Reactions of 2,2′-Methylenebis(4-chloro-6-isopropyl-3-methylphenol) with Trimethylaluminum: Highly Efficient Catalysts for the Ring-Opening Polymerization of Lactones

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The reaction of 2,2′-methylenebis(4-chloro-6-isopropyl-3-methylphenol) (MCIMP-H_2) with 1.2 molar equiv of $AlMe_3$ in THF yields [(MCIMP)AlMe(THF)] (**1**), which further reacts with a stoichiometric amount of 2-propanol (IPA), affording the isopropoxy-bridged dimer [(MCIMP)Al(μ-O^{i}Pr)]$_2$ (**2**). Compound **2** can also be obtained by the treatment of MCIMP-H_2 with a stoichiometric amount of Al(O^{i}Pr)$_3$ in refluxing toluene. However, the reaction of **1** with another 1 equiv of $AlMe_3$ in CH_2Cl_2 furnishes [Me_2Al(μ-MCIMP)$AlMe_2$(THF)] (**3**), in which the MCIMP^{2-} ligand is acting as a bridging ligand. Further treatment of compound **3** with 2 molar equiv of 2-propanol results in the formation of the isopropoxy-bridged dinuclear aluminum complex [(MCIMP)Al(μ-O^{i}Pr)$_2$$AlMe_2$] (**4**). Compound **4** can be directly obtained from the reaction of **1** with $AlMe_3$ in the presence of 2-propanol. However, in the presence of a stoichiometric amount of H_2O, hydrolysis of **1** in THF gives the trimeric aluminum compound [(MCIMP)Al(μ-OH···THF)]$_3$ (**5**), in which the hydroxy group acts as a chelating group bridging to two aluminum atoms. Compounds **2** and **4** have shown excellent catalytic activity toward the ring-opening polymerization of ϵ-caprolactone and δ-valerolactone.

Introduction

Recently, biodegradable polymers such as poly(ϵ-caprolactone) (PCL),[1] poly(lactide) (PLA),[2] and their copolymers have been attracting considerable attention due to their potential application in human life.[3] The major polymerization method used to synthesize these polymers has been the ring-opening polymerization (ROP) of lactones/lactides and functionally related compounds. For examples, stannous octate[4] as well as trivalent lanthanide,[5] magnesium,[6] and zinc[7] alkoxides have been reported to be effective initiators in the ROP of lactones/lactides, giving polymers with high molecular weights in high yields. However, the toxicity and difficulties in removal of the catalyst from the resulting polymer have limited their utilization. Therefore, developing new catalytic systems that are more compatible toward the purpose of biomedical applications become more important.

Aluminum alkoxides, aluminum hydroxides, and alumoxanes are of great interest due to their potential uses such as precursors to aluminum oxides[8] and catalysts to the organic synthesis[9] as well as to the ring-opening polymerization (ROP) of lactones or lactides.[10] Among them, aluminum alkoxides are especially interesting and well-suited as initiators for the ROP of lactones and lactides due to their high Lewis acidity and low toxic-

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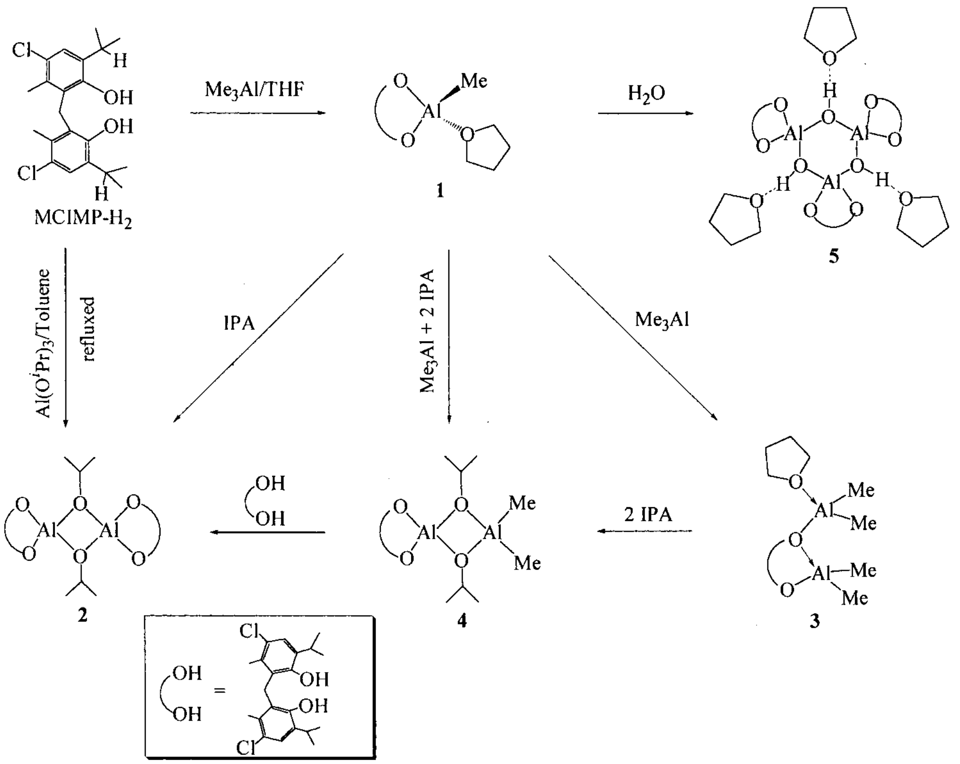
Scheme 1



ity.[11] For example, dialkylaluminum alkoxides (R_2-AlOR′) 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 many aluminum alkoxides as initiator in the ROP of lactones have been reported, both the electronic and steric alterations affecting the catalytic activities of aluminum derivatives are still fascinating. Our current interest has been in the preparation and characterization of aluminum derivatives and applying these complexes as Lewis acids in the catalysis of various reactions such as Diels−Alder reactions,[12] MPV (Meerwein−Ponndorf−Verley) reductions,[13] and ROP of lactones and lactide.[10c,14] As a result, we report herein the synthesis and characterization of novel aluminum alkoxides and aluminum hydroxides. The catalytic activities of [(MCIMP)Al(μ-O^{i}Pr)]$_2$ toward ROP of ϵ-caprolactone (CL) and δ-valerolactone (VL) are also presented. Experimental results show that this aluminum alkoxide catalyzes the polymerization of ϵ-CL in both "living" and "immortal" fashions, yielding PCL species with very narrow polydispersity indexes (PDI = M_w/M_n) in a wide range of monomer-to-initiator ratios. The "living" character of the catalyst has enabled us to synthesize PCL−b-PVL copolymer, and the "immortal" character has paved a way to prepare as much as 32-fold polymer chains of PCL in the presence of a tiny amount of an initiator.

Results and Discussion

Syntheses and Spectroscopic Studies. The free ligand 2,2′-methylene-bis(4-chloro-6-isopropyl-3-methylphenol) (MCIMP-H_2)[15] is obtained in high yield from the reaction of 4-chloro-2-isopropyl-5-methylphenol (chlorothymol) with paraformaldehyde in the presence of a catalytic amount of benzenesulfonic acid in refluxing toluene. The monomeric aluminum compound [(MCIMP)AlMe(THF)] (**1**) is prepared by the reaction of MCIMP-H_2 with 1.2 molar equiv of $AlMe_3$, as shown in Scheme 1. Compound **1** further reacts with a stoichiometric amount of 2-propanol, giving the isopropoxy-bridged aluminum dimer [(MCIMP)Al(μ-O^{i}Pr)]$_2$ (**2**). Alternatively, **2** can also be prepared directly by the reaction of MCIMP-H_2 with Al(O^{i}Pr)$_3$ in refluxing toluene. In addition, the reaction of **1** with 1 molar equiv of $AlMe_3$ in CH_2Cl_2 at room temperature furnishes [Me$_2$-Al(μ-MCIMP)AlMe$_2$(THF)] (**3**), which further reacts with 2 molar equiv of 2-propanol, yielding the isopropoxy-bridged dinuclear aluminum compound [(MCIMP)Al(μ-O^{i}Pr)$_2$AlMe$_2$] (**4**). Compound **4** can also be synthesized by the reaction of **1** with 2 molar equiv of 2-propanol in the presence of $AlMe_3$. Further reaction of **4** with a stoichiometric amount of MCIMP-H_2 at room temperature gives **2** in almost quantitative yield. Furthermore, in the presence of a stoichiometric amount of H_2O, hydrolysis of **1** in THF gives the trimeric hydroxy-bridged aluminum compound [(MCIMP)Al(μ-OH···THF)]$_3$ (**5**).

All of these compounds are isolated as off-white crystalline solids and have been characterized by spectroscopic studies as well as microanalyses. In our previous studies, we found that, in the aluminum

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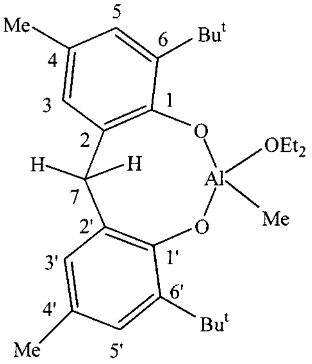
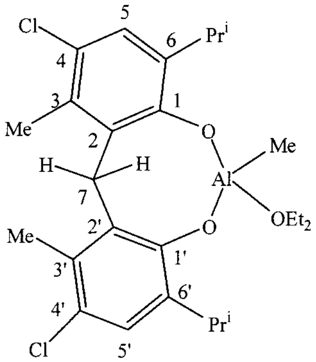
Chart 1

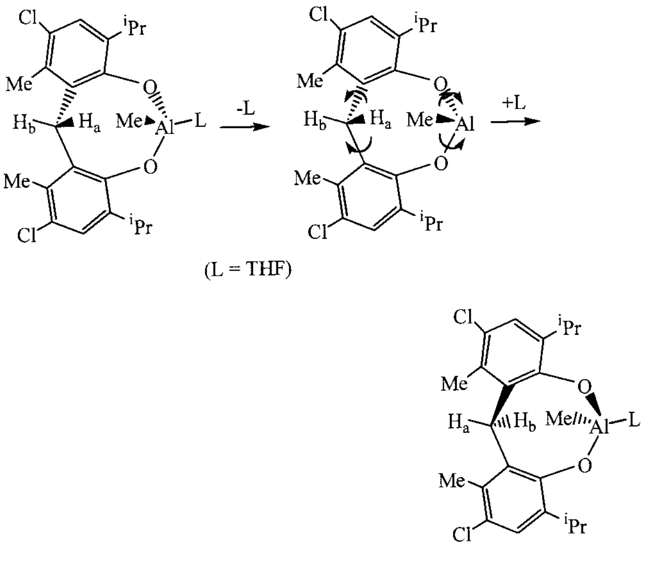


(a) [(MMBP)Al(OEt$_2$)Me]



(b) [(MCIMP)Al(OEt$_2$)Me]

Scheme 2



complexes [(MMPEP)AlMe(OEt$_2$)][16a] (MMPEP-H$_2$ = 2,2′-methylenebis(4,6-bis(1-methyl-1-phenylethyl)phenol) and [(MMBP)AlMe(OEt$_2$)][12] (MMBP-H$_2$ = 2,2′-methylenebis(4-methyl-6-*tert*-butylphenol)), a σ plane of symmetry passing through the bridging methylene carbon (C-7), two hydrogen atoms attached on the C-7 carbon, and the aluminum atom (Chart 1) makes these two C-7 protons are magnetically nonequivalent with an AB pattern in ^{1}H NMR spectroscopic studies. In addition, due to the PhC−H···O hydrogen bond, only one set of resonances appears for EDBP^{2-} (EDBP-H$_2$ = 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) and MMBP^{2-} ligands in [(EDBP)AlX(S)][16b] and [(MMBP)AlX(S)] at both 20 and −60 °C. Unlike the case for its aluminum analogues, however, the structure of [(MCIMP)AlMe(THF)] (**1**) has C_1 symmetry due to the steric hindrance of two methyl groups on the 3,3′-positions of the MCIMP^{2-} ligand. As a result, no C−H···O interaction was observed, and this has been further verified by the X-ray single-crystal structure determination of **1**. Thus, two sets of resonances for *4-chloro-6-isopropyl-3-methyl* groups attached on phenyl rings for **1** would be expected in the ^{1}H NMR spectroscopic studies. However, the ^{1}H NMR studies of **1** at 20 °C reveal only one set of resonances for the *4-chloro-6-isopropyl-3-methyl* groups of phenyl rings in the MCIMP^{2-} ligand and the two hydrogens in the bridging methylene (C-7) are observed to be magnetically equivalent with a chemical shift of δ 3.96 ppm. This observation can be attributed to the rapid dissociation of THF followed by the twisting of the MCIMP ligand and recombination of THF on the aluminum center, as shown in Scheme 2. In contrast, at −40 °C two sets of resonances with a ratio of 1:1 for *4-chloro-6-isopropyl-3-methyl* groups on phenyl rings but only one set of resonances for THF are observed. This result suggests that the dissociation constant of THF is very small. At the same time, ^{1}H NMR spectra of **2**, **4**, and **5** are as expected; however, the ^{1}H NMR spectrum of [Me$_2$Al(μ-MCIMP)AlMe$_2$(THF)] (**3**) is too complicated to be assigned.

Molecular Structure Determinations of 1−5. Suitable crystals for structure determination of **1** are obtained by slow cooling of a toluene solution. The ORTEP diagram of **1** is shown in Figure 1, and selected bond lengths and angles are listed in Table 1. The structure of **1** is feature, and the geometry around Al is distorted from tetrahedral with the bond distances Al−

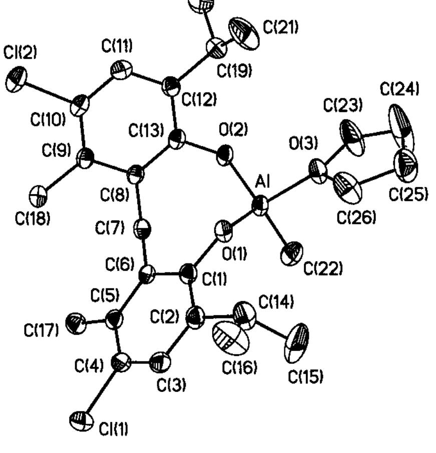


Figure 1. Molecular structure of **1** as 20% ellipsoids. All hydrogen atoms are omitted for clarity.

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

Al−O(1)	1.728(3)	Al−O(2)	1.738(2)
Al−O(3)	1.885(3)	Al−C(22)	1.940(4)
O(1)−Al−O(2)	108.11(12)	O(1)−Al−O(3)	100.96(12)
O(2)−Al−O(3)	103.15(13)	O(1)−Al−C(22)	117.56(17)
O(2)−Al−C(22)	118.36(17)	O(3)−Al−C(22)	106.12(18)

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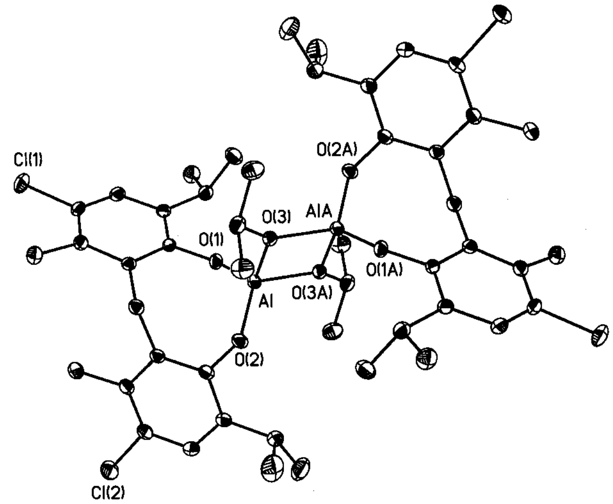

Figure 2. Molecular structure of **2** as 20% ellipsoids. All hydrogen atoms are omitted for clarity.

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

Al−O(1)	1.695(2)	Al−O(2)	1.707(2)
Al−O(3a)	1.804(2)	Al−O(3)	1.805(2)
O(1)−Al−O(2)	114.98(9)	O(1)−Al−O(3a)	112.82(9)
O(2)−Al−O(3a)	115.43(9)	O(1)−Al−O(3)	117.91(9)
O(2)−Al−O(3)	109.88(9)	O(3a)−Al−O(3)	81.68(8)

O(1) = 1.728(3) Å (phenoxy), Al−O(2) = 1.738(3) Å (phenoxy), Al−O(3) = 1.885(3) Å (THF), and Al−C(22) = 1.940(4) Å, which are all compatible with the bond lengths observed for a four-coordinated aluminum phenoxide containing bulky substituents.[17] It is interesting to note that, due to the repulsion between the 3,3′-methyl groups of MCIMP^{2-} ligand, the torsion angle between C(1)C(6) and C(8)C(13) is 40.4° and the dihedral angle between C(1)C(6) and C(8)C(13) ranges from 2.6° for [(MMPEP)Al(Me)(OEt_2)][16a] to 9.0° for [(EDBP)-Al(Me)(THF)].[16b]

The molecular structure of **2** is dimeric, containing an Al_2O_2 core bridging through the oxygen atom of the isopropoxy groups, and the geometry around Al is distorted from tetrahedral, as shown in Figure 2. Selected bond lengths and angles are given in Table 2. These two bridging oxygen atoms are roughly symmetrically bonded to two Al centers with an Al−O(3) distance of 1.805(2) Å and an Al−O(3a) distance of 1.804(2) Å. The terminal Al−O bond distances from the aryloxide ligand are Al−O(1) = 1.695(2) Å and Al−O(2) = 1.707(2) Å, well within the normal range previously reported for the four-coordinated aluminum compounds [(EDBP)AlX(S)] and [(MMBP)AlX(S)].

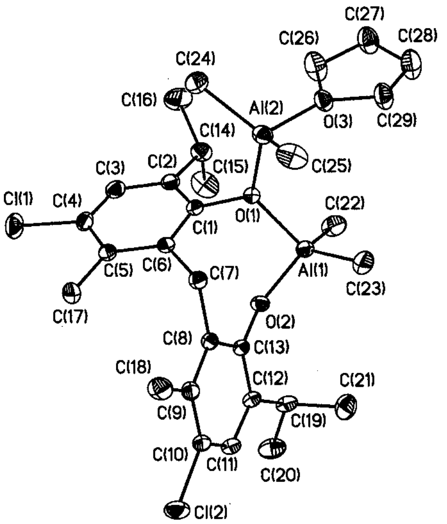

Figure 3. Molecular structure of **3** as 20% ellipsoids. All hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 3

Al(1)−O(2)	1.747(2)	Al(1)−O(1)	1.908(2)
Al(1)−C(22)	1.955(3)	Al(1)−C(23)	1.963(3)
Al(2)−O(1)	1.862(2)	Al(2)−O(3)	1.880(2)
Al(2)−C(24)	1.941(3)	Al(2)−C(25)	1.944(3)
O(2)−Al(1)−O(1)	98.58(8)	O(2)−Al(1)−C(22)	112.20(14)
O(1)−Al(1)−C(22)	107.97(12)	O(2)−Al(1)−C(23)	111.95(13)
O(1)−Al(1)−C(23)	110.48(12)	C(22)−Al(1)−C(23)	114.44(17)
O(1)−Al(2)−O(3)	98.71(8)	O(1)−Al(2)−C(24)	111.04(12)
O(3)−Al(2)−C(24)	108.04(13)	O(1)−Al(2)−C(25)	113.71(12)
O(3)−Al(2)−C(25)	107.09(13)	C(24)−Al(2)−C(25)	116.47(17)
C(1)−O(1)−Al(2)	113.70(13)	C(1)−O(1)−Al(1)	117.13(13)
Al(2)−O(1)−Al(1)	126.97(9)		

Complex **3** is recrystallized by slowly cooling a toluene solution to −23 °C. The ORTEP diagram of **3** is illustrated in Figure 3, and selected structure parameters are listed in Table 3. The molecular structure of **3** consists of a [(MCIMP)AlMe_2]$^-$ ion with a [AlMe_2-(THF)]$^+$ moiety bridging through one of the phenoxy oxygen atoms of the MCIMP^{2-} ligand. Both aluminum centers are four-coordinated, in which Al(1) is bonded to two methyl carbons and two aryloxides of the MCIMP^{2-} ligand with Al(1)−O(2) = 1.747(2) Å, Al(1)−O(1) = 1.908(2) Å, Al(1)−C(22) = 1.955(3) Å, and Al-(1)−C(23) = 1.963(3) Å. Al(2) is bonded to two methyl carbons, one oxygen atom of THF, and one bridging aryloxide with Al(2)−O(1) = 1.862(2) Å, Al(2)−O(3) = 1.880(2) Å, Al(2)−C(24) = 1.941(3) Å, and Al(2)−C(25) = 1.944(3) Å.

The molecular structure of **4** has been confirmed by X-ray crystallography, and one of the independent molecules is shown in Figure 4. Important bond distances and angles are provided in Table 4. In **4**, two isopropoxy groups act as chelating ligands bonded to [(MCIMP)Al] and [AlMe_2] fragments. The Al−O distances within the four-membered Al_2O_2 chelate ring are asymmetric, with an average bond distance of Al(1)−O = 1.775(2) Å and Al(2)−O = 1.846(3) Å. The difference in bond lengths can be attributed to the better electron-withdrawing ability of the MCIMP^{2-} ligand on Al(1) than the methyl groups on Al(2), making Al(1) more Lewis acidic than Al(2).

The trimeric compound **5** illustrated in Figure 5 crystallizes in the space group $I2_3$ with the asymmetric unit comprised of the [(MCIMP)Al(μ-OH···THF)] fragment. Selected bond lengths and angles are listed in Table 5. The trimer is composed of a six-membered ring in which each aluminum atom is connected by two bridging hydroxy oxygen atoms and each hrdroxy group is bonded to a THF molecule through hydrogen bonding. The coordination around aluminum is a distorted tet-

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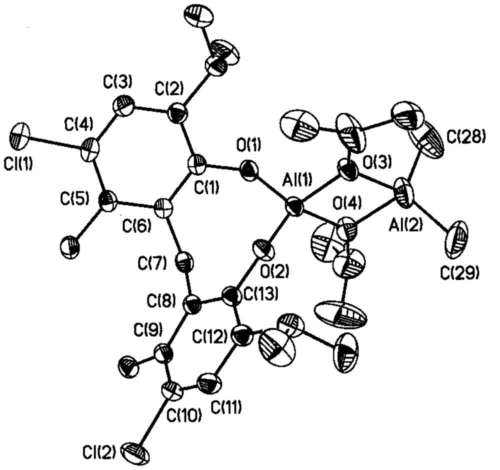

Figure 4. Molecular structure of **4** as 20% ellipsoids. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Al(1)−O(3) = 1.780(2), Al(1)−O(4) = 1.769(2), Al(2)−O(3) = 1.838(2), Al(2)−O(4) = 1.854(3).

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 4

Al(1)−O(1)	1.706(2)	Al(1)−O(2)	1.686(2)
Al(1)−O(3)	1.780(2)	Al(1)−O(4)	1.769(2)
Al(2)−O(3)	1.838(3)	Al(2)−O(4)	1.854(3)
Al(2)−C(28)	1.946(7)	Al(2)−C(29)	1.958(6)
Al(3)−O(7)	1.852(3)	Al(3)−O(8)	1.850(3)
Al(3)−C(58)	1.923(5)	Al(3)−C(59)	1.954(6)
Al(4)−O(5)	1.706(2)	Al(4)−O(6)	1.692(2)
Al(4)−O(7)	1.777(2)	Al(4)−O(8)	1.778(3)
O(2)−Al(1)−O(1)	111.73(11)	O(2)−Al(1)−O(4)	118.86(14)
O(1)−Al(1)−O(4)	113.39(13)	O(2)−Al(1)−O(3)	110.93(11)
O(1)−Al(1)−O(3)	116.33(12)	O(4)−Al(1)−O(3)	82.87(11)
O(3)−Al(2)−O(4)	79.04(10)	O(3)−Al(2)−C(28)	111.1(3)
O(4)−Al(2)−C(28)	111.3(3)	O(3)−Al(2)−C(29)	111.8(3)
O(4)−Al(2)−C(29)	112.7(2)	C(28)−Al(2)−C(29)	122.6(4)
O(8)−Al(3)−O(7)	79.05(11)	O(8)−Al(3)−C(58)	111.8(2)
O(7)−Al(3)−C(58)	111.6(2)	O(8)−Al(3)−C(59)	110.6(2)
O(7)−Al(3)−C(59)	114.2(2)	C(58)−Al(3)−C(59)	121.8(3)
O(6)−Al(4)−O(5)	111.11(11)	O(6)−Al(4)−O(7)	109.39(11)
O(5)−Al(4)−O(7)	118.51(12)	O(6)−Al(4)−O(8)	120.83(13)
O(5)−Al(4)−O(8)	111.74(12)	O(7)−Al(4)−O(8)	83.00(11)
O(6)−Al(4)−Al(3)	123.32(9)	O(5)−Al(4)−Al(3)	125.48(9)

rahedron bonded to two aryloxides of the MCIMP^{2-} ligand and two hydroxy groups with bond lengths of Al−O(1) = 1.726(2) Å (phenoxy), Al−O(2) = 1.688(2) Å (phenoxy), Al−O(3) = 1.770(2) Å (hydroxy), and Al−O(3a) = 1.783(2) Å (hydroxy). It is worthwhile to note that Al, Al(a) Al(b), O3, O(3a), and O(3b), the core of the six-membered ring, are almost coplanar, with a mean deviation of only 0.092 Å.

Ring-Opening Polymerization of ϵ-Caprolactone and δ-Valerolactone Initiated by 2 and 4. The catalytic activities of **2** and **4** toward ROP of ϵ-caprolactone (ϵ-CL), δ-valerolactone (δ-VL), and their copolymers have been examined. In general, polymerization of ϵ-caprolactone was carried out at 50 °C in toluene (30 mL) using **2** (0.116 g, 0.125 mmol) as the initiator. To a rapidly stirred solution of $[(\mathrm{MCIMP})\mathrm{Al}(\mu\text{-O}^i\mathrm{Pr})]_2$ in toluene was added ϵ-CL (2.6 mL, 25 mmol). The reaction mixture was stirred at 50 °C for 2 h, during which an increase in the viscosity of the solution was observed. After the reaction was quenched by the addition of an excess of 0.35 N aqueous acetic acid solution, the polymer was precipitated into *n*-heptane. Polymerizations of ϵ-CL and δ-VL under different reaction conditions (entries 1−15) have been systematically conducted, as shown in Table 6. It was found that the PDIs of polyesters initiated by **2** range from 1.08 to 1.25, and a linear relationship between the number-average molecular weight (M_n) and the monomer-to-initiator ratio ($[M]_0/[I]_0$) (entries 1−5) implies the “living” character of the polymerization process. The “living” character of the active polymer chain end was further confirmed from the polymerization resumption experiment and by the sequential ROP of δ-VL and ϵ-CL. In the resumption experiment (entry 6), 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. In the sequential ROP of δ-VL and ϵ-CL (entry 8), VL was polymerized using **2** as initiator. After completion of the polymerization of PVL, CL was added and the reaction was allowed to continue for further polymerization.

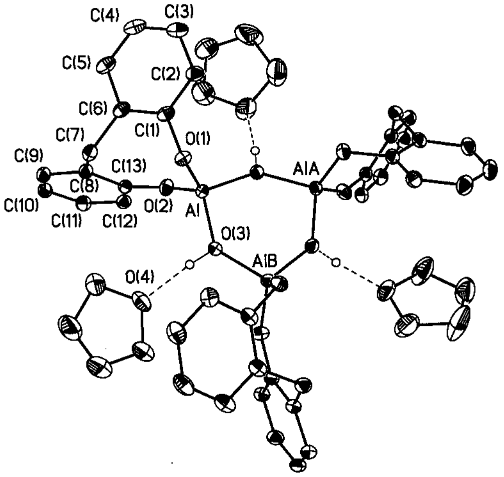

Figure 5. Molecular structure of **5** as 20% ellipsoids. All of the methyl carbons, isopropyl groups, chlorine atoms on the phenyl rings, and all hydrogen atoms except the hydroxy protons are omitted for clarity.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for 5

Al−O(1)	1.726(2)	Al−O(2)	1.688(2)
Al−O(3)	1.770(2)	Al−O(3a)	1.783(2)
O(3)−Al(a)	1.783(2)		
O(2)−Al−O(1)	113.26(10)	O(2)−Al−O(3)	114.77(10)
O(1)−Al−O(3)	108.88(9)	O(2)−Al−O(3a)	105.02(10)
O(1)−Al−O(3a)	111.69(10)	O(3)−Al−O(3a)	102.70(12)
Al−O(3)−Al(a)	134.99(12)		

The ^{1}H NMR spectrum (Figure 6) of PCL-25 (the number 25 indicates the designed $[M]_0/[I]_0$) showing an integral ratio close to 2 between H_h ($-CH_2-$ from PCL at the hydroxy chain end) and H_g ($CHMe_2$ from PCL at isopropoxy ester end) was explicit proof that the initiation occurs through the insertion of the isoproxy group from **2** into the lactone, as illustrated in Scheme 3. It is worthwhile to note that compound **2** 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 9−13). In the presence of 2-propanol 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

Table 6. Ring-Opening Polymerization of Lactones Initiated by Complexes 2 and 4 at 50 °C

entry	monomer	initiator	[M]:[Al]:[ROH]	time (h)	M_w/M_n	M_n(obsd)[a]	M_n(calcd)[b]	M_n(NMR)[c]	conversn (%)[c]	yield (%)[d]
1	ϵ-CL	**2**	25:1:0	2	1.10	5900	2900	4050	100	86
2	ϵ-CL	**2**	50:1:0	2	1.08	8000	5800	4800	100	99
3	ϵ-CL	**2**	100:1:0	2	1.11	21800	11500	10000	100	99
4	ϵ-CL	**2**	200:1:0	2	1.11	34600	22900	15500	100	99
5	ϵ-CL	**2**	400:1:0	5	1.25	52500	44300	27600	97	82
6	CL(CL)[e]	**2**	50(50):1:0	2 (2)	1.19	23100	11300	7300	100 (98)	88
7	d-VL	**2**	50:1	2	1.20	5400	4800	4900	94	64
8	VL(CL)[f]	**2**	50(50):1	2 (2)	1.17	13700	10800	8800	100 (100)	78
9	ϵ-CL	**2**	400:1:2	5	1.17	21300	14800	17900	97	96
10	ϵ-CL	**2**	400:1:4	3	1.13	17300	8900	15100	97	95
11	ϵ-CL	**2**	400:1:8	3	1.11	11000	5000	9800	98	97
12	ϵ-CL	**2**	400:1:16	3	1.11	5300	2500	5100	92	90
13	ϵ-CL	**2**	400:1:32	3	1.12	2830	1290	2500	89	
14	ϵ-CL	**4**	25:1:0	3	1.11	5100	2900	3000	100	61
15	ϵ-CL	**4**	50:1:0	2	1.12	7600	5800	5100	100	84

[a] Obtained from GPC analysis. [b] Calculated from the molecular weight of lactone times $[M]_0/[Al]_0$ times conversion yield divided by ([ROH] + 1) plus the molecular weight of ^{i}PrOH. [c] Obtained from ^{1}H NMR analysis. [d] Isolated yield. [e] Prepolymerization of ϵ-CL with initiator for 2 h followed by the addition of ϵ-CL and stirring for another 2 h. [f] Prepolymerization of δ-VL with initiator for 2 h followed by the addition of ϵ-CL and stirring for another 2 h.

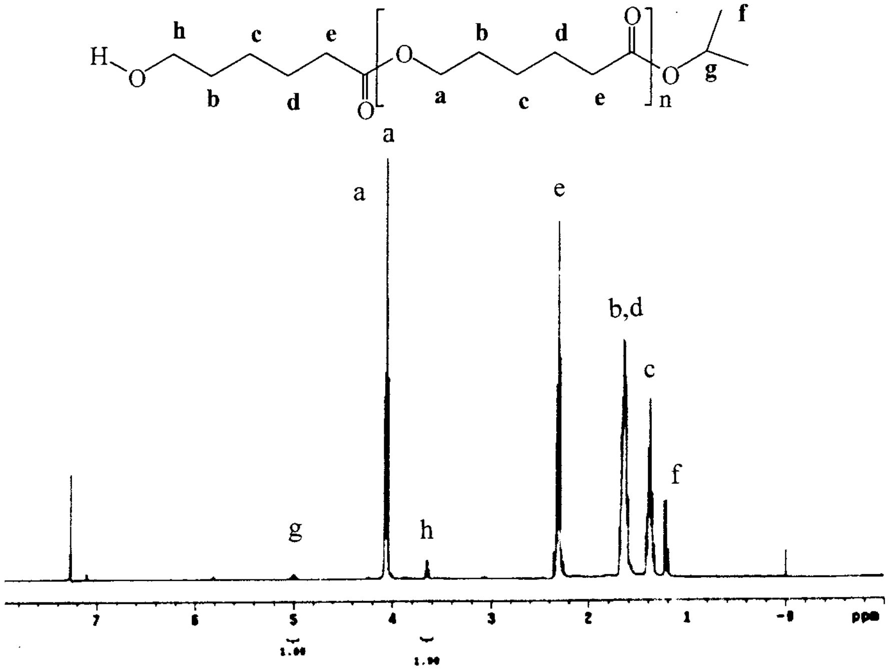

Figure 6. ^{1}H NMR spectrum of PCL-25 initiated by **2**.

much as a 32-fold amount of ^{i}PrOH can be added. In addition, preliminary results indicate that compound **4** is also active toward the ROP of ϵ-CL, giving polymers with narrow PDIs (entries 14 and 15). 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 Table 6. The unexpectedly high values of M_n(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) value, giving the actual M_n value of poly(ϵ-caprolactone).[18] This is confirmed by the M_n(NMR) values obtained from the ^{1}H NMR analysis. Further studies of its catalytic activities are currently being undertaken.

Conclusion

Several interesting aluminum alkoxides or aluminum hydroxide have been prepared and fully characterized. Among them, $[(\text{MCIMP})\text{Al}(\mu\text{-O}^i\text{Pr})]_2$ (**2**) and $[(\text{MCIMP})\text{Al}(\mu\text{-O}^i\text{Pr})_2\text{AlMe}_2]$ (**4**) have demonstrated efficient catalytic activities toward the ROP of ϵ-caprolactone and δ-valerolactone. The active polymer chain end initiated by $[(\text{MCIMP})\text{Al}(\mu\text{-O}^i\text{Pr})]_2$ has enabled us to synthesize PCL−b-PVL block copolymer, and the “immortal” character of complex **2** has paved a way to synthesize as much as 32-fold polymer chains of poly(ϵ-caprolactone) with very narrow PDIs in the presence of a small amount of initiator.

Experimental Section

General Considerations. All manipulations were carried out under a dry nitrogen atmosphere. Solvents, ϵ-caprolactone, δ-valerolactone, 2-propanol, and deuterated solvents were

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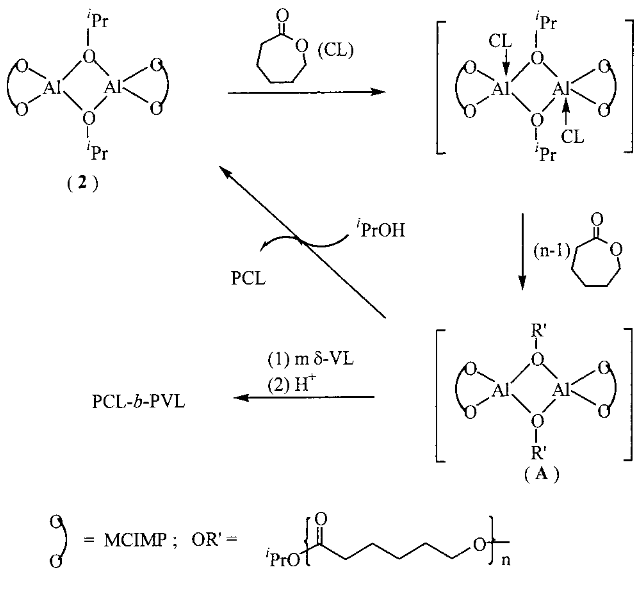
[18] McLain, S. J.; Drysdale, N. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33*, 174.

Scheme 3



purified before use. $AlMe_3$ (2.0 M in toluene), $Al(O^iPr)_3$, formaldehyde, 4-chloro-2-isopropyl-5-methylphenol, 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 for ^1H and 101 MHz for ^{13}C) or a Varian Gemini-200 (200 MHz for ^1H and 50.5 MHz for ^{13}C) spectrometer with chemical shifts given in ppm from the internal TMS or the central line of $CHCl_3$. 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 weights and molecular weight distributions were calculated using polystyrene as standard.

2,2′-Methylenebis(4-chloro-6-isopropyl-3-methylphenol) (MCIMP-H_2). To a rapidly stirred solution of 4-chloro-2-isopropyl-5-methylphenol (1.84 g, 10 mmol) and paraformaldehyde (0.18 g, 6.0 mmol) in toluene (30 mL) was added benzenesulfonic acid (0.1 mL). The reaction mixture was refluxed for 5 h and was quenched by an aqueous NaOH solution (20 mL, 0.1 N). The organic layer was dried over $MgSO_4$ and filtered, and the filtrate was concentrated under vacuum to give an orange solid which was washed with hexane (15 mL) and then dried under vacuum. Yield: 1.56 g (82%). Anal. Calcd for $C_{21}H_{26}Cl_2O_2$: C, 66.14; H, 6.87. Found: C, 66.06; H, 6.95. ^1H NMR ($CDCl_3$, ppm): δ 7.10 (s, 2H, *Ph*), 5.71 (br, 2H, $-OH$), 4.06 (s, 2H, $-CH_2-$), 3.03 (m, 2H, $CH(CH_3)_2$, $J_{H-H} = 6.8$ Hz), 2.35 (s, 6H, $-CH_3$), 1.19 (d, 12H, $CH(CH_3)_2$, $J_{H-H} = 6.8$ Hz). ^{13}C NMR ($CDCl_3$, ppm): δ 149.8, 133.5, 132.8, 127.1, 125.3, 124.9 (*Ph*), 27.1 ($CH(CH_3)_2$), 26.8 ($-CH_2-$), 22.6 ($CH(CH_3)_2$), 16.6 ($-CH_3$). IR (KBr, cm^{-1}): 3512.5 (br, s), 2960.7 (br, s), 2867.2 (s), 1461.6 (s), 1408.0 (s), 1340.3 (m), 1299.8 (s), 1276.4 (s), 1214.9 (s), 1194.7 (s), 1135.9 (s), 1087.9 (m), 1038.4 (s), 929.8 (m), 875.9 (m), 754.6 (m). Mp: 128 °C.

[(MCIMP)AlMe(THF)] (1). To a rapidly stirred solution of MCIMP-H_2 (0.76 g, 2.0 mmol) in THF (30 mL) was slowly added $AlMe_3$ (1.2 mL, 2.4 mmol), and the mixure was stirred at room temperature for 2 h and dried under vacuum. The residue was extracted with toluene (10 mL), and the extracts were cooled to −23 °C, yielding off-white crystalline solids. Yield: 0.84 g (85%). Anal. Calcd for $C_{26}H_{35}Cl_2O_3Al$: C, 63.29; H, 7.15. Found: C, 63.38; H, 7.05. ^1H NMR ($CDCl_3$, ppm): δ 7.04 (s, 2H, *Ph*), 4.17 (m, 4H, OCH_2CH_2), 3.96 (s, 2H, CH_2), 3.23 (m, 2H, $CH(CH_3)_2$, $J_{H-H} = 7$ Hz), 2.36 (s, 6H, $PhCH_3$), 2.10 (m, 4H, OCH_2CH_2), 1.16 (d, 12H, $CH(CH_3)_2$, $J_{H-H} = 7$ Hz), −0.62 (s, 3H, $Al-CH_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 153.8, 136.3, 132.2, 128.9, 125.0, 124.1 (*Ph*), 71.1 (OCH_2CH_2), 28.8 ($CH(CH_3)_2$), 26.8 (OCH_2CH_2), 25.2 ($CH(CH_3)_2$), 22.6 (CH_2), 17.0 ($PhCH_3$), −15.3 ($AlCH_3$). IR (KBr, cm^{-1}): 2962.8 (s), 2872.4 (m), 1458.7 (s), 1400.6 (s), 1340.2 (s), 1286.6 (m), 1201.4 (s), 1040.0 (m), 872.9 (s), 818.8 (s), 722.6 (m), 660.2 (s). Mp: 131−135 °C.

[(MCIMP)Al(μ-O^{i}Pr)]$_2$ (2). Method 1. To a rapidly stirred solution of **1** (0.98 g, 2.0 mmol) in CH_2Cl_2 (30 mL) was added 2-propanol (0.153 mL, 2.0 mmol), and the mixture was stirred at room temperature for 2 h, during which time an off-white powder precipitated gradually. The mixture was concentrated under vacuum. The residue obtained was extracted by hot toluene (20 mL), and the extract was cooled to room temperature to afford colorless crystalline solids. Yield: 0.75 g (81%).

Method 2. A mixture of (MCIMP-H_2) (0.76 g, 2.0 mmol) and $Al(O^iPr)_3$ (0.41 g, 2.0 mmol) in toluene (10 mL) was refluxed for 16 h, during which time an off-white solids precipitated out. After the mixture was cooled to room temperature, the solution was decanted and the solid was washed with hexane (5 mL) twice to give the pure solid. Yield: 0.57 g (62%). Anal. Calcd for $C_{48}H_{62}Cl_4O_6Al_2$: C, 61.94; H, 6.71. Found: C, 61.87; H, 6.95. ^1H NMR ($CDCl_3$, ppm): δ 7.09 (s, 2H, *Ph*), 4.51 (m, 1H, $OCH(CH_3)_2$, $J_{H-H} = 6.4$ Hz), 4.00 (m, 2H, CH_2), 3.30 (m, 2H, $CH(CH_3)_2$, $J_{H-H} = 6.8$ Hz), 2.39 (s, 6H, $PhCH_3$), 1.29 (d, 6H, $OCH(CH_3)_2$, $J = 6.4$ Hz), 1.20 (d, 12H, $CH(CH_3)_2$, $J = 6.8$ Hz). ^{13}C NMR ($CDCl_3$, ppm): δ 151.8, 136.7, 132.7, 128.1, 126.1, 124.7 (*Ph*), 71.9 ($OCH(CH_3)_2$), 28.5 ($CH(CH_3)_2$), 27.1 ($OCH(CH_3)_2$), 24.9 ($CH(CH_3)_2$), 22.6 (CH_2), 17.4 ($PhCH_3$). IR (KBr, cm^{-1}): 2962.9 (m), 1463.2 (s), 1444.4 (m), 1397.1 (m), 1204.3 (m), 938.3 (m), 860.7 (m), 830.7 (s), 682.7 (m). Mp: 154−160 °C.

[(MCIMP)Al$_2$Me$_4$(THF)] (3). To a rapidly stirred solution of **1** (0.98 g, 2.0 mmol) in CH_2Cl_2 (30 mL) was added $AlMe_3$ (1.0 mL, 2.0 mmol). The mixture was stirred at room temperature for 2 h and was dried under vacuum to give white solids. The residue was extracted by toluene (10 mL), and the extracts were cooled to −23 °C, giving colorless crystalline solids. Yield: 0.43 g (38%). Anal. Calcd for $C_{29}H_{44}Cl_2O_3Al_2$: C, 61.59; H, 7.84. Found: C, 60.96; H, 7.46. IR (KBr, cm^{-1}): 2962.08 (s), 1460.30 (s), 1398.85 (m), 1340.95 (m), 1205.25 (m), 811.21 (m), 770.20 (m), 669.44 (s). Mp: 176 °C.

[(MCIMP)Al(μ-O^{i}Pr)$_2$AlMe$_2$] (4). To a rapidly stirred solution of **3** (1.13 g, 2.0 mmol) in CH_2Cl_2 (30 mL) was added 2-propanol (0.31 mL, 4.0 mmol), and the mixture was stirred at room temperature for 16 h and was dried under vacuum to give white solids. The residue was extracted by toluene (10 mL), and the extracts were cooled to −23 °C, yielding off-white crystalline solids. Yield: 0.73 g (66%). Anal. Calcd for $C_{29}H_{44}Cl_2O_4Al_2$: C, 59.90; H, 7.60. Found: C, 59.20; H, 7.15. ^1H NMR ($CDCl_3$, ppm): δ 7.05 (s, 2H, *Ph*), 4.37 (m, 2H, $OCH(CH_3)_2$, $J_{H-H} = 6.2$ Hz), 3.96 (s, 2H, CH_2), 3.27 (m, 2H, $CH(CH_3)_2$, $J_{H-H} = 6.8$ Hz), 2.37 (s, 6H, $PhCH_3$), 1.29 (d, 12H, $OCH(CH_3)_2$, $J_{H-H} = 6.2$ Hz), 1.17 (d, 12H, $CH(CH_3)_2$, $J_{H-H} = 6.8$ Hz), −0.63 (s, 6H, $Al-CH_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 152.53, 136.76, 132.42, 128.35, 125.48, 124.50 (*Ph*), 69.26 ($OCH(CH_3)_2$), 28.41 ($CH(CH_3)_2$), 27.08 ($OCH(CH_3)_2$), 25.21 ($CH(CH_3)_2$), 22.66 (CH_2), 17.29 ($PhCH_3$), −9.02 ($AlCH_3$). IR (KBr, cm^{-1}): 2966.48 (m), 1464.44 (s), 1399.08 (m), 1341.47 (m), 1202.24 (m), 1113.56 (m), 1037.87 (m), 950.79 (m), 835.52 (m), 778.72 (m), 699.38 (s). Mp: 165−170 °C.

[(MCIMP)Al(μ-OH···THF)]$_3$ (5). To a rapidly stirred solution of **1** (1.47 g, 3.0 mmol) in THF (15 mL) was added H_2O (0.054 mL, 3.0 mmol) in THF (15 mL). The mixture was stirred for 16 h and concentrated under vacuum to remove all volatile materials. The residue was extracted by THF (10 mL), and hexane (30 mL) was then added slowly. An off-white crystalline solid was obtained after 24 h. Yield: 0.52 g (36%). Anal. Calcd for $C_{75}H_{99}Cl_6O_{12}Al_3$: C, 60.61; H, 6.71. Found: C, 59.68; H, 6.64. ^1H NMR ($CDCl_3$, ppm): δ 7.11 (s, 2H, *Ph*), 5.71 (s, 1H, $-OH-$), 4.08 (s, 2H, $PhCH_2$), 3.74 (m, 4H, OCH_2CH_2), 3.06 (m, 2H, $CH(CH_3)_2$, $J_{H-H} = 6.8$ Hz), 2.36 (s, 6H, $PhCH_3$), 1.85

Table 7. Crystallographic Data for 1−5

	1	**2**	**3**	**4**	**5**
chem formula	$C_{26}H_{35}AlCl_2O_3$	$C_{24}H_{31}AlCl_2O_3$	$C_{29}H_{44}Al_2Cl_2O_3$	$C_{58}H_{88}Al_4Cl_4O_8$	$C_{25}H_{33}AlCl_2O_4$
M_r	493.42	465.37	565.50	1163.00	495.39
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	cubic
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$I2_3$
a/Å	11.7481(19)	10.9992(7)	9.5772(6)	12.9152(9)	25.1228(8)
b/Å	19.090(3)	20.5094(13)	20.2776(13)	13.7773(11)	25.1228(8)
c/Å	12.860(2)	11.2559(7)	16.2491(10)	19.8008(15)	25.1228(8)
α/deg	90	90	90	85.655(2)	90
β/deg	110.201(3)	107.6200(10)	94.6930(10)	78.988(2)	90
γ/deg	90	90	90	74.633(2)	90
V/Å^3	2706.7(8)	2420.1(3)	3145.0(3)	3333.6(4)	15856.4(9)
Z	4	4	4	2	12
μ(Mo Kα)/mm^{-1}	0.296	0.327	0.289	0.277	0.153
N_{ref}(obsd), ($F > 4\sigma(F)$)	5348	4754	6180	12889	5198
no. of params	289	271	325	667	293
R1[a]	0.0633	0.0450	0.0472	0.0636	0.0442
wR2[b]	0.1661	0.1255	0.1393	0.1762	0.1266
GOF[c]	1.018	0.884	0.962	1.082	1.049
min, max residual density/e Å^{-3}	0.337, −0.261	0.319, −0.409	0.254, −0.313	0.431, −0.349	0.807, −0.216

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

(m, 4H, OCH_2CH_2), 1.21 (d, 12H, $CH(CH_3)_2$, $J_{H-H} = 6.8$ Hz). IR (KBr, cm^{-1}): 2963.62 (s), 1461.71 (s), 1400.64 (m), 1337.15 (m), 1203.57 (m), 1037.95 (m), 872.78 (m), 852.21 (m), 817.79 (m), 776.95 (s). Mp: 158 °C.

Synthesis of Isopropyl 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 [(MCIMP)Al(μ-O^{i}Pr)]$_2$ (0.116 g, 0.125 mmol) in toluene (30 mL) was added ϵ-CL (2.6 mL, 25 mmol). The reaction mixture was stirred at 50 °C for 2 h, during which time an increase in viscosity was observed. After the reaction was quenched by the addition of an excess of 0.35 N aqueous acetic acid solution, the polymer was precipitated into *n*-heptane. The off-white precipitate was washed with hexane three times and dried under vacuum, giving a pure solid. Yield: 2.8 g (99%).

Synthesis of Isopropyl Ester End Functionalized PCLs in the Presence of 2-Propanol. A typical polymerization was exemplified by the synthesis of PCL-400 in the presence of 8.0 molar equiv of ^{i}PrOH. To a rapidly stirred solution of [(MCIMP)Al(μ-O^{i}Pr)]$_2$ (0.116 g, 0.125 mmol) in toluene (15 mL) at 50 °C was added a mixture of ϵ-CL (10.5 mL, 100 mmol) and ^{i}PrOH (0.15 mL, 2.0 mmol) in toluene (15 mL). The solution was then stirred at 50 °C for 3 h and was quenched by adding an excess of 0.35 N aqueous acetic acid solution. The polymer was precipitated into *n*-heptane, and the white precipitate was washed with hexane three times and dried under vacuum, giving white solids. Yield: 11.1 g (97%).

Synthesis of Diblock Copolymer PCL−b-PVL. To a rapidly stirred solution of [(MCIMP)Al(μ-O^{i}Pr)]$_2$ (0.116 g, 0.125 mmol) in toluene (30 mL) was added δ-VL (1.16 mL, 12.5 mmol). The reaction mixture was stirred at 50 °C for 2 h, and ϵ-CL (1.31 g, 12.5 mmol) was added. The mixture was stirred for another 2 h, and the reaction was then quenched by following the procedures described previously. Yield: 2.13 g (78%).

X-ray Crystallographic Studies. Suitable crystals of **1**−**5** 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 **1**−**5** are shown in Table 7.

Acknowledgment. Financial support from the National Science Council and the Chinese Petroleum Cooperation of the Republic of China is gratefully acknowledged.

Supporting Information Available: For **1**−**5**, tables providing 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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