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Phenoxy-Thioether Aluminum Complexes as ε-Caprolactone and Lactide Polymerization Catalysts

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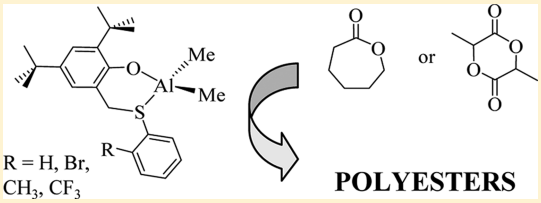
Supporting Information

ABSTRACT: A series of new phenoxy-thioether (OS) proligands have been synthesized. They were found to readily react with 1 equiv of $AlMe_3$ to afford the corresponding Al chelate complexes {4,6-tBu_2-OC_6H_2-2-CH_2S(2-R-C_6H_4)}$AlMe_2$ (R = H (**1**), Br (**2**), CH_3 (**3**), CF_3 (**4**)) in quantitative yields. All the aluminum methyl complexes are stable monomeric species. In the solid state, as determined from X-ray crystallographic studies, complex **2** consists of a four-coordinate aluminum species in which the metal center is chelated by the sulfur and oxygen atoms of the bidentate ligand. All complexes promote the ring-opening polymerization of ε-caprolactone and L- and *rac*-lactide. Upon addition of methanol, efficient binary catalytic systems for the immortal ring-opening polymerization of the cyclic esters are produced (in detail, 300 equiv of ε-CL were converted in 20 min at 50 °C and 100 equiv of *rac*-LA were converted in 1 day at 80 °C). Kinetic studies show that polymerizations promoted by **1**−**4** are first order with respect to monomer concentration. The steric and electronic characteristics of the ancillary ligands have moderate influence on the polymerization performance of the corresponding aluminum complexes. However, the introduction of a substituent at the ortho position of the thiophenol aryl ring showed an opposite effect on the catalytic activities of the two different cyclic esters, increasing the activity in the ε-caprolactone polymerization and decreasing it in the polymerization of lactide.



INTRODUCTION

The interest in the synthesis of aliphatic polyesters stems mostly from their biodegradability, in light of recent concerns with the environment, and from their biocompatibility, which make them suitable materials for medical and pharmaceutical applications.[1]

In particular, polycaprolactone (PCL) is degraded by hydrolysis of its ester bonds under physiological conditions and has therefore received a great deal of attention for use as an implantable biomaterial and as a drug delivery system.[2]

Polylactide (PLA) represents a potential candidate to replace traditional olefin-based polymers as an ecological thermoplastic resin from renewable resources.[3]

Among the various methods exploited, ring-opening polymerization (ROP) of the related cyclic esters promoted by metal initiators via a coordination−insertion mechanism is the most efficient route, allowing the production of polyesters with good control in terms of molecular weight, microstructure, and stereoregularity.[4]

Due to their high Lewis acidity and low toxicity, aluminum compounds, especially Al alkoxides and aryloxides, are well-suited initiators for the ROP of cyclic esters such as lactides and lactones.[4,5] Among these, it is worth noting that phenoxy-imine based aluminum complexes have been found to be able to initiate the ROP of lactides and lactones.[4] In particular, it was shown that the imino substituents strongly affect the performance of the initiators, in some cases providing living catalysts with high initiation efficiency.[6] Notable examples are the related salen aluminum complexes for their ability to promote stereoselective polymerization of *rac*-lactide.[7]

While the majority of these aluminum complexes bearing multidentate ligands contain nitrogen or oxygen as neutral donor atoms, anionic chelating ligands incorporating soft donors such as a phosphorus or sulfur atom have been much less explored for coordination to the hard aluminum center.[8] In this regard, Okuda described aluminum complexes containing dianionic tetradentate OSSO-type ligands which acted as efficient initiators for the *living* polymerization of *rac*-lactide in the presence of isopropyl alcohol.[9]

We recently reported new monoanionic bidentate ligands, having a phenoxo group and oxygen or sulfur atoms as additional neutral donors, for the synthesis of octahedral bis(chelate) group 4 metal complexes as catalysts for ethylene and α-olefin polymerization.[10]

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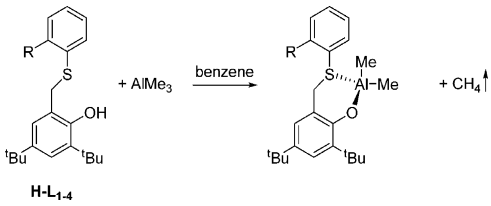
As an extension of our previous work and taking into account the interest devoted to aluminum compounds bearing phenoxy-based ligands as catalysts for polar monomer polymerization, aluminum compounds bearing this new class of ligands were synthesized, characterized, and then tested as initiators for the ROP of ε-caprolactone (ε-CL), D,L-lactide (*rac*-LA), and L-lactide (L-LA).

RESULTS AND DISCUSSION

Synthesis and Structure of Phenoxy-Thioether Dimethylaluminum Complexes 1−4. Four ligands are described in this work, each including a di-*tert*-butylphenoxo anionic donor and an aromatic thioether neutral donor differently substituted on the aromatic ring. The ligands **H-L$_1$**−**H-L$_4$** were synthesized by reacting the suitable thiophenol with 2-(bromomethyl)-4,6-di-*tert*-butylphenol using dry dimethyl formamide as the solvent according to a published procedure.[10] Aluminum complexes **1**−**4** were obtained, in quantitative yields, through a classical alkane elimination route with trimethylaluminum in benzene (Scheme 1). Solution ^{1}H NMR studies of the reactions performed in benzene-d_6 indicated that the neutral proligands were deprotonated by one metal alkyl of trimethylaluminum with the release of 1 equiv of methane. The disappearance of the O−H signal of the free ligands and the appearance of a resonance for the protons of two equivalent methyls bound to the aluminum in the high-field region of the ^{1}H NMR spectra demonstrated the formation of the desired complexes.

Scheme 1. Synthetic Route for Complexes 1−4



Complexes **1**−**4** were characterized by elemental analysis, NMR spectroscopy, and single-crystal X-ray diffraction (**2**).

Single crystals of **2** were grown from a saturated hexane solution at −20 °C. An ORTEP[11] view and selected bond distances and angles of complex **2** are shown in Figure 1 (see Tables S1 and S2 in the Supporting Information for crystallographic details). X-ray analysis established the monomeric nature of complex **2** and revealed a distorted-tetracoordinate geometry of the Al center effectively κ^2-chelated by the sulfur and oxygen atoms of the bidentate ligand. The Al−S bond length is 2.514(1) Å: i.e., in the range of other reported aluminum−thioether bond distances for coordination number 4.[12] The Al−O bond length of 1.749(2) Å is slightly lower than those of other phenolate−Al complexes. The Al(1)−O(1)−C(3)−C(8)−C(9)−S1 six-membered chelating ring displays a screw-boat S_6 conformation[13] with the following puckering parameters: Q_T = 0.872(2) Å, φ_2 = −90.9(2)°, θ_2 = 66.5(1)°.[14] Distorted-tetracoordinate Al complexes tend to adopt structures that are intermediate between the classical tetrahedral geometry and the more unusual trigonal-monopyramidal (TMP) geometry. These distortions may produce enhancement of the Lewis acidity of the metal center in comparison with that of the tetrahedral analogues, leading to very promising catalysts.[15−17] A quantitative measurement of the distortion is the angle-based parameter τ.[18] It determines the extent to which observed geometries are more like tetrahedral or TMP geometries.[19] An ideal tetrahedron has τ = 0, and an ideal vacant trigonal bipyramid has τ = 1. Using this measure, the Al atom of complex **2** has τ = 0.51; this indicates that the Al atom is about halfway between a tetrahedron and an axially vacant trigonal bipyramid.

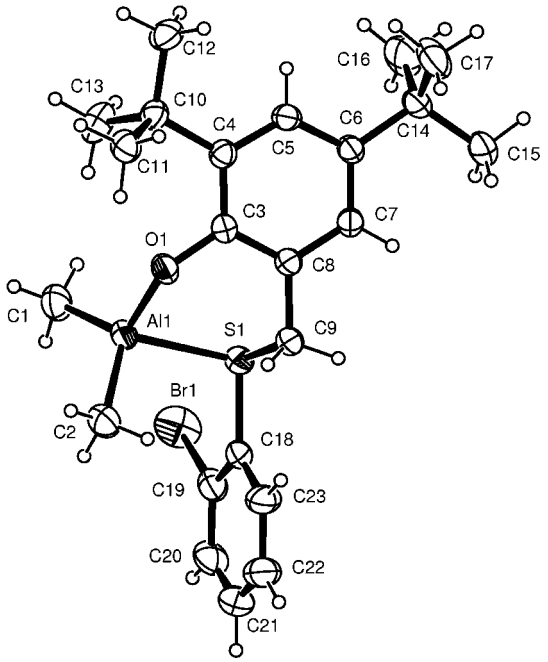


Figure 1. ORTEP view of the complex **2** showing thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): Al(1)−C(1), 1.942(3); Al(1)−C(2), 1.939(4); Al(1)−S(1) 2.514(1); Al(1)−O(1) 1.749(2); C(1)−Al(1)−C(2), 119.2(2); C(1)−Al(1)−S(1), 107.0(1); C(1)−Al(1)−O(1) 116.7(1); C(2)−Al(1)−O(1), 113.1(1); C(2)−Al(1)−S(1), 104.5(1); O(1)−Al(1)−S(1), 91.3(1).

In order to get more insight into the electronic structures of phenoxy-thioether aluminum complexes and to explore the effect of the substituents of the aromatic thioether ring, theoretical calculations were undertaken. Density functional theory (B3LYP) and Møller−Plesset second-order perturbation theory (MP2) were chosen as quantum chemical methods.

Complex **2** was chosen to evaluate the performance of the selected methods. The Al−ligand bond lengths in the optimized structures were measured and compared with corresponding experimental values from the X-ray structure. The results show that the B3LYP functional reproduces with moderate accuracy the geometry of the selected complex. In particular, the Al−S bond distance is overestimated by 0.10 Å. MP2 was found to perform much better and led to an acceptable value for the same Al−S distance, with an underestimation of 0.01 Å. In order to shed light on the strength of Al−ligand interactions in this class of complexes, Mayer bond orders were computed. The results of the calculations are summarized in Table 1. Very low bond orders were found for the Al−S bonds (ranging between 0.28 and 0.31), suggesting a small overlap between orbitals (or weak covalent bonding), whereas for the Al−C bonds the values were close to 1.

We were also interested in evaluating the influence of the substituent of the aromatic thioether ring on the Lewis acidity

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Table 1. Results of the Natural Bond Orbital (NBO) Analysis for the Aluminum Complexes: Bond Distances (d in Å), Mayer Bond Orders (bo), and Natural Charges at Aluminum (Q_{Al} in e) and Sulfur (Q_S in e)

complex	d_{Al-S}	bo	Q_{Al}	Q_S
1	2.536	0.309	1.797	0.311
2	2.567	0.282	1.823	0.353
3	2.540	0.302	1.810	0.327
4	2.545	0.305	1.801	0.330

of the metal center in complexes **1**–**4**. Two aspects were considered: the Al–S bond distance and the natural charges on the S and Al atoms (Table 1). The electronic charge on the Al atom and the Al–S bond distance can give indirect measurements of the Lewis acidity at the metal center: the greater the charge (or the longer the bond), the greater the Lewis acidity. The longest bond distance was observed for complex **2**, while the shortest distance was observed for complex **1**. The other two complexes featured intermediate values. Natural population analysis for Al and S atoms shows that the partial charges on these atoms have a similar trend. The phenoxo-thioether Al complexes reported in this study should display the following order of increasing Lewis acidity: **1** < **3** ≈ **4** < **2**. However, the changes in electronic charges and bond distances are moderate and the influence of the substituent of the aromatic thioether is expected to be modest.

Solution Structures of Aluminum Complexes 1–4. The ^{1}H NMR spectra of complexes **1**–**4** at room temperature showed no complexity and indicated the presence of symmetric structures; a sharp single resonance assigned to the Al–Me protons in the range −0.31 to −0.25 ppm, a sharp singlet ascribed to the S-CH_2-Ar methylene protons, and resonances corresponding to hydrogens of the aromatic rings were observed.

The uniqueness and the symmetry of these species in benzene-d_6 solution at room temperature are corroborated by the observation of a single set of resonances in the ^{13}C NMR spectra. The ^{13}C NMR spectra of complexes **1**–**4** all exhibited a single characteristic resonance for the carbon atoms of the $AlMe_2$ group in the region −8.60 to −7.80 ppm.

These data agree with an overall C_s symmetry for complexes **1**–**4** on the NMR time scale at room temperature and suggest a stereochemically nonrigid coordination environment at the metal center. The fluxionality supposed for the phenoxy-thioether aluminum complexes **1**–**4** in solution at room temperature has been investigated by variable-temperature (VT) NMR analyses.

The VT NMR analysis of complex **2** showed that, at subambient temperature, the resonance of methyl groups bonded to aluminum and that of the methylene bridge broaden and resolve each into two separate peaks (Figure 2). Coalescence of the signals was observed at −40 °C; below this temperature the resonances became sharp and well resolved and the ^{1}H NMR spectra are consistent with the chelation of one bidentate ligand to the metal center and with the solid-state structure being retained in solution.

Analogous fluxional behavior was observed for complexes **1**, **3**, and **4**, with coalescence temperatures in the range −40 °C to −50 °C.

Kinetic parameters were calculated for complexes **1** and **2** using line shape analysis of the ^{1}H NMR data measured over the temperature range 293–193 K in dichloromethane-d_2; selected ^{1}H NMR spectra and calculated exchange rates are shown in the Supporting Information. The free energies of activation for the fluxional processes were calculated from the line shape analysis of the Al–Me protons to be $\Delta G^{\ddagger}$ = 11.61 ± 0.90 kcal mol^{-1} and $\Delta G^{\ddagger}$ = 11.81 ± 0.09 kcal mol^{-1} at 293 K for **1** and **2**, respectively. The activation parameters were $\Delta H^{\ddagger}$ = 8.37 ± 0.08 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −11.05 ± 3.36 cal mol^{-1} K^{-1} for complex **1** and $\Delta H^{\ddagger}$ = 6.04 ± 0.26 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −19.38 ± 1.19 cal mol^{-1} K^{-1} for complex **2**. The data are consistent with a fast conformation change of the six-membered-ring aluminum metallacycle. A similar fluxional behavior was observed for other tetracoordinate aluminum complexes.[8,20,21]

Formation and Reactivity of Cationic Species. There has been a growing interest in the synthesis of cationic aluminum complexes, since the enhanced Lewis acidity of the aluminum center should yield higher catalytic activity and may lead to new applications.[22]

The ionization chemistry of N,N- and N,O-based Al neutral dialkyls has yielded novel families of highly Lewis acidic Al species, differently the synthesis and the study of the reactivity of cationic Al alkyl species supported by "softer" chelating ligands has still been scarcely explored.[8,23] Within this context, the synthesis of cationic aluminum compounds supported by bidentate OS ligands could be interesting, as these ligands combine a hard oxygen donor with a soft sulfur donor for the coordination to the reactive center.

Thus, the reaction of Al methyl complex **1** was carried out with 1 equiv of $B(C_6F_5)_3$, a classical methide abstracting reagent, to generate the corresponding Al cation.

The addition of 1 equiv of $B(C_6F_5)_3$ to a benzene-d_6 solution of (OS)$AlMe_2$ (**1**) afforded the neutral complex (OS)Al-(C_6F_5)Me in 24 h. The ^{1}H NMR spectrum exhibited a triplet at

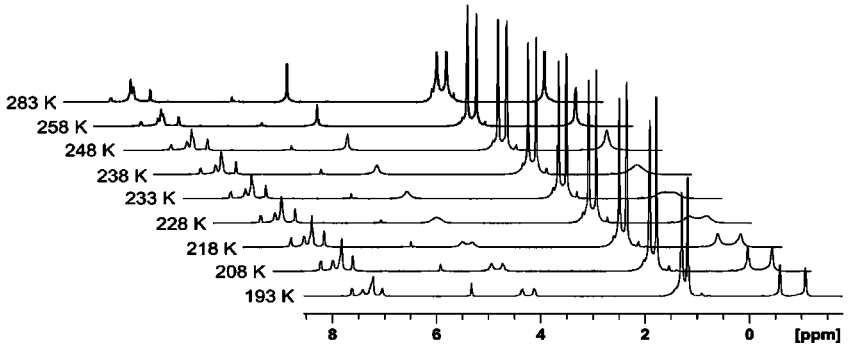

Figure 2. Variable-temperature ^{1}H NMR spectra of **2** in dichloromethane-d_2.

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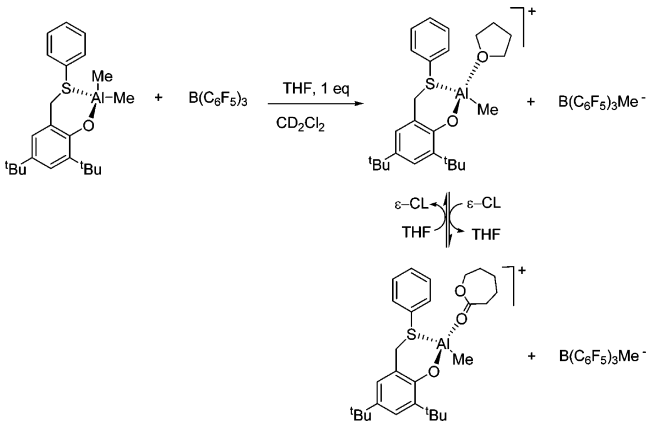
−0.16 ppm (J_{HF} = 1.12 Hz) characteristic of an Al−Me resonance coupled to the α-fluorines of a coordinated C_6F_5 group.[24] The methylene bridge of the OS fragment gave a well-resolved AB resonance centered at 3.68 ppm ($\Delta\delta$ = 0.21 ppm, J = 12.44 Hz); the diasterotopic nature of these protons is consistent with a strong coordination of the sulfur atom to the asymmetric aluminum center. Two quintets in the same ^{1}H NMR spectrum at 1.33 and 0.96 indicated the presence of $MeB(C_6F_5)_2$ and $Me_2B(C_6F_5)$ in a 4:1 molar ratio, respectively. The ^{19}F NMR spectrum revealed, inter alia, the presence of $MeB(C_6F_5)_3^-$, suggesting that the species $(OS)Al(C_6F_5)Me$ is formed by the transfer of a C_6F_5 group from $MeB(C_6F_5)_3^-$ by the first formed coordinatively unsaturated cationic intermediate.

Analogous results have been previously reported for the reaction of dialkylaluminum complexes bearing bidentate N,N or N,O ligands with $B(C_6F_5)_3$, leading to unstable tricoordinate alkylaluminum cations which react quite quickly by abstracting a C_6F_5 group from $MeB(C_6F_5)_3^-$ anions to form neutral $L_nAl(C_6F_5)R$ products.[24] Several studies have shown that the presence of a Lewis base B can stabilize the aluminum cation by forming $L_nAlR(B)^+$ adducts.[20,25] Gibson et al. showed that a pendant donor group, which is weakly bonding or nonbonding in the neutral aluminum complexes, becomes a normal donor group in the cationic derivatives upon reaction with $B(C_6F_5)_3$, thus stabilizing these species.[26]

Therefore, the "trapping" of the cationic species was obtained in the presence of THF as donor molecule in dichloromethane-d_2 solution. When $B(C_6F_5)_3$ (1 equiv) was added to a dichloromethane-d_2 solution of **1** containing 1 equiv of THF, a THF-coordinated aluminum methyl cation was formed (Scheme 2). Characteristic resonances in the ^{1}H NMR spectrum are signals at δ −0.31 for Al−Me, appearing at lower field in comparison with the resonance of the neutral compound **1** (δ −0.63 in dichloromethane-d_2) as a consequence of the positive charge on the aluminum atom, and a broad resonance at δ 0.46 for $B(C_6F_5)_3Me^-$, characteristic of the "free" anion,[27] thus suggesting that there are no relevant interactions between the cation and anion, at least under the experimental conditions used. The methylene bridge of the OS fragment gave in this case a singlet at 4.06 ppm, shifted to higher field with respect to the same signal in the neutral compound (4.20 ppm): this opposite effect, with respect to the $AlMe^+$ shift behavior, may be due to a decreased coordination of the "soft" sulfur atom, supplied by the presence of the "harder" oxygen of the THF external donor. As a matter of fact, the signals for the THF coordinated to the aluminum atom appeared at 4.20 and 2.18 ppm (OCH_2 and OCH_2CH_2, respectively), downfield with respect to the resonances of the "free" THF in the same solvent. Analogous results were previously observed for closely related phenoxy-imine and anilinotroponato aluminum compounds.[28]

Scheme 2. Formation of Cationic Species of Complex 1

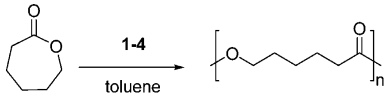


The reactivity of the cationic species thus formed toward ε-caprolactone was successively studied. One equivalent of ε-caprolactone was added to the same NMR tube, and a ^{1}H NMR spectrum was registered. Interestingly, the resonances of the THF were shifted to higher field (3.90 and 1.93, OCH_2 and OCH_2CH_2, respectively), toward those of the free THF species (3.69 and 1.82), while the resonances of the ε-caprolactone appeared as broad multiplets and were shifted downfield (4.47 ppm, $O-CH_2$; 2.71 ppm, $COCH_2$). Notably, the same resonances of the "free" ε-caprolactone in dichloromethane-d_2 appeared at 4.17 and 2.57 ppm, respectively. Moreover, the $AlMe^+$ and the $B(C_6F_5)_3Me^-$ singlet signals still appear at the previous chemical shifts, as well as the ligand's resonances. The whole picture may suggest a rapid intermolecular exchange process between the THF and the ε-caprolactone coordinated to the aluminum cation (Scheme 2). A similar exchange process between bound and "free" THF molecule was previously observed by Gibson[28a] for analogous systems.[29]

The same sequence of experiments was performed on compound **3** and produced analogous results.

Polymerization Studies. *Ring-Opening Polymerization of ε-Caprolactone.* The reactivity of compounds **1**−**4** in the ring-opening polymerization of ε-CL was studied (Scheme 3).

Scheme 3. Ring-Opening Polymerization of ε-Caprolactone Initiated by Complexes 1−4



Polymerization screenings were performed under a nitrogen atmosphere in a toluene solution of ε-CL and the proper aluminum compound. The polymers, precipitated from the reaction solution by addition of hexane, were analyzed by NMR and gel permeation chromatography (GPC).

The main results of the polymerization studies performed with complex **1** are summarized in Table 2.

Aluminum complex **1** exhibits good activity toward the ROP of ε-CL in the absence of alcohols (runs 1 and 2, Table 2). Two polymerization experiments carried out at 50 and 70 °C demonstrated that the conversion increased significantly with temperature (runs 1 and 2, Table 2). At 50 °C full conversion was obtained in 180 min. Under these reaction conditions, the initiation efficiency was 52%, suggesting that only half of the catalytic centers were active. The broad molecular weight distribution would reflect, at least in part, the poor initiation efficiency of the methyl group. On the other hand, when the same experiment was performed at 70 °C, 250 equiv of monomer were converted in 40 min with a slightly better agreement between calculated and experimental molecular weight values, suggesting that when temperature is increased, the efficiency of monomer first insertion on the Al−methyl bond increases.

As is well known in the literature, amido and alkyl initiators are usually inferior initiating groups with respect to metal

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Table 2. Ring-Opening Polymerization of ε-CL Promoted by Complex 1

run[a]	amt of MeOH (equiv)	temp (°C)	time (min)	conversn (%)[b]	M_n(th) (×10³)[c]	M_n(GPC) (×10³)[d]	M_w/M_n[d]
1		50	180	100	41.1	79.6	1.77
2		70	40	70	28.8	44.1	1.46
3	1	25	1140	100	41.1	50.3	1.40
4	1	50	130	100	41.1	50.8	1.30
5	1	70	30	100	41.1	44.2	1.49
6	2	70	30	96	19.7	23.9	1.26
7	10	70	30	94	3.9	5.2	1.11
8[e]	1	70	30	100	4.1	2.8	1.31

[a]General conditions: complex **1**, 25 μmol; toluene, 4 mL; [ε-CL]/[Al] = 360; MeOH, 1 equiv. [b]Conversion of ε-CL as determined by ^{1}H NMR spectral data. [c]M_n(th) (g mol^{-1}) = 114.14([ε-CL]$_0$/[I]$_0$) × conversion of ε-CL. [d]Experimental M_n (g mol^{-1}) and M_w/M_n values determined by GPC in THF against polystyrene standards and corrected using the factor 0.56. [e][ε-CL]/[Al] = 36.

alkoxides for the ROP of cyclic esters. The alkoxide initiating group mimics the propagating groups of the presumed active species and complexes with these moieties produce polymers of predictable molecular weights and with narrow molecular weight distributions. Alkoxide initiators can be generated in situ by alcoholysis of amido and alkyl complexes with alcohols.[5,6a,30] In this context, three polymerization experiments were conducted at different temperature by adding 1 equiv of methanol (runs 3−5, Table 2). Aside from confirming the beneficial effect of the temperature on the polymerization rate, it was observed that all the obtained PCLs possess quite narrow molecular weight distributions (M_w/M_n = 1.30−1.49) with unimodal characteristics. The M_n values determined by GPC (and corrected by the factor 0.56)[31] match excellently those calculated for a controlled polymerization, on the assumption that a single PCL chain is produced per metal center through initiation of the polymerization by the alkoxide group. These observations reflected the single-site nature of the active species and confirmed that, under these conditions, all the aluminum centers are active.

To explore the possibility of achieving immortal polymerization[32] with these systems, experiments were conducted in the presence of an excess of methanol as chain transfer agent. Representative results are shown in Table 2 (runs 6 and 7). Increasing the amount of methanol did not significantly affect the polymerization rate, and the obtained PCLs showed monomodal, narrow distributions with a good correlation between the experimental and calculated M_n values. These observations establish that the metal complex is stable in the presence of large amounts of free alcohol (i.e., the ligand is not displaced) and a fast reversible exchange between free alcohol and growing PCL chains takes place during the polymerization process. These processes compete with monomer propagation; however, since the observed PCL polydispersivities are low, this exchange reaction between alkoxides and free alcohol molecules takes place faster than chain propagation.[32b]

In order to confirm that the alkoxide ligand for this complex is the true initiatior of the ROP process, low-molecular-weight PCL was obtained by carrying out a polymerization experiment at a low CL/Al ratio (run 8, Table 2). ^{1}H NMR analysis of this PCL sample disclosed the presence of methyl ester end groups (−COOCH$_3$; 3.65 ppm), generated via insertion of the monomer unit into the Al−OCH$_3$ bond with cleavage of the acyl−oxygen bond of the monomer, and hydroxyl end groups (CH$_2$CH$_2$OH; 3.62 ppm), generated by hydrolysis of the growing chain. No signals were observed in the aromatic region. These data confirm that the terminal alkoxide OMe group is the only initiating moiety involved in the polymerization process; therefore, a coordination−insertion mechanism, proceeding through acyl−oxygen cleavage of the monomer, should be operative in this system.[33] Moreover, the agreement between the M_n value determined by GPC (M_n(GPC) = 2804) and that determined by NMR (M_n = 3424) indicated that the polymerization proceeds exclusively by the mechanism detailed above.

To evaluate the potential of cationic aluminum compounds supported by bidentate OS ligands in the ROP of ε-caprolactone, a polymerization test was performed under the same reaction conditions used for the neutral species (see run 1 in Table 2). The cationic species, generated in situ by reaction of complex **1** and 1 equiv of B(C$_6$F$_5$)$_3$, was found to initiate the ROP of ε-CL with a very low activity in comparison with the corresponding neutral derivative (a conversion of 15% was obtained in 180 min). The lack of activity of the cationic species in ε-CL polymerization under the conditions studied can be ascribed to the strong Lewis acidity of the Al metal center of the cationic species that should form a robust Lewis acid/base adduct with the cyclic ester.

In an effort to investigate the effects of modifying the steric and electronic environment around the reactive center, we carried out a study of the polymerization behavior of phenoxy-thioether aluminum complexes **1**−**4** by performing ε-CL polymerization under the same reaction conditions (see Table 3).

The aluminum complexes **1**−**4** were all effective initiators for the ROP of ε-CL at 50 °C. Good activities were observed under these conditions with turnover frequencies (TOF) up to 900 h^{-1}. These activity data compare favorably with those of related phenoxy-imine and -amine catalysts under the same reaction

Table 3. Ring-Opening Polymerization of ε-CL Initiated by Complexes 1−4

run[a]	complex	conversn (%)[b]	M_n(th) (×10³)[c]	M_n(GPC) (×10³)[d]	M_w/M_n[d]
9	**1**	36	14.8	18.2	1.37
10	**2**	82	33.7	34.6	1.27
11	**3**	79	32.5	38.7	1.39
12	**4**	78	32.0	24.0	1.27

[a]General conditions: complex, 12.5 μmol; toluene, 2 mL; CL/Al = 360; cocatalyst (MeOH), 1 equiv; temperature, 50 °C; reaction time, 20 min. [b]Conversion of ε-CL as determined by ^{1}H NMR spectral data. [c]M_n(th) (g mol^{-1}) = 114.14([ε-CL]$_0$/[I]$_0$) × conversion of ε-CL. [d]Experimental M_n (in g mol^{-1}) and M_w/M_n values determined by GPC in THF against polystyrene standards and corrected using the factor 0.56.

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conditions,[6] and result much better than those obtained with the O,P-phosphinophenolate aluminum complexes.[8]

From the data reported in Table 3 it is found that the presence of a substituent in the ortho position of the aromatic thiophenol ring results in a beneficial effect in terms of catalytic activity; in fact, complexes **2**−**4** all were more active than unsubstituted complex **1**, giving similar conversions.

Kinetic investigations were conducted by NMR experiments to establish the reaction order with respect to monomer concentration.

The polymerization kinetics were studied with $[\varepsilon\text{-CL}]_0/[\text{Al}]_0$ = 100 at 50 °C using toluene-d_8 as solvent. For all complexes the polymerization obeyed first-order kinetic in monomer with instantaneous initiation (Figure 3). Within the series of

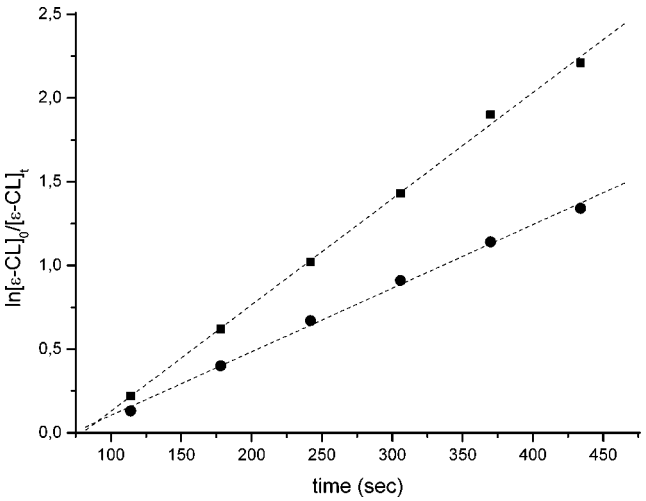
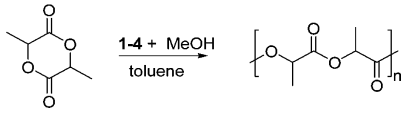


Figure 3. Pseudo-first-order kinetic plots for ROP of ε-CL promoted by **1** (●) and **2** (■). The pseudo-first-order rate constants are (3.80 ± 0.10) × 10^{-3} s^{-1} (●) (R = 0.999) and (6.34 ± 0.13) × 10^{-3} s^{-1} (■) (R = 0.998). Conditions: [Al] = 1.0 × 10^{-2} M; [ε-CL]/[Al] = 100; T = 50 °C; toluene-d_8 as solvent.

complexes, the relative rates correlate well with the activities observed in the polymerization runs reported in Table 3. The fastest polymerization was observed for complex **2**, having the pseudo-first-order rate constant k_{app} = 6.34 × 10^{-3} s^{-1}. Kinetic plots for complexes **1** and **2** are reported in Figure 3.

Ring-Opening Polymerization of Lactides. Polymerizations of L- and *rac*- lactide were performed with **1**−**4** in toluene solution at 80 °C, in the presence of MeOH (Scheme 4). Polymers were characterized by NMR and GPC.[34] The main results of the polymerization studies are summarized in Table 4.

Scheme 4. Ring-Opening Polymerization of Lactide Initiated by Complexes 1−4



In the ROP of L-lactide the **1**/MeOH system exhibited the highest catalytic activity among complexes **1**−**4** under the same polymerization conditions (cf. runs 13−16, Table 4). The polymerization data may suggest that the catalytic activity decreases with the increase of steric hindrance offered by the ortho substituent on the aromatic ring of the sulfur donor. This could be explained in light of the sterically demanding character of the monomer lactide and with the increased steric encumbrance around the reactive center due to the possible chelation by a carbonyl group of the lactate arm to form a five-membered-ring η^2-lactate−Al unit. This coordination is frequently observed, for both cationic and neutral aluminum species.[21]

All polymerizations proceeded in a living fashion, leading to polymers with monomodal and very narrow molecular weight distributions (M_w/M_n = 1.12−1.16). In fact, the experimental number average molecular weights (M_n) showed a good agreement with the theoretical values and a linear correlation with monomer conversion (Figure 4).

The addition of excess alcohol as an initiator/chain transfer agent accelerated the reaction and an effective immortal polymerization was achieved (cf. runs 14 and 17, Table 4).

Complexes **1**−**4** were active in the polymerization of *rac*-lactide (runs 18−21, Table 4). In all cases the homodecoupled ^{1}H NMR spectra of the methine regions of PLAs show atactic microstructures.

The ^{1}H NMR spectra in $CDCl_3$ of PLAs (see Figure S8 in the Supporting Information) obtained with methoxide systems (**1**−**4**/MeOH) show a resonance at δ 3.73 ppm for the methyls of a $COOCH_3$ group and a broadened quartet at δ 4.35 and a doublet at 2.66 ppm characteristic of the CH(Me)OH terminal group (the doublet for the methylic protons of the same group mostly overlaps with those of PLA). The observation of these end groups suggests that the ROP proceeds via a classical coordination/insertion mechanism: i.e., initial acyl−oxygen bond cleavage by the transfer of the nucleophilic methoxide group of the metal complex to the monomer with the eventual formation of a metal alkoxide propagating species, which is hydrolyzed at the end of the reaction. A strictly agreement between the M_n value determined by GPC (M_n(GPC) = 10400) and that determined by NMR (M_n ^{1}H NMR 10800) was observed.

■ CONCLUSIONS

The present work shows that bidentate phenoxy-thioether (OS) ligands, which combine a hard phenoxide donor with a soft sulfur donor, are suitable ligands in the coordination chemistry of the hard Lewis acid aluminum(III), as they readily form stable and monomeric monoadducts of the type $OSAlMe_2$. All aluminum complexes have been synthesized via alkane elimination reactions in almost quantitative yields.

Their catalytic performances in ε-CL, L-LA, and *rac*-LA ring-opening polymerization have been explored. In all cases the polymerizations proceed in a controlled fashion and immortal polymerization are achieved upon addition of an excess of methanol, as a chain transfer agent. End group analyses of the obtained oligomer samples support a classical coordination−insertion mechanism.

The substituents at the ortho position of the aromatic ring bound to the sulfur atom have a moderate effect on the catalytic behavior of the aluminum complexes. In particular, the presence of a substituent at the ortho position of the thiophenol aryl ring resulted in an increase of the catalytic activity in the ε-caprolactone polymerization, regardless of the size and the electronic character of the substituent, whereas in the polymerization of lactide a decrease in the catalytic activity was observed by increasing the size of the substituent.

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Table 4. Polymerization of L- and *rac*-Lactide Initiated by Complexes 1−4

run[a]	cat.	amt of MeOH (equiv)	mon	time (h)	conversn (%)[b]	M_n(th) (×10³)[c]	M_n(GPC) (×10³)[d]	M_w/M_n[d]
13	**1**	1	L-LA	48	77	11.1	11.6	1.14
14	**2**	1	L-LA	48	54	7.8	8.7	1.12
15	**3**	1	L-LA	48	57	8.2	7.3	1.14
16	**4**	1	L-LA	48	38	5.5	4.0	1.16
17	**2**	4	L-LA	24	98	3.5	3.8	1.11
18	**1**	4	*rac*-LA	24	98	3.5	3.1	1.14
19	**2**	4	*rac*-LA	24	99	3.5	3.2	1.16
20	**3**	4	*rac*-LA	24	99	3.6	3.1	1.15
21	**4**	4	*rac*-LA	24	97	3.5	3.3	1.18

[a]General conditions: complex, 12.5 μmol; toluene, 2 mL; T = 80 °C, [LA]/[Al] = 100. [b]Conversion of LA was determined by ^{1}H NMR analysis. [c]M_n(th) (in g mol^{-1}) =144.14([LA]$_0$/[I]$_0$) × conversion of LA. [d]Experimental M_n (g mol^{-1}) and M_w/M_n values determined by GPC in THF against polystyrene standards and corrected using the factor 0.58.

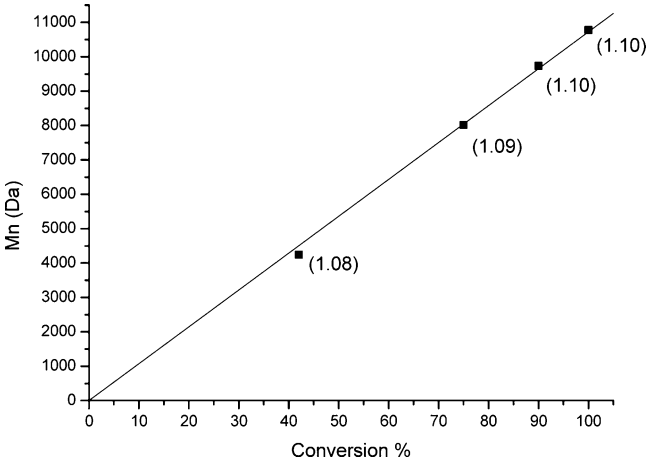

Figure 4. Plot of number-averaged molecular weights, M_n (Da), and PDI values versus conversion for PLLA produced by catalyst **2**/MeOH (1/1) at 80 °C. PDI values are given in parentheses.

EXPERIMENTAL SECTION

Materials and Methods. All manipulations of air- and/or water-sensitive compounds were carried out under a dry nitrogen atmosphere using a Braun Labmaster drybox or standard Schlenk-line techniques. Glassware and vials used in the polymerization were dried in an oven at 120 °C overnight and exposed three times to vacuum−nitrogen cycles.

Benzene, hexane, and toluene were distilled over sodium benzophenone. THF was distilled over $LiAlH_4$. Dimethylformamide and $AlMe_3$ were used as received. Deuterated solvents were dried using molecular sieves. Lactide was purified by crystallization from dry toluene. MeOH was purified by distillation over sodium. ε-CL was dried with CaH_2 for 24 h at room temperature and then distilled under reduced pressure.

All other chemicals were commercially available and used as received unless otherwise stated.

H-L$_1$ was prepared according to a published procedure.[10]

Instruments and Measurements. Elemental analyses were recorded on a Thermo Finningan Flash EA 1112 series C, H, N, S analyzer in the microanalytical laboratory of the institute.

The NMR spectra were recorded on a Bruker Avance 400 spectrometer (^{1}H, 400.13 MHz; ^{13}C, 100.62 MHz) at 25 °C, unless otherwise stated. Chemical shifts (δ) are given in parts per million and coupling constants (J) in hertz. ^{1}H NMR spectra are referenced using the residual solvent peak at δ 7.16 for C_6D_6 and δ 7.27 for $CDCl_3$. ^{13}C NMR spectra are referenced using the residual solvent peak at δ 128.39 for C_6D_6 and δ 77.23 for $CDCl_3$. ^{19}F NMR spectra are referenced to external $CFCl_3$.

Variable-temperature ^{1}H NMR experiments were performed with a Bruker AVANCE 400 (operating at 400.13 MHz) in CD_2Cl_2 using NMR tubes equipped with J. Young valves. NMR spectral simulations were performed using WINDNMR (DNMR71.EXE)[35] by taking into account the ^{1}H chemical shift variation of complex **1** as a function of temperature: shifts were measured below the exchange region and extrapolated into the temperature range where simulations were performed. Final simulated line shapes were obtained via an iterative parameter search upon the exchange constant k. Estimated standard deviations (s) in the slope and the y intercept of the Eyring plot determined the errors in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, respectively. The standard deviation in $\Delta G^{\ddagger}$ was determined from the formula $\sigma^2(\Delta G^{\ddagger}) = \sigma^2(\Delta H^{\ddagger}) + T^2\sigma^2(\Delta S^{\ddagger}) - 2T\sigma(\Delta H^{\ddagger})\sigma(\Delta S^{\ddagger})$.

The molecular weights (M_n and M_w) and the molecular mass distribution (M_w/M_n) of polymer samples were measured by gel permeation chromatography (GPC) at 30 °C, using THF as solvent, an eluant flow rate of 1 mL/min, and narrow polystyrene standards as reference. The measurements were performed on a Waters 1525 binary system equipped with a Waters 2414 RI detector using four Styragel columns (range 1 000−1 000 000 Å). Every value was the average of two independent measurements. It was corrected using the factor 0.58 for polylactide and 0.56 for polycaprolactone according to the literature.

Computational Details. All calculations were performed using the Gaussian 03 program package.[36] The complexes were energy-minimized without symmetry constraints at the B3LYP[37] levels of theory using the standard 6-31G(d) basis set for C and H and the 6-311G(d,p) basis set for all other atoms. Stationary point geometries were characterized as local minima on the potential energy surfaces. The absence of imaginary frequencies verified that structures were true minima at their respective levels of theory.

The structure optimized at B3LYP levels of theory was used as a starting point for successive reoptimization at the MP2 level using the same combination of basis sets.

The chemical bonding in the complexes was analyzed by employing the natural bond orbital (NBO) partition scheme by Weinhold and co-workers[38] using the natural bond orbital program (NBO 3.1),[39] as implemented in Gaussian 03. The NPA analysis was obtained by performing MP2 single-point calculations at the previously MP2 optimized structures.

Synthesis of Proligands and Complexes. *Synthesis of H-L$_2$.* The reaction was performed according the procedure previously reported in the literature.[10] To a stirred solution of 2-bromothiophenol (0.927 g, 5.01 mmol) and K_2CO_3 in 50 mL of DMF at room temperature was added a solution of 2-(bromomethyl)-4,6-di-*tert*-butylphenol (1.50 g, 5.01 mmol) in 20 mL of DMF. The mixture was stirred at room temperature for 3 h. The product was extracted with 50 mL of diethyl ether and 50 mL of water. The organic layer was washed with water (3 × 25 mL). The organic solution was dried over sodium sulfate. The solvent was removed under vacuum, giving a pale yellow solid. Yield: 1.12 g; 50%.

^{1}H NMR (400.13 MHz, $CDCl_3$, 298 K): δ 7.57 (d, J = 8 Hz, 1 H, Ar*H*), 7.37 (d, J = 8 Hz, 1 H, Ar*H*), 7.22 (d, ^4J = 2 Hz, 1 H, Ar*H*), 7.08 (t, 1 H, J = 8 Hz, Ar*H*), 7.07 (t, J = 8 Hz, 1 H, Ar*H*), 6.90 (d, ^4J = 2

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Hz, 1 H, ArH), 6.00 (s, 1 H, OH), 4.20 (s, 2 H, CH_2), 1.44 (s, 9 H, CCH_3), 1.23 (s, 9 H, CCH_3). $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$, 298 K): 151.6 (q, CO), 142.7 (q, CS), 137.2 (q, CBr), 135.42 q, 133.3 (CH), 132.8 (CH), 128.8 (CH), 128.0 (CH), 126.8 q, 125.6 (CH), 124.2 (CH), 121.3 q, 36.7 (CH_2), 35.2 (CCH_3), 34.4 (CCH_3), 31.7 (CCH_3), 30.1 (CCH_3).

Synthesis of H-L₃. The synthesis of **H-L₃** was performed according to the same procedure as for **H-L₂**. Yield: 0.858 g; 52%.

^1H NMR (400.13 MHz, C_6D_6, 298 K): δ 7.40 (d, J = 2.5 Hz, 1H, ArH), 7.16 (m, 2H, ArH), 6.86 (m, 3H, ArH), 6.74 (d, J = 2.5 Hz, 1H, ArH), 6.16 (s, 1H, ArOH), 3.73 (s, 2H, CH_2), 2.14 (s, 3H, CH_3), 1.59 (s, 9H, CCH_3), 1.22 (s, 9H, CCH_3). $^{13}C\{^1H\}$ NMR (100.62 MHz, C_6D_6, 298 K): δ 152.1 q (CO), 142.4 q (CS), 139.6 q, 137.2 q, 133.8 q, 131.7 (CH), 130.4 (CH), 127.4 (CH), 126.7 (CH), 125.7 (CH), 123.8 (CH), 122.3 q, 36.7 (CH_2), 35.3 ($C(CH_3)_3$), 34.3 ($C(CH_3)_3$), 31.7 (CCH_3), 30.0 (CCH_3), 20.7 (CH_3Ar).

Synthesis of H-L₄. The synthesis of **H-L₄** was performed according to the same procedure as for **H-L₂**. Yield: 1.25 g; 52%.

^1H NMR (400.13 MHz, $CDCl_3$, 298 K): δ 7.62 (d, J = 8 Hz, 1H, ArH), 7.40 (d, J = 8 Hz, 1 H, ArH), 7.36 (t, J = 8 Hz, 1 H, ArH), 7.29 (t, J = 8 Hz, 1 H, ArH), 7.18 (d, J = 2.5 Hz, 1 H, ArH), 6.77 (d, J = 2.5 Hz, 1 H, ArH), 5.87 (s, 1H, ArOH), 4.15 (s, 2H, CH_2), 1.40 (s, 9H, CCH_3), 1.16 (s, 9H, CCH_3). $^{13}C\{^1H\}$ NMR (100.62 MHz, C_6D_6, 298 K): δ 152.1 q (CO), 142.5 q (CS), 137.5 q, 134.3 (CH), 131.7 q, 127.2 (CH), 126.9 (m, CF_3), 125.8 (CH), 133.97 q, 124.1 (CH), 121.7 q, 37.6 (CH_2), 35.2 ($C(CH_3)_3$), 34.2 ($C(CH_3)_3$), 31.6 ($C(CH_3)_3$), 30.0 ($C(CH_3)_3$). $^{19}F\{^1H\}$ NMR (376.45 MHz, C_6D_6, 298 K): δ −60.6.

Complex 1 (L₁AlMe₂). To a stirred solution containing $AlMe_3$ (0.110 g, 1.52 mmol) in benzene (4 mL) was added dropwise a solution of the ligand precursor (0.500 g, 1.52 mmol) in benzene (3 mL). The solution was stirred for 1 h at room temperature. The solvent was removed under vacuum, forming a pale yellow solid that was pure according to ^1H NMR and elemental analysis. Yield: 0.584 g; 95%.

^1H NMR (400.13 MHz, C_6D_6, 298 K): δ 7.53 (d, ^4J = 2.5 Hz, 1H, ArH), 6.90 (m, 2H, o-H Ph), 6.78 (m, 3H, m-H, p-H Ph), 6.59 (d, ^4J = 2.5 Hz, 1H, ArH), 3.73 (s, 2H, CH_2), 1.68 (s, 9 H, CCH_3), 1.26 (s, 9 H, CCH_3), −0.25 (s, 6 H, $AlCH_3$). ^1H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ 7.32−7.11 (overlapped multiplets, 4H, ArH), 6.47 (d, 1H, ArH), 4.20 (s, 2H, CH_2), 1.42 (s, 9 H, CCH_3), 1.17 (s, 9 H, CCH_3), −0.63 (s, 6 H, $AlCH_3$). $^{13}C\{^1H\}$ NMR (100.62 MHz, C_6D_6, 298 K): δ 156.1 q (CO), 140.9 q (CS), 139.6 q, 131.7 (2 CH), 129.8 (CH), 129.7 (2 CH), 129.5 q, 126.4 (CH), 125.7 (CH), 121.1 q, 40.3 (CH_2), 36.0 (CCH_3), 34.6 (CCH_3), 32.1 (CCH_3), 31.0 (CCH_3), −7.8 ($AlCH_3$). Anal. Calcd for $C_{23}H_{33}AlOS$: C, 71.84; H, 8.65; S, 8.34. Found: C, 71.69; H, 8.43; S, 8.22.

Complex 2 (L₂AlMe₂). To a stirred solution containing $AlMe_3$ (0.088 g, 1.23 mmol) in benzene (4 mL) was added dropwise a solution of the ligand precursor (0.500 g, 1.23 mmol) in benzene (4 mL). The solution was stirred for 1 h at room temperature. The solvent was removed under vacuum, forming a pale yellow solid that was pure according to ^1H NMR and elemental analysis. Yield: 0.553 g; 97% yield.

^1H NMR (400.13 MHz, C_6D_6, 298 K): δ 7.07 (d, ^4J = 2.5 Hz, 1H, ArH), 6.79 (m, 2H, ArH), 6.63 (dt, 1H, ArH), 6.26 (dt, 1H, ArH), 3.80 (s, 2H, CH_2), 1.64 (s, 9 H, CCH_3), 1.28 (s, 9 H, CCH_3), −0.29 (s, 6 H, $AlCH_3$). $^{13}C\{^1H\}$ NMR (75.47 MHz, C_6D_6, 298 K): δ 157.0 (q, CO), 140.5 (q, CS), 139.4 (q, CBr), 133.7 (CH), 131.2 (CH), 130.5 (CH), 129.5 q, 128.4 (CH), 125.9 (CH), 125.6 (CH), 125.1 q, 119.7 q, 38.5 (CH_2), 35.8 (CCH_3), 34.6 (CCH_3), 32.2 (CCH_3), 30.8 (CCH_3), −8.7 ($AlCH_3$). Anal. Calcd for $C_{23}H_{32}AlBrOS$: C, 59.61; H, 6.96; S, 6.9. Found: C, 58.83; H, 6.14; S, 6.77.

Complex 3 (L₃AlMe₂). To a stirred solution containing $AlMe_3$ (0.042 g, 0.58 mmol) in benzene (2 mL) was added dropwise a solution of the ligand precursor (0. 200 g, 0.58 mmol) in benzene (2 mL). The solution was stirred for 1 h at room temperature. The solvent was removed under vacuum, forming a pale yellow solid that was pure according to ^1H NMR and elemental analysis. Yield: 0.220 g,; 95%.

^1H NMR (400.13 MHz, C_6D_6, 298 K): δ 7.56 (d, ^4J = 2.4 Hz, 1H, ArH), 6.90−6.68 (m, 5H, ArH), 3.73 (s, 2H, CH_2), 2.06 (s, 3H, CH_3), 1.68 (s, 9 H, CCH_3), 1.30 (s, 9 H, CCH_3), −0.30 (s, 6 H, $AlCH_3$). $^{13}C\{^1H\}$ NMR (62.89 MHz, C_6D_6, 298 K): δ 156.6 (q, CO), 140.7 (q,CS), 139.4 q, 138.9 q, 131.2 (CH), 129.8 (CH), 129.2 (CH), 127.3 (CH), 126.0 (CH), 125.6 (CH), 120.6 q, 38.2 (CH_2), 35.9 (CCH_3), 34.6 (CCH_3), 32.2 (CCH_3), 30.9 (CCH_3), 20.3 ($ArCH_3$), −8.3 ($AlCH_3$). Anal. Calcd for $C_{24}H_{35}AlOS$: C, 72.32; H, 8.85; S, 8.04. Found: C, 72.21; H, 8.74; S, 8.17.

Complex 4 (L₄AlMe₂). To a stirred solution containing $AlMe_3$ (0.036 g, 0.50 mmol) in benzene (2 mL) was added dropwise a solution of the ligand precursor (200 mg, 0.50 mmol) in benzene (2 mL). The solution was stirred for 1 h at room temperature. The solvent was removed under vacuum, forming a pale yellow solid that was pure according to ^1H NMR and elemental analysis. Yield: 0.226 g; 95%.

^1H NMR (400.13 MHz, C_6D_6, 298 K): δ 7.51 (d, ^4J = 2.3 Hz, 1H, ArH), 7.16 (d, 1H, J = 6.5 Hz, ArH), 6.95 (d, 1H, J = 6.5 Hz, ArH), 6.58 (m, 2H, ArH), 6.53 (d, 2H, ^4J = 2.3 Hz, ArH), 3.79 (s, 2H, CH_2), 1.64 (s, 9 H, CCH_3), 1.19 (s, 9 H, CCH_3), −0.31 (s, 6 H, $AlCH_3$). $^{13}C\{^1H\}$ NMR (62.89 MHz, C_6D_6, 298 K): δ 155.9 (q, CO), 141.6 (q, CS), 139.7 q, 134.2 (CH), 132.4 (CH), 129.8 (CH), 127.7 (CH), 127.06 q, 126.3 (CH), 126.0 (CH), 120.7 q, 40.7 (CH_2), 35.9 (CCH_3), 34.5 (CCH_3), 32.1 (CCH_3), 31.0 (CCH_3), −7.9 ($AlCH_3$). Anal. Calcd for $C_{22}H_{27}F_3OS$: C, 63.70; H, 7.13; S, 7.09. Found: 63.65; H, 7.06; S, 7.11.

ε-Caprolactone Polymerizations. In a typical polymerization, a magnetically stirred reactor vessel (50 cm^3) was charged sequentially with a solution of precatalyst (25 μmol in 4 mL of dry toluene) and monomer (1 mL, 9.0 mmol). Subsequently, 0.25 mL of a solution 0.1 M of methanol in toluene (25 μmol) was added. The mixture was thermostated at the required temperature and, after the required polymerization time, poured into hexane. The precipitated polymer was recovered by filtration and dried at 40 °C in a vacuum oven. The polymer was characterized by NMR spectroscopy and GPC analysis. ^1H NMR ($CDCl_3$, 25 °C): δ 1.34 (m, 2H, $-CH_2-$), 1.62 (m, 4H, $-CH_2-$), 2.29 (t, 2H, $-CH_2C(O)O-$), 4.04 (t, 2H, $-CH_2OC(O)-$), 3.62 (t, 2H, $-CH_2OH$), 3.65 (s, 3H, $-C(O)OCH_3$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 24.7, 25.7, 28.5, 34.3, 64.3 ($-OCO(CH_2)_5-$), 51.7 ($-C(O)OCH_3$), 62.7 ($-CH_2OH$), 173.7 ($-COO-$).

Lactide Polymerizations. In a typical polymerization, a magnetically stirred reactor vessel (50 cm^3) was charged sequentially with the monomer (*rac*- or L-lactide, 350 mg, 2.4 mmol), the precatalyst (25 μmol), and 4 mL of dry toluene. Subsequently, 0.25 mL of a 0.1 M solution of methanol in toluene (25 μmol) was added. The mixture was thermostated at the required temperature and, after the required polymerization time, poured into hexane. The precipitated polymer was recovered by filtration and dried at 40 °C in a vacuum oven. Conversions were determined by integration of the monomer vs polymer methine resonances in the ^1H NMR spectrum of crude product (in $CDCl_3$). The polymer was purified by redissolving in CH_2Cl_2 and precipitating from rapidly stirred methanol. The polymer was characterized by NMR spectroscopy and GPC analysis. ^1H NMR ($CDCl_3$, 25 °C): δ 1.56 (m, 6H, $-CHCH_3-$), 3.79 (s, 3H, $-C(O)OCH_3$), 5.18 (m, 2H, $-CHCH_3-$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 16.8 ($-C(O)OCHCH_3-$), 69.2 ($-C(O)OCHCH_3-$), 169.5, 169.8 ($-COO-$).

Kinetic Experiments. In a typical experiment carried out in a Braun Labmaster glovebox, initiator solution, from a stock solution in toluene-d_8, was injected into a in Teflon-valved J. Young NMR tube loaded with the monomer dissolved in a suitable amount of toluene-d_8 as dry solvent. The sample was thermostated at the required temperature. The polymerization reaction was monitored via ^1H NMR analysis.

The characteristic chemical shift for each monomer in toluene-d_8 is 4.12 ppm (q, CH; lactide), and 3.63 ppm (m, CH_2; ε-caprolactone). The characteristic chemical shift for each polymer in toluene-d_8 is 5.12 ppm (q, CH; polylactide), and 4.00 ppm (t, CH_2; poly-ε-caprolactone).

Crystal Structure Determination. The crystal data of complex **2** were collected at room temperature using a Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα radiation. The data sets were integrated with the Denzo-SMN package[40] and corrected for Lorentz, polarization, and absorption effects (SORTAV[41]). The structure was solved by direct methods (SIR97[42]) and refined using full-matrix least squares with all non-hydrogen atoms anisotropic and hydrogens included on calculated positions, riding on their carrier atoms.

All calculations were performed using SHELXL-97[43] and PARST[13] implemented in the WINGX[44] system of programs. The crystal data are given in Table S1 (Supporting Information). Selected bond distances and angles are given in Table S2 (Supporting Information).

Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 859040. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or on application to the CCDC, Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223-336033; e-mail, deposit@ccdc.cam.ac.uk).

■ ASSOCIATED CONTENT

Supporting Information

Figures, tables, and a CIF file giving ^{1}H NMR spectra of complexes **1**–**4**, details on variable-temperature experiments, and crystallographic data for complex **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(33) Following a reviewer's suggestion, in order to discriminate between the "coordination−insertion" and the "activated monomer" mechanisms, both resulting in the same end groups, the ^{1}H NMR monitoring of the reaction of complex **1** with 1 equiv of MeOH was carried out in C_6D_6 at room temperature. Although a complex mixture of products was observed, the formation of methane (signal at 0.16 ppm) suggested the alcoholysis of the aluminum−methyl bond, ruling out the "activated monomer" mechanism.
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