7968 *Macromolecules* **2004,** *37,* 7968−7973

Aluminum Complexes Supported by Tridentate Aminophenoxide Ligand as Efficient Catalysts for Ring-Opening Polymerization of ϵ-Caprolactone

Chi-Tien Chen,* Chi-An Huang, and Bor-Hunn Huang

Department of Chemistry, National Chung-Hsing University, Taichung 402, Taiwan

Received April 25, 2004; Revised Manuscript Received July 27, 2004

ABSTRACT: Aluminum complexes bearing dianionic amine bis(phenolate) ligand are described. Reactions of ligand precursors H_2O_2NMe or H_2O_2NPr [$H_2O_2NMe = (CH_3)N\text{-}(CH_2\text{-}2\text{-}HO\text{-}3,5\text{-}C_6H_2(^tBu)_2)_2$; $H_2O_2NPr = (CH_3CH_2CH_2)N\text{-}(CH_2\text{-}2\text{-}HO\text{-}3,5\text{-}C_6H_2(^tBu)_2)_2$] with 1.1 mol equiv of $AlMe_3$ in toluene afford $MeAl(O_2NMe)$ (**1**) and $MeAl(O_2NPr)$ (**2**) as four-coordinate aluminum methyl complexes. The molecular structures are reported for compounds **1** and **2**. Both compounds show excellent catalytic activity toward the ring-opening polymerization of ϵ-caprolactone in the presence of benzyl alcohol.

Introduction

Aluminum complexes with ancillary ligands applied in ring-opening polymerization of poly(ϵ-caprolactone) (PCL) and poly(lactide) (PLA) as well as their copolymers have attracted considerable attention, mainly due to their great success in making materials with narrow molecular weight distribution and in high yield.[1−5] Various metal alkoxides supported by bulky ancillary ligands have been synthesized; the high Lewis acidity and low toxicity of the aluminum alkoxide-based system bearing bulky phenolate ligands seems to be active and suitable in preparing the well-defined polyesters.[2−8] Both "living" and "immortal" properties also encourage the researcher to develop novel (phenolate)aluminum alkoxides, which are expected to produce polymers with controlled properties.[2−8]

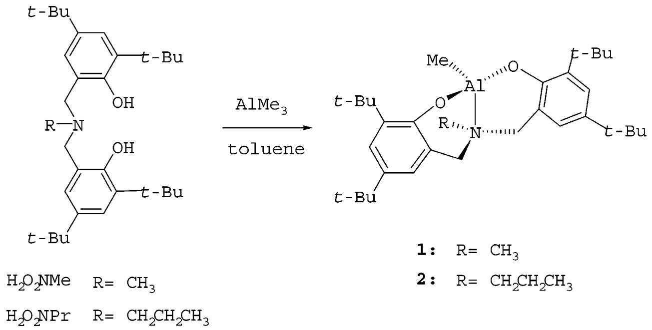
Based on Tolman's[7] and our[8] work on the application of amine bis(phenolate) aluminum complexes in ring-opening polymerization, the Lewis acidity on the central metal center could be modulated by pendant functionality or substituents on the phenyl ring. In some cases, the existence of pendant arm could play an important role in determining the constitution of the resulting complexes[9] or affecting the reactivity of metal complexes in catalytic reactions.[10−13]

In this paper, we report aluminum complexes supported by the bulky amine bis(phenolate) ligands without bearing a dative arm. The geometry and catalytic activities of aluminum methyl complexes are under investigation.

Results and Discussion

Syntheses and Characterization of Aluminum Amine Bis(phenolate)s. Ligand precursors H_2O_2NMe or H_2O_2NPr [$H_2O_2NMe = (CH_3)N-(CH_2\text{-}2\text{-}HO\text{-}3,5\text{-}C_6H_2(^tBu)_2)_2$; $H_2O_2NPr = (CH_3CH_2CH_2)N\text{-}(CH_2\text{-}2\text{-}HO\text{-}3,5\text{-}C_6H_2(^tBu)_2)_2$] are prepared using the Mannich condensation reaction.[13,14] Reactions of ligand precursors H_2O_2NMe or H_2O_2NPr with 1.1 mol equiv of $AlMe_3$ in toluene yield $MeAl(O_2NMe)$ (**1**) and $MeAl(O_2NPr)$ (**2**) as four-coordinate aluminum methyl complexes, as shown in Scheme 1. Both compounds were isolated as colorless crystalline solids and were characterized by spectroscopic studies as well as microanalyses. ^1H and $^{13}C\{^1H\}$ NMR spectra of **1** and **2** are indicative of a highly symmetric species in solution, with two diastereotopic signals corresponding to the methylene protons of N-CH_2-aryl found around 3.6−3.9 ppm (3.65 and 3.79 ppm for **1**; 3.73 and 3.83 ppm for **2**). Crystals of **1** or **2** for structural determination were obtained from concentrated hexane solution. The molecular structure of **1** is shown in Figure 1, and selected bond lengths and angles of **1** and **2** are listed in Table 1. Basically, the chelate of compound **2** is quite similar to compound **1** with a different substituent $-CH_2CH_2CH_3$ on nitrogen of amine instead of $-CH_3$ for **1**. Both structures exhibit a monomeric structure with four-coordinate aluminum center, including two six-membered amine phenolate metalla-rings. Bond angles (98.52(9)°−117.23(13)° for **1**; 99.00(18)°−115.4(2)° for **2**) around the central Al atom adopt a distorted tetrahedral geometry. The Al−O bond lengths (1.740(2) and 1.735(2) Å for **1**; 1.714(4)−1.736(3) Å for **2**) for the chelates are slightly shorter than those (1.748(3)−1.7842(10) Å) for aluminum pendant amine bis(phenolate) complexes.[7,8] The Al−C bond length (1.919(3) Å for **1**; 1.930(7), 1.925(6), and 1.939(6) Å for **2**) is shorter than that (1.981(2) Å) found in aluminum pendant amine bis(phenolate) complexes.[8] The Al−N bond length (1.988(2) Å for **1**; 1.985(4), 1.988(4), and 1.991(3) Å for **2**) of the amine donor is shorter than those (2.186(4)−2.1969(12) Å) found in aluminum pendant amine bis(phenolate) complexes.[7,8]

Scheme 1



Ring-Opening Polymerization of ϵ-Caprolactone Catalyzed by 1 and 2 in the Presence of Benzyl

---

* Corresponding author. E-mail: ctchen@mail.nchu.edu.tw.

10.1021/ma0492014 CCC: $27.50

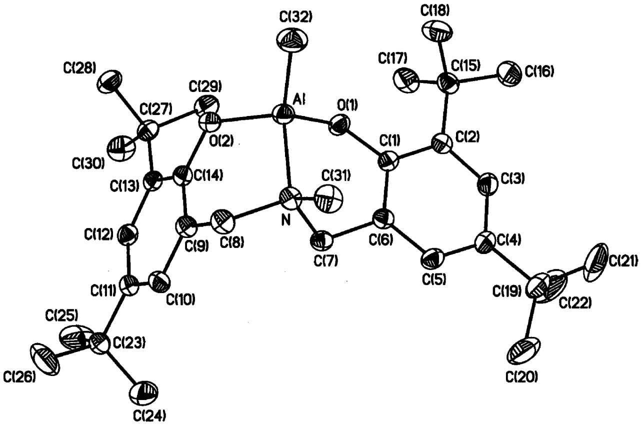


Figure 1. Molecular structure of MeAl(O_2NMe) (**1**). Hydrogen atoms on carbon atoms omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1 and 2

	1	2
Al−CH_3	1.919(3)	1.930(7), 1.925(6), 1.939(6)
Al−$O_{phenoxide}$	1.740(2)	1.714(4), 1.736(3), 1.734 (3)
	1.735(2)	1.734(4), 1.720(4), 1.724(3)
Al−N	1.988(2)	1.985(4), 1.988(4), 1.991(3)
O−Al−O	112.56(10)	114.23(19), 114.60(18), 114.63(19)
O−Al−N	99.16(9)	99.79(18), 99.58(16), 99.79(16)
	98.52(9)	99.25(18), 99.00(18), 100.15(16)
C−Al−N	113.60(13)	116.0(2), 115.2(2), 115.5(2)
C−Al−O	113.35(13)	115.3(2), 110.6(2), 111.7(2)
	117.23(13)	114.9(2), 115.4(2), 110.7(2)

Alcohol. According to the “immortal” property demonstrated by several aluminum amine bis(phenolate) derivatives[8] and the evidence of in situ formation of metal alkoxide in the presence of alcohol,[15,16] the methyl derivatives **1** and **2** were expected to work as catalysts toward the ROP of ϵ-caprolactone in the presence of alcohol. Basically, polymerization reactions were carried out in toluene (30 mL) at 50 °C with a prescribed equivalent ratio on the catalyst (0.25 mmol), monomers, and benzyl alcohol for the prescribed time.[8] After the reaction was quenched with an excess amount of aqueous acetic acid solution, the polymer was precipitated in *n*-heptane. The results of the polymerization of ϵ-CL initiated by **1** or **2** and benzyl alcohol under different reaction conditions have been summarized in Table 2. On the basis of the low molecular weight distribution values of polyesters (range from 1.04 to 1.12), both four-coordinated aluminum complexes **1** and **2** behave in a controlled manner in the presence of benzyl alcohol. Similar to those aluminum complexes supported by pendant amine bis(phenolate) ligands, the linear relationship between the number-average molecular weight (M_n) and the monomer-to-initiator ratio ($[M]_0/[I]_0$), as shown in Figure 2 (entries 1−5) and Figure 3 (entries 10−14), also exhibits the “living” character of the polymerization process, however, with better catalytic activity. Further experiments for the confirmation of this character were taken by the addition of another portion of ϵ-CL monomer after the polymerization of the first addition had gone to completion (entries 6 and 15). To examine the “immortal” character of **1** and **2**, 2 equiv of benzyl alcohol is used as the chain transfer agent (entry 7 for **1** and entry 16 for **2**). The M_n of the polymer in each case became half of that found in the reaction with addition of 1 equiv of benzyl alcohol. This character can be further confirmed by using different [M]:[Al]:[BnOH] ratios in each case (entries 8−9 and 17−18). The ratios between M_n(calcd) and M_n(obsd) are quite close to the average value of the respective correcting coefficient (0.56 ± 0.05) for poly(ϵ-CL).[17] To prove the polymer produced by the “in situ” manner is ended with benzyl oxide group, a polymer produced from ϵ-CL, **2**, and BnOH ([M]:[Al]:[BnOH] = 50:1:1) was purified from THF/hexane and subjected to ^{1}H NMR spectroscopy. As shown in Figure 4, peaks are assignable to the corresponding protons in the proposed structure.[4,6] From this spectrum, the polymer is almost the same as the one produced by using pendant amine bis(phenolate) aluminum benzyl oxide as initiator.[8] To prove the existence of the metal benzyl oxide species in the “in situ” manner, reaction of compound **2** (0.1 mmol) and benzyl alcohol in a 1:1 molar ratio was allowed to proceed in $CDCl_3$ at 50 °C for 4 h, as shown in Figure 5. A new species corresponding to the metal benzyl oxide complex appears gradually, accompanying the disappearance of peaks corresponding to the metal methyl compound. After removal of the volatiles, the residue was redissolved in toluene and heated at 50 °C with 50 mol equiv of ϵ-CL for 15 min in a flask. Polymer was purified from the normal manner and subjected to ^{1}H NMR spectroscopy. As shown in Figure 6, the spectrum is almost the same as the one shown in Figure 4 with a similar property (entry 19 in Table 2). On the basis of these results and by analogy with the mechanisms accepted for the ROP of cyclic esters mediated with metal alkoxides,[4,5,8,18,19] the metal−benzyl oxide species will form first, followed by the procedures similar to those proposed for pendant amine bis(phenolate)aluminum benzyl oxide complexes.[8] Finally polyesters can be released by the addition of benzyl alcohol or acidic solution, as shown in Scheme 2. Because of the poor stability of metal benzyl oxide compounds, isolation of pure compounds for characterization was proved unsuccessfully.

Conclusion

Novel monomeric four-coordinate aluminum methyl complexes supported by dianionic amine bis(phenolate) ligand have been prepared and fully characterized. The aluminum methyl complexes were found to catalyze the polymerization of ϵ-caprolactone in the presence of benzyl alcohol with narrow PDIs. The “in situ” formed aluminum benzyl oxide initiators can produce the same polymer as the one found in other system using aluminum benzyl oxides as initiators. They also exhibit both “living” and “immortal” characters with better catalytic ability than those with dative pendant functionalities. It seems presumable that lack of the dative pendant groups makes a better tuning on the Lewis acidity and steric hindrance of the metal center that gives a better combination of monomer binding and alkoxide nucleophilicity in this system, thus leading to a higher catalytic ability in polymerization.

Experimental Section

All manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk-line or drybox techniques. Solvents were refluxed over the appropriate drying agent and distilled prior to use. Deuterated solvents were dried over molecular sieves.

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded either on a Varian Mercury-400 (400 MHz) or a Varian Inova-600 (600 MHz) spectrometer in chloroform-*d* at ambient temperature unless stated otherwise and referenced internally to the residual solvent peak and reported as parts per million relative

Table 2. Ring-Opening Polymerization of ϵ-Caprolactone Initiated by Compounds 1 and 2 in the Presence of BnOH at 50 °C

entry	compd	[M]:[Al]:[ROH]	time (min)	M_n (obsd)[a]	M_n (calcd)[b]	M_n (NMR)[c]	conv (%)[c]	yield (%)[d]	PDI
1	**1**	50:1:1	20	10 800	5700	5800	99	98	1.05
2	**1**	100:1:1	30	17 800	11 400	10 600	99	91	1.04
3	**1**	150:1:1	30	31 800	17 100	17 000	99	92	1.09
4	**1**	200:1:1	30	47 100	22 700	23 700	99	96	1.07
5	**1**	300:1:1	30	71 600	33 900	30 800	99	95	1.13
6	**1**	100 (100):1:1	30 (30)	39 000	11 200 (22 500)	22 200	97 (98)	91	1.05
7	**1**	100:1:2	20	10 900	5800	5400	99	92	1.06
8	**1**	200:1:4	20	11 300	5700	6000	99	96	1.07
9	**1**	400:1:8	20	10 900	5800	5400	99	98	1.07
10	**2**	50:1:1	15	9300	5700	6000	99	88	1.06
11	**2**	100:1:1	20	18 800	11 400	9500	99	92	1.06
12	**2**	150:1:1	20	26 700	16 700	17 700	99	87	1.06
13	**2**	200:1:1	20	36100	22 600	21 900	98	87	1.05
14	**2**	300:1:1	20	58 000	34 000	34 600	99	91	1.12
15	**2**	100 (100):1:1	20 (20)	34100	10 600 (22500)	23 000	92 (98)	87	1.05
16	**2**	100:1:2	15	10 000	5800	5700	99	98	1.05
17	**2**	200:1:4	15	10 300	5700	5600	99	99	1.04
18	**2**	400:1:8	15	10 700	5700	5800	99	99	1.04
19	[AlOBn]	50:1:0	15	10 800	5800	5300	99	81	1.07

[a] Obtained from GPC analysis. [b] Calculated from [M(lactone) × $[M]_0/[Al]_0$ × conversion yield/($[BnOH]_{eq}$)] + M(BnOH). [c] Obtained from ^1H NMR analysis. [d] Isolated yield.

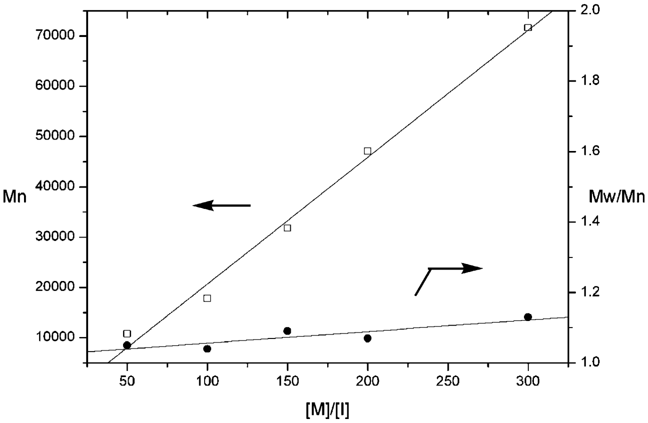


Figure 2. Polymerization of ϵ-CL initiated by **1** and BnOH in toluene at 50 °C.

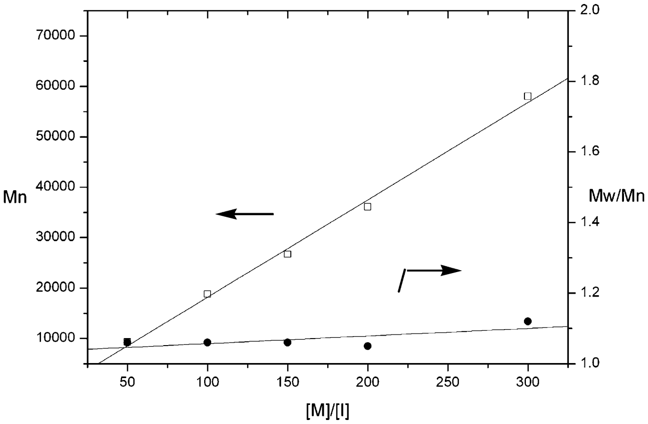


Figure 3. Polymerization of ϵ-CL initiated by **2** and BnOH in toluene at 50 °C.

to tetramethylsilane. Elemental analyses were performed by a Heraeus CHN-O-RAPID instrument. 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 weights and molecular weight distributions were calculated using polystyrene as standard.

Benzyl alcohol was dried over magnesium sulfate and distilled before use. ϵ-Caprolactone was dried over magnesium sulfate and distilled under reduced pressure. $AlMe_3$ (2 M in toluene, Acros) was used as supplied. The compounds H_2O_2-NMe[14] and H_2O_2NPr[13] were prepared according to previously reported procedures.

Preparations. MeAl(O_2NMe) (1). To a solution of H_2O_2-NMe (8.5 g, 18.2 mmol) in 40 mL of toluene, 10 mL of $AlMe_3$ (2 M in toluene, 20 mmol) was added dropwise at room temperature. After 17 h of stirring, the volatiles were removed under reduced pressure, and the residue was washed with 30 mL of hexane to afford white powder. Yield: 6.3 g, 68%. ^1H NMR (600 MHz): δ −0.63 (s, Al−CH_3, 3H), 1.27 (s, C(CH_3)$_3$, 18H), 1.41 (s, C(CH_3)$_3$, 18H), 2.51 (s, N−CH_3, 3H), 3.65 (d, CH_2, 2H, J = 12.6 Hz), 3.79 (d, CH_2, 2H, J = 13.2 Hz), 6.86 (d, CH−phenoxide, 2H, J = 2.4 Hz), 7.29 (d, CH−phenoxide, 2H, J = 2.4 Hz).$^{13}C\{^1H\}$ NMR (150 MHz): δ −16.1 (s, Al−CH$_3$), 29.5, 31.7 (s, C(CH$_3$)$_3$), 34.1, 35.1 (s, C(CH$_3$)$_3$), 43.4 (s, N-CH$_3$), 60.8 (s, N−(CH$_2$)−Ph), 124.3, 124.9 (s, CH−Ph), 120.8, 138.4, 139.9, 154.8 (s, *tert*-C). Anal. Calcd for $C_{32}H_{50}AlNO_2$: C, 75.7; H, 9.9; N, 2.8. Found: C, 75.1; H, 9.4; N, 2.4.

MeAl(O_2NPr) (2). To a solution of H_2O_2NPr (9.0 g, 18.2 mmol) in 30 mL of toluene, 10 mL of $AlMe_3$ (2 M in toluene, 20 mmol) was added dropwise at room temperature. After 24 h of stirring, the volatiles were removed under reduced pressure, and the residue was washed with 30 mL of hexane to afford white powder. Yield: 7.2 g, 74%. ^1H NMR (600 MHz): δ −0.62 (s, Al−CH_3, 3H), 0.90 (t, (CH$_2$)$_2$−CH_3, 3H, 7.2 Hz), 1.26 (s, C(CH_3)$_3$, 18H), 1.40 (s, C(CH_3)$_3$, 18H), 1.74 (m, (CH_2)$_2$−CH$_3$, 2H), 2.74 (m, (CH_2)$_2$−CH$_3$, 2H), 3.73 (d, CH_2, 2H, J = 13.2 Hz), 3.83 (d, CH_2, 2H, J = 13.2 Hz), 6.85 (d, CH−phenoxide, 2H, J = 2.4 Hz), 7.27 (d, CH−phenoxide, 2H, J = 3.0 Hz). $^{13}C\{^1H\}$ NMR (150 MHz): δ −15.2 (s, Al−CH$_3$), 11.6 (s, (CH$_2$)$_2$−CH$_3$), 14.6 (s, (CH$_2$)$_2$−CH$_3$), 29.5, 31.7 (s, C(CH$_3$)$_3$), 34.1, 35.0 (s, C(CH$_3$)$_3$), 55.3 (s, (CH$_2$)$_2$−CH$_3$), 56.3 (s, N−(CH$_2$)−Ph), 124.2, 124.7 (s, CH−Ph), 120.7, 138.2, 139.8, 155.0 (s, *tert*-C). Anal. Calcd for $C_{34}H_{54}AlNO_2$: C, 76.2; H, 10.2; N, 2.6. Found: C, 75.8; H, 10.7; N, 2.6.

Polymerization Studies. Typically, to a rapid stirring solution of prescribed amount of ϵ-CL and benzyl alcohol in toluene (20 mL) at 50 °C for 5 min was added a solution (10 mL in toluene) containing a prescribed amount of catalyst (0.25 mmol). The reaction mixture was stirred at 50 °C for the prescribed time. After the reaction was quenched by the addition of an excess amount of acetic acid solution, the resulting mixture was poured into excess n-heptane to precipitate PCL (poly-ϵ-caprolactone). Crude products were recrystallized from THF/hexane and dried in vacuo up to a constant weight. ^1H NMR (400 MHz) for the PCL-50 (Figure 4): δ 1.38 (m, H_e, 121H), 1.65 (m, H_d, 228H), 2.31 (m, H_c, 108H), 3.65 (t, H_g, 3H), 4.06 (m, H_f, 102H), 5.12 (s, H_b, 2H), 7.36 (br, H_a, 5H).

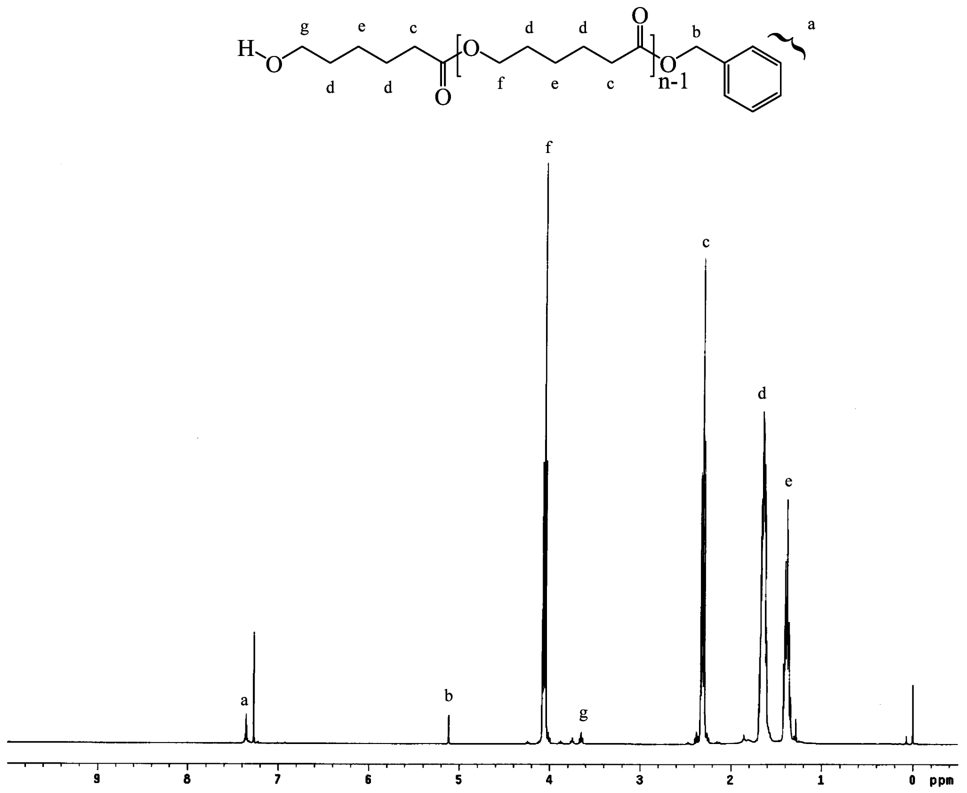


Figure 4. ^{1}H NMR spectrum of PCL-50 initiated by **2** and BnOH in $CDCl_3$.

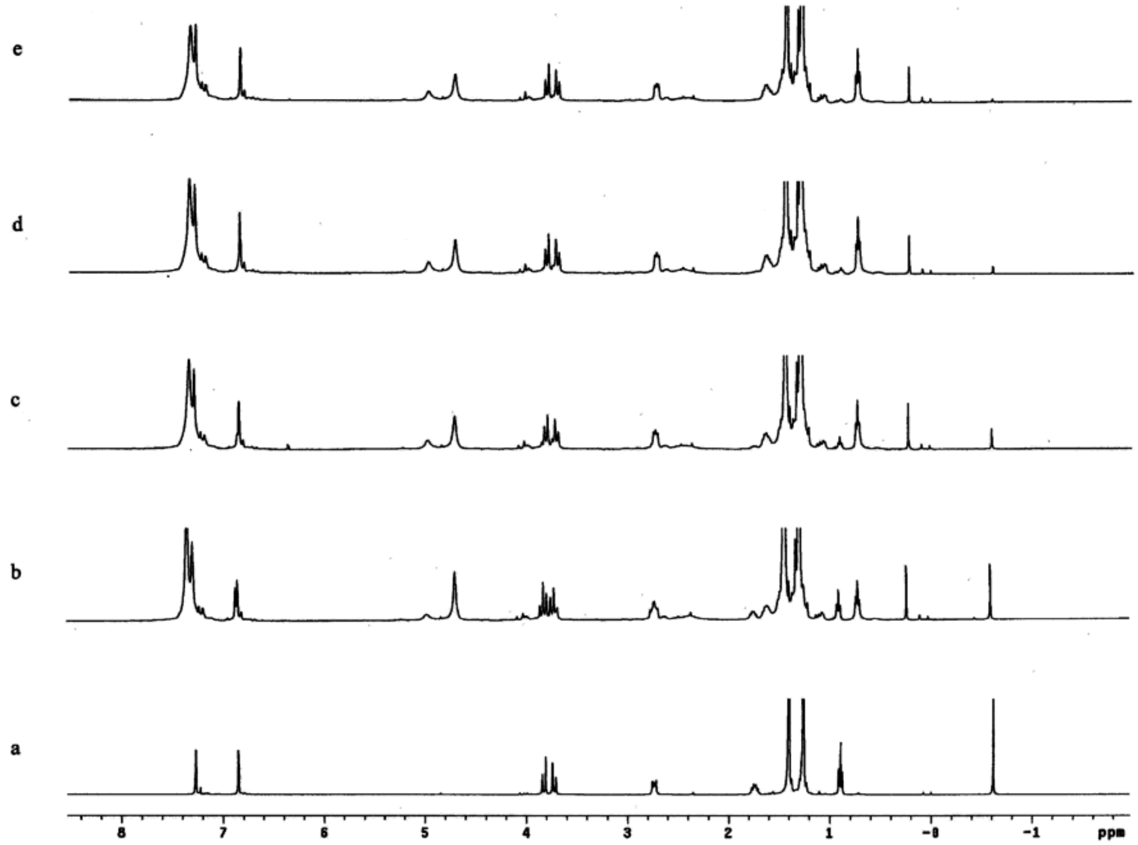


Figure 5. ^{1}H NMR specta of the reaction of **2** and BnOH in $CDCl_3$ at 50 °C: (a) without the addition of BnOH; (b) 1 h after the addition of BnOH; (c) 2 h after the addition of BnOH; (d) 3 h after the addition of BnOH; (e) 4 h after the addition of BnOH (from bottom to top).

NMR Study of the Formation of Metal Benzyl Oxide Species. To a solution containing **2** (0.053 g, 0.1 mmol) and $CDCl_3$ (0.9 g), benzyl alcohol (0.016 mL, 0.15 mmol) was added at 50 °C. The ^{1}H NMR spectra were taken with a period of 1 h, as shown in Figure 5. ^{1}H NMR (400 MHz)for the new species (Figure 5e): δ 0.72 (m, $(CH_2)_2{-}CH_3$, 3H), 1.26 (s, $C(CH_3)_3$,

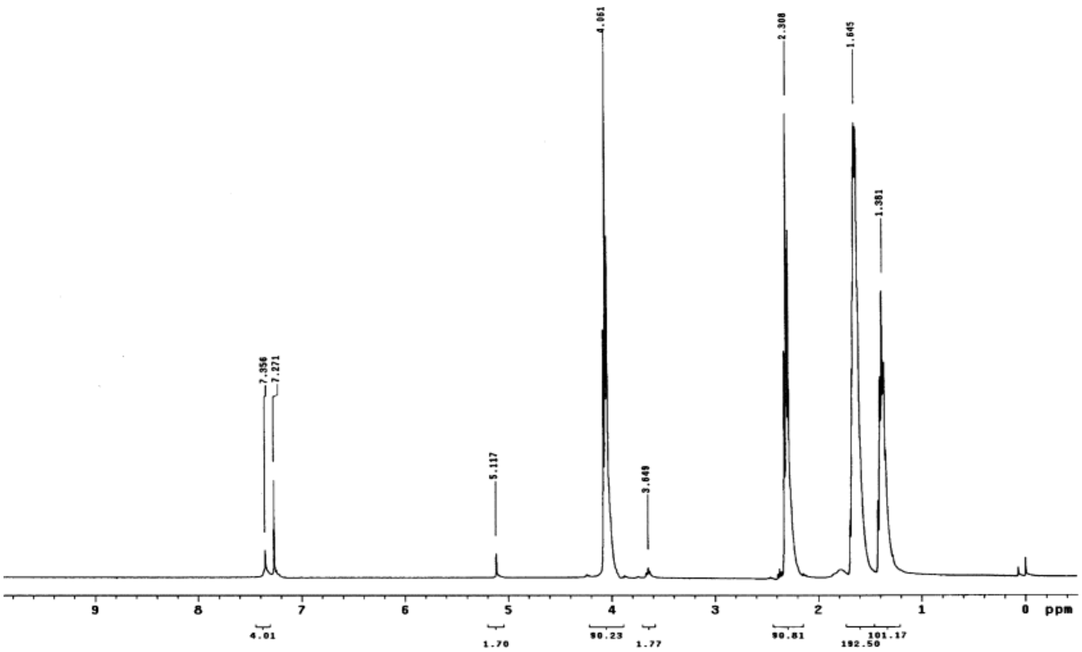
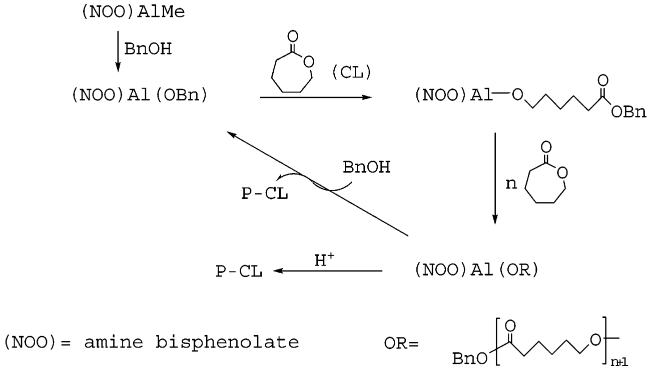


Figure 6. ^{1}H NMR spectrum of PCL-50 initiated by new metal benzyl oxide species in $CDCl_3$.

Scheme 2



18H), 1.42 (s, C(CH_3)$_3$, 18H), 1.61 (m, (CH_2)$_2$−CH_3, 2H), 2.71 (m, (CH_2)$_2$−CH_3, 2H), 3.69 (d, CH_2, 2H, J = 13.2 Hz), 3.79 (d, CH_2, 2H, J = 13.2 Hz), 4.70 (s, OCH_2Ph, 2H), 6.83 (s, CH−phenoxide, 2H), 7.27 (s, CH−phenoxide, 2H), 7.32 (br, OCH$_2$$Ph$, 5H).

After 4 h of heating, the volatiles were removed, and the residue was transferred into a 125 mL flask with 12 mL of toluene. To this toluene solution, ϵ-CL (0.525 mL, 5 mmol) was added at 50 °C and reacted for 15 min. After the reaction was quenched by the addition of an excess amount of acetic acid solution, the resulting mixture was poured into excess n-heptane to precipitate PCL (poly-ϵ-caprolactone). Crude products were recrystallized from THF/hexane and dried in vacuo up to a constant weight. ^{1}H NMR (400 MHz) for the PCL-50 initiated by new species (Figure 6): δ 1.38 (m, H_e, 103H), 1.65 (m, H_d, 193H), 2.31 (m, H_c, 91H), 3.65 (t, H_g, 2H), 4.06 (m, H_f, 91H), 5.12 (s, H_b, 2H), 7.36 (br, H_a, 4H). GPC data are listed in Table 2 (entry 19).

Crystal Structure Data. Crystals of **1** or **2** were grown from concentrated hexane solution and isolated by filtration. Suitable crystals of **1** or **2** were sealed in thin-walled glass capillaries under a nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. 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. Some details of the data collection and refinement are given in Table 3.

Table 3. Summary of Crystal Data for Compounds 1 and 2

	1	2
formula	$C_{32}H_{50}AlNO_2$	$C_{102}H_{162}Al_3N_3O_6$
FW	507.71	1607.29
T, K	293(2)	293(2)
crystal system	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_12_12_1$
a, Å	15.3605(11)	12.3430(15)
b, Å	18.3417(14)	28.695(3)
c, Å	12.3191(9)	28.695(3)
α, deg	90	90
β, deg	110.225(2)	90
γ, deg	90	90
V, Å^3	3256.8(4)	10163(2)
Z	4	4
ρ_{calc}, mg/m^3	1.035	1.050
μ(Mo Kα), mm^{-1}	0.088	0.087
reflections collected	18474	57942
no. of parameters	325	1027
$R1^a$	0.0555	0.0832
$wR2^a$	0.1464	0.1951
GoF^b	0.905	1.047

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

Acknowledgment. We thank the National Science Council of the Republic of China for financial support and Professor Chu-Chieh Lin for the useful discussion.

Supporting Information Available: CIF file for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Uhrich, K. E.; Cannizzaro, S. M.; Langer, R. S. *Chem. Rev.* **1999**, *99*, 3181.
(2) O'Keefe, B. J.; Hillmyer, M. A.; Tolman, W. B. *J. Chem. Soc., Dalton Trans.* **2001**, 2215.

(3) Coates, G. W. *J. Chem. Soc., Dalton Trans.* **2002**, 467.
(4) Ko, B.-T.; Lin, C.-C. *Macromolecules* **1999**, *32*, 8296.
(5) Chen, H.-L.; Ko, B.-T.; Huang, B.-H.; Lin, C.-C. *Organometallics* **2001**, *20*, 5076.
(6) Liu, Y.-C.; Ko, B.-T.; Lin, C.-C. *Macromolecules* **2001**, *34*, 6196.
(7) Alcazar-Roman, L. M.; O'Keefe, B. J.; Hillmyer, M. A.; Tolman, W. B. *Dalton Trans.* **2003**, 3082.
(8) Chen, C.-T.; Huang, C.-A.; Huang, B.-H. *Dalton Trans.* **2003**, 3799.
(9) Tshuva, E. Y.; Goldberg, I.; Kol, M.; Goldschmidt, Z. *Inorg. Chem.* **2001**, *40*, 4263.
(10) Tshuva, E. Y.; Versano, M.; Goldberg, I.; Kol, M.; Weitman, H.; Goldschmidt, Z. *Inorg. Chem. Commun.* **1999**, *2*, 371.
(11) Tshuva, E. Y.; Goldberg, I.; Kol, M.; Goldschmidt, Z. *Inorg. Chem. Commun.* **2000**, *3*, 611.
(12) Tshuva, E. Y.; Goldberg, I.; Kol, M.; Weitman, H.; Goldschmidt, Z. *Chem. Commun.* **2000**, 379.
(13) Tshuva, E. Y.; Goldberg, I.; Kol, M.; Goldschmidt, Z. *Organometallics* **2001**, *20*, 3017.
(14) Burke, W. J.; Glennie, E. L. M.; Weatherbee, C. *J. Org. Chem.* **1964**, *29*, 909.
(15) Martin, E.; Dubois, P.; Jérôme, R. *Macromolecules* **2000**, *33*, 1530.
(16) Martin, E.; Dubois, P.; Jérôme, R. *Macromolecules* **2003**, *36*, 5934.
(17) Save, M.; Schappacher, M.; Soum, A. *Macromol. Chem. Phys.* **2002**, *203*, 889.
(18) Ropson, N.; Dubois, P.; Jérôme, R.; Teyssie, P. *Macromolecules* **1995**, *28*, 7589.
(19) Takashima, Y.; Nakayama, Y.; Watanabe, K.; Itono, T.; Ueyama, N.; Nakamura, A.; Yasuda, H.; Harada, A. *Macromolecules* **2002**, *35*, 7538.

MA0492014