# Articles

## Ring-Opening Polymerization of ϵ-Caprolactone and L-Lactide Using Aluminum Thiolates as Initiator

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ABSTRACT: Polyesters containing thiolate chain end were obtained from the "controlled" ring-opening polymerization (ROP) of ϵ-caprolactone or δ-valerolactone initiated by several novel aluminum thiolates. The initiators, [(MOBT)$_2$AlR] (**1**, R = Me; **2**, R = Cl) can be obtained in high yield from the interaction of Me$_3$Al or Et$_2$AlCl with 2 molar equiv of 2-methoxybenzenethiol (MOBT-H). [(μ-TMBM)AlR$_2$]$_2$ (**3**, R = Et; **4**, R = Me; **5**, R = Bu$^i$) were prepared from the reactions of R$_3$Al with 1 molar equiv of 2,4,6-trimethylbenzylmercaptan (TMBM−H) in dichloromethane at ambient temperature. The X-ray structures of **1**−**3** have been determined and have shown that **1** and **2** are monomeric while **3** is dimeric in the solid state. The "controlled" character of the aluminum complex shown in the polymerization process has enabled us to synthesize a P-δ-VL-*b*-P-ϵ-CL block copolymer, and the thioester end group may provide a suitable method for the design of PCL conjugates. In addition, ROP of L-lactide initiated by **1** can be achieved under refluxing toluene conditions.

### Introduction

Polyesters such as poly(ϵ-caprolactone) (PCL),[1] polylactide (PLA),[2] and their copolymers are of great interest for their applications in the medical field as biodegradable surgical sutures or as a delivery medium for controlled release of drugs[3] due to their biodegradable, biocompatible, and permeable properties.[4] The major polymerization method used in the syntheses of these polymers has been ring-opening polymerization (ROP) of lactones and related compounds by a coordination, anionic, and cationic initiator.[5] In particular, aluminum alkoxide based initiator systems seem to be active and suited for this purpose due to their high Lewis acidity and low toxicity. For example, we have described recently that the "living" and "immortal" polymerization of CL and valerolactone (VL) could be promoted by a novel aluminum benzyl alkoxide, giving polyesters with very narrow molecular weight distribution.[6] Despite the fact that some excellent initiators have been reported for the living polymerization of these monomers, the synthesis of well-defined polyesters with precisely controlled end group functionalities still remains of interest.[7] Aluminum thiolates are chosen as initiators for their excellent properties. For instance, dimethylaluminum thiolates (Me$_2$AlSR′) initiate polymerization of lactones in a living fashion, leading to the formation of polyesters with a hydroxy functional end and an alkanethiolate (−COSR′) end group from the initiator which further reacts with poly(ethylene glycol) (PEG) derivatives affording a PCL−PEG copolymer.[8] Though many aluminum thiolates have been synthesized, only three examples of aluminum thiolates as initiators for the ROP of lactones have been reported.[9,10] Among these initiators, only one of them has been fully structurally characterized.[9] Therefore, we report here the synthesis, characterization, and X-ray structure determinations of several novel aluminum thiolates. Their activities toward ROP of caprolactone, valerolactone, and L-lactide are also presented.

### Results and Discussion

**Syntheses and Molecular Structure Studies.** The reaction of Me$_3$Al or Et$_2$AlCl with 2 molar equiv of 2-methoxybenzenethiol (MOBT-H) in hexane yields a pentacoordinated monomeric aluminum complex [(MOBT)$_2$AlR] (**1**, R = Me; **2**, R = Cl) as shown in Scheme 1. Both compounds are isolated as colorless crystalline solid. The $^{27}$Al NMR peak position (δ 121.4 ppm) and width ($W_{1/2}$ = 5853 Hz) of **1** are consistent with a five-coordinate aluminum center.[11] The methyl group bound to aluminum of compound **1** occurs as sharp signals in the $^1$H NMR and $^{13}$C NMR spectra at δ = −0.39 and −8.06 ppm, respectively. Besides this, $^1$H NMR spectroscopic studies of **1** at both 20 and −60 °C show only one set of resonances for the methoxy group on the phenyl ring as well as the Al−Me group. These results tell us that among the five possible trigonal pyramidal isomers for [(MOBT)$_2$AlR] (Chart 1), only the most stable conformation **A** exists in the solution. This is further verified by the X-ray single-crystal structure determinations of **1** and **2**. In addition, [(μ-TMBM)AlR$_2$]$_2$ (**3**, R = Et; **4**, R = Me; **5**, R = Bu$^i$) were obtained in high yield from the reactions of R$_3$Al with 1 molar equiv of 2,4,6-trimethylbenzylmercaptan (TMBM−H) in dichloromethane at ambient temperature, followed by crystallization from hexane to afford the white crystalline solids (Scheme 2). $^1$H NMR spectra and microanalyses of **3**−**5** are consistent with our expectations. Their structures are

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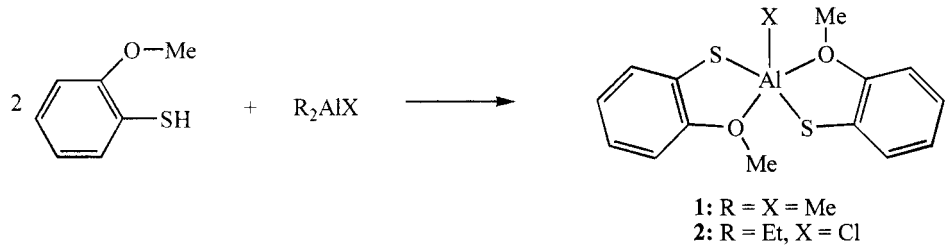
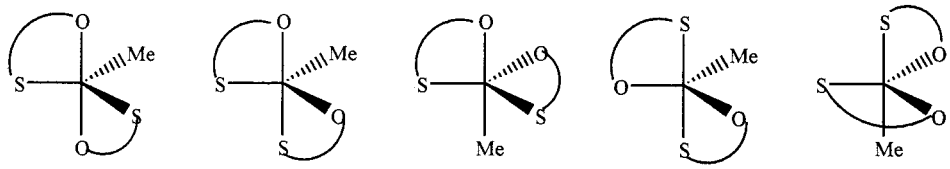
**Scheme 1**

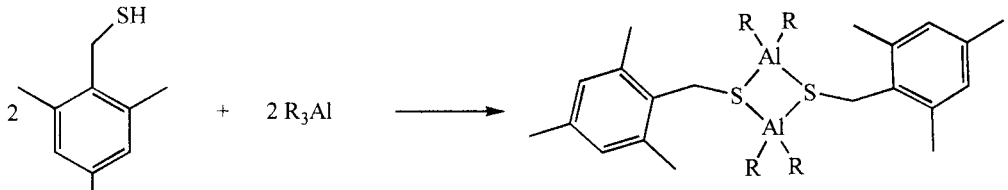



**1:** R = X = Me
**2:** R = Et, X = Cl

**Chart 1**




**Scheme 2**




**3**: R = Et; **4**: R = Me; **5**: R = $Bu^i$

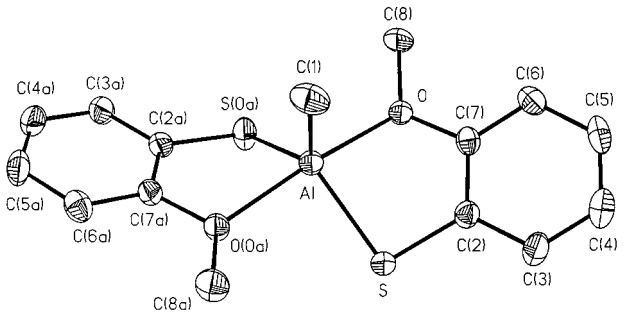



**Figure 1.** Molecular structure of **1** as 20% ellipsoids. All hydrogen atoms are omitted for clarity.

further verified by the X-ray single-crystal structure determination of **3**.

The molecular structure of **1** is shown in Figure 1, and the comparison of selected bond lengths and bond angles of **1** and **2** is listed in Table 1. Compound **1** crystallizes in the space group *C*2/*c* with the Al and C(1) atoms are residing on the crystallographic $C_2$ axis. The geometry around Al is a distorted trigonal bipyramid with C(1), S and S(0a) in the equatorial positions and O and O(0a) atoms in the axial positions. The total angles of the basal triangular face, defined by the two equatorial sulfurs and the carbon atom, equal to the ideal value 360° due to its $C_2$ symmetry. The bond distances of Al−C(1) = 1.941(4) Å, Al−S 2.257(1) = Å and Al−O = 2.087(2) Å are all within the normal range for Al−C, Al−O, and Al−S bonds for pentacoordinated aluminum complexes.[9] Compound **2**, which differs from compound **1** only by replacing the Me group with Cl, is isomorphic with **1**. The average Al−S distance of 2.231(1) Å and Al−O distance of 2.008(1) Å in **2** are all slightly shorter than those observed in **1**. This result is consistent with our expectation due to the higher electronegativity of a chlorine atom than a carbon atom.

**Table 1. Comparison of Selected Bond Distances (Å) and Bond Angles (deg) for 1 and 2**

| | **1** | **2** |
|---|---|---|
| Al−X | 1.941(4) | 2.1617(13) |
| Al−O(a) | 2.0867(15) | 2.0082(14) |
| Al−O | 2.0867(15) | 2.0082(14) |
| Al−S(a) | 2.2565(8) | 2.2306(7) |
| Al−S | 2.2565(8) | 2.2306(7) |
| X−Al−O(a) | 95.10(5) | 92.60(6) |
| X−Al−O | 95.10(5) | 92.60(6) |
| O(a)-Al−O | 169.80(10) | 174.80(11) |
| X−Al−S(a) | 120.51(3) | 118.39(3) |
| O(a)−Al−S(a) | 82.66(4) | 85.38(5) |
| O−Al−S(a) | 92.15(5) | 92.14(5) |
| X −Al−S | 120.51(3) | 118.39(3) |
| O(a)−Al−S | 92.15(5) | 92.14(5) |
| O−Al−S | 82.66(4) | 85.38(5) |
| S(a)−Al−S | 118.98(6) | 123.22(6) |

[a] X = C(1) for **1** and X = Cl for **2**.

A single crystal suitable for X-ray determination of **3** is obtained from the slowly cooling of a hexane solution. The ORTEP of **3** is shown in Figure 2 and the selective bond lengths and bond angles are listed in Table 2. The molecular structure of **3** is a dimeric feature bridging through the S atoms, and the coordination geometry around Al is a distorted tetrahedral. Atomic parameters such as Al−S distances of the thiolato ligands [2.343(2), 2.353(2) Å] and Al−$CH_3$ distances [1.965(5), 1.973(6) Å] are all within the expected range for a four-coordinated aluminum with a $Al_2S_2$ ring.[12]

**Ring-Opening Polymerization of ϵ-Caprolactone and δ-valerolactone.** The catalytic activities of **1**, **2**, **3**, and **5** toward ϵ-caprolactone (ϵ-CL) and δ-valerolactone (δ-VL) have been studied, and all four compounds have shown efficient activities. In general, polymerization of caprolactone was carried out at 25 °C in toluene (20 mL) using **1** (0.20 mmol) as the initiator. To a

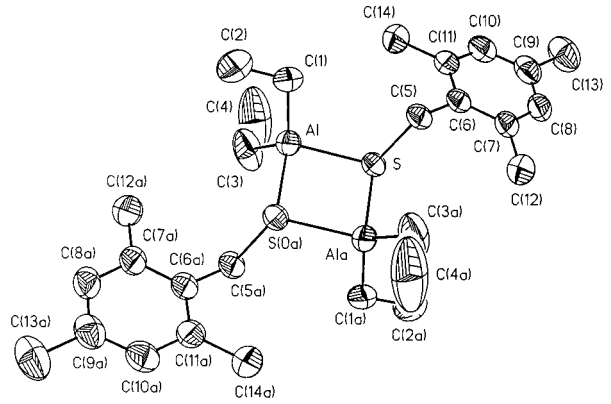



**Figure 2.** Molecular structure of **3** as 20% ellipsoids. All hydrogen atoms are omitted for clarity.

**Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 3**

| | | | |
|---|---|---|---|
| Al−C(1) | 1.965(5) | Al−C(3) | 1.973(6) |
| Al−S(a) | 2.3434(16) | Al−S | 2.3530(16) |
| S−C(5) | 1.849(3) | S−Al(a) | 2.3434(16) |
| C(1)−Al−C(3) | 124.2(3) | C(1)−Al−S(a) | 105.01(17) |
| C(3)−Al−S(a) | 111.5(2) | C(1)−Al−S | 110.26(16) |
| C(3)−Al−S | 106.7(3) | S(a)−Al−S | 95.50(5) |
| C(5)−S−Al(a) | 109.47(15) | C(5)−S−Al | 107.05(14) |
| Al(a)−S−Al | 84.50(5) | | |

rapidly stirred solution of [(MOBT)$_2$AlMe] (0.064 g, 0.20 mmol) in toluene (20 mL) was added $\epsilon$-CL (0.63 mL, 6.0 mmol). The reaction mixture was stirred at 25 °C for 2 h, during which an increase in viscosity was observed. After the reaction was quenched by adding excess 0.35 N acetic acid solution, the polymer was precipitated into *n*-heptane. The experimental result shows that these aluminum thiolates initiate the polymerization of lactones in a "controlled" fashion, giving polymers with low polydispersity indexes (PDI = $M_w/M_n$) in a wide range of monomer to initiator ($[M]_0/[I]_0$) ratios. To understand the initiating process, $^1$H NMR studies on the PCL initiated by **1** were carried out as shown in Figure 3. The $^1$H NMR spectrum of PCL-30 (the number 30 indicates the designed $[M]_0/[I]_0$ ratio) gives an intensity ratio closed to 1 between $H_c$ ($CH_2$ from $\epsilon$-CL at the thioester chain end) and $H_h$ ($CH_2$ from $\epsilon$-CL at the hydroxy end). The observed result tells us that the initiation occurs through the insertion of a thiolyl group from compound **1** to caprolactone, giving an aluminum alkoxide intermediate, which further reacts with excess lactones, giving polyesters. The result is in agreement with our expectation that the polymer chain should be capped with one thioester and one hydroxy end.

Polymerizations of $\epsilon$-CL under different reaction conditions (entries 1−17) have been systematically conducted as shown in Table 3. It was found that the PDIs of polyesters initiated by **1** range from 1.19 to 1.44, and a linear relationship between the number-average molecular weight ($M_n$) and the monomer-to-initiator ratio ($[M]_0/[I]_0$) exists as shown in Figure 4 (entries 1−5), implying the controlled character of the polymerization process. The "controlled" character was further confirmed from the polymerization resumption experiment. In the resumption experiment (entry 6), more $\epsilon$-CL monomer was added after the polymerization of the first addition had gone to completion. The molecular weight increased for the final polymer ($M_n$ = 21 400, PDI = 1.25), relative to the first ($M_n$ = 11 300, PDI = 1.39). It is interesting to note that polymerization initiated by **2** is noticeably less controlled than **1**, as can be judged by the higher PDIs as well as by the rather erratic ratios ranging from 0.33 to 0.40 (Table 3, entries 7−11). The reason for the higher PDIs and erratic ratios of polyesters obtained from the ROP of caprolactone initiated by **2** is not known. In addition, compound **3** also shows good activity toward polymerization of caprolactone in a controlled manner with a much slower rate than that of **1** and **2** (entries 12−17). This result may be contributed to the fact that there is only one Al−S function in **3** compared to two Al−S functions in **1** and **2**.

In addition, compound **5** is also active for the ROP of caprolactone and valerolactone (Table 4, entries 1−7). By use of this convenient initiating system, we attempted the synthesis of a narrow PDI block copolymer from $\delta$-VL and $\epsilon$-CL. Thus, the poly($\delta$-VL-*b*-$\epsilon$-CL) (PVL-*b*-PCL) block polymer ($M_n$ = 23900, $M_w/M_n$ = 1.21 and WPCL = 53%, entry 7) was synthesized by the sequential ROP of $\delta$-VL ($[M]_0/[Al]_0$ = 30) monomer in the presence of [Bu$^i_2$Al($\mu$-TMBM)]$_2$ (**5**) at room temperature for 20 h followed by the addition of $\epsilon$-CL ($[M]_0/[Al]_0$ = 30) and stirred for another 20 h. However, the initiation rate of **5** is much slower than that of **3**, probably due to the steric hindrance of isobutyl groups on aluminum retarding the interaction between the Al center and lactones.

Notably, in these experiments, the experimental values of $M_n$(GPC) obtained from the GPC are always much higher than the theoretical values, $M_n$(calcd) as shown in Tables 3 and 4. The ratio between $M_n$(calcd) and $M_n$(GPC) has a value of about 0.25 per Al−S function for the polyester initiated by **1**. One of the possible reasons for the unexpected high values of $M_n$(GPC) is that $M_n$ values obtained from GPC, based on the polystyrene standard, differ substantially from the actual molecular masses of the poly(aliphatic esters). Maclain and Drysdale have suggested that a factor of 0.45 should be multiplied by the $M_n$(GPC), giving the actual $M_n$ of poly($\epsilon$-caprolactone).[13] This is confirmed by the $M_n$(NMR) values obtained from the $^1$H NMR analysis. Another reason is that transesterfication occurs during the polymerzation process. If transesterfication effectively competes with ROP, the PDIs of resultant polymer should broaden with increasing conversion, and molecular weight distributions may be bimodal.[14] However, our observations are not consistent with the predicted effect of transesterfication.

**Ring-Opening Polymerization of L-Lactide Initiated by 1.** Lactide is made of lactic acid derived from natural renewable sources and is a good candidate to replace nonbioresorbable polymers due to its excellent mechanical properties.[15] Therefore, the ring-opening polymerization of L-lactide initiated by complexes **1**, **2**, **3**, or **5** is studied. Among them, only compound **1** is active for the ROP of L-lactide under refluxing toluene condition. GPC analyses reveal that the PDIs of poly(L-lactide) initiated by **1** are quite narrow, ranging from 1.15 to 1.25, and the "controlled" character of **1** can be concluded from the linear relationship between the number-average molecular weight ($M_n$) and the monomer-to-initiator ratio ($[M]_0/[I]_0$) as shown in Table 5. (entries 1−5). For the lactide-to-initiator ratio of 20 to 1, a conversion yield of 66% was achieved after 24 h at 110 °C based on the NMR spectroscopic studies. However, the conversion is obtained in 88% with similar molecular weight when the reaction was run under refluxing xylene temperature.

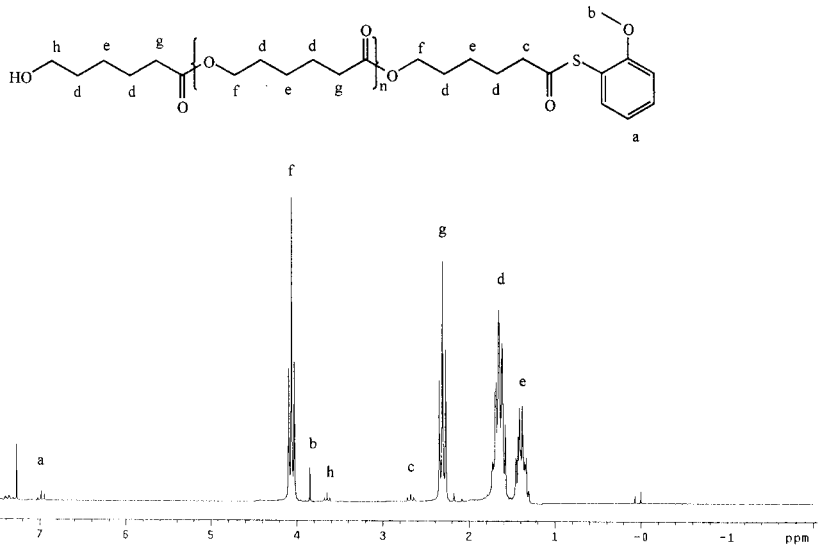



**Figure 3.** $^1$H NMR spectrum of PCL-30 initiated by **1** in $CDCl_3$.

**Table 3. Ring-Opening Polymerization of $\epsilon$-Caprolactone Initiated by Complexes 1, 2, and 3**

| entry | initiator | $[M]_o/[Al]_o$ | time (h) | $M_w/M_n$ | $M_n$(GPC)[a] | $M_n$(calcd)[b] | $M_n$(NMR)[c] | convn (%)[c] | yield[d] | ratio[e] |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **1** | 20 | 2 | 1.40 | 5300 | 2430 | 2900 | 100 | 80 | 0.46 |
| 2 | **1** | 30 | 2 | 1.44 | 6900 | 3570 | 4400 | 100 | 96 | 0.52 |
| 3 | **1** | 50 | 2 | 1.39 | 11300 | 5850 | 7100 | 100 | 89 | 0.52 |
| 4 | **1** | 100 | 2 | 1.30 | 23100 | 11400 | | 100 | 99 | 0.50 |
| 5 | **1** | 200 | 2 | 1.19 | 45300 | 21300 | | 93 | 93 | 0.47 |
| 6 | **1** | 50 (50) | 4 | 1.25 | 21400 | 11600 | | | 93 | 0.54 |
| 7 | **2** | 50 | 1 | 2.21 | 17700 | 5850 | 6100 | 100 | 99 | 0.33 |
| 8 | **2** | 50 | 2 | 2.17 | 16900 | 5850 | 6400 | 100 | 99 | 0.35 |
| 9 | **2** | 80 | 1 | 1.40 | 23600 | 9270 | 10500 | 100 | 99 | 0.39 |
| 10 | **2** | 100 | 1 | 1.77 | 28800 | 11600 | 12400 | 100 | 96 | 0.40 |
| 11 | **2** | 200 | 2 | 1.41 | 58300 | 23000 | | 100 | 99 | 0.39 |
| 12 | **3** | 30 | 5 | 1.44 | 9900 | 3570 | 4000 | 100 | 99 | 0.36 |
| 13 | **3** | 50 | 5 | 1.28 | 20300 | 5850 | 6600 | 100 | 96 | 0.29 |
| 14 | **3** | 100 | 5 | 1.46 | 42300 | 10300 | 13900 | 89 | 89 | 0.24 |
| 15 | **3** | 150 | 5 | 1.41 | 73300 | 17300 | 18600 | 100 | 99 | 0.24 |
| 16 | **3** | 200 | 5 | 1.37 | 117200 | 23000 | | 100 | 99 | 0.20 |
| 17 | **3** | 50 (50)[f] | 10 | 1.53 | 37600 | 11600 | | | 99 | 0.31 |

[a] Obtained from GPC analysis. [b] Calculated from the molecular weight of $\epsilon$-caprolactone times $[M]_0/[Al]_0$ times conversion yield plus the molecular weight of RSH. [c] Obtained from $^1$H NMR analysis. [d] Isolated yield. [e] Calculated from the $M_n$(calcd) relative to $M_n$(GPC). [f] Prepolymerization of $\epsilon$-CL with initiator for 2 h followed by the addition of $\epsilon$-CL and stirred for another 2 h.

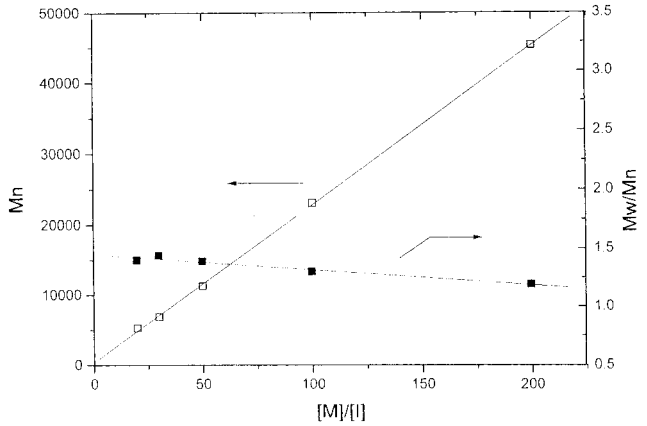



**Figure 4.** Polymerization of $\epsilon$-CL initiated by **1** in toluene at 25 °C. Relationship between $M_n$ (□) ($M_w/M_n$ (■)) of the polymer and the initial mole ratio [M]/[I].

In conclusion, we have discovered several structurally characterized aluminum thiolates, and all of them have demonstrated efficient catalytic activities in the ROP of $\epsilon$-caprolactone. Besides this, compound **1** is also active for the ring-opening polymerization of L-lactide. The "controlled" character of the aluminum complexes shown in the polymerization process has enabled us to synthesize P-$\delta$-VL-*b*-P-$\epsilon$-CL block copolymer. Polyesters with a thioester chain end group may provide a suitable method for the design of PCL conjugates.

## Experimental Section

**General Data.** All manipulations were carried out under a dry nitrogen atmosphere. Solvents, $\epsilon$-caprolactone, $\delta$-valerolactone, L-lactide, and deuterated solvents were purified before uses. $AlMe_3$ (2.0 M in toluene), $AlEt_3$ (1.9 M in toluene), $AlBu^i_3$ (15% in hexane), $Et_2AlCl$ (15% in *n*-hexane), 2-methoxybenzenethiol, and 2,4,6-trimethylbenzylmercaptan were purchased and used without further purification. $^1$H and $^{13}$C NMR spectra were recorded on a Varian VXR-300 (300 MHz) or a Varian Gemini-200 (200 MHz) spectrometer with chemical shifts given in ppm from the internal TMS. $^{27}$Al NMR spectra were recorded on a Varian-600 (600 MHz) spectrometer with chemical shifts given in ppm from the internal $(acac)_3Al$. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument. Infrared spectra were obtained from a Bruker Equinox 55 spectrometer. The GPC measurements were performed on a Hitachi L-7100 system equipped with a differential Bischoff 8120 RI detector using THF (HPLC grade) as an eluent. Molecular weight and molecular weight distributions were calculated using polystyrene as standard.

**[(MOBT)$_2$AlMe] (1).** To a rapidly stirred solution of 2-methoxybenzenethiol (MOBT-H) (0.24 mL, 2.0 mmol) in hexane (30

**Table 4. Polymerization and Copolymerization of ϵ-Caprolactone (CL) and δ-Valerolactone (VL) Initiated by 5**

| entry | monomer | initiator | $[M]_0/[Al]_0$ | time (h) | $M_w/M_n$ | $M_n$(obsd)[a] | $M_n$(calcd)[b] | convn (%)[c] | yield (%) | ratio[d] |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | VL | **5** | 30 | 20 | 1.39 | 12600 | 3170 | 100 | 97 | 0.25 |
| 2 | VL | **5** | 60 | 20 | 1.27 | 24200 | 6170 | 100 | 87 | 0.25 |
| 3 | VL | **5** | 100 | 20 | 1.16 | 40300 | 10200 | 100 | 93 | 0.25 |
| 4 | CL | **5** | 30 | 20 | 1.11 | 11300 | 3590 | 100 | 79 | 0.32 |
| 5 | CL | **5** | 60 | 20 | 1.21 | 26100 | 7010 | 100 | 96 | 0.27 |
| 6 | CL-CL[e] | **5** | 30(30) | 20(20) | 1.22 | 25700 | 7010 | - | 88 | 0.27 |
| 7 | VL-CL[f] | **5** | 30(30) | 20(20) | 1.21 | 23900 | 6600 | - | 93 | 0.28 |

[a] Obtained from GPC analysis. [b] Calculated from the molecular weight of ϵ-caprolactone or δ-valerolactone times $[M]_0/[Al]$ times conversion yield plus the molecular weight of the chain end, RSH. [c] Obtained from $^1$H NMR analysis. [d] Calculated from the $M_n$(calcd) relative to $M_n$(obsd). [e] Prepolymerization of CL with initiator for 20 h followed by the addition of CL and then stirred for another 20 h. [f] Prepolymerization of VL with initiator for 20 h followed by the addition of CL and then stirred for another 20 h.

**Table 5. Ring-Opening Polymerization of L-Lactide Initiated by Complex 1**

| entry | monomer | initiator | $[M]_0/[Al]_0$ | solvent | time (h) | $M_w/M_n$ | $M_n$(obsd)[a] | $M_n$(calcd)[b] | convn (%)[c] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | L-lactide | **1** | 10 | toluene | 24 | 1.18 | 3600 | 1004 | 60 |
| 2 | L-lactide | **1** | 20 | toluene | 24 | 1.15 | 5700 | 2041 | 66 |
| 3 | L-lactide | **1** | 30 | toluene | 24 | 1.25 | 8400 | 3062 | 88 |
| 4 | L-lactide | **1** | 50 | toluene | 24 | 1.16 | 13800 | 6764 | 92 |
| 5 | L-lactide | **1** | 20 | xylene | 24 | 1.19 | 5200 | 2473 | 88 |

[a] Obtained from GPC analysis. [b] Calculated from the molecular weight of L-lactide times $[M]_0/[Al]_0$ times conversion yield plus the molecular weight of the chain end, RSH. [c] Obtained from $^1$H NMR analysis.

mL) at 0 °C was added $AlMe_3$ (0.55 mL, 1.1 mmol) slowly. The mixture was stirred for 3 h while the temperature was raised to room temperature during which a white solid was observed. The volatile materials were removed under vacuum, and the residue was extracted with toluene (10 mL). Colorless crystals were obtained in 24 h at −18 °C. Yield: 0.28 g (88%). Anal. Calcd for $C_{15}H_{17}AlO_2S_2$: C, 56.26; H, 5.35. Found: C, 56.51; H, 5.61. $^1$H NMR ($CDCl_3$, ppm): δ 7.45−6.86 (m, 8H, Ph), 4.15 (s, 6H, $OCH_3$), −0.39 (s, 3H, $AlCH_3$). $^{13}$C NMR ($CDCl_3$, ppm): δ 152.4, 131.8, 127.5, 123.9, 123.7, 109.4 (Ph), 56.8 ($OCH_3$), −8.1 ($AlCH_3$). $^{27}$Al NMR ($CDCl_3$, ppm): δ 121.4 ($W_{1/2}$ = 5853 Hz). IR (KBr, cm$^{-1}$): 1579.8 (m), 1469.0 (s), 1243.9 (s), 1217.6 (s), 1178.2 (s), 1071.7 (s), 1039.7 (m), 1025.0 (m), 996.0 (s), 791.0 (m), 745.9 (s), 683.0 (s), 641.0 (s), 592.4 (m), 451.7 (m). Mp: 114−116 °C

**[(MOBT)$_2$AlCl] (2).** This compound was prepared according to the method described for **1** using $Et_2AlCl$ (5.8 mL, 5.0 mmol). Yield: 0.58 g (85%). Anal. Calcd for $C_{14}H_{14}AlClO_2S_2$: C, 56.26; H, 5.35. Found: C, 56.51; H, 5.61. $^1$H NMR ($CDCl_3$, ppm): δ 7.44−6.98 (m, 8H, Ph), 4.31 (s, 6H, $OCH_3$).$^{13}$C NMR ($CDCl_3$, ppm): δ 151.7, 131.8, 126.1, 124.6, 124.5, 109.8 (Ph), 58.1 ($OCH_3$). Mp: 138−140 °C.

**[(μ-TMBM)AlEt$_2$]$_2$ (3).** To a rapidly stirred solution of 2,4,6-trimethylbenzylmercaptan (TMBP−H) (0.33 g, 2.0 mmol) in $CH_2Cl_2$ (20 mL) at 0 °C was added $AlEt_3$ (2.3 mL, 2.1 mmol) slowly. The mixture was stirred for 3 h while the temperature was raised to room temperature. The volatile materials were removed under vacuum, and the residue was extracted with hexane (40 mL). Colorless crystals were obtained in 24 h at −18 °C. Yield: 0.41 g (82%). Anal. Calcd for $C_{28}H_{46}Al_2S_2$: C, 67.34; H, 9.17. Found: C, 67.16; H, 9.26. $^1$H NMR ($CDCl_3$, ppm): δ 6.84 (s, 2H, Ph), 3.92 (s, 2H, $SCH_2$), 2.34 (s, 6H, $PhCH_3$), 2.25 (s, 3H, $PhCH_3$), 1.11 (t, 3H, $AlCH_2CH_3$, $J$ = 7.8 Hz), 0.30 (q, 2H, $AlCH_2CH_3$, $J$ = 7.8 Hz).$^{13}$C NMR ($CDCl_3$, ppm): δ 137.3, 136.4, 132.6, 129.3 (Ph), 25.9 ($PhCH_3$), 20.9 ($PhCH_3$), 20.0 ($SCH_2$), 8.5 ($AlCH_2CH_3$), 0.6 ($AlCH_2CH_3$). IR (KBr, cm$^{-1}$): 2907.3 (br, s), 1607.2 (w), 1456.0 (s), 1415.6 (s), 1375.1 (s), 1232.6 (s), 682.5 (br, s) Mp: 132−134 °C dec.

**[(μ-TMBM)AlMe$_2$]$_2$ (4).** This compound was prepared according to the method described for **3** using $AlMe_3$ (0.6 mL, 2.0 mmol). Yield: 0.41 g (93%). Anal. Calcd for $C_{24}H_{38}Al_2S_2$: C, 64.83; H, 8.61. Found: C, 65.37; H, 8.94. $^1$H NMR ($CDCl_3$, ppm): δ 6.87 (s, 2H, Ph), 3.94 (s, 2H, $SCH_2$), 2.34 (s, 6H, $PhCH_3$), 2.27 (s, 3H, $PhCH_3$), −0.33 (s, 6H, $AlCH_3$).$^{13}$C NMR ($CDCl_3$, ppm): δ 137.1, 136.1, 132.2, 129.2 (Ph), 26.8 ($PhCH_3$), 21.0 ($PhCH_3$), 20.2 ($SCH_2$), −8.3 ($AlCH_3$). IR (KBr, cm$^{-1}$): 2965.5 (br, w), 1261.8 (s), 1095.4 (br, w), 1019.9 (br, m), 801.8 (s). Mp: 128−130 °C dec.

**[(μ-TMBM)AlBu$^i_2$]$_2$ (5)** This compound was prepared according to the method described for **3** using $Bu^i_3Al$ (4.0 mL, 2.0 mmol). Yield: 0.58 g (95%). Anal. Calcd for $C_{30}H_{50}Al_2S_2$: C, 70.54; H, 10.22. Found: C, 70.69; H, 10.00. $^1$H NMR ($CDCl_3$, ppm): δ 6.84 (s, 2H, Ph), 3.90 (s, 2H, $SCH_2$), 2.33 (s, 6H, $PhCH_3$), 2.25 (s, 3H, $PhCH_3$), 1.95 (m, 2H, $AlCH_2CH$), 0.96 (d, 12H, $CH(CH_3)_2$, $J$ = 7.2 Hz), 0.38 (d, 4H, $AlCH_2$, $J$ = 7.2 Hz).$^{13}$C NMR ($CDCl_3$, ppm): δ 137.0, 136.3, 132.4, 129.1 (Ph), 26.6 ($PhCH_3$), 21.0 ($PhCH_3$), 20.4 ($SCH_2$), 28.1 ($AlCH_2CH$), 25.9 ($CH(CH_3)_2$), 22.6 ($AlCH_2$). IR (KBr, cm$^{-1}$): 2953.8 (br, m), 2864.1 (br, w), 1459.8 (br, w), 852.2 (w). Mp: 173−174 °C dec.

**Polymerization of ϵ-Caprolactone and δ-Valerolactone** A typical polymerization procedure was exemplified by the synthesis of PCL-30 (the number 30 indicates the designed $[M]_0/[I]_0$ ratio). To a rapidly stirred solution of [MeAl(MOBT)$_2$] (0.064 g, 0.20 mmol) in toluene (20 mL) was added ϵ-CL (0.63 mL, 6.0 mmol). The reaction mixture was stirred at 25 °C for 2 h during which an increase in viscosity was observed. After quenching the reaction by adding excess 0.35 N acetic acid solution, the polymer was precipitated into *n*-heptane. The white precipitate was washed with hexane three times and dried under vacuum overnight, giving a white solid.

**Polymerization of L-Lactide Initiated by 1.** A typical polymerization procedure was exemplified by the synthesis of PLA-50. To a rapidly stirred solution of [MeAl(MOBT)$_2$] (0.064 g, 0.20 mmol) in toluene (20 mL) was added L-lactide (1.44 g, 10.0 mmol). The reaction mixture was refluxed for 24 h during which an increase in viscosity was observed. The volatile materials were removed under vacuum and the residue was extracted with THF (30 mL). The extraction was dried again and the white precipitate was washed with hexane three times and dried under vacuum overnight, giving a white solid.

**X-ray Crystallographic Studies.** Suitable crystals of **1**−**3** were sealed in thin-walled glass capillaries under nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. Intensity data were collected in 1350 frames with increasing ω (width of 0.3° per frame). The absorption corrections were based on the symmetry equivalent reflections using the SADABS program. The space group determinations were based on a check of the Laue symmetry and systematic absences and was confirmed using the structure solution. The structures were solved by direct methods using a SHELXTL package. All non-H atoms were located from successive Fourier maps and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms.

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**Supporting Information Available:** For **1**, **2**, and **3**, tables giving full details of the crystal data and figures showing the ORTEP structure of **2** and GPC profiles of polymerization resumption experiments initiated by **1** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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