the way in which stereoselectivity is achieved is not well understood[3] or significant uncertainties concern the role of the Lewis acidity of

the metal center.[4] Another particularly intriguing aspect concerns both the potential occurrence of chelation involving growing polymer chain donor sites and the effect of chelating groups on the reactivity of active species (Scheme 1). The latter issue has been a recurring theme in the literature, albeit without clear statements.[5] The mentioned mechanistic uncertainties, which are vital to the development and improvement of catalytic processes, partly result from a paucity of the structurally authenticated intermediate species.[6]

Aluminum alkoxides have been employed extensively as efficient initiators for the controlled polymerization

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(1) For recent reviews see: (a) Kuran, W. *Principles of Coordination Polymerisation*; Wiley: Chichester, 2001; Chapter 9. (b) O'Keefe, B. J.; Hillmyer, M. A.; Tolman, W. B. *J. Chem. Soc., Dalton Trans.* **2001**, 2215. (c) Stridsberg, K. M.; Ryner, M.; Albertsson, A. C. *Adv. Polym. Sci.* **2002**, *157*, 41. (d) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. *Chem. Rev.* **2004**, *104*, 1647. (e) Chisholm, M. H.; Zhou, Z. *J. Mater. Chem.* **2004**, *14*, 3081.

(2) Selected recent examples: (a) Hormnirun, P.; L. Marshall, E.; Gibson, V. C.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **2004**, *126*, 2688. (b) Byrne, C. M.; Allen, S. D.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2004**, *126*, 11404. (c) Majerska, K.; Duda, A. *J. Am. Chem. Soc.* **2004**, *126*, 1026. (d) Lewiński, J.; Horeglad, P.; Dranka, M.; Justyniak, I. *Inorg. Chem.* **2004**, *43*, 5789. (e) Doherty, S.; Errington, R. J.; Housley, N.; Clegg, W. *Organometallics* **2004**, *23*, 2382. (f) Williams, C. K.; Breyfogle, L. E.; Choi, S. K.; Nam, W.; Young, V. G.; Hillmyer, M. A.; Tolman, W. B. *J. Am. Chem. Soc.* **2003**, *125*, 11350. (g) Zhong, Z. Y.; Dijkstra, P. J.; Feijen, J. *J. Am. Chem. Soc.* **2003**, *125*, 11291.

(3) For an example of recent studies directed to this issue see: (a) Chisholm, M. H.; Patmore, N. J.; Zhou, Z. *Chem. Commun.* **2005**, 127. (b) Marshall, E. L.; Gibson, V. C.; Rzepa, H. S. *J. Am. Chem. Soc.* **2005**, *127*, 6048.
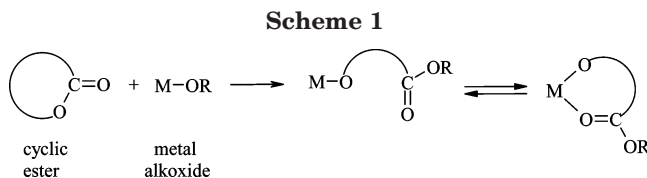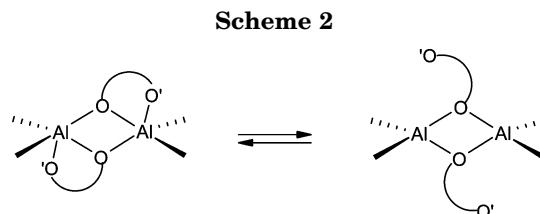
(4) Recent studies on the ROP of cyclic esters have demonstrated that the electrophilicity of the metal center is much less important than conventionally thought, see: (a) Lewiński, J.; Horeglad, P.; Tratkiewicz, E.; Grzenda, W.; Lipkowski, J.; Kołodziejczyk, E. *Macromol. Rapid Commun.* **2004**, *25*, 1939. (b) Alcazar-Roman, L. M.; O'Keefe, B. J.; Hillmyer, M. A.; Tolman, W. B. *J. Chem. Soc., Dalton Trans.* **2003**, 3082.

<div style="column: left">

Scheme 1

of lactones and lactides in recent years.[1,2a,c,3a,4b,7] On the other hand, α-hydroxycarbonyl compounds and alcohols with an ethereal termini have been developed with success in extensive studies on the nature of aluminum alkoxides.[8] We anticipated that alkylaluminum derivatives of alcohols with neutral Lewis base termini may act as model complexes mimicking intermediate species in the initiation and propagation steps in the ROP of cyclic esters mediated by metal alkoxides. As a part of our systematic studies on the activation of heterocyclic monomers by the well-designed group 13 complexes,[2d,4a,9] herein we describe the isolation and structure characterization of the novel intermediate formed by primary insertion of a lactide (LA) molecule into the Al−OR bond of the dialkylaluminum derivative of 2-methoxyethanol and report on the effect of the Lewis base functionality of both the alkoxide ligand and the first polymer chain repeating unit on initiation and propagation steps in the ROP of cyclic esters.

Results and Discussion

As a direct probe of the effect of the Lewis base termini on the initiation efficiency of metal alkoxides in the ROP of *rac*-lactide and ε-caprolactone (ε-CL), well-defined aluminum alkoxides derived from 2-methoxyethanol and *rac*-ethyl lactate, $[R_2Al(\mu\text{-}OCH_2CH_2OMe)]_2$ [where R = Me (**1a**)[10] and ^tBu (**1b**)[8a] and $[Me_2Al(\mu\text{-}OCH(Me)CO_2Et)]_2$ (**2**),[8b,11] were used. Pertinent to the

(5) For selected examples see the following. Al initiators: (a) Jacobs, C.; Dubois, P.; Jerome, R.; Teyssie, P. *Macromolecules* **1991**, *24*, 3027. (b) Vanhoorne, P.; Dubois, P.; Jerome, R.; Teyssie, P. *Macromolecules* **1992**, *25*, 37. (c) Duda, A.; Penczek, S. *Macromolecules* **1995**, *28*, 5981. (d) Ropson, N.; Dubois, P.; Jérôme, R.; Teyssiè, P. *Macromolecules* **1995**, *28*, 7589. (e) Kowalski, A.; Duda, A.; Penczek, S. *Macromolecules* **1998**, *31*, 2114. (f) Chisholm, M. H.; Navarro-Llobet, D.; Simonsick, W. J. W. *Macromolecules* **2001**, *34*, 8851. Sn initiators: (g) Chisholm, M. H.; Delbridge, E. E. *Chem. Commun.* **2001**, 1308. (h) Chisholm, M. H.; Delbridge, E. E. *New J. Chem.* **2003**, *27*, 1167. (i) Chisholm, M. H.; Delbridge, E. E. *New J. Chem.* **2003**, *27*, 1177. Zn initiators: (j) Chamberlain, B. M.; Cheng, M.; Moore, D. R.; Ovitt, T. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 3229.

(6) (a) For the first structurally characterized aluminum-ε-caprolactone complex, see ref 4a. (b) For rare earth metal complexes with ε-CL, see: Evans, W.; Shreeve, J. L.; Doedens, R. J. *Inorg. Chem.* **1993**, *32*, 245. Evans, W.; Shreeve, J. L.; Ziller, J. W.; Doedens, R. J. *Inorg. Chem.* **1995**, *34*, 576. (c) For the alumoxane-(R,S)-β-butyrolactone adduct see: Harlan, C. J.; Bott, S. G.; Wu, B.; Lenz, R. W.; Barron, A. R. *Chem. Commun.* **1997**, 2183. (d) To our knowledge, there is a lack of structurally authenticated metal-lactide adducts.

(7) For other selected examples see: (a) Liao, T. C.; Huang, Y. L.; Huang, B. H.; Lin, C. C. *Macromol. Chem. Phys.* **2003**, *204*, 885. (b) Ma, H. Y.; Melillo, G.; Oliva, L.; Spaniol, T. P.; Englert, U.; Okuda, J. *J. Chem. Soc., Dalton Trans.* **2005**, 721.
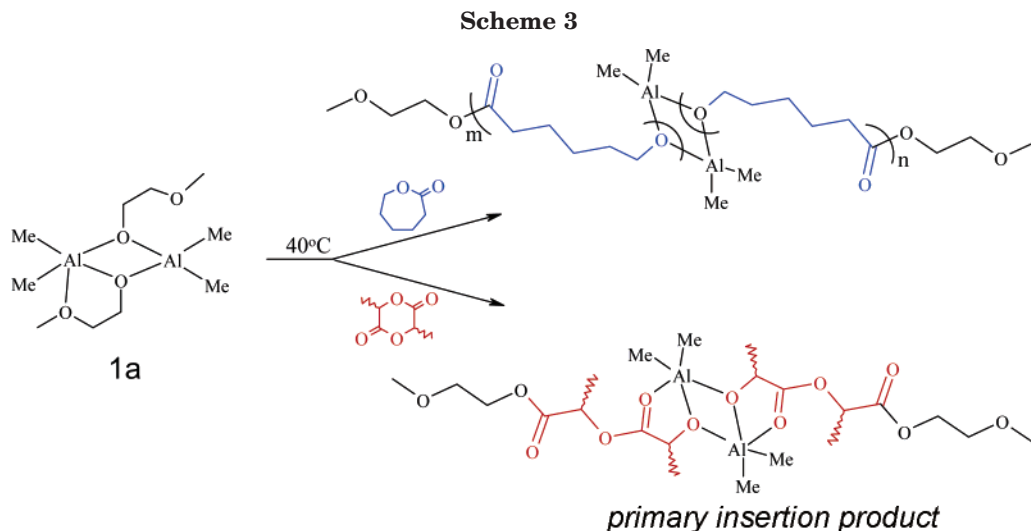
(8) For extensive discussion on this issue see for example: (a) Francis, J. A.; McMahon, C. N.; Bott, S. G.; Barron A. R. *Organometallics* **1999**, *18*, 4399. (b) Lewiński, J.; Justyniak, I.; Horeglad, P.; Tratkiewicz, E.; Zachara, J.; Ochal, Z. *Organometallics* **2004**, *23*, 4430.

(9) (a) Lewiński, J.; Zachara, J.; Horeglad, P.; Glinka, D.; Lipkowski, J.; Justyniak, I. *Inorg. Chem.* **2001**, *40*, 6086. (b) Lewiński, J.; Horeglad, P.; Tratkiewicz, E.; Justyniak, I.; Ochal, Z. *J. Organomet. Chem.* **2005**, *690*, 3697.

(10) Benn, R.; Rufinska, A.; Lemkuhl, H.; Janssen, E.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 779.

(11) (a) Lewiński, J.; Zachara, J.; Justyniak, I. *Chem. Commun.* **1997**, 1519. (b) Lewiński, J.; Zachara, J.; Justyniak, I. *Organometallics* **1997**, *16*, 4597.

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Scheme 2

subject of our studies is the fact that **1a**, **1b**, and **2** are dimeric in solution and the ligand-dependent equilibria between five-coordinate $[R_2Al(\mu,\eta^2\text{-}O,O')]_2$ and four-coordinate $[R_2Al(\mu,\eta^1\text{-}O,O')]_2$ species have been observed.[8a,10] It involves dissociation and recoordination of the neutral donor site O′, while the central Al_2O_2 bridging ring remains intact (Scheme 2); that is, an "on/off" rather than a monomer/dimer equilibrium is present.

Compound **1a** was found to initiate efficiently the polymerization of ε-CL in CH_2Cl_2 at 40 °C with almost complete conversion after 12 h (Scheme 3 and Table 1, entry 1). Insertion of ε-CL occurred exclusively into the Al−OR bond, which was confirmed by ^{1}H NMR and MALDI TOF analysis (Figure 1S), leading to polycaprolactone of a relatively low polydispersity. The observed polydispersity is similar to that reported for the polymerization of ε-CL initiated by diethylaluminum ethoxide.[12] In contrast, the polymerization of LA with **1a** was not observed at the same conditions even after prolonged time (96 h) (Table 1, entry 7). Astonishingly, an analysis of the postreaction mixture revealed the presence of novel compound $[Me_2Al(\mu\text{-}OCH(Me)C(O))_2O\text{-}(CH_2)_2OMe]_2$ (**1-LA**) formed by the insertion of two LA molecules into the 2-methoxyethoxide−aluminum bonds of **1a** and corresponding to the primary insertion product (Scheme 3). The formation of **1-LA** was confirmed independently by the reaction of **1a** with 2 equiv of LA in CH_2Cl_2, which was completed after ca. 96 h at 40 °C. The ^{1}H NMR spectrum of the postreaction mixture showed two sets of signals (Figure 2S), and the observed pattern clearly indicated the presence of the homochiral $(R*,R*)(R*,R*)$-**1-LA** and the heterochiral $(R,R)(S,S)$-**1-LA** stereoisomers in equimolar ratio (Figure 1). The characteristic feature of this ^{1}H NMR spectrum is the occurrence of a single resonance due to the Al-Me groups of the homochiral species (Figure 1), which indicates the operation of a dynamic process with very fast, on the NMR time scale, intramolecular exchange of the ester groups between the different aluminum sites.

Thus, the insertion process of LA into the aluminum−alkoxide bonds of **1a** is not stereoselective, in contrast to the reaction of Me_3Al with *rac*-ethyl lactate previously reported by our group that resulted in the formation of an exclusively racemic mixture of the homochiral dimers $[Me_2Al(\mu\text{-}OCH(Me)CO_2Et)]_2$ (**2**). These data are rather surprising; nevertheless it confirms our earlier observation that subtle changes may have a profound effect on chiral recognition of donor-functionalized metal alkoxides.[13] Furthermore, the IR spectrum of **1-LA** in CH_2Cl_2 appeared to be a sensitive probe for detecting the chelated and pendant ester groups, as it displays two strong $\nu_{C=O}$ bands of similar intensity at 1756 and 1704

(12) (a) Duda, A.; Penczek, S. *Macromol. Rapid Commun.* **1994**, *15*, 559. (b) Gadzinowski, M.; Sosnowski, S.; Słomkowski, S. *Macromolecules* **1996**, *29*, 6404.

</div>

Scheme 3

primary insertion product

cm^{-1}. The former band corresponds to the pendant uncoordinated carbonyl groups, and the red-shifted band is due to the intramolecularly coordinated carbonyl groups. Thus, the IR data indicate that the five-coordinate chelate species dominate at ambient temperature.

The lack of any structure representing the inserted lactide into the metal−alkoxide bond of an initiator encouraged us to confirm the structure of **1-LA** by X-ray diffraction. Compound **1-LA** was found to crystallize as a centrosymmetric dimer with five-coordinate aluminum centers (Figure 2). The alkoxide ligands resulting from the insertion of a LA molecule into the 2-methoxyethox-ide−aluminum bond form two five-membered chelate rings with aluminum atoms, which lie approximately in one plane with the central Al$_2(\mu$-O)$_2$ ring. The methyl group bonded to the chiral C$_\alpha$ atom in the μ,η^2-alkoxide ligands lies on the opposite side of the plane outlined by the three fused heterocyclic rings. The aluminum atoms adopt a distorted trigonal bipyramidal geometry, with the most significant distortion found for the angle defined by axial substituents [O(2)Al(1)O(1′), 153.46-(7)°]. The Al−O bridging distances are typical for this group of compounds, and the ester Al(1)−O(2) distance [2.147(4) Å] in **1-LA** is comparable with the analogous Al−O distance in **2**[11a] and slightly shorter than the corresponding Al−O$_{ether}$ linkage in **1a** [2.268(2) Å].[10]

In contrast to the 2-methoxyethanol derivative **1a**, compound **1-LA** was essentially inactive in the reaction

with ε-CL and LA at 40 °C (Table 1, entries 5 and 12), and this observation strongly confirms the influence of the ester functionality on the catalytic efficiency of aluminum alkoxides (Scheme 2). However, when the corresponding reaction mixtures involving **1-LA** or **1a** were heated to 70 °C, PCL and PLA were obtained in high yields (Table 1, entries 6, 8, and 13). The ^{1}H NMR and MALDI TOF analysis revealed that PLA was formed by exclusive insertion of the monomer molecule into the Al−OR bond, and the Al−C bond remains intact. The MALDI-TOF spectrum of the resulting polylactide revealed two sets of signals (Figure 3). One of two distributions (difference between peaks = 144 Da) represents polylactide chains of mass 72*n (n = even number) and the end group of 76 Da corresponding to H[OCH(Me)C(O)]$_n$OCH$_2$CH$_2$OMe (72.09*n+76 Da). The second distribution (difference between peaks = 144 Da) represents polylactide chains of mass 72*(n+1) and of the end group of 76 Da corresponding to H[OCH(Me)C-(O)]$_{n+1}$OCH$_2$CH$_2$OMe (72.09*(n+1)+76 Da). The presence of two mentioned distributions indicates the occurrence of transesterification side reactions during the

Figure 2. ORTEP drawing of the solid-state structure of **1-LA** (probability ellipsoids are shown at the 50% level). Selected bond lengths (Å) and angles (deg): Al1−C1 = 1.969(4), Al1−C2 = 1.967(4), Al1−O1 = 1.858(4), Al1−O1′ = 1.925(4), Al1−O2 = 2.147(4); O2−Al1−O1′ = 153.46(7), O1−Al1−C1 = 117.1(1), O1−Al1−C1 = 119.41(11), C1−Al1−C2 = 122.83(12).

Figure 1. The ^{1}H NMR spectrum of **1-LA** in the region of the Al−Me signals.
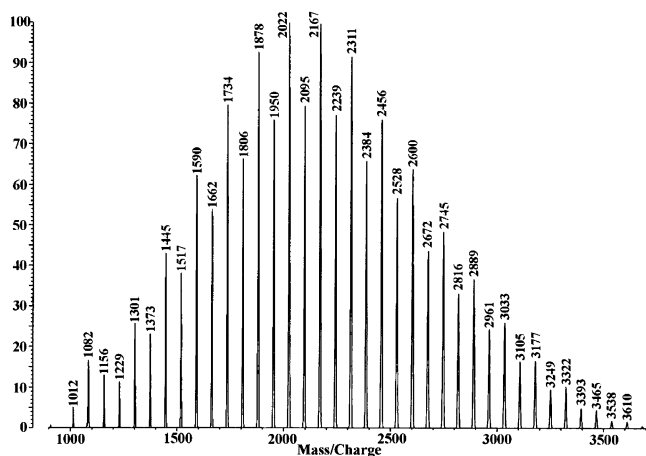
Figure 3. Polylactide obtained with **1-LA** as the initiator at 70 °C.

polymerization process, which significantly impairs any stereoregular structure of PLA.

Similarly to **1-LA**, the methylaluminum derivative of *rac*-ethyl lactate **2** was essentially inactive in the reaction of both ϵ-CL and LA at 40 °C (Table 1, entries 3 and 10), and this observation strongly confirms the influence of the α-carbon-bonded ester functionality on the catalytic efficiency of aluminum alkoxides. However, when the corresponding reaction mixtures were heated to 70 °C, PCL and PLA were obtained in high yields (Table 1, entries 4 and 11). Both PCL and PLA were found on the basis of ^{1}H NMR analysis to be formed by insertion of the monomer molecule exclusively into the Al–OR bond. It should be noted that while the reported studies indicate the strong influence of the ester functionality on the reactivity of aluminum alkoxides, the analogous effect was much less pronounced in the case of zinc alkoxides. The latter was shown by the study on the effect of initiating group upon lactide polymerization using isopropoxide and methyl lactate zinc complexes supported by a β-diiminate ligand, [(BDI)ZnO^{i}Pr]$_2$ and (BDI)ZnOCH(Me)CO$_2$Me.[5j]

The direct relationship between the size of aluminum-bonded alkyl substituent and the lower strength of the chelate bond in dialkylaluminum derivatives of donor-functionalized alcohols was proved by Barron et al.[8a] Therefore, in the next step we turned our attention to the *tert*-butylaluminum derivative of 2-methoxyethanol **1b**. According to the expectation, **1b** was found to initiate efficiently the polymerization of both ϵ-CL and LA at 40 °C (Table 1, entries 2 and 9), and both PCL and PLA were found on the basis of ^{1}H NMR analysis to be formed by insertion of the monomer molecule exclusively into the Al–OR bond. It clearly indicates that the species formed after the initial insertion of a LA molecule do not strongly suppress the propagation process when more bulky alkyl substituents are bonded to the metal center.

The different behavior of **1a**, **1b**, **2**, and **1-LA** toward ϵ-CL and LA may be rationalized by discussing the relationship between their structure and reactivity as well as the intermediate species formed during the polymerization. All the considered aluminum alkoxides exist as dimers with bridging alkoxide groups and differ in both the strength and the extent of chelation, i.e., the position of the equilibrium between the four- and five-coordinate species shown in Scheme 2. For the 2-methoxyethoxide derivatives **1a** and **1b**, the equilibrium is far shifted toward the four-coordinate species at ambient temperature,[8a] allowing for the efficient primary insertion of the first two ϵ-CL or LA molecules into the aluminum–alkoxide bonds. However, the insertion of an ϵ-CL molecule into the Al–O(CH$_2$)$_2$OMe bond produces the intermediate **1-CL** bearing the new ester-functionalized alkoxide ligand –O(CH$_2$)$_5$CO$_2$(CH$_2$)$_2$OMe, which exhibits much lower efficiency for the metal center chelation than the 2-methoxyethoxide ligand due to the increased carbon chain length between the bridging alkoxide oxygen and the donor site from C$_2$ in **1a** and **1b** to C$_6$ in the resulting intermediate species. Thus, the absence of the chelation in **1-CL** would rationalize efficient propagation in the ϵ-CL polymerization. On the other hand, the reaction of **1a** with LA leads to **1-LA**, with the five-coordinate chelate species dominating at room temperature, and a limited accessibility of an incoming cyclic ester molecule to the effective coordinate site, i.e., the metal coordinate site allowing for the efficient propagation process. Accordingly, for **1-LA** and its homologue **2**, the polymerization of both ϵ-CL and LA is suppressed at mild conditions. For these alkoxides both the fraction of the four-coordinate species and the accessibility of the effective coordinate site increase significantly at higher temperature,[14] which allows for the insertion of the cyclic ester molecules into the aluminum–alkoxide bond and promotes the propagation process. On the other hand, the observed higher reactivity of the *tert*-butylaluminum complex **1b** toward LA strongly supports the above considerations as Barron et al. nicely demonstrated that the chelation stabilization is weaker, and the fraction of the four-coordinate species in di-*tert*-butylaluminum alkoxides derived from donor-functionalized alcohols is higher than those found in the less sterically hindered related aluminum alkyls.[8a,15] That is why the ester functionality of the growing PLA chain does not suppress the polymerization in this case.

Thus, the initiation process is affected by the extent of chelation to a similar degree for ϵ-CL and LA, as the character of the donor-functionalized alkoxide ligand determines the access of an incoming cyclic ester molecule to the effective coordinate site. The significant chelation effect on the propagation step is observed only in the polymerization of LA, while this does not affect the polymerization of ϵ-CL. This divergent influence of chelation interference on the polymerization efficiency results from the different character of intermediate species resulting from the primary insertion, particularly from their inherent tendency to coordinate intramolecularly. The chelation effect may be minimized by increasing the reaction temperature; however, this procedure usually makes the polymerization process

(13) The factors controlling the stereoselective association of metal alkoxides are unclear and therefore our continuous interest in this subject, see: (a) Ref 11. (b) Lewiński, J.; Justyniak, I.; Ochal, Z.; Zachara, J. *J. Chem. Soc., Dalton Trans.* **1999**, 2909. (c) Lewiński, J.; Zachara, J.; Kopeć, T.; Starowieyski, K. B.; Lipkowski, J.; Justyniak, I.; Kołodziejczyk, E. *Eur. J. Inorg. Chem.* **2001**, 1123.

(14) For studies on the temperature dependence of the equilibrium process between coordinated and uncoordinated species for the dimeric dialkylaluminum alkoxide compounds, see ref 8a.

(15) Francis, J. A.; Boot, S. G.; Barron, A. R. *Polyhedron* **1999**, *18*, 2211.

difficult to control, as it favors undesirable transesterification reaction, which in any case causes the formation of atactic PLA. Accordingly, our reported results for aluminum complexes in combination with Coates results for zinc complexes[5j] lead to the assumption that the strong Lewis acidic centers should be least advisable as the active centers in polymerization of LA. Instead, a relatively soft character of the metal center should enable rational control of the polyesters molecular and physical properties.

Conclusion

In conclusion, several experiments were designed to probe for structural features controlling the initiation and propagation events in the polymerization of ϵ-caprolactone and *rac*-lactide. Using well-defined dimeric dialkylaluminum derived from bifunctional alcohols as well as the first structurally authenticated intermediate resulting from primary insertion of a lactide molecule into the aluminum–alkoxide bonds of the initiator, we have demonstrated that the activity of aluminum alkoxides in the ring-opening polymerization varied considerably with steric demands of alkyl substituents bonded to the metal center and the character of donor sites attached to the alkoxide ligand and/or the first polymer chain repeating unit. We have also shown the direct relationship between the extent of intramolecular coordination in both initiating species and putative intermediates, and initiation and propagation steps. The initiation process is affected by the extent of chelation to a similar degree for ϵ-CL and LA, as the character of the donor-functionalized alkoxide ligand determines the access of an incoming cyclic ester molecule to the effective coordinate site. On the other hand, a significant chelation effect on the propagation step was observed only in the polymerization of LA. Finally, our observation represents an important impact that should be considered in the design of new efficient catalysts for the polymerization and copolymerization of heterocyclic monomers.

Experimental Section

General Procedures. All reactions were carried out under dry nitrogen using standard Schlenk techniques. Solvents were dried and distilled prior to use, hexane from potassium and methylene chloride from calcium chloride. ϵ-Caprolactone was purified by distillation from calcium hydride. *rac*-Lactide was purified by recrystallization from 2-propanol and toluene, followed by vacuum sublimation. 2-Methoxyethanol and ethyl lactate were purchased from Aldrich and dried by distillation from calcium chloride and later stored over molecular sieves. Trimethylaluminum was purchased from Aldrich and used as received. Compounds **1a**,[10] **1b**,[8a] and **2**[11] and tri-*tert*-butylaluminum[16] were prepared according to the literature procedures. ^{1}H NMR spectra were recorded on a Varian Mercury-400 spectrometer, GPC measurements were recorded on a LabAlliance chromatograph, and MALDI TOF analyses were performed on a Kratos Kompact MALDI 4 V5.2.1 spectrometer. Samples for the MALDI-TOF analyses were dissolved in CH₃-Cl and analyzed with addition of 2-(4hydroxyphenolato)benzoic acid (HABA) or 2,5-dihydroxybenzoic acid (DHB) THF solution as matrix. For the presented MALDI-TOF spectra, peaks other

(16) Lewiński, J.; Zachara, J.; Gœ, P.; Grabska, E.; Kopeć, T.; Madura, I.; Marciniak, W.; Prowotorow, I. *Chem.-Eur. J.* **2000**, *6*, 3215.

than indicated in the description originate from the matrix. Sodium iodide (NaI) was added to every polymer sample.

Synthesis of 1-LA. Compound **1a** (0.66 g, 2.5 mmol) and *rac*-lactide (0.72 g, 5.0 mmol) were placed in a Schlenk vessel and dissolved in CH₂Cl₂ (10 mL). The solution was mixed at 40 °C for 96 h, and the resulting colorless solid crystallized from CH₂Cl₂/hexane solution at −18 °C to give colorless crystals in 80% yield (1.10 g). Anal. Calcd for $C_{22}H_{42}Al_2O_{12}$: C, 47.82; H, 7.66; Al, 9.77. Found: C, 48.15; H, 7.53; Al, 9.45. ^{1}H NMR (CDCl₃, δ, ppm): −1.02, −0.99, −0.93 (s, 6H, AlC*H₃*), 1.53, 1.55, (d, 3H, J_{HH} 7.2 Hz, AlOCHC*H₃*), 1.58, 1.60, (d, 3H, J_{HH} 7.2 Hz, −OCHC*H₃*), 3.37, 3.38 (s, 3H, −OC*H₃*), 3.59, 4.30 (t, 2H, J_{HH} 4.1 Hz, −OC*H₂*CH₂OCH₃), 3.59, 4.30 (t, 2H, J_{HH} 4.1 Hz, −OCH₂C*H₂*OCH₃) 4.54, 4.55 (q, 1H, J_{HH} 7.2 Hz AlOC*H*CH₃) 5.28, 5.29 (2q, 1H, J_{HH} 7.2 Hz, J_{HH} 1.2 Hz −OC*H*CH₃). IR (CH₂Cl₂, cm⁻¹): 1756 (s), 1704 (s) 1694 (s), 1456 (s), 1384 (m), 1368 (m), 1344 (m), 1200 (s), 1140 (s), 1092 (s), 1052 (m), 1032 (m), 952 (m), 868 (m), 836 (m), 676 (s), 604 (m), 400 (m). Molecular weight (cryoscopically in benzene): found 542, calcd 552.5.

General Procedure for Polymerization of ϵ-Caprolactone and *rac*-Lactide with 1a, 1b, 2, and 1-LA Initiators. Polymerization reactions were carried out under a nitrogen atmosphere. In a typical run, a monomer solution in CH₂Cl₂ was added to the corresponding aluminum alkoxide initiator. The polymerization was then thermostated for the indicated time in the sealed tube. The reaction was then quenched by addition of 5% HCl (20 mL) solution. The organic phase was separated, washed with water (3 × 50 mL), dried over sodium sulfate, and filtered. In the case of ϵ-caprolactone polymerization the resulting solution was concentrated and polycaprolactone was precipitated by the addition of methanol. Then, for both polycaprolactone and polylactide the polymer samples were dried under vacuum.

Polymerization of ϵ-Caprolactone with 1a. ϵ-Caprolactone (1.85 g, 16.25 mmol) was added to the solution of **1a** (0.08 g, 0.325 mmol) in CH₂Cl₂ (20 mL) and left for 12 h at 40 °C. The polycaprolactone was precipitated as a white solid in 98% yield (3.60 g). ^{1}H NMR (CDCl₃, δ, ppm), signals of the polycaprolactone chain: 1.37 (m, 2H, −C*H₂*−), 1.63 (m, 4H, −C*H₂*−), 2.30 (t, 2H, −C*H₂*C(O)−), 4.05 (t, 2H, −C*H₂*OC-(O)−); signals of the end group: 3.38 (s, 3H, −OC*H₃*), 3.58 (t, 2H, −OC*H₂*CH₂OCH₃), 4.22 (t, 2H, −OCH₂C*H₂*OCH₃).

Polymerization of *rac*-Lactide with 1a. *rac*-Lactide (1.87 g, 13.00 mmol) was added to the solution of **1** (0.08 g, 0.325 mmol) in CH₂Cl₂ (20 mL) and left for 96 h at 40 °C and for 24 h 70 °C. No polylactide was obtained for polymerization at 40 °C. For the polymerization at 70 °C polylactide was obtained in 96% yield (1.80 g). ^{1}H NMR (CDCl₃, δ, ppm), signals of polylactide chain: 1.45−1.60 (br, 3H, −OCH(C*H₃*)C(O)−), 5.08−5.26 (br, 1H, −OC*H*(CH₃)C(O)−); signals of the end group: 3.36 (s, 3H, −OC*H₃*), 3.57 (t, 2H, −OC*H₂*CH₂OCH₃), 4.26 (t, 2H, −OCH₂C*H₂*OCH₃); ^{1}H NMR after decoupling at 1.54 ppm, methine proton region: 4 signals 5.15, 5.14, 5.20, 5.21.

Polymerization of ϵ-Caprolactone with 1b. ϵ-Caprolactone (1.85 g, 16.25 mmol) was added to the solution of **1b** (0.14 g, 0.325 mmol) in CH₂Cl₂ (20 mL) and left for 12 h at 40 °C. The polycaprolactone was precipitated as a white solid in 99% yield (3.64 g). ^{1}H NMR (CDCl₃, δ, ppm), signals of the polycaprolactone chain: 1.37 (m, 2H, −C*H₂*−), 1.63 (m, 4H, −C*H₂*−), 2.30 (t, 2H, −C*H₂*C(O)−), 4.05 (t, 2H, −C*H₂*OC-(O)−); signals of the end group: 3.37 (s, 3H, −OC*H₃*), 3.58 (t, 2H, −OC*H₂*CH₂OCH₃), 4.23 (t, 2H, −OCH₂C*H₂*OCH₃).

Polymerization of *rac*-Lactide with 1b. *rac*-Lactide (1.87 g, 13.00 mmol) was added to the solution of **1b** (0.14 g, 0.325 mmol) in CH₂Cl₂ (20 mL) and left for 24 h at 40 °C. Polylactide was obtained in 65% yield (1.33 g). ^{1}H NMR (CDCl₃, δ, ppm), signals of the polylactide chain: 1.45−1.60 (br, 3H, −OCH-(C*H₃*)C(O)−), 5.08−5.26 (br, 1H, −OC*H*(CH₃)C(O)−); signals of the end group: 3.36 (s, 3H, −OC*H₃*), 3.57 (t, 2H, −OC*H₂*-

Table 1. Results of ε-Caprolactone and *rac*-Lactide Polymerization with 1a, 1b, 2, and 1-LA

entry	initiator	monomer	[mon]:[Al]	temp (°C)	time (h)	yield (%)	$M_n{}^a$	$M_n{}^b$	PDI^b
1	**1a**	ε-CL	25:1	40	12	98	2820	4653	1.38
2	**1b**	ε-CL	25:1	40	12	99	2855	4735	1.27
3	**2**	ε-CL	25:1	40	12	1			
4	**2**	ε-CL	25:1	70	12	95	9582	16 350	1.35
5	**1-LA**	ε-CL	25:1	40	12	2			
6	**1-LA**	ε-CL	25:1	70	12	96	7445	12 575	1.39
7	**1a**	LA	20:1	40	96	<1			
8	**1a**	LA	20:1	70	24	96	3054	5492	1.19
9	**1b**	LA	20:1	40	24	65	1853	3038	1.15
10	**2**	LA	20:1	40	96	<1			
11	**2**	LA	20:1	70	24	97	2803	4681	1.15
12	**1-LA**	LA	20:1	40	96	<1			
13	**1-LA**	LA	20:1	70	24	95	2758	4655	1.17

^{a} Obtained by integration of the monomer vs polymer resonances in the ^{1}H NMR spectra. ^{b} Obtained from GPC analysis and calibrated for polystyrene standard.

CH$_2$OCH$_3$), 4.26 (t, 2H, −OCH$_2$C*H*$_2$OCH$_3$); ^{1}H NMR after decoupling at 1.54 ppm, methine proton region: 4 signals 5.15, 5.14, 5.20, 5.21.

Polymerization of ε-Caprolactone with 1-LA. ε-Caprolactone (1.85 g, 13.25 mmol) was added to the solution of **1-LA** (0.18 g, 0.325 mmol) in CH$_2$Cl$_2$ (20 mL) and left for 12 h at 40 and 70 °C. Only traces of polycaprolatone were obtained for polymerization at 40 °C. For the polymerization at 70 °C polycaprolactone was obtained in 96% yield (1.78 g). ^{1}H NMR (CDCl$_3$, δ, ppm), signals of the polycaprolactone chain: 1.37 (m, 2H, −C*H*$_2$−), 1.63 (m, 4H, −C*H*$_2$−), 2.30 (t, 2H, −C*H*$_2$C-(O)−), 4.05 (t, 2H, −C*H*$_2$OC(O)−); signals of the end group: 1.46, 1.51 (d, 6H, −OCHC*H*$_3$), 3.34 (s, 3H, −OC*H*$_3$), 3.56 (t, 2H, −OC*H*$_2$C*H*$_2$OCH$_3$), 4.27, 4.33 (t, 2H, −OC*H*$_2$CH$_2$OCH$_3$), 5.17 (2q, 2H, −OC*H*CH$_3$).

Polymerization of *rac*-Lactide with 1-LA. *rac*-Lactide (1.87 g, 13.00 mmol) was added to the solution of **1-LA** (0.18 g, 0.325 mmol) in CH$_2$Cl$_2$ (20 mL) and left for 96 h at 40 °C and for 12 h at 70 °C. No polylactide was obtained for polymerization at 40 °C. For the polymerization at 70 °C polylactide was obtained in 97% yield (1.81 g). ^{1}H NMR (CDCl$_3$, δ, ppm) signals of the polylactide chain: 1.45−1.60 (br, 3H, −OCH(C*H*$_3$)C(O)−), 5.08−5.26 (br, 1H, −OC*H*(CH$_3$)C(O)−); signals of the end group: 3.36 (s, 3H, −OC*H*$_3$), 3.57 (t, 2H, −OC*H*$_2$CH$_2$OCH$_3$), 4.26 (t, 2H, −OCH$_2$C*H*$_2$OCH$_3$). ^{1}H NMR spectrum after decoupling at 1.54 ppm: the methine proton region, 4 signals 5.15, 5.14, 5.20, 5.21.

Polymerization of ε-Caprolactone with 2. ε-Caprolactone (1.85 g, 16.25 mmol) was added to the solution of **2** (0.11 g, 0.325 mmol) in CH$_2$Cl$_2$ (20 mL) and left for 12 h at 40 and 70 °C. Only traces of polycaprolatone were obtained for polymerization at 40 °C. For the polymerization at 70 °C polycaprolactone was obtained in 95% yield (1.76 g). ^{1}H NMR (CDCl$_3$, δ, ppm) signals of the polycaprolactone chain: 1.37 (m, 2H, −C*H*$_2$−), 1.63 (m, 4H, −C*H*$_2$−), 2.30 (t, 2H, −C*H*$_2$C-(O)−), 4.05 (t, 2H, −C*H*$_2$OC(O)−); signals of the end group: 1.24 (t, 3H, C(O)CH$_2$C*H*$_3$), 1.47 (d, 3H, −OCHC*H*$_3$), 4.17 (br, 2H, C(O)C*H*$_2$CH$_3$), 4.23 (q, 1H, −OC*H*(CH$_3$)).

Polymerization of *rac*-Lactide with 2. *rac*-Lactide (1.87 g, 13.00 mmol) was added to the solution of **1** (0.11 g, 0.325 mmol) in CH$_2$Cl$_2$ (20 mL) and left for 96 h at 40 °C and 24 h at 70 °C. No polylactide was obtained for polymerization at 40 °C. For the polymerization at 70 °C polylactide was obtained in 95% yield (1.77 g). ^{1}H NMR (CDCl$_3$, δ, ppm) signals of the polylactide chain: 1.45−1.60 (br, 3H, −OCH(C*H*$_3$)C(O)−), 5.08−5.26 (br, 1H, −OC*H*(CH$_3$)C(O)−); signals of the end group: 1.33 (t, 3H, C(O)CH$_2$C*H*$_3$), 1.63 (d, 3H, −OCHC*H*$_3$), 4.25 (q, 2H, C(O)C*H*$_2$CH$_3$), 4.32 (q, 1H, −OC*H*(CH$_3$)). ^{1}H NMR

spectrum after decoupling at 1.54 ppm, the methine proton region: 4 signals 5.15, 5.14, 5.20, 5.21.

Crystal Structure Determination of Compound 1-LA. C$_{22}$H$_{42}$Al$_2$O$_{12}$: $M = 552.52$, triclinic, space group $P\bar{1}$ (no. 2), $a = 8.1070(4)$ Å, $b = 9.0890(5)$ Å, $c = 12.6240(8)$ Å, $\alpha = 69.858$-$(3)°$, $\beta = 70.465(3)°$, $\gamma = 62.466(3)°$, $V = 757.05(7)$ Å^3, $Z = 2$, $F(000) = 296$, $D_c = 1.212$ g m^3, $\theta_{max} = 21.97°$. X-ray diffraction data for a crystal of dimensions of $0.40 \times 0.30 \times 0.20$ mm were collected at 100(2) K on a Kappa CCD diffractometer using Mo Kα radiation ($\lambda = 0.71073$). The data were collected using the "Collect" software [17] and were processed using the "Denzo" and "Scalepak" software.[18] The structure was solved by direct methods using the SHELXS97[19] and SHELXL97[20] programs. All structural analyses and drawings were done using the WinGX software[21] with 1854 unique reflections, which are used in all calculations. H atoms were included in idealized positions and refined isotropically. Refinement converged at $R_1 = 0.0466$, $wR_2 = 0.0823$ for all data and 168 parameters ($R_1 = 0.0389$, $wR_2 = 0.0799$ for 1667 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on F^2 was equal to 1.104. A weighting scheme $w = [\sigma^2(F_o^2 + (0.0418P)^2 + 3.1964P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the final stage of refinement. The residual electron density = $+0.36/-0.20$ e Å^{-3}. See www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)-1223-336-033; or deposit@ccdc.cam.ac.uk.

Supporting Information Available: Crystallographic data in CIF format, MALDI TOF data for polycaprolactone obtained with **1a**, and ^{1}H NMR spectra of **1-LA**. This material is available free of charge via the Internet at http://pubs.acs.org.

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