A Highly Efficient Catalyst for the “Living” and “Immortal” Polymerization of ϵ-Caprolactone and L-Lactide

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Received March 15, 2001; Revised Manuscript Received May 21, 2001

ABSTRACT: A novel ligand, 2,2′-methylenebis(4,6-di(1-methyl-1-phenylethyl)phenol) (MMPEP-H_2) (**1**), has been prepared by the reaction of 2,4-bis(α,α-dimethylbenzyl)phenol with formaldehyde in the presence of a catalytic amount of benzenesulfonic acid. Further reaction of compound **1** with Me_3Al in diethyl ether produces a four-coordinated monomeric aluminum complex [(MMPEP)AlMe(OEt_2)] (**2**). [(MMPEP)-Al(μ-OBn)]$_2$ (**3**) can then be synthesized from the reaction of **2** with 1 molar equiv of benzyl alcohol at ambient temperature. **3** has demonstrated highly efficient catalytic activities in the ROP of ϵ-caprolactone and the ROP of L-lactide. The “living” character of complex **3** enable us to prepare PCL-*b*-PLA copolymer, and the “immortal” character of **3** has paved a way to synthesize as much as 160-fold polymer chains of poly(caprolactone) with very narrow PDI in the presence of a small amount of initiator.

Introduction

Biodegradable polymers have been attracting considerable attention recently due to their potential application in human life.[1] Among them, the aliphatic polyesters, such as poly(ϵ-caprolactone) (PCL)[2] and poly(lactide) (PLA),[3] and their copolymers are especially interesting for their applications in the medical field as biodegradable surgical sutures or as a delivery medium for controlled release of drugs[4] due to their biodegradable, biocompatible, and permeable properties.[5] There has been increasing interest in the development of efficient catalytic systems for the preparation of PLA and PCL. The major polymerization method used to synthesize these polymers has been the ring-opening polymerization (ROP) of lactones/lactides and functionally related compounds. Stannous,[6] trivalent lanthanide,[7] magnesium,[8] and zinc derivatives[8,9] have been reported to be effective initiators that initiate ROP of lactones/lactides, giving polymers with both high molecular weights and high yields. However, the cytotoxicity and difficulties in removal of the catalyst from the resulting polymer have limited their utilization.

An important task for developing new catalytic systems is to make the catalyst more compatible with the purpose of biomedical application. Aluminum alkoxide-based initiator systems seem to be active and suited for this purpose due to their high Lewis acidity and low toxicity.[10] For example, dialkylaluminum alkoxides (R_2AlOR') initiate polymerization of lactones in a living fashion, leading to the formation of polyesters with a hydroxy functional end and an alkyl ester (−COOR′) end group. Though several aluminum derivatives of monodentate bulky phenol have demonstrated efficient catalytic activities toward the ROP of lactones,[11] these catalysts decrease activities in the presence of excess 2-propanol because the metathesis occurs between aluminum phenolate and 2-propanol. Recently, we have developed the synthesis, characterization, and catalytic studies of many aluminum alkoxides[12] and aluminum thiolates.[13] Among them, [(EDBP)Al(OBn)]$_2$[12a] catalyzes the polymerization of ϵ-caprolactone in both “living” and “immortal” fashions, yielding polymers with very narrow polydispersity index (PDI $= M_w/M_n$). However, it becomes inactive in the presence of a very large amount of BnOH and is inactive toward ROP of L-lactide.

We report herein the synthesis, characterization, and catalytic studies of several novel aluminum alkoxides. The catalytic activities of [(MMPEP)Al(OBn)]$_2$ toward ROP of ϵ-caprolactone and L-lactide are also presented. Experimental results show that this aluminum alkoxide catalyzes the polymerization of ϵ-CL in both “living” and “immortal” fashions, yielding PCL with very narrow PDI in a wide range of monomer-to-initiator ratios.

Results and Discussion

Syntheses and Spectroscopic Studies. The reaction of formaldehyde with 2 molar equiv of 2,4-bis(α,α-dimethylbenzyl)phenol in the presence of a catalytic amount of benzenesulfonic acid under refluxing hexane gives 2,2′-methylenebis(4,6-di(1-methyl-1-phenylethyl)-phenol) (MMPEP-H_2) (**1**) in moderate yield as shown in Scheme 1. Further reaction of compound **1** with 1 molar equiv of Me_3Al in diethyl ether produces a four-coordinated monomeric aluminum complex [(MMPEP)-AlMe(OEt_2)] (**2**) in almost quantitative yield. The initiator, [(MMPEP)Al(μ-OBn)]$_2$ (**3**), can then be prepared from the reaction of **2** with 1 molar equiv of benzyl alcohol at ambient temperature. All of these compounds are isolated as colorless crystalline solids. Compound **1** has been characterized by spectroscopic studies as well as microanalyses. The ^{1}H NMR data of **2** and **3** reveal only one set of resonances for 1-methyl-1-phenylethyl groups of phenyl rings in MMPEP^{2-} ligand. These observations suggest that these two aryl moieties are equivalent, and that requires a σ plane of symmetry passing through the C-7 methine carbon and the aluminum atom (Chart 1). The two hydrogens in the bridging methylene (C-7) are observed to be magnetically nonequivalent with the ^{1}H chemical shifts at δ 3.56 and 3.06 ppm ($^2J_{HH} = 13.6$ Hz) for **2**, and the value is similar to the one reported for the aluminum derivatives of MDBP^{2-} or MMBP^{2-}.[14] However, it is interesting to note that the ^{1}H chemical shifts of the C-7 protons in **3** observed at δ 2.43 and 2.17 ppm ($^2J_{HH} = 15.2$ Hz) are about 1 ppm upfield than its EDBP^{2-} analogue. The reason for this abnormal phenomenon is probably resulting from deshielding of the ring current of the phenyl ring

10.1021/ma0104579 CCC: $20.00

Scheme 1

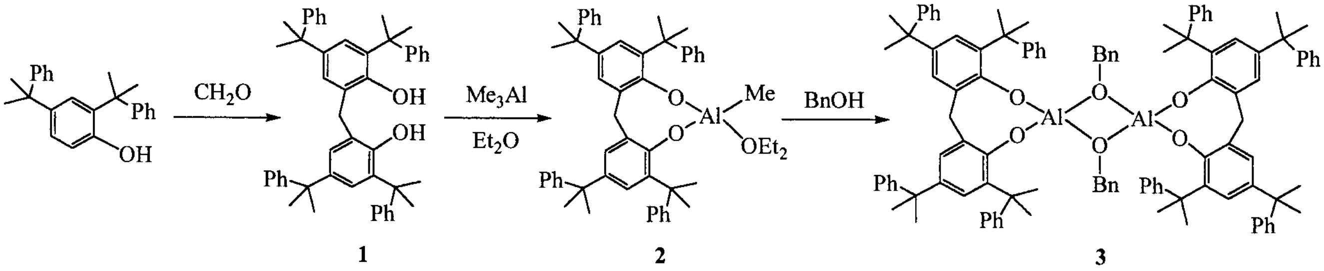
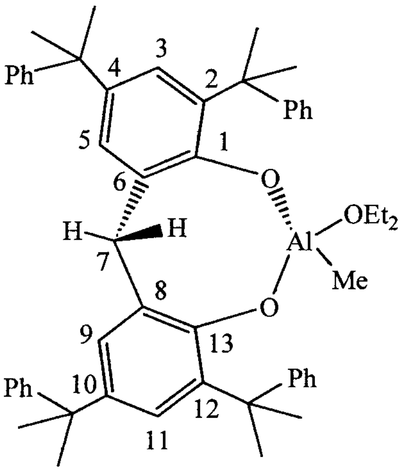


Chart 1



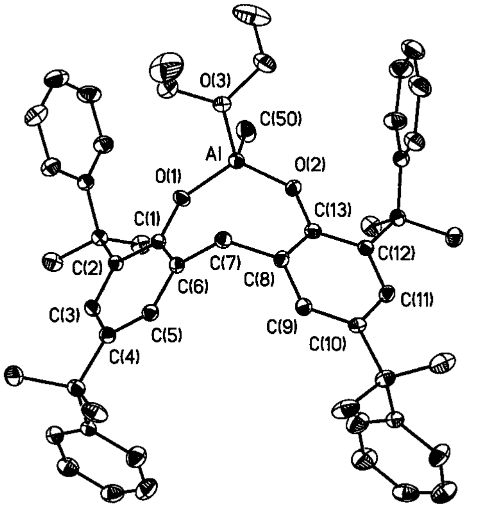


Figure 1. Molecular structure of **2** as 20% ellipsoids. All hydrogen atoms are omitted for clarity. Selected bond distances: Al–O(1) 1.703(3), Al–O(2) 1.709(3), Al–O(3) 1.888(3), Al–C(50) 1.936(4).

in the phenylethyl group, and this can be further verified by the crystal structure studies of **2** and **3**.

Molecular Structure Determinations of 2 and 3. Suitable crystals for structure determination of **2** are obtained from slowly cooling a hot toluene solution, and its ORTEP is shown in Figure 1. The structure of **2** shows a monomeric feature, and the geometry around Al is distorted from tetrahedral with the bond distances Al–O(1) 1.703(3) (phenoxy), Al–O(2) 1.709(3) (phenoxy), Al–O(3) 1.888(3) (ethereal), and Al–C(50) 1.936(4), which are all compatible with the bond lengths for the observed results for four-coordinated aluminum phenoxide containing steric bulky substituents.[15] The structure of **3** shows a dimeric feature containing an Al_2O_2 core bridging through the oxygen atom of the benzyl alkoxide groups, and the geometry around Al is distorted from tetrahedral as shown in Figure 2. The bridging oxygen atom bond distances are roughly equivalent to the two Al centers with the Al–O(3) distance of 1.821(1) Å and Al–O(3a) distance of 1.816(1) Å. The terminal Al–O bond distances from the aryl oxide ligand are Al–O(1) 1.692(1) Å and Al–O(2) 1.704(1) Å, well within the normal range previously reported for a four-coordinated aluminum compound, [(EDBP)AlX(S)].

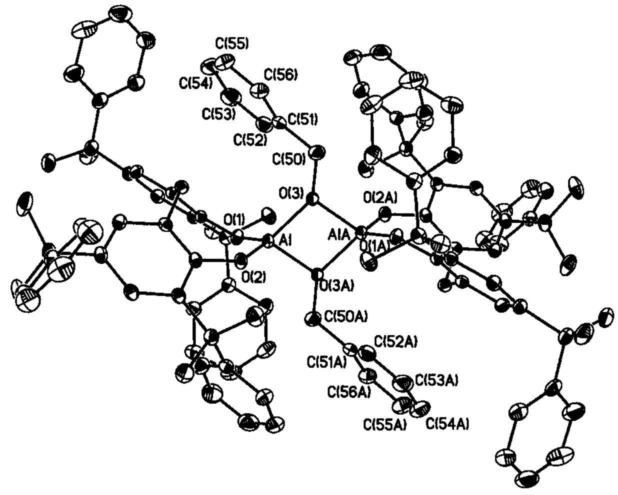
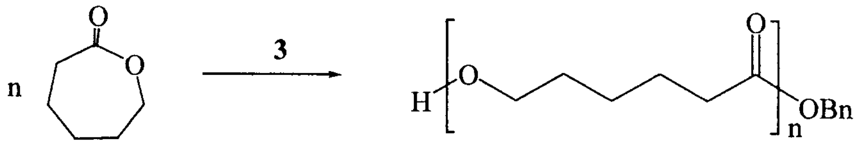


Figure 2. Molecular structure of **3** as 20% ellipsoids. All hydrogen atoms are omitted for clarity. Selected bond distances: Al–O(1) 1.692(1), Al–O(2) 1.704(1), Al–O(3) 1.821(1), Al–O(3a) 1.816(1).

Ring-Opening Polymerization of ε-Caprolactone Initiated by 3. $[(EDBP)Al(\mu\text{-}OBn)]_2$ has demonstrated efficient catalytic activities toward ring-opening polymerization (ROP) of ε-caprolactone.[12a] MMPEP-H_2 is considered as a much more sterically hindered ligand than EDBP-H_2. Therefore, we expect that the catalytic activities of $[(MMPEP)Al(\mu\text{-}OBn)]_2$ (**3**) will be more active than that of $[(EDBP)Al(\mu\text{-}OBn)]_2$ because a four-coordinated intermediate instead of five-coordinated intermediate may be generated during the polymerization process catalyzed by **3**. The catalytic activities of **3** toward ε-caprolactone (ε-CL) have been examined. In general, polymerization of ε-caprolactone was carried out at 53 °C in toluene (30 mL) using **3** (0.16 g, 0.10 mmol) as the initiator. To a rapidly stirring solution of $[(MMPEP)Al(\mu\text{-}OBn)]_2$ in toluene was added ε-CL (2.1 mL, 20 mmol). The reaction mixture was stirred at 53 °C for 1 h during which an increase in viscosity was observed. After the reaction was quenched by the addition of an excess 0.35 N acetic acid aqueous solution, the polymer was precipitated into *n*-heptane. Polymerizations of ε-CL under different reaction conditions (entries 1–9) have been systematically conducted as

Table 1. Ring-Opening Polymerization of ϵ-Caprolactone Initiated by Complex 3



entry	[M]/[Al]/[ROH]	time (h)	M_w/M_n	M_n(GPC)[a]	M_n(calcd)[b]	M_n(nmr)[c]	conv (%)[c]	yield (%)[d]	ratio[e]
1	25:1:0	1	1.06	7 900	2 960	3 900	100	71	0.37
2	50:1:0	1	1.04	13 200	5 800	5 600	100	71	0.45
3	100:1:0	1	1.08	29 000	11 500	15 000	100	81	0.40
4	200:1:0	2	1.10	54 700	22 900	25 800	100	86	0.42
5	400:1:0	5	1.16	99 800	43 900	41 500	96	94	0.46
6	400:1:2	3	1.04	27 900	15 200	13 600	99	93	0.55
7	800:1:40	6	1.04	4 400	2 200	2 300	95	94	0.52
8	800:1:160	7	1.17	1 100	650	660	95		0.64
9	50(50):1:0[f]	1(1)	1.11	22 700	11 500	12 100	100	89	0.51

[a] Obtained from GPC analysis. [b] Calculated from the molecular weight of ϵ-caprolactone times $[M]_0/[Al]_0$ times conversion yield divided by ([ROH] + 1) plus the molecular weight of BnOH. [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 ϵ-CL with initiator for 1 h followed by the addition of ϵ-CL and stirred for another 1 h.

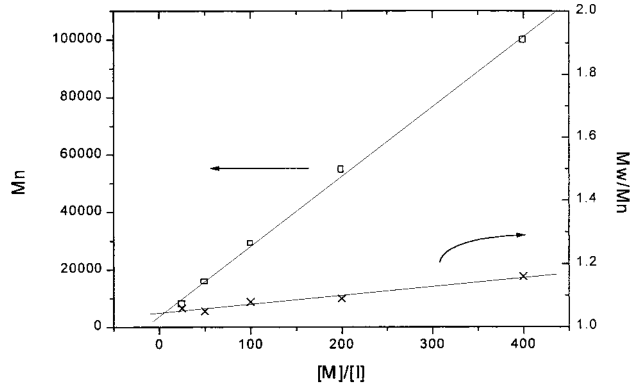


Figure 3. Polymerization of ϵ-CL initiated by **3** in toluene at 53 °C. The relationship between M_n (□) (M_w/M_n (×)) of the polymer and the initial mole ratio $[M]_0/[I]_0$ is shown.

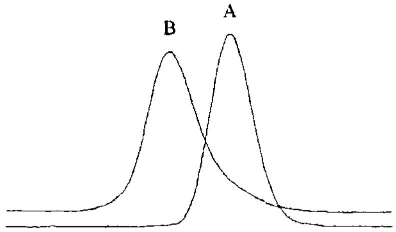


Figure 4. GPC profiles of polymerization resumption experiment: (peak A) after prepolymerization of CL (50 equiv to **3**, 1 h), $M_n = 13\,200$ (PDI = 1.04)); (peak B) after polymerization of 50 equiv more CL (1 h), $M_n = 22\,700$ (PDI = 1.11).

shown in Table 1. It was found that the PDIs of polyesters initiated by **3** range from 1.04 to 1.16, 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 3 (entries 1–5), implying the "living" character of the polymerization process. The "living" character was further confirmed from the polymerization resumption experiment and by the sequential ROP of ϵ-CL and L-LA. In the resumption experiment (entry 9), another portion of ϵ-CL monomer ($[M]_0/[I]_0 = 50$) was added after the polymerization of the first addition ($[M]_0/[I]_0 = 50$) had gone to completion. Figure 4 shows that the molecular weight increases for the final polymer (peak B, $M_n = 22\,700$ g/mol, PDI = 1.11), relative to the first (peak A, $M_n = 13\,200$, PDI = 1.04).

To understand the initiating process, ^{1}H NMR studies on the PCL initiated by **3** were carried out as shown in Figure 5. The ^{1}H NMR spectrum of PCL-25 (the number of 25 indicates the designed $[M]_0/[I]_0$ ratio) gives an intensity ratio close to 1 between H_b (CH_2 from ϵ-CL at the benzyl alkoxy chain end) and H_g (CH_2 from ϵ-CL at the hydroxy end). The observed result tells us that the initiation occurs through the insertion of a benzyl alkoxy group from compound **3** to ϵ-CL, 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 benzyl ester and one hydroxy end.

Synthesis of Benzyl Ester End-Functionalized PCLs in the Presence of Benzyl Alcohol. Recently, we found that $[(EDBP)Al(OBn)]_2$ can initiate ROP of CL in the presence of as much as 16-fold BnOH.[12a] Therefore, the polymerization of ϵ-CL initiated by **3** was performed in the presence of benzyl alcohol. In the presence of benzyl alcohol as the chain transfer agent, the exchange between the growing alkoxide species and alcohol leads to chain transfer reaction, since the resulting aluminum alkoxide is able to reinitiate the polymerization. It is interesting to note that compound **3** catalyzes ROP of lactones not only livingly but also immortally in which a narrow PDI polymer is obtained with a number of polymer molecules exceeding the number of initiator molecules (entries 6–8). Experimental results show that as much as 160-fold of BnOH can be added, resulting in a narrow PDI polymer with a M_n of only 1/160th of that without the addition of BnOH. The result is much better than its $[(EDBP)Al(OBn)]_2$ analogue, probably due to the fact that $MMPEP^{2-}$ is a much more sterically hindered ligand than $EDBP^{2-}$. Therefore, $[(MMPEP)Al(OBn)]_2$ is somewhat more inert toward H_2O than $[(EDBP)Al(OBn)]_2$ is.

Ring-Opening Polymerization of L-Lactide Initiated by 3. Due to its excellent mechanical properties, polylactide is a good candidate to replace nonbioresorbable polymers.[16] Therefore, the ring-opening polymerization of L-lactide initiated by complexes **3** is studied. GPC analyses reveal that the PDIs of poly(L-lactide) initiated by **3** are quite narrow, ranging from 1.06 to 1.11 as shown in Table 2. For the lactide-to-initiator ratio of 20 to 1, a conversion yield of 68% was achieved after 25 h at 110 °C based on the NMR spectroscopic studies. However, when the reaction was performed in

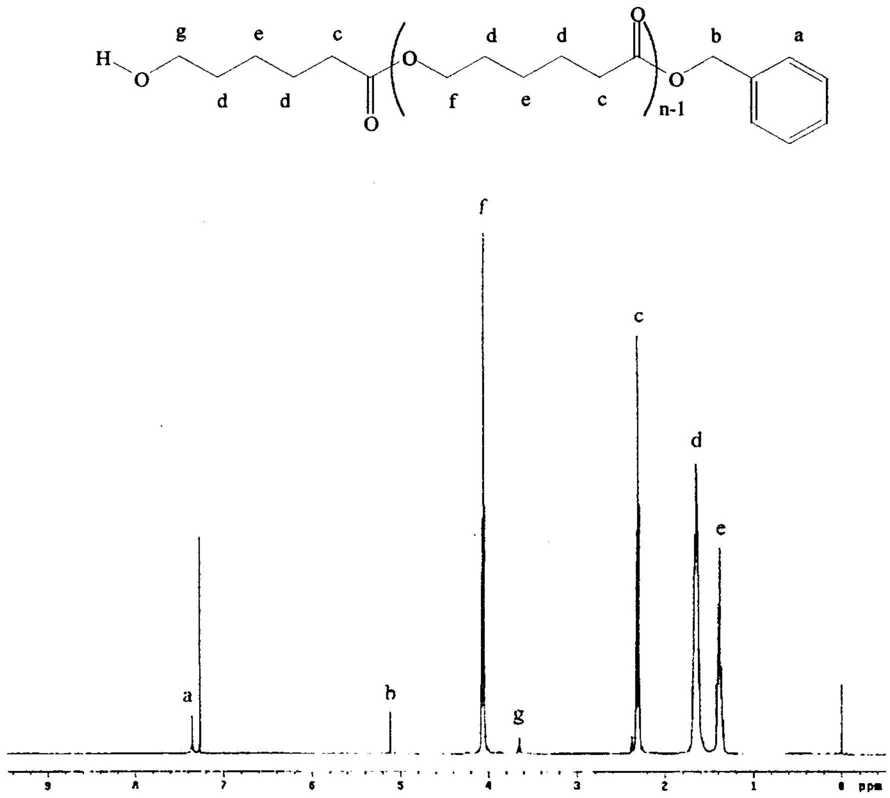
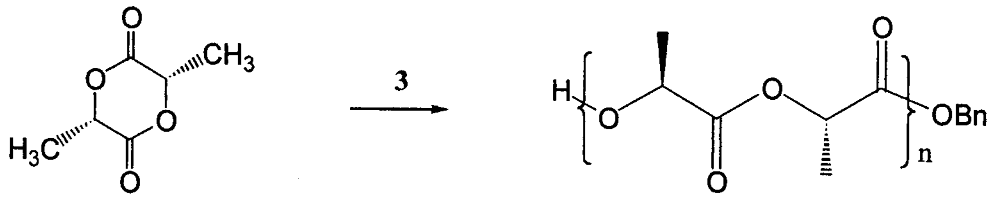


Figure 5. ^{1}H NMR spectrum of PCL-25 initiated by **3** in CDCl$_3$.

Table 2. Polymerization of L-Lactide and Copolymerization of PCL-b-PLA Initiated by Complex 3



entry	monomer	[M]$_0$/[Al]$_0$/[ROH]	time (h)	M_w/M_n	M_n(GPC)[a]	M_n(calcd)[b]	M_n(NMR)[c]	conv (%)[c]
1	LA	10/1/0	25	1.07	3300	1100	1700	66
2	LA	20/1/0	25	1.11	3800	2100	2400	68
3	LA	25/1/0	25	1.08	5800	2600	3500	70
4	LA	40/1/0	25	1.06	7200	3600	4200	61
5	LA	50/1/0	25	1.07	10200	4900	6000	66
6	LA	20/1/0	48	1.08	6600	2600	3800	87
7	LA	50/1/0	48	1.09	13000	5900	7000	81
8	CL(LA)[d]	50(20)/1/0	1(24)	1.09	15700	8000	8800	100(77)
9	LA	50/1/1[e]	25	1.07	8900	3600	4500	97

[a] Obtained from GPC analysis. [b] Calculated from the molecular weight of L-lactide times [M]$_0$/[Al]$_0$ times conversion yield divided by ([ROH] + 1) plus the molecular weight of BnOH. [c] Obtained from ^{1}H NMR analysis. [d] Prepolymerization of ϵ-CL in toluene at 53 °C with initiator for 1 h followed by the addition of LA and refluxed in toluene for another 24 h. [e] Polymerization of LA in the presence of 1 molar equiv of benzyl alcohol.

a longer period of time (entry 6), the conversion yield up to 87% along with a higher molecular weight polymer can be achieved. The ^{1}H NMR spectrum of PLA-20 (Figure 6) indicates the polymer chain should be capped with one benzyl ester and one hydroxy end, suggesting that back-reactions leading to the formation of macrocycles do not occur. The linear relationship between M_n and [M]$_0$/[I]$_0$ suggests the "controlled" character of **3**. The PCL-*b*-PLA block polymer (M_n = 15 700, M_w/M_n = 1.09, entry 8) was synthesized by the sequential ROP of CL ([M]$_0$/[I]$_0$ = 50) and LA monomer ([M]$_0$/[I]$_0$ = 20) in the presence of **3** as shown in Figure 7. It is worthwhile to note that compound **3** is also able to initiate ROP of lactide in the presence of BnOH. Preliminary results show that, in the presence of 2 molar equiv of benzyl alcohol as the chain transfer agent, the exchange between the growing alkoxide species and alcohol leads to chain transfer reaction, giving a PLA with only one third molecular weight of that without the addition of BnOH (entry 6).

In conclusion, a novel aluminum alkoxide, [(MMPEP)-Al(OBn)]$_2$, **3**, has been synthesized and structurally characterized which has demonstrated efficient catalytic activities in the ROP of ϵ-caprolactone and the ROP of L-lactide. The "living" character of this aluminum complex shown in the polymerization process has enabled us to synthesize PCL-*b*-PLA block copolymer. The "immortal" character of complex **3** has paved a way to

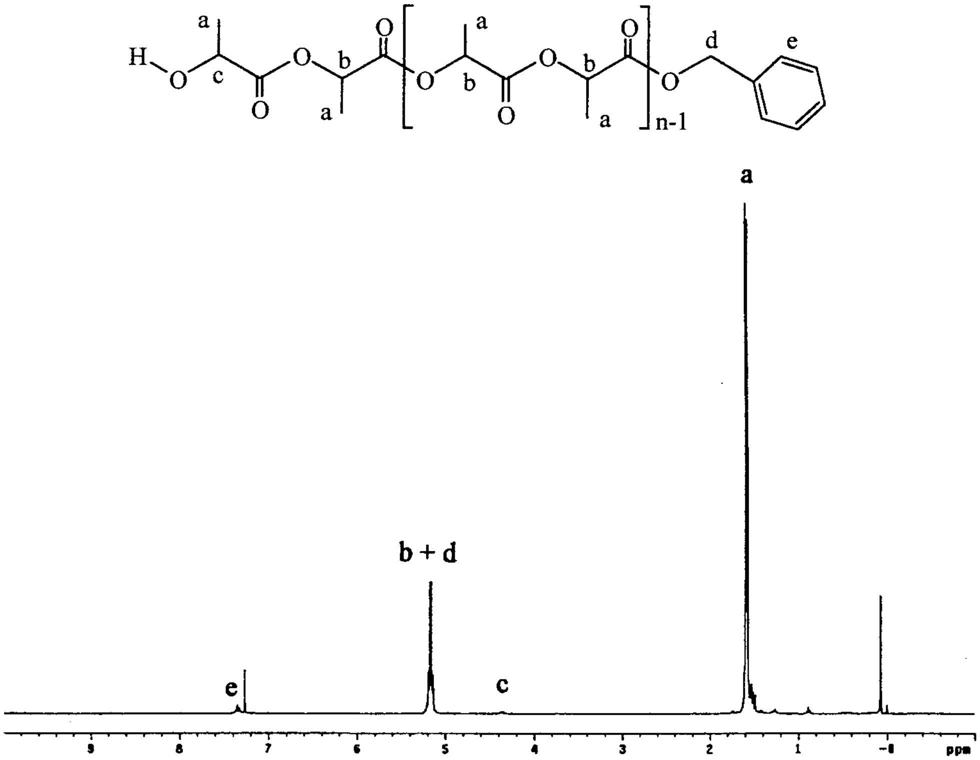


Figure 6. ^1H NMR spectrum of PLA-20 initiated by **3** in $CDCl_3$.

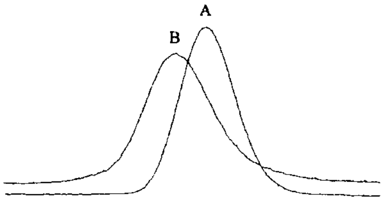


Figure 7. GPC profiles of copolymerization of PCL-*b*-PLA: (peak A) after prepolymerization of CL (50 equiv to **3**, M_n = 13 200 (PDI = 1.04)); (peak B) after block copolymerization of PCL-*b*-PLA ($[CL]_0/[3]_0/[LA]_0$ = 50/1/20, M_n = 15 700 (PDI = 1.09)).

synthesize as much as 160-fold polymer chains of poly(caprolactone) with very narrow PDI in the presence of a small amount of initiator.

Experimental Section

General. All manipulations were carried out under a dry nitrogen atmosphere. Solvents, ϵ-caprolactone, L-lactide, benzyl alcohol, and deuterated solvents were purified before use. $AlMe_3$ (2.0 M in toluene), formaldehyde, 2,4-bis(α,α-dimethylbenzyl)phenol, and benzenesulfonic acid were purchased and used without further purification. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury-400 (400 MHz) or a Varian Gemini-200 (200 MHz) spectrometer with chemical shifts given in ppm from the internal TMS. 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.

2,2′-Methylenebis(4,6-di(1-methyl-1-phenylethyl)phenol (MMPEP-H_2) (1). A mixture of 2,4-bis(α,α-dimethylbenzyl)phenol (6.6 g, 20 mmol), formaldehyde (0.3 g, 10 mmol), and benzenesulfonic acid (0.40 mL) in hexane (40 mL) was refluxed for 5 h. After neutralization by an aqueous NaOH solution (0.1 N, 20 mL), the organic layer was extracted with water (10 mL) twice. The hexane layer was then dried over $MgSO_4$ and concentrated to 25 mL. White crystalline solids were obtained after 5 days at −20 °C. Yield: 0.95 g (71%). Anal. Calcd for $C_{49}H_{46}O_2$: C, 87.46; H, 7.79%. Found: C, 87.34; H, 7.85%. ^1H NMR ($CDCl_3$, ppm): δ 6.84−7.26 (m, 24H, Ph); 3.59 (s, 2H, CH_2); 5.13 (s, 2H, OH); 1.54, 1.63 (s, 24H, CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 151.08, 149.05, 148.90, 141.98, 134.57, 128.72, 127.84, 127.30, 126.65, 126.29, 125.88, 125.75, 125.39, 123.23 (Ph); 42.48, 41.97 (Ph**C**(CH_3)$_2$); 31.01, 29.69 (PhC(**C**H_3)$_2$); δ 30.92 (−**C**H_2−). IR (KBr, cm^{-1}): 3449 (s), 3055 (m), 3024 (m), 2969 (s), 2873 (s), 1481 (s), 1467 (s), 1451 (s), 1371 (m), 1277 (m), 1224 (s), 1201 (s), 1142 (s), 773 (s), 699 (s), 550 (m). Mass spectrum (EI, *m*/*e*): 672 (M^+, 96%). Mp: 112−113 °C.

[(MMPEP)Al(CH_3)(Et_2O)] (2). To an ice cold solution (0 °C) of 2,2′-methylenebis(4,6-di(1-methyl-1-phenylethyl)phenol (1.35 g, 2.0 mmol) in diethyl ether (20 mL) was added slowly an $AlMe_3$ (1.20 mL, 2.0 M in toluene, 2.4 mmol) solution. After all of the solution was added, the mixture was stirred for 2 h during which a white precipitate formed. The mixture was then dried in vacuo, and the residue was extracted with 30 mL of toluene. The extract was then concentrated to ca. 10 mL and cooled to −20 °C to furnish colorless crystals. Yield: 0.77 g (98%). Anal. Calcd for $C_{54}H_{63}AlO_3$: C, 82.41; H, 8.07%. Found: C, 81.98; H, 8.38%. ^1H NMR ($CDCl_3$, ppm): δ 6.96−7.32 (m, 24H, Ph); 3.56 (d, 1H, C**H_2**, J_{H-H} = 13.6 Hz); 3.06 (d, 1H, C**H_2**, J_{H-H} = 13.6 Hz); 3.02 (q, 4H, OC**H_2**CH_3, J_{H-H} = 7.2 Hz); 1.67, 1.63, 1.38 (s, 24H, C**H_3**), 0.75 (t, 6H, OCH_2C**H_3**, J_{H-H} = 7.2 Hz), −0.99 (s, 3H, AlC**H_3**). ^{13}C NMR ($CDCl_3$, ppm): δ 153.3, 151.9, 151.6, 138.9, 137.3, 129.9, 127.8, 127.4, 126.9, 125.5, 125.2, 124.0, 123.5 (Ph); 65.5 (O***C***H_2CH_3); 42.4, 42.2 (***C***(CH_3)$_2$); 33.2 (CH_2); 31.3, 31.1 (C(***C***H_3)$_2$). IR (KBr, cm^{-1}): 2964 (s), 2934 (s), 2870 (m), 1479 (s), 1443 (s), 1316 (s), 1261 (m), 1201 (m), 1095 (m), 1027 (s), 926 (m), 884 (m), 843 (m), 796 (m), 767 (s), 700 (s). Mp = 168−170 °C.

[(MMPEP)Al(*μ*-OBn)]$_2$ (3). To a rapidly stirring solution of [(MMPEP)Al(CH_3)(Et_2O)] (1.57 g, 2 mmol) in toluene (30 mL) was added benzyl alcohol (0.21 mL, 2.0 mmol), and the reaction mixture was stirred at 25 °C for 2 h. The volatile materials were removed under vacuum, and the residue was redissolved in hot toluene (30 mL). The extraction was then concentrated to ca. 10 mL and was allowed to cool to room temperature, affording colorless crystalline solids after 12 h. Yield: 1.14 g (71%). Anal. Calcd for $C_{112}H_{114}Al_2O_6$: C, 83.55; H, 7.14%. Found: C, 83.86; H, 6.84%. ^1H NMR ($CDCl_3$, ppm): δ 6.65−7.28 (m, 58H, Ph); 3.30 (s, 4H, OC**H**$_2$); 2.43 (d, 2H, C**H**$_2$, $J_{H-H} = 15.2$ Hz); 2.17 (d, 2H, C**H**$_2$, $J_{H-H} = 15.2$ Hz); 1.82, 1.56, 1.45 (s, 48H, CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 151.50, 151.31, 150.85, 140.25, 136.18, 135.75, 129.22, 128.23, 127.91, 127.86, 127.76, 126.85, 126.76, 126.65, 125.80, 125.65, 125.03, 124.72 (Ph); 66.50 (O**C**H$_2$); 42.95, 42.28 (Ph**C**(CH_3)$_2$); 33.10 (**C**H$_2$); 33.57, 31.01, 30.80, 27.82 (PhC(**C**H$_3$)$_2$). IR (KBr, cm^{-1}): 3024 (s), 2965 (m), 1442 (s), 1288 (m), 1203 (m), 1028 (m), 926 (m), 840 (m), 791 (m), 765 (m), 734 (m), 700 (s). Mp = 186−188 °C.

Synthesis of Benzyl Ester End-Functionalized PCLs. A typical polymerization procedure was exemplified by the synthesis of PCL-100 (the number 100 indicates the designed $[M]_0/[I]_0$). To a rapidly stirring solution of $[(MMPEP)Al(\mu\text{-}OBn)]_2$ (0.161 g, 0.10 mmol) in toluene (30 mL) was added ϵ-CL (2.1 mL, 20 mmol). The reaction mixture was stirred at 53 °C for 1 h during which an increase in viscosity was observed. After the reaction was quenched by the addition of an 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 giving a white solid. Yield: 1.83 g (81%).

Synthesis of Benzyl Ester End-Functionalized PCLs in the Presence of Benzyl Alcohol. A typical polymerization was exemplified by the synthesis of PCL-800 in the presence of 40 molar equiv of BnOH. ϵ-CL (16.8 mL, 160 mmol) and BnOH (0.84 mL, 8.0 mmol) were dissolved in 15 mL of toluene at 53 °C, and then the mixture was added to a rapidly stirring solution of $[(MMPEP)Al(\mu\text{-}OBn)]_2$ (0.161 g, 0.10 mmol) in toluene (15 mL). The reaction mixture was stirred at 53 °C for 6 h. After the reaction was quenched by adding an 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 giving white solids. Yield: 17.06 g (94%).

Synthesis of Diblock Copolymer PCL-*b*-PLA. To a rapidly stirring solution of $[(MMPEP)Al(\mu\text{-}OBn)]_2$ (0.161 g, 0.10 mmol) in toluene (30 mL) was added ϵ-CL (1.05 mL, 10 mmol). The reaction mixture was stirred at 53 °C for 1 h, and the mixture was concentrated to 10 mL. L-Lactide (0.58 g, 4.0 mmol) was added, and the mixture was refluxed for 25 h. The reaction was quenched using the procedures described previously. Yield: 1.21 g (71%).

Polymerization of L-Lactide Initiated by 3. A typical polymerization procedure was exemplified by the synthesis of PLA-50. To a rapidly stirred solution of $[(MMPEP)Al(\mu\text{-}OBn)]_2$ (0.160 g, 0.10 mmol) in toluene (10 mL) was added L-lactide (1.44 g, 10.0 mmol). The reaction mixture was refluxed for 25 h, and the volatile materials were removed under vacuum and the residue was redissolved in toluene (10 mL). The mixture was then quenched by the addition of an aqueous acetic acid solution (0.35 N, 10 mL) and the polymer was precipitated on pairing into *n*-hexane (10 mL) to give white crystalline solid.

X-ray Crystallographic Studies. Suitable crystals of **2** and **3** were sealed in thin-walled glass capillaries under a 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 correction was based on the symmetry equivalent reflections using SADABS program. The space group determination was based on a check of the Laue symmetry and systematic absences and was confirmed using the structure solution. The structure was 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.

Acknowledgment. Financial support from the National Science Council of the Republic of China is gratefully appreciated.

Supporting Information Available: Tables giving full details of the crystal data for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA0104579