Reactions of 2,2′-(2-Methoxybenzylidene)bis(4-methyl-6-*tert*-butylphenol) with Trimethylaluminum: Novel Efficient Catalysts for "Living" and "Immortal" Polymerization of ϵ-Caprolactone

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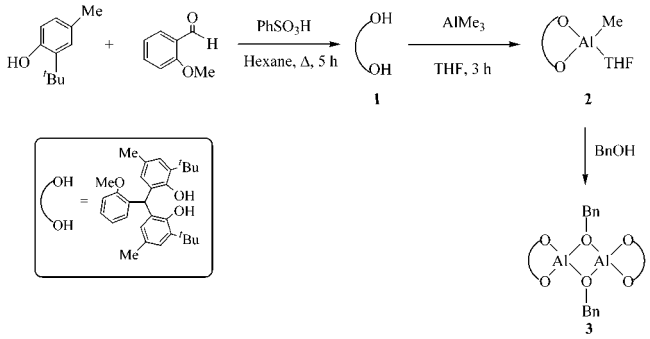
ABSTRACT: A sterically hindered biphenol 2,2′-(2-methoxybenzylidene)bis(4-methyl-6-*tert*-butylphenol) (MEBBP-H_2) (**1**) has been prepared by the reaction of *o*-anisaldehyde with 2-*tert*-butyl-4-methylphenol in the presence of a catalytic amount of benzenesulfonic acid. Further reaction of compound **1** with a stoichiometric amount of Me_3Al in tetrahydrofuran produces a four-coordinated monomeric aluminum complex [(MEBBP)AlMe(THF)] (**2**). [(MEBBP)Al(μ-OBn)]$_2$ (**3**) can then be synthesized by the reaction of **2** with 1 mol equiv of benzyl alcohol at ambient temperature. Compound **3** has demonstrated highly efficient activities toward ring-opening polymerization of ϵ-caprolactone. The "living" and the "immortal" character of **3** has paved a way to synthesize as much as 256-fold polymer chains of poly(ϵ-caprolactone) with a very narrow polydispersity index in the presence of a small amount of initiator. In addition, the polystyrene-*b*-poly(ϵ-caprolactone) copolymer has also been prepared using polystyrene containing a hydroxy chain end as an initiator in the presence of **2**.

Introduction

Biodegradability, biocompatibility, and permeable properties of aliphatic polyesters, such as poly(ϵ-caprolactone) (PCL)[1] and poly(lactide) (PLA),[2] and their copolymers show their potential applications in the medical field as biodegradable surgical sutures or as a delivery medium for controlled release of drugs.[3] Therefore, there has been increasing interest in the development of efficient catalytic systems for the preparation of PCL and PLA. The major polymerization method used to synthesize these polymers has been the ring-opening polymerization (ROP) of CL and functionally related compounds. An important task for developing new catalytic systems is to make the catalyst more compatible with the purpose of biomedical application. Though several effective initiators that initiate ROP of lactones have been reported,[4−9] the cytotoxicity and difficulties in removal of the catalyst from the resulting polymer have limited their utilization.

High Lewis acidity and low toxicity[10] of aluminum alkoxide-based initiator systems seem to be active and suited for this purpose. 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 reported the synthesis, characterization, and catalytic studies of many aluminum alkoxides[12] and aluminum thiolates.[13] Among them, [(EDBP)Al(μ-OBn)]$_2$ (**A**),[12a] [(MMPEP)Al(μ-OBn)]$_2$ (**B**),[12d] and [(MCIMP)Al(μ-OBn)]$_2$ (**C**)[12c] catalyze the polymerization of ϵ-caprolactone in both "living" and "immortal" fashions, yielding polymers with a very narrow polydispersity index (PDI = M_w/M_n). The differences between these compounds are substituents in the phenyl rings of biphenol and the methine carbon (C-7). On the basis of the catalytic activities of compounds **A**, **B**, and **C**, we conclude that bulky substituents in the ortho carbon of the hydroxyl group of biphenol affect the reactivity of the aluminum center dramatically. Encouraged by our pervious results, we want to find out how a sterically bulky group at the bridged methine carbon (C-7) affects the reactivity of aluminum. As a result, we reported here synthesis and characterization of two novel aluminum complexes and their reactivities toward ROP of ϵ-caprolactone. We have also reported herein the synthesis of polystyrene-*block*-poly(ϵ-caprolactone) copolymers using a bifunctional ligand 4-hydroxy-TEMPO as an initiator.

Scheme 1



Results and Discussion

Syntheses and Characterization. The reaction of *o*-anisaldehyde with 2 mol equiv of 2-*tert*-butyl-4-methylphenol in the presence of a catalytic amount of benzenesulfonic acid under refluxing hexane gives 2,2′-(2-methoxybenzylidene)bis(4-methyl-6-*tert*-butylphenol) (MEBBP-H_2) (**1**) in moderate yield as shown in Scheme 1. Further reaction of compound **1** with a stoichiometric amount of Me_3Al in tetrahydrofuran produces a four-coordinated monomeric aluminum complex [(MEBBP)-AlMe(THF)] (**2**) in almost quantitative yield. The ini-

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

entry	[M]/[Al]/[ROH]	time (h)	M_w/M_n	M_n(obsd)[a]	M_n(calcd)[b]	M_n(NMR)[c]	conv (%)[c]	yield (%)[d]
1	25:1:0	2	1.08	5500	2960	2730	100	72
2	50:1:0	3	1.08	9300	5800	5900	100	81
3	100:1:0	3	1.09	19900	11300	10800	98	83
4	200:1:0	5	1.09	38000	21800	22100	95	91
5	400:1:0	5	1.21	78600	42100	43400	92	90
6	50(50):1:0	3(3)	1.12	23100	11500	10900	100	85
8	400:1:2	4	1.08	33900	15200	15000	99	96
9	400:1:4	4	1.08	19500	9200	9500	100	94
10	400:1:8	2	1.07	10500	4900	5000	95	94
11	400:1:16	2	1.12	5800	2790	2390	100	96
12	400:1:32	1	1.10	2850	1490	1250	100	91
13	800:1:128	1	1.14	1230	750	770	91	*f*
14	800:1:256	1	*f*	*f*	460	440	100	*f*

[a] Obtained from GPC analysis. [b] Calculated from the molecular weight of ϵ-caprolactone times $[M]_0/[Al]_0$ times conversion yield divides 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] Not available.

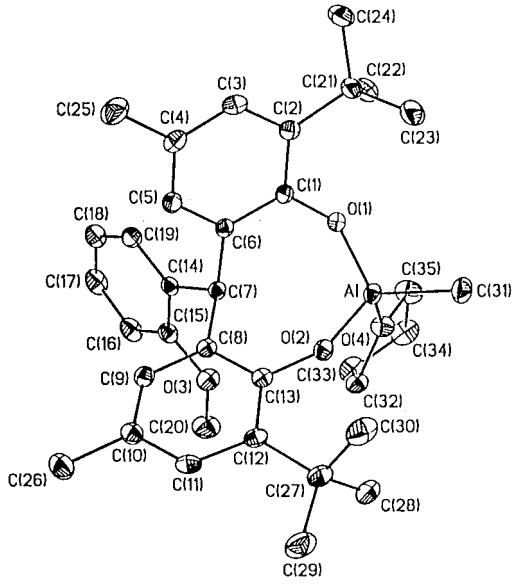

Figure 1. Molecular structure of **2** as 20% ellipsoids. All hydrogen atoms are omitted for clarity.

tiator, [(MEBBP)Al(−OBn)]$_2$ (**3**), can then be prepared from the reaction of **2** with 1 mol equiv of benzyl alcohol at ambient temperature. All of these compounds are isolated as colorless crystals, and elemental analysis and spectroscopic analysis are well consistent with the proposed molecular formula. The chemical equivalence of two phenyl moieties in the MEBBP^{2-} of **2** and **3** is confirmed by the appearance of one singlet for both butyl groups in the ^{1}H NMR. It is interesting to note that due to the acidic nature of hydrogen in the bridging methine carbon (C-7), the chemical shift (6.05 and 5.89 ppm for **2** and **3**, respectively) appeared downfield from the expected value. A similar result has been found in the [(EDBP)AlMe(S)] system.[14] Suitable crystals for structure determination of **2** are obtained from slow cooling a hot toluene solution, and its ORTEP is shown in Figure 1. The structure of **2** shows a monomeric feature, and the immediate geometry around Al is a distorted tetrahedron.

Ring-Opening Polymerization of ϵ-Caprolactone Initiated by 3. Recently, we have reported that [(EDBP)Al(μ-OBn)]$_2$ (**A**), [(MMPEP)Al(μ-OBn)]$_2$ (**B**), and [(MCIMP)Al(μ-O^{i}Pr)]$_2$ (**C**) can initiate ROP of CL in an efficient way. The differences between these compounds are substituents in the phenyl rings of biphenol and the methine carbon (C-7). We found that the catalytic

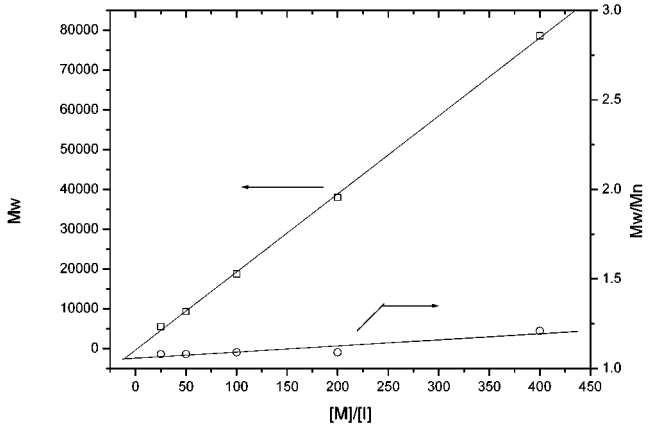

Figure 2. Polymerization of ϵ-CL initiated by **3** in toluene at 50 °C. The relationship between M_n (O) (M_w/M_n (×)) of the polymer and the initial mole ratio $[M]_0/[I]_0$ is shown.

activities of compound **B** is much higher than that of **A**. This result indicates that the sterically bulky group at the ortho position of the hydroxyl group in biphenol dramatically affects the reactivity of aluminum. In the present work, the catalytic activities of **3** toward ϵ-caprolactone (ϵ-CL) have been examined in which MEBBP^{2-} in compound **3** has a sterically much more bulky substituent at the methine carbon (C-7) than that of EDBP^{2-}, and the rest is similar to the ligand EDBP^{2-}. A typical polymerization experiment exemplified for PCL-100 ($[M]_0/[I]_0 = 100$) is described as follows. To a rapidly stirring solution of [(MEBBP)Al(μ-OBn)]$_2$ in toluene was added ϵ-CL (2.1 mL, 20 mmol). The reaction mixture was stirred at 50 °C for 1 h, during which an increase in viscosity was observed. After the reaction was quenched by the addition of excess 0.35 N acetic acid aqueous solution, the polymer was precipitated into *n*-heptane. Polymerizations of ϵ-CL under different reaction conditions (entries 1−14) have been systematically examined as shown in Table 1. It was found that the PDIs of polyesters initiated by **3** range from 1.07 to 1.21, 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 2 (entries 1−5), implying the "living" character of the polymerization process. The "living" character was further confirmed from the polymerization resumption experiment (entry 6) in which 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.

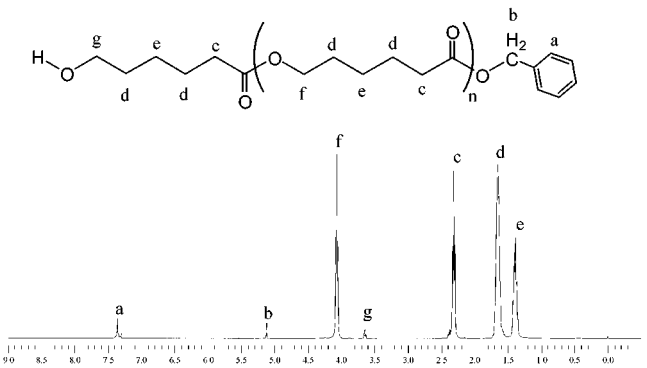

Figure 3. ^1H NMR spectrum of PCL-25 initiated by **3** in $CDCl_3$.

The ^1H NMR spectrum (Figure 3) of PCL-25 (the number 25 indicates the designed $[M]_0/[I]_0$) shows an integral ratio close to 1 between H_b (CH_2 from −CL at the benzyl alkoxy chain end) and H_g (CH_2 from −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 good agreement with our expectation that the polymer chain should be capped with one benzyl ester and one hydroxy end. It is worthwhile to note that compound **3** catalyzes the ROP of lactones not only in a "living" fashion but also in an "immortal" way, in which a narrow-PDI polymer is obtained with a number of polymer molecules exceeding the number of initiator molecules (entries 8−14). In the presence of benzyl alcohol as the chain transfer agent, the exchange between the growing alkoxide species and alcohol leads to a chain transfer reaction, since the resulting aluminum alkoxide is able to reinitiate the polymerization. The experimental results show that as much as a 256-fold amount of BnOH can be added (entry 14). The result is much better than its $[(EDBP)Al(\mu\text{-}OBn)]_2$ analogue, but similar to $MMPEP^{2-}$.

Synthesis of Diblock Copolymer PS-*b*-PCL. Copolymers containing poly(ϵ-caprolactone) are especially interesting because they are miscible with a wide range of polymers,[15] and they have features like crystallizability,[16] lack of toxicity, ability to disperse pigments, low-temperature adhesiveness, and printability.[17] Moreover, physical properties of polystyrene after degradation of PCL from PS-*b*-PCL copolymer are of great interest. To develop a convenient synthetic route of copolymers with control over molecular weight is the challenging task in the material chemistry research. Recently, Youshida et al.[18] have reported PS-*b*-PCL from ROP of CL followed by the polymerization of styrene with PDIs ranging from 1.23 to 1.42. We reported here a different way to prepare PS-*b*-PCL copolymers with a much narrower molecular weight distribution.

Polystyrene with 4-hydroxy-TEMPO terminal was synthesized by a free radical polymerization approach similar to the method reported by Georges et al.[19] In this method polymerization of styrene was initiated by dibenzoyl peroxide (BPO) in the presence of 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinoxyl (4-OH-TEMPO), yielding high molecular weight polystyrene (M_n = 20 800) with low polydispersities (PDI = 1.1). This prepolymer (**PS-2**) with a hydroxy terminal then reacts with [(MEBBP)Al(CH_3)(THF)] in toluene, giving a macroinitiator as shown in Scheme 2. The macroinitiator further reacts with ϵ-CL by ROP to give PS-*block*-PCL. This polymerization experiment was conducted with different condition, and the results are tabulated in Table 2. The molecular weight of block copolymers increases with increasing $[CL]_0/[Al]_0$ ratio with reasonable PDIs ranging from 1.14 to 1.17. In the ^1H NMR spectrum of PS-*b*-PCL (Figure 4), a broad signal in the aromatic region and the typical triplets at 4.05 and 2.23 show the block nature of the PS−PCL copolymer. Moreover, in the GPC profile (Figure 5) peak A corresponds to polystyrene (M_n = 20 800, PDI = 1.10), and peak B corresponding to PS-*b*-PCL after polymerization with 50 equiv of CL increase in molecular weight (M_n = 34 400, PDI = 1.16) was observed (peak B) to confirm the formation of block copolymer. In every case block copolymers showed sharp, unimodal distribution GPC curves, indicating that the PS had completely reacted with CL.

In conclusion, two novel aluminum alkoxides [(MEBBP)Al(CH_3)(THF)] (**2**) and $[(MEBBP)Al(\mu\text{-}OBn)]_2$ (**3**) have been synthesized, and compound **2** has been structurally characterized by the single-crystal diffraction method. The "immortal" character of complex **3** has paved a way to synthesize as much as 256-fold polymer chains of PCL with very narrow PDI in the presence of a small amount of initiator. From our earlier reports and this research, we found that substituents in the biphenol, especially the presence of a bulky substituent

Scheme 2

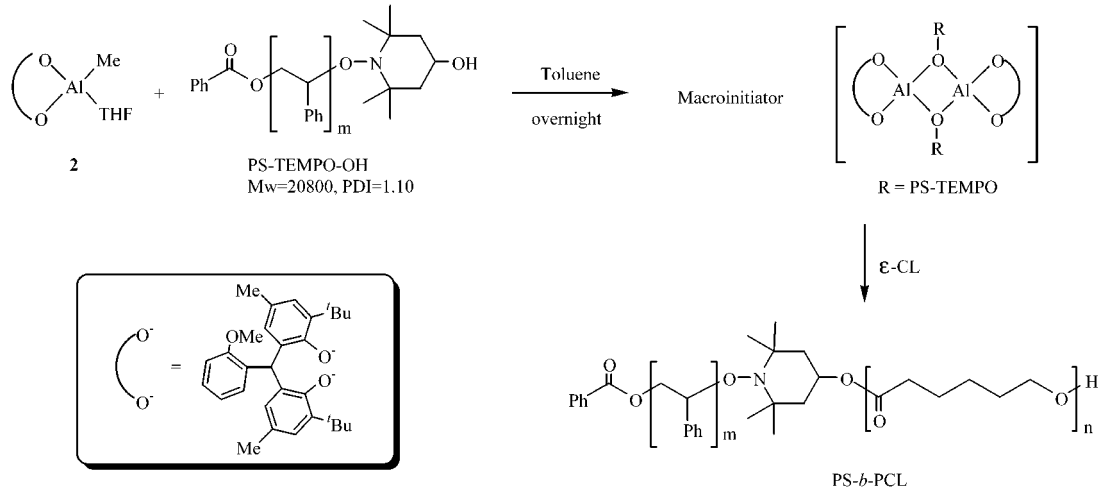

Table 2. Polymerization of ϵ-Caprolactone Initiated by Aluminum Alkoxide Macroinitiator Containing TEMPO-Supported PS

	prepolymer					PS-*b*-PCL		PCL	
entry	M_n	PDI	[CL]/[Al]	time (h)	conv[a] (%)	M_n(GPC)[b]	PDI	M_n(NMR)[c]	PS ratio[d]
1	20 800	1.10	50	3	93	34 400	1.16	6 200	0.64
2	20 800	1.10	100	3	100	56 700	1.14	15 100	0.39
3	20 800	1.10	150	5	100	70 600	1.17	21 900	0.32
4	20 800	1.10	200	5	98	84 200	1.17	29 500	0.27
5	20 800	1.10	50	3	100	32 600	1.17	5 800	0.66

[a] Obtained from ^{1}H NMR analysis. [b] Obtained from GPC analysis. [c] Calculated from the molecular weight of ϵ-caprolactone times $[M]_0/[Al]_0$ times conversion yield plus the molecular weight of BnOH. [d] Volume of PS divived the total volume of PS and PCL.

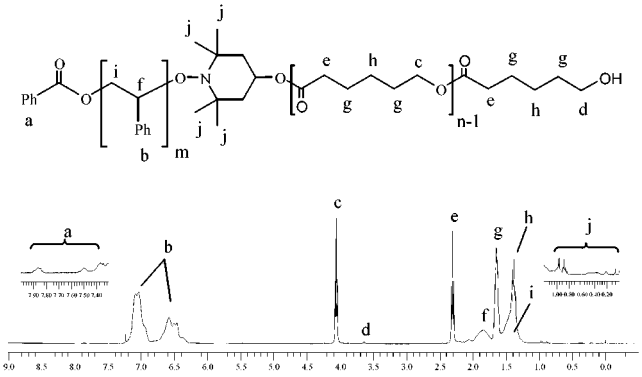

Figure 4. ^{1}H NMR spectrum of PS-*b*-PCL initiated by PS-TEMPO-OH in the presence of **2** in $CDCl_3$.

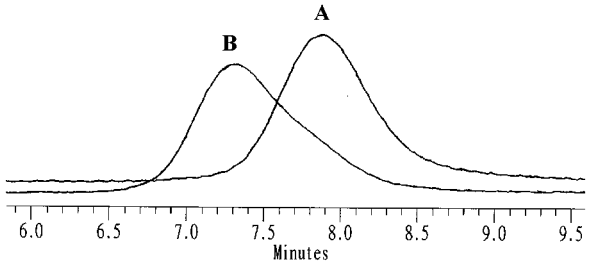

Figure 5. GPC profiles of copolymerization of PS-*b*-PCL: (peak A) 4-OH-TEMPO−PS (prepolymer, M_n = 20 800, PDI = 1.10); (peak B) after block copolymerization of PS-*b*-PCL ($[PS]_0/[\mathbf{2}]_0/[CL]_0$ = 1/1/50, M_n = 34 400, PDI = 1.16).

either in the bridged methine carbon (C-7) or at the ortho position of the hydroxyl group of biphenol, dictate the efficiency of the initiator. Furthermore, an effective method to prepare PS-*b*-PCL by combination of free radical polymerization of styrene and ROP of CL using a bifunctional ligand 4-OH-TEMPO has been found.

Experimental Section

General. All manipulations were carried out under a dry nitrogen atmosphere. The solvents ϵ-caprolactone, styrene, benzyl alcohol, and deuterated solvents were purified by distillation before use. $AlMe_3$ (2.0 M in toluene), *o*-anisaldehyde, 2-*tert*-butyl-4-methylphenol, and benzenesulfonic acid were purchased and used without further purification. ^{1}H 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 using $CDCl_3$ as deuterated solvent. 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 a standard.

2,2′-(2-Methoxybenzylidene)bis(4-methyl-6-*tert*-butylphenol) (MEBBP-H_2) (1). A mixture of 2-*tert*-butyl-4-methylphenol (3.29 g, 20 mmol), *o*-anisaldehyde (1.45 mL, 10 mmol), and benzenesulfonic acid (0.40 mL) in hexane (30 mL) was refluxed for 5 h. The volatile materials were removed under vacuum, and the residue was redissolved in toluene (30 mL). After neutralization with aqueous NaOH solution (0.1 N, 20 mL), the organic layer was extracted with water (10 mL) twice. The toluene layer was then dried over $MgSO_4$ and concentrated to 15 mL. White crystalline solids were obtained after 5 days at −20 °C. Yield: 3.82 g (81%). Anal. Calcd for $C_{30}H_{38}O_3$: C, 80.59; H, 8.39%. Found: C, 80.52; H, 8.05%. ^{1}H NMR ($CDCl_3$, ppm): δ 7.32−6.53 (m, 8H, Ph); 5.89 (s, 1H, CH); 4.94 (br, 2H, OH); 3.80 (s, 3H, OCH_3); 2.17 (s, 6H, CH_3); 1.35 (s, 18H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 156.62, 151.00, 137.32, 130.57, 129.01, 128.57, 128.44, 127.45, 127.23, 126.93, 121.18, 110.86 (Ph); 55.61 (OCH_3); 39.59 (CH); 34.63 ($PhCH_3$); 29.72 ($PhC(CH_3)_3$); 21.01 ($PhC(CH_3)_3$). IR (KBr, cm^{-1}): 3539 (br, s), 3008 (m), 2962 (s), 2914 (s), 2865 (m), 1487 (s), 1469 (s), 1439 (s), 1416 (s), 1391 (m), 1361 (m), 1319 (m), 1243 (s), 1218 (s), 1179 (s), 1105 (m), 869 (m). Mass spectrum (EI, *m/e*): 446 (M^+, 91%). IR (KBr, cm^{-1}): 3539 (br, s), 3008 (m), 2962 (s), 2914 (s), 2865 (m), 1487 (s), 1469 (s), 1439 (s), 1416 (s), 1391 (m), 1361 (m), 1319 (m), 1243 (s), 1218 (s), 1179 (s), 1105 (m), 869 (m). Mp: 166−168 °C.

[(MEBBP)Al(CH_3)(THF)] (2). To an ice cold solution (0 °C) of MEBBP-H_2 (1.34 g, 3.0 mmol) in tetrahydrofuran (20 mL) was added slowly an $AlMe_3$ (1.80 mL, 2.0 M in toluene, 3.6 mmol) solution. After all of the solution was added, the mixture was stirred for 3 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: 1.31 g (78%). Anal. Calcd for $C_{35}H_{47}AlO_4$: C, 75.24; H, 8.48%. Found: C, 74.44; H, 8.64%. ^{1}H NMR ($CDCl_3$, ppm): δ 7.57−6.80 (m, 8H, Ph); 6.05 (s, 1H, CH); 4.31 (br, 4H, $-OCH_2-$); 3.33 (s, 3H, OCH_3); 2.17 (s, 6H, CH_3); 2.06−2.03 (m, 4H, $-CH_2-$); 1.37 (s, 18H, $C(CH_3)_3$); −0.61 (s, 3H, $AlCH_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 157.92, 152.96, 137.44, 133.94, 132.87, 129.44, 127.29, 126.88, 125.49, 124.47, 120.24, 112.78 (Ph); 71.53 (OCH_2CH_2); 55.93 (OCH_3); 36.85 (CH); 34.75 ($PhCH_3$); 29.97 ($PhC(CH_3)_3$); 25.14 (OCH_2CH_2); 21.13 ($PhC(CH_3)_3$); −13.74 ($AlCH_3$). IR (KBr, cm^{-1}): 2991 (s), 2865 (s), 2832 (m), 1543 (m), 1483 (m), 1401 (s), 1355 (m), 1270 (m), 1118 (m), 916 (s), 828 (m), 697 (m). Mp = 214−216 °C.

[Al(MEBBP)(μ-OBn)]$_2$ (3) To a rapidly stirred solution of [(MEBBMP)Al(CH_3)(THF)] (1.12 g, 2.0 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 3 h. The volatile materials were removed under vacuum, and the residue was redissolved in hot toluene (50 mL). The extraction was then concentrated to ca. 30 mL and was allowed to cool −20 °C, affording colorless crystalline solids after 12 h. Yield: 1.03 g (89%). Anal. Calcd for $C_{74}H_{86}Al_2O_8$: C, 76.79; H, 7.49%. Found: C, 76.14; H, 8.01%. ^{1}H NMR ($CDCl_3$, ppm): 7.35−6.57 (m, 26H, Ph); 5.15 (s, 2H, CH); 3.30 (s, 6H, OCH_3); 2.99 (s, 4H, OCH_2); 2.15 (s, 12H, $PhCH_3$); 1.34 (s, 36H, $PhC(CH_3)_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 157.84, 151.39, 137.59, 134.75, 132.05, 131.92, 129.27, 129.04, 128.23, 127.81, 127.64, 127.17, 126.94, 126.87, 126.00, 124.94, 119.88, 112.02 (Ph); 66.66 (OCH_2); 55.27 (OCH_3); 39.21 (CH); 34.90 ($PhCH_3$); 30.25, 21.08

Table 3. Crystallographic Data for 2

complex	**2**
empirical formula	C_{35} H_{47} Al O_4
formula weight	558.71
crystal system	triclinic
space group	*P*-1
a (Å)	8.3163(8)
b (Å)	11.8938(11)
c (Å)	18.1431(17)
α (deg)	75.384(2)
β (deg)	84.707(2)
γ (deg)	72.860(2)
V (Å^3)	1659.1(3)
Z	2
D(calcd), mg/m^3	1.118
absorption coefficient (mm^{-1})	0.095
F(000)	604
θ range for data collection	2.60−26.03°
reflections collected	5128
independent reflections	4466 [*R*(int) = 0.0268]
completeness to *θ* = 25.02°	68.1%
absorption correction	SADABS
refinement method	full matrix least squares on F^2
data/restraints/parameters	4466/0/361
goodness-of-fit on F^2	1.022
final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0528$, $wR2 = 0.1410$
R indices (all data)	$R1 = 0.0747$, $wR2 = 0.1561$
largest diff peak and hole	0.227 and −0.222 e Å^{-3}

[a] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]]^{1/2}$; $w = 0.10$. [c] GoF $= [\Sigma w(F_o^2 - F_c^2)^2/(N_{rflns} - N_{params})]^{1/2}$.

($PhC(CH_3)_3$). IR (KBr, cm^{-1}): 3012 (s), 2981 (s), 2844 (m), 1392 (m), 1342 (m), 1289 (s), 1203 (s), 877 (m), 762 (s), 657 (m). Mp = 232−234 °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 stirred solution of [(MEBBP)Al(μ-OBn)]$_2$ (0.116 g, 0.10 mmol) in toluene (30 mL) was added ϵ-CL (2.1 mL, 20 mmol). The reaction mixture was stirred at 50 °C for 3 h, during which an increase in viscosity was observed. After the reaction was quenched by the addition of excess 0.35 N acetic acid solution, the polymer was precipitated in *n*-heptane. The white solid was precipitated from a mixed hexane/THF (5:1) solvent twice and was dried under vacuum, giving a white solid. Yield: 1.91 g (83%).

Synthesis of Benzyl Ester End-Functionalized PCLs in the Presence of Benzyl Alcohol. A typical polymerization was exemplified by the synthesis of PCL-400 in the presence of 2.0 mol equiv of BnOH. ϵ-CL (8.4 mL, 80 mmol) and BnOH (0.042 mL, 0.4 mmol) were dissolved in 20 mL of toluene at 50 °C, and then the mixture was added to a rapidly stirring solution of [(MEBBP)Al(μ-OBn)]$_2$ (0.116 g, 0.10 mmol) in toluene (10 mL). The reaction mixture was stirred at 50 °C for 4 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: 8.8 g (96%).

Synthesis of 4-Hydroxy-TEMPO-Terminated Polystyrene. A typical free radical polymerization procedure was exemplified by the synthesis of **PS-2**. A mixture of styrene (St, 46 mL, 400 mmol), dibenzoyl peroxide (BPO, 0.39 g, 1.6 mmol), and 4-OH-TEMPO (0.33 g, 1.92 mmol) (molar ratio of 4-OH-TEMPO/BPO = 1.2) was preheated in a 250 mL round-bottom flask with a stirring bar in a nitrogen atmosphere at 95 °C for 3 h to allow BPO to decompose completely. Then the system was heated at 130 °C for 4 h to yield PS-TEMPO-4-OH. The resulting polystyrene was precipitated with methanol (300 mL) from a THF (50 mL) solution. The product was then precipitated from CH_2Cl_2/MeOH (1:5) mixture solution twice and dried in vacuo overnight. Yield: 31.22 g (74.7%). M_n(GPC): 20 800, PDI = 1.10. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.46−7.09 (br, 5H, ArH), 1.84 (br, 1H, CH), 1.42 (br, 2H, CH_2).

Synthesis of Diblock Copolymer PS-*b*-PCL. To a rapidly stirred solution of [(MEBBP)Al(CH_3)(THF)] (0.123 g, 0.22 mmol) in toluene (30 mL) was added 4-hydroxy-TEMPO-terminated polystyrene (PDI = 1.10, M_w = 20 800) (4.16 g, 2 mmol), and the reaction mixture was stirred at 25 °C for 16 h. ϵ-CL (2.1 mL, 20 mmol) was then added, and the reaction mixture was stirred at 50 °C for 3 h during which an increase in viscosity was observed. After the reaction was quenched by the addition of an excess acetic acid aqueous solution (10 mL, 0.35 N), the polymer was precipitated into *n*-hexane (20 mL). The white solid was precipitated from a mixed hexane/THF (5:1) solvent twice and was dried under vacuum, giving a white solid. Yield: 3.45 g (65%).

X-ray Crystallographic Studies. Suitable crystals of **2** 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 the 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. Crystallographic data for **2** are listed in Table 3.

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

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