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Catalysts for the ring-opening polymerization of ε-caprolactone and L-lactide and the mechanistic study

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Abstract

Two novel magnesium aryloxides have been prepared and their catalytic activities toward ring-opening polymerization (ROP) of ε-caprolactone and L-lactide have been investigated. The reaction of 2,2′-(2-methoxybenzylidene)-bis(4,6-di(1-methyl-1-phenylethyl)phenol) (MEMPEP-H_2) (**1**) and 2,2′-methylene-bis(4,6-di(1-methyl-1-phenylethyl)phenol) (MMPEP-H_2) with $^nBu_2Mg$ yield dimeric magnesium complexes [Mg(μ-MEMPEP)(THF)]$_2$ (**2**) and [Mg(μ-MMPEP)(THF)]$_2$ (**3**), respectively. Catalytic studies of complexes **2** and **3** illustrate that both **2** and **3** are good catalysts in ε-caprolactone and L-lactide polymerization. Theoretical study of the ROP mechanism of ε-caprolactone catalyzed by **2** demonstrates that the initiator, benzyl alcohol, is activated by the formation of a hydrogen bond with the phenoxy oxygen of $MEMPEP^{2-}$ ligand.

Keywords: Magnesium; Catalyst; L-Lactide

1. Introduction

Over the past two decades, biodegradable polyesters, such as poly(ε-caprolactone) (PCL), poly(lactide) (PLA) and their copolymers have been attracting considerable attention due to their potential applications in human life [1]. Therefore, there has been increasing interest in the development of efficient catalytic systems for the preparation of PLA and PCL. Ring-opening polymerization (ROP) of lactones/lactides and functionally related compounds initiated by metal alkoxides have been the major polymerization method used to synthesize these polymers [2]. Many metal alkoxides, such as aluminum [3], tin [4], trivalent lanthanide [5], magnesium [6] and zinc derivatives [7,8] have been reported to be effective initiators that initiate ROP of lactones/lactides giving polymers with both high and controlled molecular weights.

We have systematically studied the catalytic activity of aluminum alkoxides coordinated by sterically bulky biphenoxide and found that the reactivity of aluminum alkoxide is enhanced by using a sterically more bulky ligand [9]. Recently, Chisholm and coworkers have compared the catalytic activities of magnesium, zinc and aluminum alkoxides toward ROP of lactones/lactide and summarized that the activity toward polymerization of lactide is Mg > Zn > Al [10]. Most recently, we have investigated the catalytic activity of lithium [11] and magnesium [12] complexes coordinated by a sterically bulky biphenoxide and found that the activity toward polymerization of lactide is Li > Mg > Al. In order to study the activities of magnesium complexes affecting by sterically bulky ligands, we report herein the synthesis, characterization and catalytic studies of two novel magnesium aryloxides, [Mg(μ-MEMPEP)(THF)]$_2$ (**2**) and [Mg(μ-MMPEP)(THF)]$_2$ (**3**). Theoretical study of the ROP mechanism of ε-caprolactone (CL) with **2** will also be presented.

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2. Results and discussion

2.1. Syntheses and spectroscopic studies

It has been reported previously that in aluminum system, a sterically bulky ligand on either the *ortho*-position or the bridging carbon (C-7) of the phenoxy group (Chart 1) can dramatically affect the catalytic activities of aluminum alkoxides toward ring-opening polymerization of ε-caprolactone [9]. In order to understand the effect of a sterically hindered group on the phenoxy ligand influencing the activity of magnesium complexes, 2,2′-(2-methoxybenzylidene)-bis(4,6-di(1-methyl-1-phenylethyl)phenol) (MEMPEP-H_2) (**1**) is prepared in moderate yield by the reaction of *o*-anisaldehyde 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 (Scheme 1). Further reaction of MEMPEP-H_2 with a stoichiometric amount of $^{n}Bu_2Mg$ in tetrahydrofuran produces a four-coordinated dimeric magnesium complex [Mg(μ-MEMPEP)(THF)]$_2$ (**2**) in almost quantitative yield. Similarly, [Mg(μ-MMPEP)(THF)]$_2$ (**3**) can be obtained in high yield by reaction of 2,2′-methylene-bis(4,6-di(1-methyl-1-phenylethyl)phenol) (MMPEP-H_2) with 1 molar equiv of $^{n}Bu_2Mg$ in THF. All of these compounds are isolated as colorless crystalline solids and have been characterized by spectroscopic studies as well as X-ray structural determination.

Suitable crystals for structure determination of **2** are obtained from slowly cooling a hot toluene solution, and its ORTEP is shown in Fig. 1. The structure of **2** shows a dimeric feature containing an Mg_2O_2 core bridging through one of the phenoxy oxygen atoms with the center of the Mg_2O_2 core sitting on the crystallographic center. The geometry around Mg is distorted from tetrahedral and the bridging oxygen atom bond distances are asymmetric to the two Mg centers with the bond distances Mg–O(1) 2.0005(15) (bridging oxygen), Mg–O(1A) 1.9812(16) (bridging oxygen), Mg–O(2) 1.8676(16) (phenoxy), Mg–O(4) 2.0618(17) (THF). These lengths are similar to those found for its analogous [(EDBP)Mg(THF)]$_2$ [12]. The molecular structure of **3** is similar to that of **2** and its ORTEP is shown in Fig. 2. The geometry around Mg is distorted from tetrahedral and the bridging oxygen atom bond distances are asymmetric to the two Mg centers with the bond distances Mg–O(2) 1.9616(18) (bridging oxygen), Mg–O(2A) 2.0056(19) (bridging oxygen), Mg–O(1) 1.8594(19) (phenoxy), Mg–O(3) 2.004(2) (THF).

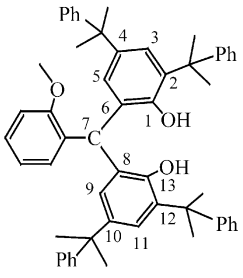
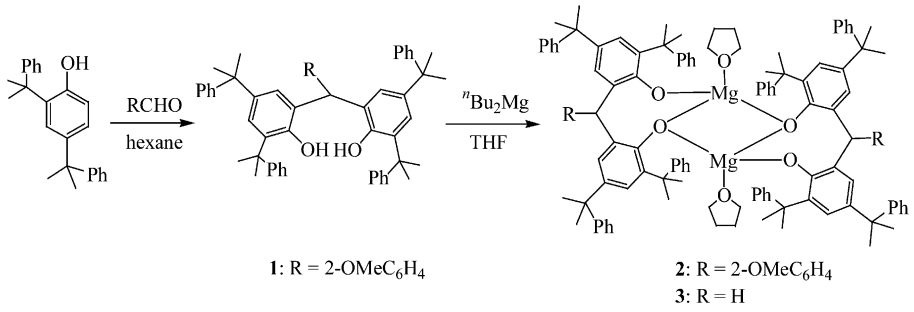


Chart 1.

2.2. Ring-opening polymerization of ε-caprolactone catalyzed by **2** and **3**

The catalytic activities of **2** and **3** toward ε-caprolactone (CL) have been systematically examined and found that the polymerization of CL proceeded smoothly as shown in Table 1. It was found that the polydispersity indexes (PDIs) of polyesters are reasonable narrow ranging from 1.06 to 1.10 using **2** and from 1.13 to 1.25 using **3** as catalyst and a linear relationship between the number-average molecular weight (M_n) and the initial monomer-to-initiator ratio ($[M]_0$/[BnOH]) existed (Fig. 3), implying the controlled character of the polymerization process (entries 1–4 and entries 6–10). The molecular weight of PCL and the chemical nature of the structure chain ends can be established by the ^1H NMR studies. For example, the ^1H NMR spectrum of PCL-25 (the number 25 indicates the designed $[M]_0$/[BnOH]) gave an integral ratio close to 2:2:48 for H_b (–OCH_2Ph from PCL at the benzyl ester chain end), H_g (–CH_2 from PCL at the hydroxy end) and H_f ({–$CH_2OC(O)$–}$_n$), respectively (Fig. 4). The result indicates that the polymerization is initiated through the insertion of the benzyl alkoxy group to ε-caprolactone. In addition, experimental results show that as much as 16 folds of benzyl alcohol can be added resulting in a low PDI polymer with a much smaller M_n (entry 5). This property is very much useful while fabrication of biomedical material concerned. It is worthwhile to note that when the reaction is performed in the higher [BnOH/catalyst] ratio, the conversion rate is much faster. This result is probably attributed from a rapid equilibrium between Mg–OR and alcohol and a much faster initiation rate than the propagation rate of the polymer chain.

While compare the reactivity of **2** with **3** toward the ring-opening polymerization of ε-caprolactone, we found that the reactivity of **3** is much lower than that of **2**. For instance, ROP of CL in the same condition, up to 97% conversion can be achieved within 2 h using **2** as catalyst (entry 2). However, only 92% can be achieved after 12 h at 40 °C when **3** is used (entry 6). This result is consistent with our expectation that a sterically more bulky ligand in the C-7 position will speed up the reaction rate. As expected, the reaction rate increases with the temperature increases as seen in entry 6 and entry 8. In the resumption experiment (entry 12), an excess of 50 equiv of CL monomer was added after the polymerization effected by the first addition of 50 equiv of CL monomer had gone to completion. The molecular weight obtained in this process is similar to the polymer obtained by the polymerization of 100 molar equiv of CL catalyzed by **3** (entry 8). Useful mechanical properties for biomedical applications require molar masses of poly(ε-caprolactone) higher than $M_n = 45{,}000$. This can be achieved as shown in entry 11. Due to the hydrodynamic



Scheme 1.

volumes difference, the molecular weight obtained by GPC does not provide the actual molar masses of aliphatic polyesters (M_n (NMR)) [13]. Though a ratio between 0.45 and 0.56 have been proposed by several research groups. M_n (GPC) values are compatible with M_n (NMR) and M_n (Calcd) after applied the ratio.

2.3. Ring-opening polymerization of L-lactide catalyzed by 2

Due to its excellent mechanical properties, polylactide is a good candidate to replace nonbioresorbable polymers [14]. In this context, ROP of L-lactide employing **2** (0.1 mmol) as catalyst is systematically examined in ClC_2H_4Cl/toluene (12 mL) at 25 °C as shown in Table 2. It was found that compound **2** is also an efficient catalyst for the ROP of L-lactide. ROP of L-lactide goes to completion within 3 h at room temperature, and the PDIs of poly(L-lactide)s (PLLAs) obtained are narrow, ranging from 1.10 to 1.30. A linear relationship between the number-average molecular weight (M_n) and the monomer-to-initiator ratio ($[M]_0/[BnOH]$) are existed. The ^1H NMR spectrum of PLLA-25 (the number of 25 indicates the designed $[M]_0/[BnOH]$ ratio) (Fig. 5) indicates that the polymer chain should be capped with one benzyl ester and one hydroxy end.

2.4. Mechanistic studies

Theoretical study of the ROP mechanism of 1,5-dioxepan-2-one (DXO) and L-lactide initiated by $Sn(Oct)_2$ and methanol has been investigated by Albertsson et al. [15]. The calculated result exhibits that the initiator, methanol is activated by the formation of a hydrogen bond through a carboxyl ligand. Most recently, the formation of a hydrogen bond between BnOH and phenoxyl oxygen of $EDBP^{2-}$ ligand has been found in a lithium complex, which displays excellent activity toward ROP of L-lactide [16]. In this paper, theoretical study of ROP of CL catalyzed by **2** in the presence of benzyl alcohol has been performed using semiempirical PM3 (tm) [17] molecular modeling as implemented in the Spartan 04 [18] software package. On the basis of the catalytic, structural and theoretical studies of **2**, it is believed that, during polymerization of ε-caprolactone, the initial step involves the replacement of THF by ε-caprolactone of the dimeric compound **2** gives the dimeric intermediate (**A**) as shown in Scheme 2. When BnOH approachs intermediate **A**,

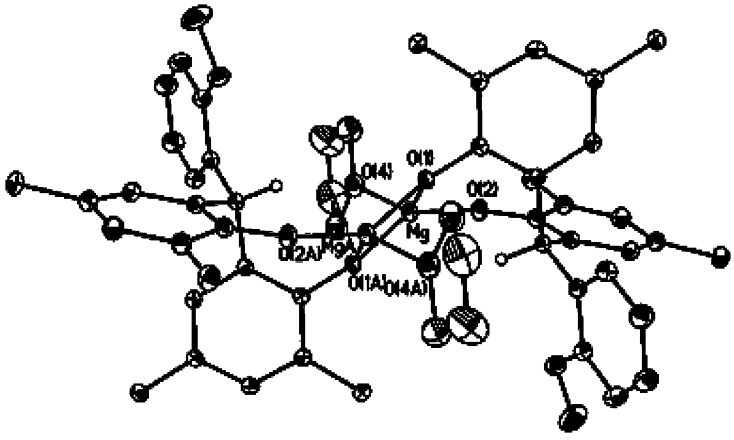


Fig. 1. Molecular structure of **2** as 20% ellipsoids (methyl and phenyl carbons of the ethyl groups and all of the hydrogen atoms are omitted for clarity, except the H atom on C-7).

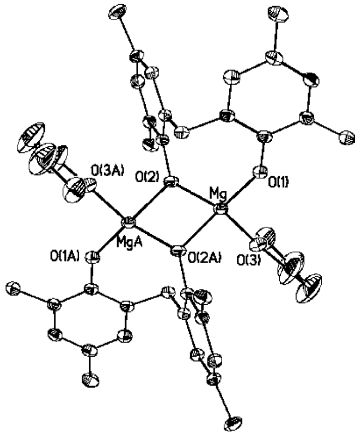


Fig. 2. Molecular structure of **3** as 20% ellipsoids (methyl and phenyl carbons of the ethyl groups and all of the hydrogen atoms are omitted for clarity).

formation of hydrogen bond occurs between BnOH and the terminal phenoxyl oxygen atom of $MEMPEP^{2-}$ ligand (**B**). The insertion of benzyl alkoxyl group, in which benzyl alcohol is activated by the formation of hydrogen bond and a weak interaction with Mg center (**TS1**), to the carbonyl carbon of ε-caprolactone leads to the ring-opening polymerization forming **C**. Truly ring-opening of monomer occurs between **C** and **TS2**. After dissociation of BnO···Mg bond, rotation of Mg–O=C bond gives **TS2**. Finally, followed by the transfer of H atom to the O atom of the C–O of ε-caprolactone, the C–O single bond breaks almost at the same time to give intermediate (**D**).

3. Experimental section

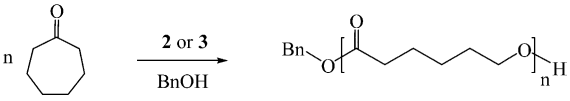
3.1. General

All experiments were carried out under a dry nitrogen atmosphere. Solvents were dried by refluxing at least for 24 h over sodium/benzophenone (toluene, and tetrahydrofuran), phosphorus pentaoxide (CH_2Cl_2), or over anhydrous magnesium sulfate (benzyl alcohol and ClC_2H_4Cl) and freshly distilled prior to use. Deuterated solvents and ε-caprolactone were dried over molecular sieves. $^nBu_2Mg$ (1.0 M in heptane), hexane, *o*-anisaldehyde, benzenesulfonic acid, and 2,4-bis(α,α-dimethylbenzyl)phenol were purchased and used as received. 2,2′-Methylene-bis(4,6-di(1-methyl-1-phenylethyl)phenol) was prepared according to the method described previously [9c]. Melting points were determined with a Buchi 535 digital melting point apparatus. ^1H and ^{13}C NMR spectra were recorded on a Mercury-400 (400 MHz) spectrometer with chemical shifts given in ppm with TMS as internal standard. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument. Infrared spectra were obtained from a Bruker Equinox 55 spectrometer.

3.2. 2,2′-(2-Methoxybenzylidene)-bis(4,6-di(1-methyl-1-phenylethyl)phenol) (MEMPEP-H_2) (*1*)

To a rapidly stirred solution of 2,4-bis(α,α-dimethylbenzyl)phenol (33 g, 100 mmol) in hexane (30 mL) was added *o*-anisaldehyde (6.8 g, 50 mmol) and benzenesulfonic acid (0.4 mL). The mixture was then heated under refluxing for

Table 1
Ring-opening polymerization of ε-CL catalyzed by **2** and **3** in the presence of benzyl alcohol



Entry	Cat.[a]	$[M]_0$:[Mg]:[BnOH]	Toluene (mL)	Temp. (°C)	Time (h)	M_n (Calcd)[b]	M_n (NMR)[c]	M_n (GPC)[d]	PDI[d]	Conv. (%)[c]
1	**2**	50:2:2	30	25	2	2700	3500	6300(3550)	1.06	> 99
2	**2**	100:2:2	30	25	2	5100	5600	9300(5200)	1.06	97
3	**2**	200:2:2	30	25	5	9700	9000	19,500(10,900)	1.07	93
4	**2**	400:2:2	30	25	8	19,800	22,600	43,200(24,200)	1.07	95
5	**2**	400:2:32	30	25	1	1500	1400	2900(1600)	1.10	> 99
6	**3**	100:2:2	10	40	12	5350	5450	10,100(5650)	1.08	92
7	**3**	50:2:2	10	70	2	2900	3000	5600(3150)	1.25	99
8	**3**	100:2:2	10	70	3	5700	5800	10,600(5950)	1.24	98
9	**3**	150:2:2	10	70	3	8600	7300	15,000(8400)	1.22	99
10	**3**	200:2:2	10	70	4	11,000	11,400	21,700(12,100)	1.13	90
11	**3**	900:2:2	25	110	12	51,400	54,200	82,500(46,200)	1.35	99
12	**3**	50(50):2:2	10	70	2(2)	5800	4900	9600(5400)	1.20	98(99)
13	**3**	400:2:4	10	70	5	11,000	9500	20,100(11,300)	1.18	95

[a] **2**, 0.1 mmol; **3**, 0.05 mmol.
[b] Calculated from the molecular weight of ε-caprolactone times $[M]_0$/[BnOH] times conversion yield plus the molecular weight of BnOH.
[c] Obtain from ^1H NMR analysis.
[d] Obtain from GPC analysis. Values in parentheses are the values obtained from GPC times 0.56 [13].

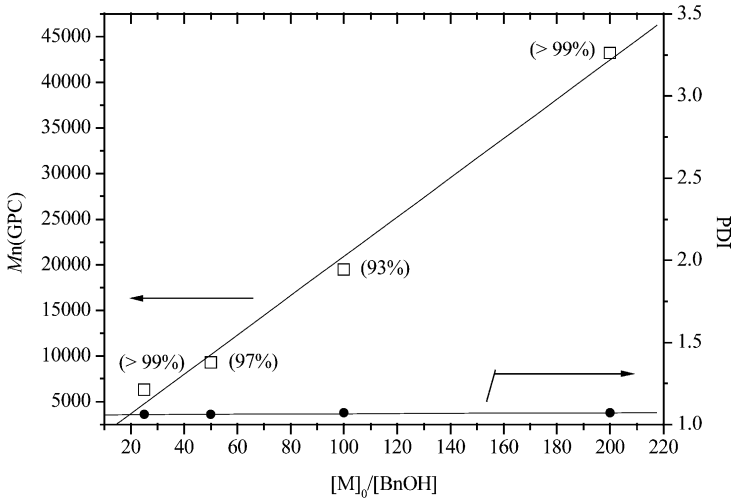


Fig. 3. Polymerization of CL catalyzed by **2** in toluene at 25 °C. Relationship between M_n (□)/PDI (●) of the polymer and the initial mole ratio $[M]_0/[I]_0$. Values in the bracket is the conversion (%) of the monomer.

30 h and volatile materials were removed under vacuum. The resulting solid was redissolved in toluene (50 mL) and neutralized by NaOH (aq) (0.1 N, 20 mL). The aqueous solution was extracted with toluene (50 mL) twice and the organic layer was collected and dry over $MgSO_4$. *n*-Hexane (30 mL) was added to the toluene solution to yield white precipitate. Yield: 21 g (54%).

*3.3. [Mg(μ-MEMPEP)THF]$_2$ (**2**)*

To an ice cold solution (0 °C) of 2,2′-(2-methoxybenzylidene)-bis(4,6-di(1-methyl-1-phenylethyl)phenol) (1.56 g, 2.0 mmol) in THF (20 mL) was added slowly an $^{n}Bu_2Mg$ (2.4 mL, 2.4 mmol in heptane) solution. After all of the solution was added, the mixture was stirred for 3 h. The

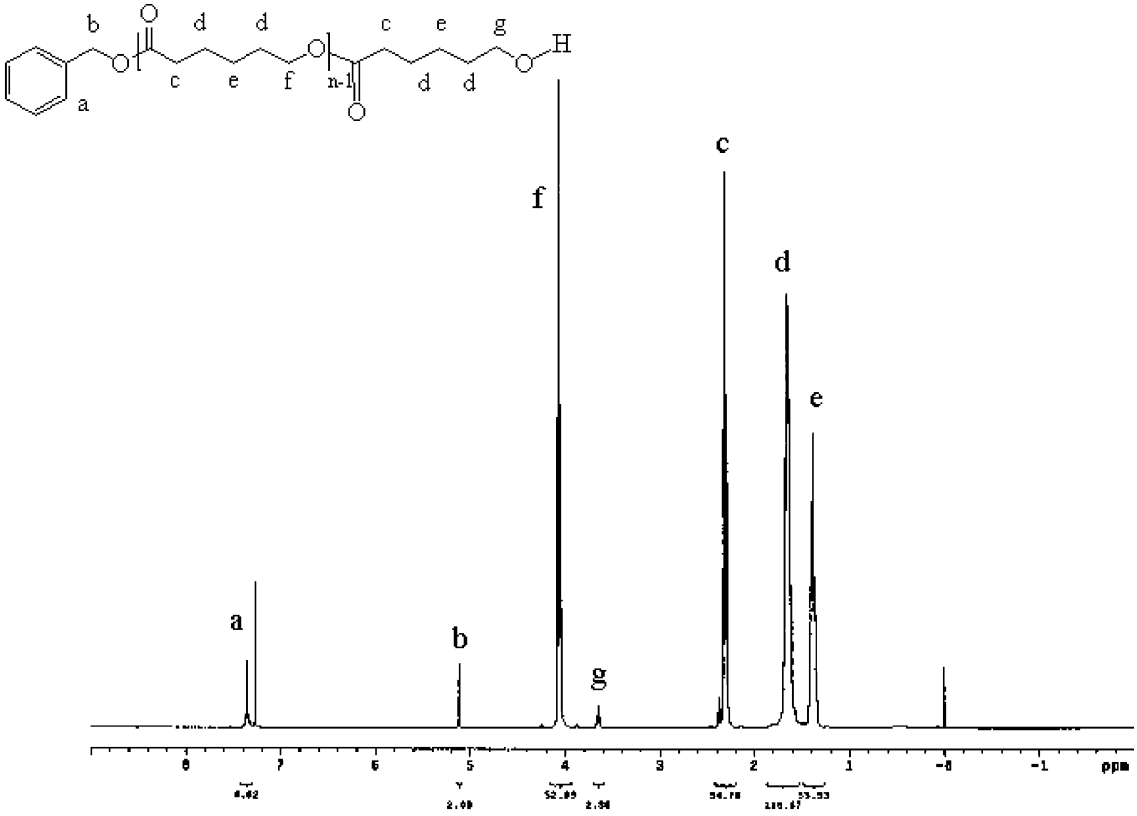
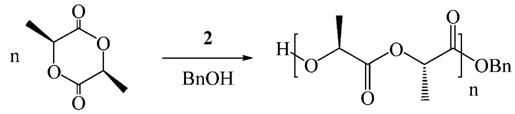


Fig. 4. ^{1}H NMR spectrum of PCL-25 in $CDCl_3$.

Table 2
Ring-opening polymerization of L-lactide catalyzed by **2** in the presence of benzyl alcohol



Entry	$[M]_0$/[Mg]/[BnOH]	ClC_2H_4Cl/toluene (mL)	Time (h)	Temp (°C)	M_n (Calcd)[a]	M_n (NMR)[b]	M_n (GPC)[c]	PDI[c]	Conv. (%)[b]
1	50:2:2	12	3	25	3700	3000	5700(3300)	1.18	87
2	100:2:2	12	3	25	7300	5100	13,100(7600)	1.10	92
3	200:2:2	12	2	25	14,500	14,200	43,500(25,200)	1.28	> 99
4	400:2:2	12	1	25	28,900	30,300	75,600(44,100)	1.30	99

2, 0.1 mmol.
[a] Calculated from the molecular weight of L-lactide times $[M]_0$/[BnOH] times conversion yield plus the molecular weight of BnOH.
[b] Obtain from [1]H NMR analysis.
[c] Obtain from GPC analysis. Values in parentheses are the values obtained from GPC times 0.58 [13].

mixture was then dried in vacuo, and the residue was extracted with 40 mL of dichloromethane. The extract was then concentrated to ca. 15 mL and was cooled to −20 °C to furnish colorless crystals. Yield: 1.43 g (82%). Anal. Calcd for $C_{134}H_{128}Mg_2O_8$: C, 82.50, H, 7.30. Found: C, 82.60, H, 7.39%. ^{1}H NMR ($CDCl_3$, ppm): δ 7.35–6.40 (m, 28H, Ph); 5.72 (s, 1H, C*H*); 3.27 (br, 4H, OCH_2CH_2); 2.56 (br, 3H,OCH_3); 1.65–1.37 (br, 28H, CH_3 and OCH_2CH_2). ^{13}C NMR ($CDCl_3$, ppm): δ 158.28, 152.56, 151.86, 151.11, 139.42, 137.81, 137.19, 134.30, 133.39, 130.05, 129.00, 128.20, 127.72, 127.58, 127.48, 127.20, 126.98, 126.69, 126.39, 126.24, 125.27, 124.99, 124.68, 123.89, 122.87, 120.23, 112.05 (Ph); 68.65 (OCH_3); 43.23, 42.80 (OCH_2CH_2); 42.14, 42.00 (Ph*C*(CH_3)); 31.22 (Ph*C*H); 30.86, 30.39 (Ph*C*(CH_3)); 24.96 (OCH_2CH_2); 29.45, 21.45 (PhC(CH_3)$_2$). mp 218–220 °C (dec).

3.4. [Mg(μ-MMPEP)THF]$_2$ (3)

To an ice cold solution (0 °C) of 2,2-methylene-bis(4,6-di(1-methyl-1-phenylethyl)phenol) (1.35 g, 2.0 mmol) in THF (40 mL) was added slowly an ^{n}Bu$_2$Mg (2.4 mL, 2.4 mmol in heptane) 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 10 mL of dichloromethane. The extractor was then concentrated to ca. 5 mL and cooled to −20 °C to furnish white solid.

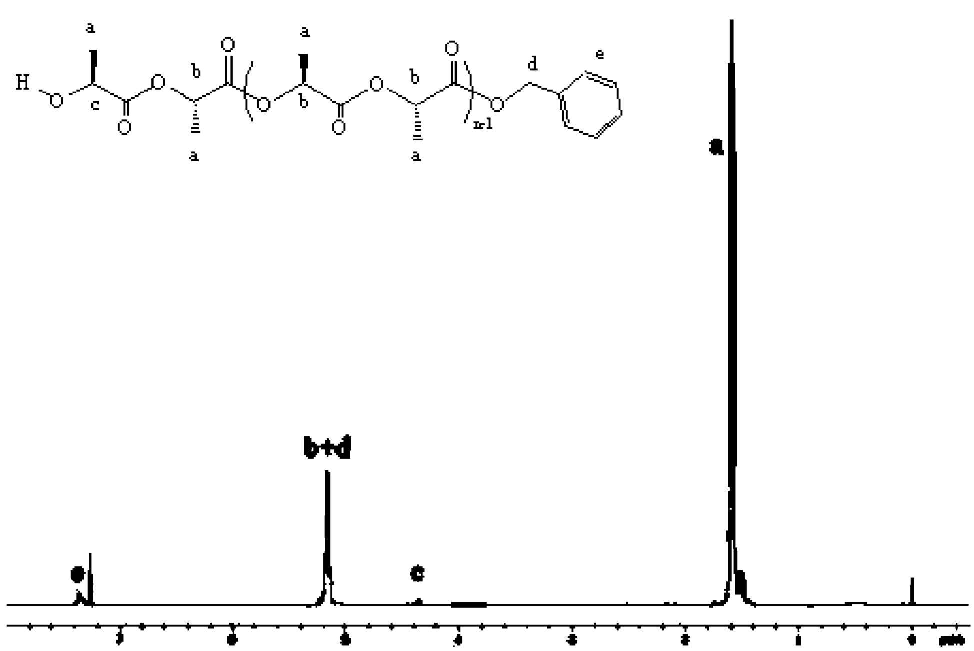
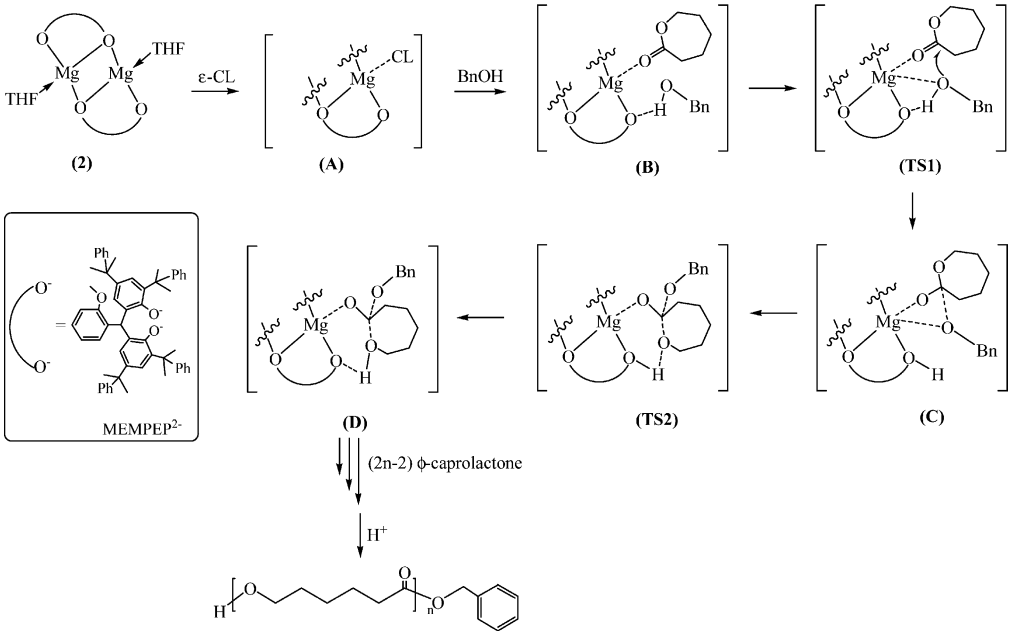


Fig. 5. ^{1}H NMR spectrum of PLLA-25 in $CDCl_3$.



Scheme 2. Proposed mechanism for ring-opening polymerization of ε-caprolactone catalyzed by compound **2** (half of the molecule is shown from (**A**) to (**TS2**) for clarity).

Yield: 1.16 g (75%). Anal. Calcd for $C_{106}H_{116}Mg_2O_6$: C, 82.96; H, 6.23. Found: C, 83.19; H, 7.37%. ^{1}H NMR ($CDCl_3$, ppm): δ 5.29–7.38 (m, 24H, Ph), 3.33 (d, 1H, CH_2, J_{H-H} = 14 Hz), 2.76 (d, 1H, CH_2, J_{H-H} = 14 Hz), 2.58 (b, 2H, OCH_4), 1.71–1.28 (br, 28H, CH_3 and OCH_2CH_2). ^{13}C NMR ($CDCl_3$, ppm): δ 159.26, 153.19, 152.47, 151.75, 151.49, 139.71, 136.39, 133.89, 132.63, 130.85, 130.46, 128.13, 127.68, 127.65, 127.55, 127.25, 126.98, 126.47, 126.44, 125.12, 125.00, 124.84, 124.61, 123.94, 123.73, 123.45 (Ph); 69.23 (OCH_2); 42.67, 42.47, 42.25, 42.18 (PhC(CH_3)$_2$); 34.29, 33.43, 33.06, 31.54, 31.51, 31.12, 30.70, 29.27, 28.72 (PhC(CH_3)$_2$ and PhCH_2), 25.03 (OCH_2CH_2). IR (KBr, cm^{-1}): 3081(m), 3055(m), 3022(s), 2965(s), 2870(m), 1600(m), 1469(s), 1442(s), 1381(m), 1360(m), 1323(m), 1283(m), 1234(m), 1199(m), 1146(m), 1028(m). mp: 150–154 °C (dec).

3.5. Synthesis of benzyl ester end-functionalized PCLs

A typical polymerization procedure was exemplified by the synthesis of PCL-75 (the number 75 indicates the designed $[M]_0/[BnOH]$). To a rapidly stirring solution of $[Mg(\mu\text{-MMPEP})THF]_2$ (0.0768 g, 0.05 mmol) in toluene (6 mL) was added CL (0.26 mL, 7.5 mmol) and BnOH (0.1 mmol) in toluene (4 mL). The reaction mixture was stirred at 70 °C for 3 h. After the reaction was quenched by the addition of an excess 0.35 N acetic acid solution, the polymer was precipitated into *n*-hexane. The white precipitate was purified by redissolving the polymer in dichloromethane and then precipitated into *n*-hexane. Finally, the white polymer was dried under vacuum giving white solid. Yield: 0.73 g (84%).

3.6. Synthesis of benzyl ester end-functionalized PLLAs

A typical polymerization procedure was exemplified by the synthesis of PLLA-25 (the number 25 indicates the designed $[M]_0/[BnOH]$). To a rapidly stirring solution of $[Mg(\mu\text{-MMPEP})THF]_2$ (0.1747 g, 0.1 mmol) and L-lactide (0.72 g, 50 mmol) in ClC_2H_4Cl (10 mL) was added BnOH/toluene mixture solution (0.2 mmol, 2 mL). The reaction mixture was stirred under refluxing temperature for 3 h. After the reaction was quenched by the addition of an excess 0.35 N acetic acid solution, the polymer was precipitated into *n*-hexane. The white precipitate was resolved in dichloromethane and then precipitated into *n*-hexane. The obtained white precipitate was dried under vacuum to yield white solid.

3.7. GPC measurements

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. The chromatographic column was Phenomenex Phenogel 5 10∼3 A and the calibration curve is made by polystyrene standards to calculate M_n (GPC). A typical GPC measurements description was exemplified by the measurement of PCL-25 (the number 25 indicates $[M]_0/[BnOH]$). 0.025 g PCL-25 was dissolved by 3.975 g THF (HPLC grade) and filtered through a filter (13 mm Millex-HN Filter 0.45 μm NY Non-Sterile). Then 25 μL of the solution were injected into the GPC and the flow eluent rate is 1 mL/min. Full study was be finished in 15 min. The results were calculated by SISC chromatography data station 1.0 edition.

3.8. NMR measurements

PCL-25 (ca. 0.01 g) was dissolved in $CDCl_3$ (ca. 1 mL) in a NMR tube and was determined by a Mercury-400 (400 MHz) spectrometer. The spectrum was obtained from at least 10 Fid files. M_n (NMR) for PCL was calculated based on the comparison of integral between peaks at 5.12 (–OCH_2Ph), 4.05 (–CH_2OC(=O)) and at 3.65 (–CH_2OH) ppm. M_n (NMR) for PLLA was calculated based on the comparison of integral between peaks at 7.27–7.37 (–CH$_2$*Ph*), 5.18 (–OC*H*MeC(O)), 4.36 (–C*H*MeOH) ppm.

3.9. X-ray crystallographic studies

Suitable crystals of **2** and **3** were sealed in thin-walled glass capillaries under nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. Intensity data were collected in 1350 frames with increasing ω (width of 0.3°/frame). Unit cell dimensions were determined by a least-squares fit of 4081 reflections for **2** and 2998 reflections for **3**. 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 Siemens SHELXTL PLUS 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.

3.10. Computational methods

Theoretical study of the polymerization of CL catalyzed by **2** in the presence of benzyl alcohol was performed. The calculations were carried out using semiempirical PM3 (tm) [17] molecular modeling as implemented in the Spartan 04 [18] software package. All calculated structures were characterized by frequency calculations.

4. Conclusion

In conclusion, two interested magnesium aryloxides **2** and **3** have been prepared and have demonstrated their efficient catalytic activities in the ROP of ε-caprolactone/L-lactide. The catalytic character of complex **2** paved the way to synthesize as much as 16-fold polymer-chains of polymer with low PDIs in the presence of a small amount of catalyst. Theoretic studies of ROP mechanism of CL using **2** as a catalyst indicating that benzyl alcohol is activated by the formation of a hydrogen bond through one of the phenoxy oxygen atom.

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Supplementary data

Crystallographic data and further details of the crystal structure determination of **2** and **3** and theoretical study of the polymerization of CL catalyzed by **2** in the presence of benzyl alcohol are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2005.04.079

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