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Reactions of 2,2′-Methylenebis(4-chloro-6-isopropyl-3-methylphenol) and 2,2′-Ethylidenebis(4,6-di-*tert*-butylphenol) with Mg^nBu_2: Efficient Catalysts for Ring-Opening Polymerization of ϵ-Caprolactone and L-Lactide

Mao-Ling Shueh,[†] Yi-Shen Wang,[†] Bor-Hunn Huang,[†] Chen-Yuan Kuo,[‡] and Chu-Chieh Lin*,[†]

Department of Chemistry, National Chung-Hsing University, Taichung, Taiwan 402, and Department of Chemical Engineering, Yung-Ta Institute of Technology and Commerce, Pingtung, Taiwan 909, ROC

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ABSTRACT: Three novel magnesium aryloxides, $[(MCIMP)_2Mg_2(THF)]_2$ (**1**), $[(EDBP)Mg(Et_2O)]_2$ (**2**), and $[(EDBP)Mg(THF)]_2$ (**3**), have been synthesized by the reaction of 2,2′-methylenebis(4-chloro-6-isopropyl-3-methylphenol) ($MCIMP-H_2$) or 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) ($EDBP-H_2$) with Mg^nBu_2 in diethyl ether or tetrahydrofuran, respectively. Experimental results show that **1**−**3** efficiently catalyze the ring-opening polymerization of ϵ-caprolactone and L-lactide in a controlled fashion, yielding polymers with very narrow polydispersity indexes in a wide range of monomer-to-initiator ratios. Compound **1** has paved a way to synthesize as much as 500-fold polymer chains of poly(ϵ-caprolactone) with a very narrow polydispersity index. In addition, block copolymers such as poly(ϵ-caprolactone)-*b*-poly(L-lactide), poly(ethylene glycol) methyl ether-*b*-poly(L-lactide), and polystyrene-*b*-poly(L-lactide) have also been prepared.

Introduction

Recently, biodegradable polymers have been attracting considerable attention due to their potential application in human life.[1] Among them, the aliphatic polyesters, such as poly(ϵ-caprolactone) (PCL) and poly(lactide) (PLA) 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 due to their biodegradable, biocompatible, and permeable properties.[2] Therefore, there has been increasing interest in the development of efficient catalytic systems for the preparation of PCL and PLA. The major polymerization method employed to synthesize these polymers has been the ring-opening polymerization (ROP) of lactones/lactides and functionally related compounds. Aluminum alkoxides,[3] zinc,[4] stannous,[5] yttrium,[6] and trivalent lanthanide derivatives[7] have been reported to be effective initiators of ROP of lactones/lactides, giving polymers with both high molecular weights and high yields. Recently, we became interested in magnesium alkoxides due to their low toxicity as well as their high reactivity.

When using metal alkoxides as initiators for ROP of lactones and lactides, back-reactions leading to the formation of macrocycles always occur as side reactions. The undesired back-biting reaction can be solved by using a suitable sterically bulky ligand to interact coordinatively with the active center and therefore provides a steric barrier to a certain extent around that metal center to minimize the side reactions. This strategy has been successfully applied in the anionic polymerization of (methyl)acrylates[8] and the ring-opening polymerization of lactones/lactides.[9] In this paper, we report the synthesis, characterization, and catalytic studies of three magnesium derivatives coordinated with sterically bulky ligands.

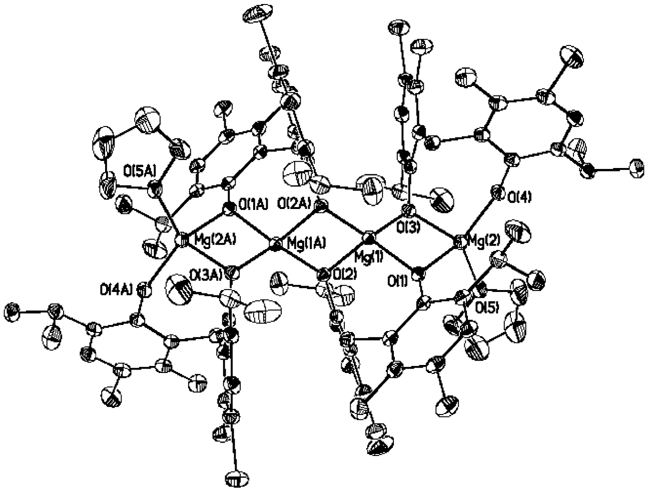

Figure 1. Molecular structure of **1** as 20% ellipsoids (all of the hydrogen atoms are omitted for clarity).

Results and Discussion

Syntheses. A highly efficient catalyst, $[(MCIMP)_2Mg_2(THF)]_2$ (**1**), for the ROP of lactone and lactide is prepared in moderate yield from the reaction of 2,2′-methylenebis(4-chloro-6-isopropyl-3-methylphenol) ($MCIMP-H_2$) with 1.2 molar equiv of Mg^nBu_2 in tetrahydrofuran (THF) as shown in Scheme 1. Compound **1** is isolated as a tetranuclear magnesium complex. However, 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) ($EDBP-H_2$) reacts with 1.2 molar equiv of Mg^nBu_2 in diethyl ether or in THF, yielding a dinuclear magnesium complex, $[(EDBP)Mg(S)]_2$ (**2**, $S = Et_2O$; **3**, $S = THF$), in high yield as shown in Scheme 2. All of these compounds are isolated as colorless crystals, and

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[†] National Chung-Hsing University.
[‡] Yung-Ta Institute of Technology and Commerce.

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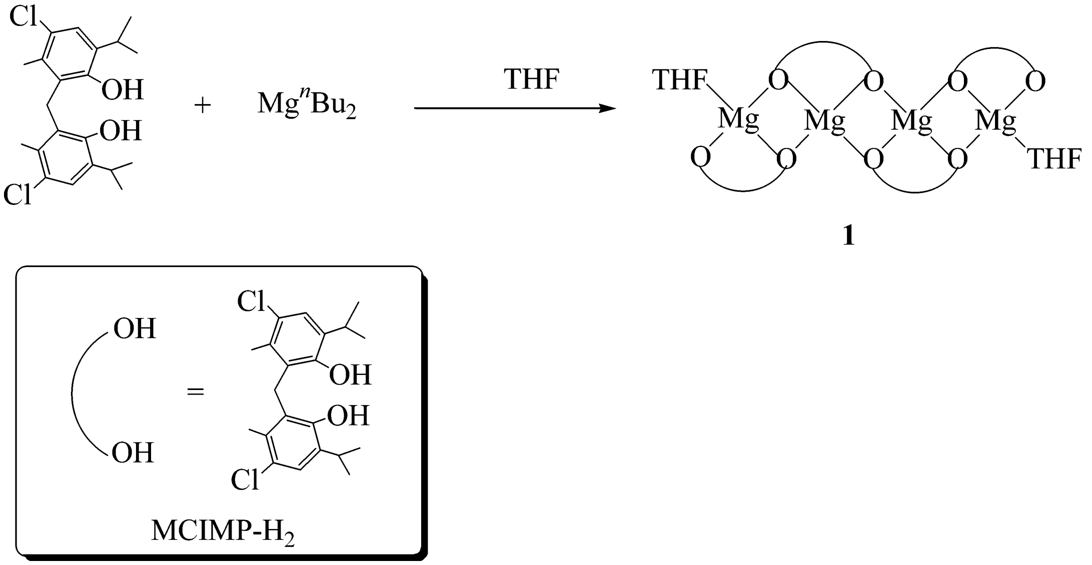
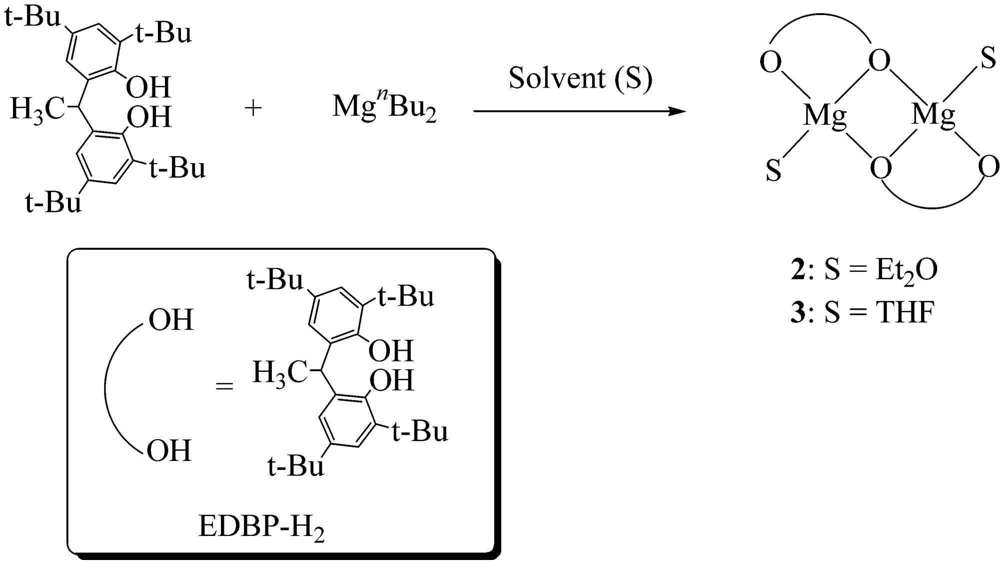
Scheme 1. Preparation of Compound 1

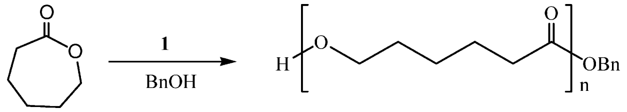


Scheme 2. Preparation of Compounds 2 and 3



2: S = Et_2O
3: S = THF

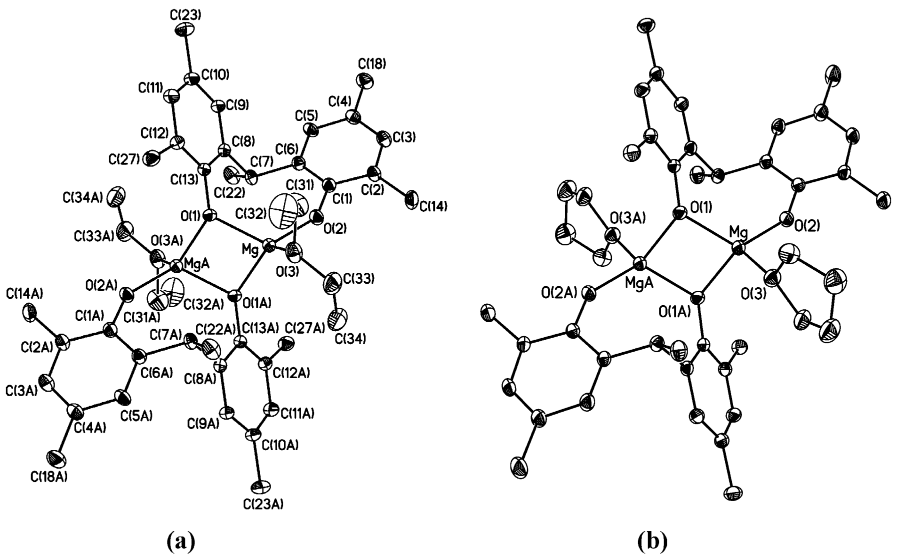
Table 1. Ring-Opening Polymerization of ϵ-Caprolactone Catalyzed by 1



entry	$[M]_0/[Mg]_0/[BnOH]_0$	temp (°C)	time (h)	M_w/M_n	M_n(obsd)[a]	M_n(calcd)[b]	M_n(NMR)[c]	conv[c] (%)
1	50/1/2	56	0.5	1.11	5600 (3100)	2900	2000	99
2	100/1/2	56	1	1.14	11000 (6200)	5800	5100	99
3	200/1/2	56	3	1.11	24600 (13800)	11500	9400	99
4	400/1/2	56	3	1.19	43100 (24100)	22900	19000	99
5	400/1/16	56	1	1.06	5400 (3000)	2900	3300	99
6	800/1/320	56	0.5	*d*	*d*	390	470	97
7	5000/1/500	56	2	1.12	2200 (1200)	1100	1100	86

[a] Obtained from GPC analysis and calibrated by a polystyrene standard. Values in parentheses are the values obtained from GPC times 0.56.[13] [b] Calculated from the molecular weight of ϵ-caprolactone times $[M]_0/[BnOH]_0$ times the conversion yield. [c] Obtained from ^1H NMR analysis. [d] Not available.

their elemental analysis and spectroscopic analysis are very consistent with the proposed molecular formula. A suitable crystal for structural determination of **1** is obtained from slow cooling of a THF solution, and its ORTEP is shown in Figure 1. The tetranuclear species **1** consists of two different kinds of four-coordinated Mg atoms, where Mg(1) and Mg(1A) are bonded to the two oxygen atoms of two MCIMP^{2-} ligands. Mg(2) and Mg(2A) are each bonded to one oxygen atom of two MCIMP^{2-} groups and one oxygen of THF. Single crystals suitable for X-ray determination of compounds **2** and **3** are obtained from slow cooling of a hexane (**2**)



(a) **(b)**

Figure 2. Molecular structures of **2** (a) and **3** (b) as 20% ellipsoids (methyl carbons of the *tert*-butyl groups and all of the hydrogen atoms are omitted for clarity).

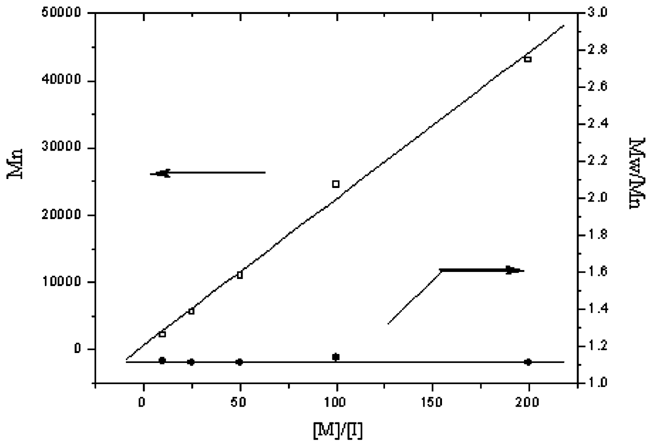
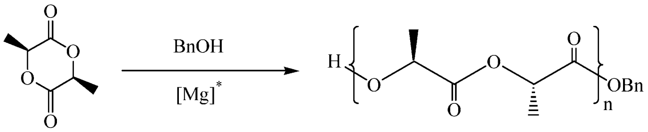


Figure 3. Polymerization of ϵ-CL catalyzed by **1** in toluene at 56 °C. The relationship between M_n (□) (M_w/M_n (●)) of the polymer and the initial mole ratio $[M]_0/[I]_0$ is shown.

or a toluene (**3**) solution, and their molecular structures are shown in Figure 2. Compound **2** is a dimeric compound in which two magnesium atoms are bonded through one of the oxygens of the EDBP^{2-} ligand. Both Mg atoms of compound **2** are equivalent and attain the ability to act as Lewis acids. The immediate geometry of **2** around Mg is distorted tetrahedral. The molecular structure of **3** is analogous to that of **2** with only a slightly difference in bond distances and angles.

Ring-Opening Polymerization of ϵ-Caprolactone. The catalytic activities of **1** toward ROP of ϵ-caprolactone (ϵ-CL) have been examined. In general, polymerization of ϵ-caprolactone was carried out at 56 °C in toluene (15 mL) using **1** (0.05 mmol) as the catalyst. To a rapidly stirred solution of $[(MCIMP)_2Mg_2(THF)]_2$ (**1**) in toluene were added ϵ-CL (0.53 mL, 5 mmol) and BnOH (0.01 mL, 0.1 mmol). The reaction mixture was stirred at 56 °C for 1 h, during which time 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, the polymer was precipitated into *n*-heptane. Polymerizations of ϵ-CL under different reaction conditions (entries 1−7) have been systematically conducted as shown in Table 1. It was found that the polydispersity indexes (PDIs) of polyesters initiated by **1** range from 1.06 to 1.19, and a linear relationship between the number-average molecular weight (M_n) and the monomer-to-initiator ratio ($[M]_0/[I]_0$) exists as shown in Figure 3, implying the

Table 2. Ring-Opening Polymerization of L-Lactide Catalyzed by 1−3



entry	initiator	$[M]_0/[Mg]_0/[BnOH]_0$	solvent (mL)	time (h)	temp (°C)	M_w/M_n	M_n(obsd)[a]	M_n(calcd)[b]	M_n(NMR)[c]	conv[c] (%)	yield[d] (%)
1	1	50/1/2	THF (15)	6	68	1.07	5000 (2900)	2800	3000	76	51
2	2	50/1/2	CH_2Cl_2 (10)	24	30	1.04	7300 (4200)	3670	3560	99	75
3	2	100/1/2	$C_2H_4Cl_2$ (10)	2	83	1.08	9900 (5700)	6600	6200	92	82
4	2	200/1/2	$C_2H_4Cl_2$ (10)	2	83	1.10	19400 (11300)	14200	13900	98	88
5	2	300/1/2	$C_2H_4Cl_2$ (10)	2	83	1.18	33900 (19700)	20600	21100	95	85
6	2	400/1/2	$C_2H_4Cl_2$ (10)	2	83	1.21	45200 (26200)	27800	30200	96	90
7	2	400/1/20	$C_2H_4Cl_2$ (10)	1	83	1.14	6000 (3500)	2960	2840	99	86
8	3	100/1/2	$C_2H_4Cl_2$ (10)	3	83	1.06	10800 (300)	6800	6900	94	86
9	1	30 (20)/1/2[e]	toluene (15)	1 (4)	56 (110)	1.18	13300	6100	8400	99 (93)	77

[a] Obtained from GPC analysis and calibrated by a polystyrene standard. Values in parentheses are the values obtained from GPC times 0.58.[13,14] [b] Calculated from the molecular weight of L-lactide times $[M]_0/[BnOH]_0$ times the conversion yield. [c] Obtained from ^1H NMR analysis. [d] Isolated yield. [e] Polymerization of ϵ-CL in toluene at 56 °C with compound **1** for 1 h followed by the addition of LA and refluxed in toluene for another 4 h.

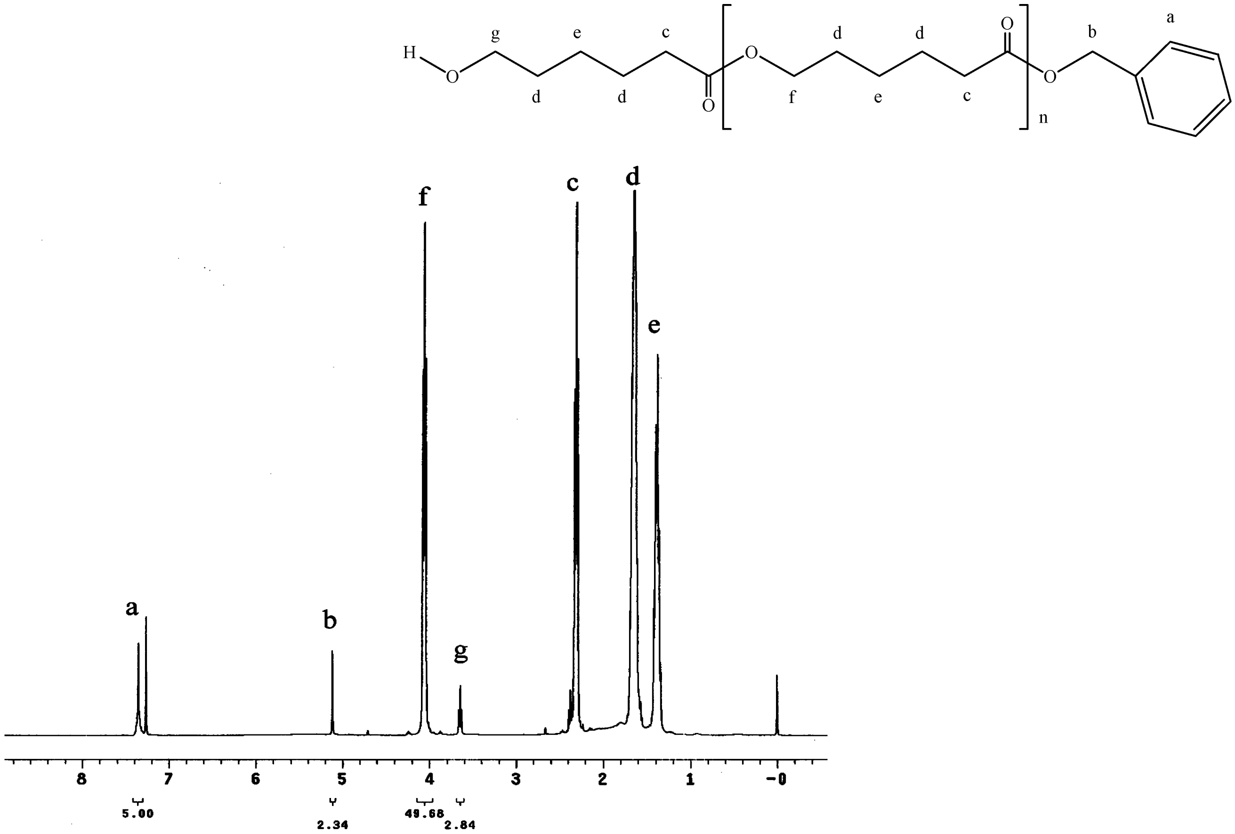


Figure 4. ^1H NMR spectrum of PCL-25 in $CDCl_3$.

"living" character of the polymerization process. It is worthwhile to note that compound **1** has paved a way to synthesize as much as 500-fold polymer chains of poly(ϵ-caprolactone) with a very narrow polydispersity index in the presence of a small amount of compound **1**. The ^1H NMR spectrum of PCL-25 (the number 25 indicates the designed $[M]_0/[I]_0$ ratio) (Figure 4) indicates the polymer chain should be capped with one benzyl ester and one hydroxy end, suggesting that back-reactions leading to the formation of macrocycles do not occur.

Ring-Opening Polymerization of L-Lactide. In this context, ROP of L-lactide (LLA) employing **2** (0.05 mmol) as a catalyst is systematically examined in CH_2Cl_2 (10 mL) at 25 °C or in refluxed 1,2-dichloroethane (10 mL) as shown in Table 2. It was found that compound **2** is an efficient catalyst for the ROP of L-lactide. ROP of L-lactide goes to completion within 24 h at room temperature (entry 2), and the reaction rate increases with the increase in temperature (entries 3−7). However, the PDIs of poly(L-lactide)s obtained are all quite narrow, ranging from 1.04 to 1.21, and a linear relationship between M_n and $[M_0]/[I_0]$ existes (Figure 5). The ^1H NMR spectrum of PLA (Figure 6) indicates that the polymer chain should be capped with one benzyl ester and one hydroxy end. This result suggests that the polymerization occurs through the insertion of a benzyl alkoxy group into the lactide. Additionally, compounds **1** and **3** have also shown excellent activity toward the ROP of L-lactide (entries 1 and 8). The PCL-*b*-PLA block polymer (M_n = 13300, PDI = 1.18, entry 9) was synthesized by the sequential ROP of ϵ-CL ($[M]_0/[I]_0$ = 30) and L-LA monomer ($[M]_0/[I]_0$ = 20) in the presence of **1** as shown in Figure 7.

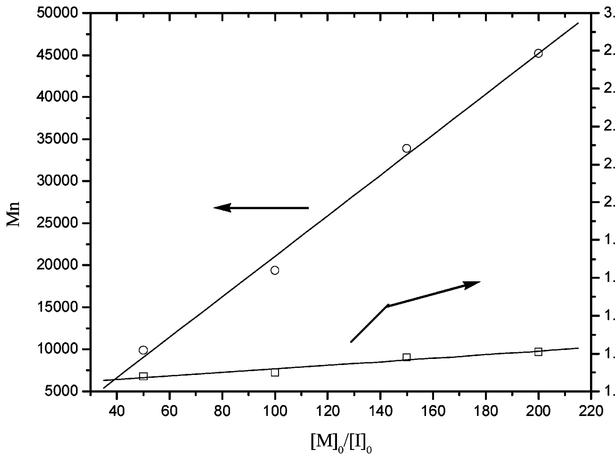


Figure 5. Polymerization of L-LA catalyzed by **2** in refluxed 1,2-dichloroethane. The relationship between M_n (○) (M_w/M_n (□)) of the polymer and the initial mole ratio $[M]_0/[I]_0$ is shown.

Proposed Mechanism for ROP of L-Lactide Catalyzed by 2. On the basis of the catalytic and structural studies of compound **2**, it is believed that, during polymerization of LLA, both Mg atoms of compound **2** are equivalent and attain the ability to act as Lewis acids. In the presence of an excess of LLA, dissociation of Et_2O followed by the coordination of lactide on both Mg and Mg(A) atoms occurs. The insertion of benzyl alcohol, which is activated by the formation of a hydrogen bond through the terminal oxygen atom of $EDBP^{2-}$ (**A**), to the carbonyl group of LLA leads to the ring-opening polymerization as shown in Scheme 3. However, an attempt to isolate the intermediate has failed.

Synthesis of Diblock Copolymer MPEG-*b*-PLA. Copolymers containing poly(L-lactide) and poly(ethylene glycol) methyl ether (MPEG) have been explored as biodegradable scaffolds because they ultimately degrade

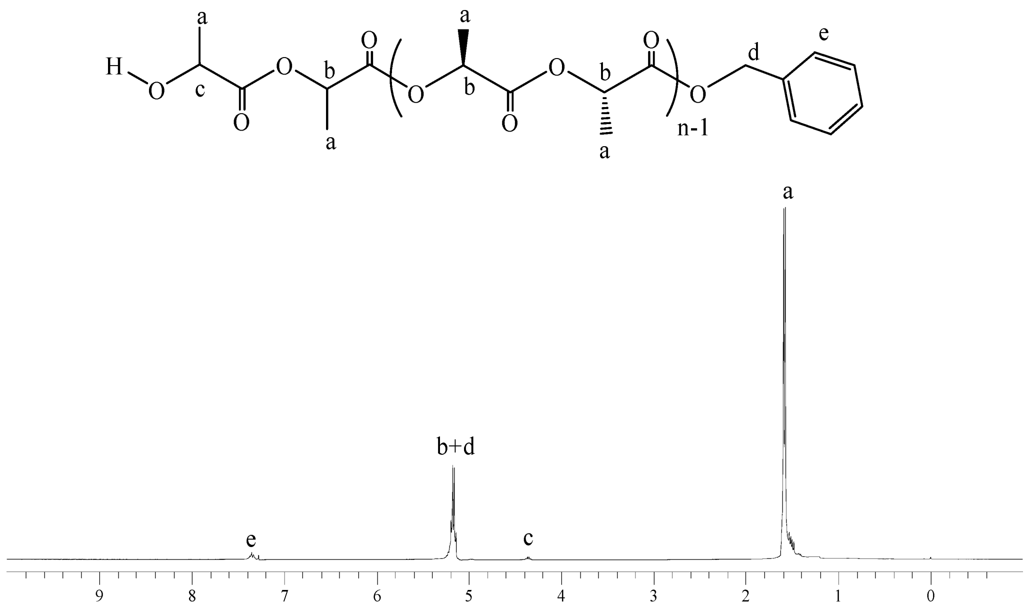
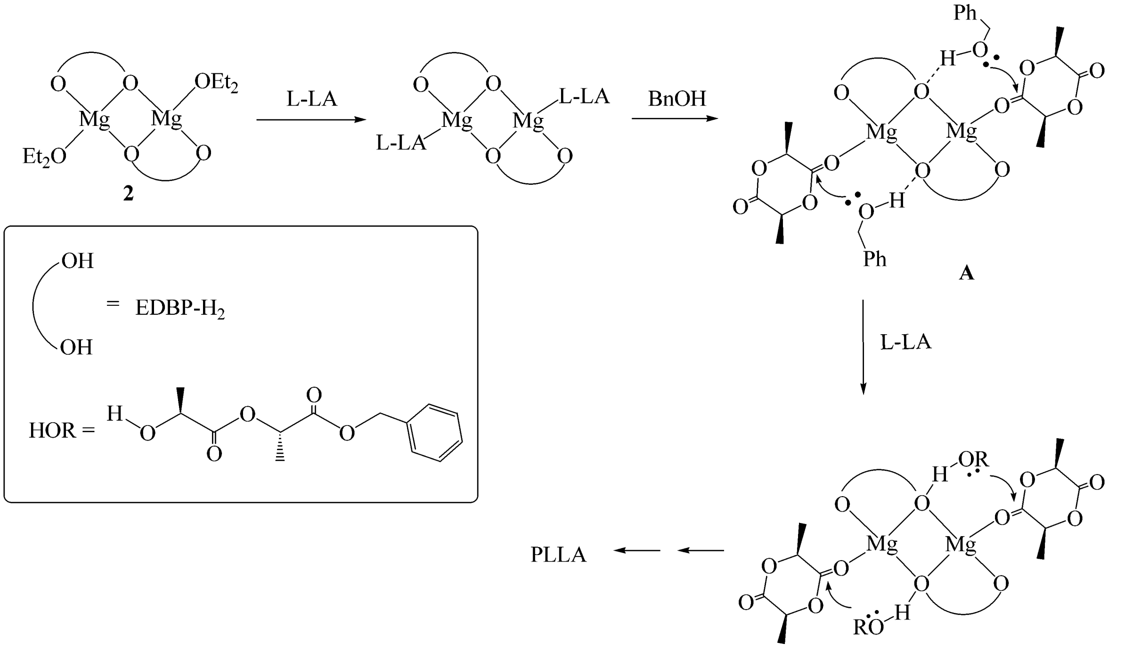


Figure 6. ^{1}H NMR spectrum of PLA-25 in CDCl$_3$.

Scheme 3. Proposed Mechanism for the Ring-Opening Polymerization of L-Lactide Catalyzed by 2



to natural metabolites. Scaffolds may be readily formed from these materials as bonded fibers or porous sponges.[10] A block copolymer of MPEG-*b*-PLA was prepared by the ring-opening polymerization of L-lactide in the presence of MPEG catalyzed by compound **1**. The result is tabulated in Table 3. The molecular weight of the block copolymer increases with reasonable PDI. In the ^{1}H NMR spectrum of MPEG-*b*-PLA (Figure 8), a sharp singlet of methylene protons (3.72 ppm) and a singlet of methoxy protons (3.25 ppm) show the block nature of the MPEG-*b*-PLA copolymer. It is further verified by the GPC profile.

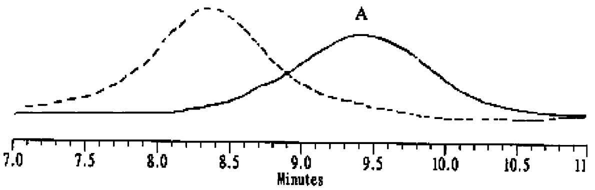


Figure 7. GPC profiles of copolymerization of PCL-*b*-PLA: (peak A) after prepolymerization of CL (30 equiv of **1**); (peak B) after block copolymerization of PCL-*b*-PLA ([CL]/[LA]/**1**/BnOH = 30/20/1/2, M_n = 13300, PDI = 1.18).

Synthesis of Diblock Copolymer PS-*b*-PLA. Copolymers containing poly(L-lactide) are especially interesting due to the physical properties of polystyrene after biodegradation of PLA from PS-*b*-PLA copolymer. More recently, a mesoporous polystyrene monolith has been prepared from PS-*b*-PLA block copolymer.[11] This may provide new applications of block copolymers in the field of nanotechnologies. Developing a convenient synthetic route of copolymers with control over molecular weight is a challenging task in material chemistry research. Despite polyesters containing block coplymers having been synthesized through the controlled ring-opening polymerization using lithium alkoxide macroinitiators,

Table 3. Preparation of MPEG-*b*-PLA and PS-*b*-PLA Catalyzed by 1 and 2 Using MPEG or PS as Initiator with $[LA]_0/[ROH]_0 = 50$

	prepolymer (GPC)					temp	time	conv[a]	copolymer (GPC)		M_n(NMR)[c]
entry	M_n	PDI	cat.	ROH	solvent (mL)	(°C)	(h)	(%)	M_n[b]	PDI[b]	[PS−PLA (PLA)]
1	6300	1.04	**1**	MPEG	toluene (15)	110	8	94	13300	1.15	15700 (9400)
2	28900	1.13	**2**	PS−OH	$C_2H_4Cl_2$ (30)	83	5	81	38800	1.16	28900 (5100)

[a] As determined via integration of the methine resonances of LA and poly(L-lactide) ($CDCl_3$, 400 MHz). [b] Obtained from GPC analysis and calibrated by a polystyrene standard. [c] Calculated from the molecular weight of L-lactide times $[LA]_0/[ROH]_0$ times the conversion yield plus the molecular weight of ROH.

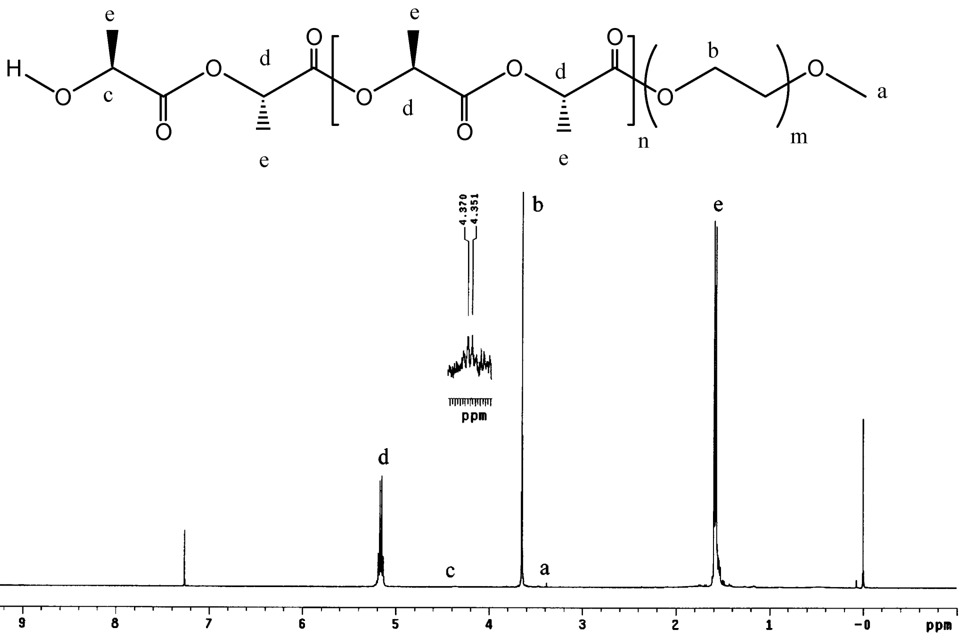


Figure 8. ^1H NMR spectrum of MPEG-*b*-PLA (Table 3, entry 1) in $CDCl_3$.

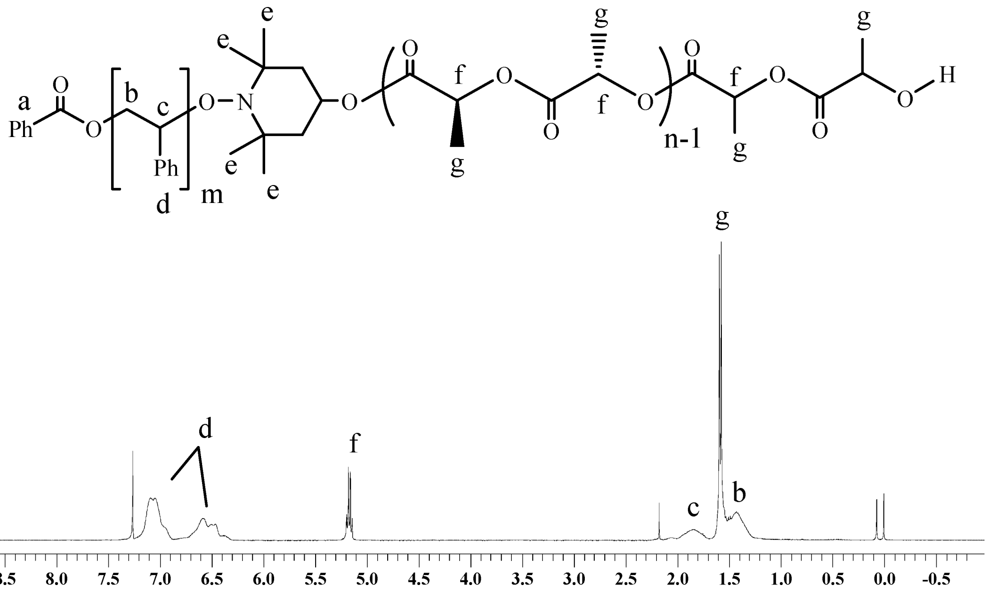


Figure 9. ^1H NMR spectrum of PS-*b*-PLA (Table 3, entry 2) in $CDCl_3$.

we reported here a different way to prepare PS-*b*-PLA copolymer.

Polystyrene with a 4-hydroxy-TEMPO terminal was synthesized by a free radical polymerization approach similar to the method reported by Georges et al.[12] 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 = 28900) with low polydispersity (PDI = 1.13). The block copolymer of PS and PLA was further prepared by the ring-opening polymerization of L-lactide in the presence of polystyrene (PS−TEMPO−OH) catalyzed by compound **2**. The result is tabulated in Table 3. The molecular weight of the block copolymer increases with reasonable PDI. In the ^1H NMR spectrum of PS-*b*-PLA (Figure 9), a broad signal in the aromatic region at 1.84 ppm and the typical quartet at 5.16 ppm show the block nature of the PS-*b*-PLA copolymer. Moreover, in the GPC profile (Figure 10) peak A corresponds to polystyrene

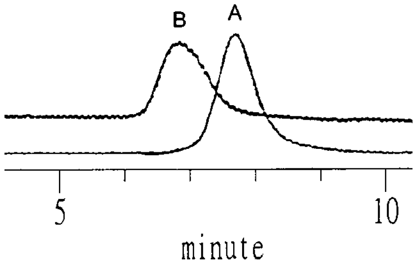


Figure 10. GPC profiles of copolymerization of PS-*b*-PLA: (peak A) the prepolymer (M_n = 28900, PDI = 1.13); (peak B) after block copolymerization of PS-*b*-PLA (M_n = 38800, PDI = 1.16).

(M_n = 28,900, PDI = 1.13) and peak B to PS-*b*-PLA after polymerization with 50 equiv of L-LA. An increase in molecular weight (M_n = 38800, PDI = 1.16) was observed (peak B) to confirm the formation of the block copolymer.

In conclusion, three novel magnesium aryloxides, $[(MCIMP)_2Mg_2(THF)]_2$ (**1**), $[(EDBP)Mg(Et_2O)]_2$ (**2**), and $[(EDBP)Mg(THF)]_2$ (**3**), have been synthesized and characterized by X-ray diffraction. Compound **1** has been demonstrated to efficiently catalyze the ROP of ϵ-caprolactone, and it has paved a way to synthesize as much as 500-fold polymer chains of PCL with very narrow PDI in the presence of a small amount of **1**. Compounds **1**−**3** have been demonstrated to efficiently catalyze the ROP of L-lactide. Furthermore, an effective method to prepare PCL-*b*-PLA, MPEG-*b*-PLA, and PS-*b*-PLA by the ring-opening copolymerization of ϵ-caprolactone and L-lactide catalyzed by magnesium aryloxides has been reported.

Experimental Section

General Procedures. All manipulations were carried out under a dry nitrogen atmosphere. Solvents, ϵ-caprolactone, L-lactide, styrene, benzyl alcohol, and deuterated solvents were purified before use. 2,2′-Ethylidenebis(4,6-di-*tert*-butylphenol) and Mg^nBu_2 (1.0 M in heptane) were purchased and used without further purification. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury-400 (400 MHz) or a Varian Gemini-200 (200 MHz) spectrometer with chemical shifts given in parts per million from the peak for internal TMS. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument. Infrared spectra were obtained from a Bruker Equinox 55 spectrometer. The GPC measurements were performed on a Hitachi L-7100 system equipped with a differential Bischoff 8120 RI detector using THF (HPLC grade) as an eluent. Molecular weight and molecular weight distributions were calculated using polystyrene as standard.

$[(MCIMP)_2Mg_2(THF)]_2$ (1). To an ice cold solution (0 °C) of 2,2′-methylenebis(4-chloro-6-isopropyl-3-methylphenol) (0.76 g, 2.0 mmol) in tetrahydrofuran (20 mL) was slowly added a Mg^nBu_2 (2.2 mL, 1.0 M in heptane, 2.2 mmol) solution. The mixture was stirred for 3 h and was then concentrated in vacuo. The residue was extracted with tetrahydrofuran (25 mL), and the extract was then concentrated to ca. 10 mL. Colorless crystals were obtained on cooling to −20 °C overnight. Yield: 1.12 g (64%). Anal. Calcd for $C_{92}H_{112}Cl_8Mg_4O_{10}$: C, 62.83; H, 6.42. Found: C, 62.15; H, 6.86. ^1H NMR ($CDCl_3$, ppm): δ 7.11−7.26 (m, 8H, Ph); 4.08 (s, 8H, $-CH_2-$); 3.64 (br, 8H, $-OCH_2CH_2$); 3.05 (m, 8H, $-CH(CH_3)_2$); 2.36 (m, 24H, $-CH_3$); 1.82 (br, 8H, $-OCH_2CH_2$); 1.22 (d, 48H, $-CH(CH_3)_2$).

$[(EDBP)Mg(Et_2O)]_2$ (2). To an ice cold solution (0 °C) of 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) (0.88 g, 2.0 mmol) in diethyl ether (20 mL) was slowly added a Mg^nBu_2 (2.2 mL, 1.0 M in heptane, 2.2 mmol) solution. The mixture was stirred for 2 h and was then concentrated in vacuo. The residue was extracted with hot hexane (30 mL), and the extract was then concentrated to ca. 15 mL. Colorless crystals were obtained on cooling to −20 °C overnight. Yield: 0.91 g (85%). Anal. Calcd for $C_{68}H_{108}Mg_2O_6$: C; 76.32, H, 10.17. Found: C, 76.70; H, 10.96. ^1H NMR ($CDCl_3$, ppm): δ 7.44−7.05 (m, 8H, Ph); 4.71 (q, 2H, $CH(CH_3)$, J = 6.8 Hz); 3.74 (q, 8H, OCH_2CH_3, J = 7.2 Hz); 1.58 (d, 6H, $CH(CH_3)$, J = 7.2 Hz); 1.52−1.15 (m, 72H, $C(CH_3)_3$); 0.96 (t, 12H, OCH_2CH_3, J = 7.2 Hz).

$[(EDBP)Mg(THF)]_2$ (3). To an ice cold solution (0 °C) of 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) (0.88 g, 2.0 mmol) in tetrahydrofuran (20 mL) was slowly added a Mg^nBu_2 (2.2 mL, 1.0M in heptane, 2.2 mmol) solution. The mixture was stirred for 2 h and was then concentrated in vacuo. The residue was extracted with toluene (20 mL), and the extract was then concentrated to ca. 10 mL. Colorless crystals were obtained on cooling to −20 °C overnight. Yield: 0.93 g (87%). Anal. Calcd for $C_{68}H_{104}Mg_2O_6$: C; 76.60, H, 9.83. Found: C, 78.33; H, 10.89. ^1H NMR ($CDCl_3$, ppm): δ 7.41−7.01 (m, 8H, Ph); 4.70 (q, 2H, $CH(CH_3)$, J = 6.8 Hz); 3.71 (br, 8H, OCH_2CH_3); 1.86 (br, 8H, OCH_2CH_3) 1.69 (d, 6H, $CH(CH_3)$, J = 6.8 Hz); 1.60, 1.33, 1.29, 1.24 (m, 72H, $C(CH_3)_3$).

Polymerization of ϵ-Caprolactone Catalyzed by 1. A typical polymerization procedure was exemplified by the synthesis of PCL-50 (the number 50 indicates the designed $[CL]_0/[BnOH]_0$) at 56 °C. The conversion yield (99%) of PCL-50 was analyzed by ^1H NMR spectroscopic studies. To a rapidly stirred solution of $[(MCIMP)_2Mg_2(THF)]_2$ (**1**) (0.088 g, 0.05 mmol) in toluene (5 mL) was added a mixture of ϵ-caprolactone (0.53 mL, 5 mmol) and benzyl alcohol (0.01 mL, 0.1 mmol). The reaction mixture was stirred for 1 h, during which time an increase in viscosity was observed. The reaction was then quenched by the addition of an aqueous acetic acid solution (0.35 N, 10 mL), and the polymer was precipitated on pouring the mixture into *n*-hexane (40 mL) to give white crystalline solids.

Polymerization of L-Lactide Catalyzed by 2. A typical polymerization procedure was exemplified by the synthesis of PLA-50 (the number 50 indicates the designed $[LA]_0/[BnOH]_0$) at 83 °C. The conversion yield (92%) of PLA-50 was analyzed by ^1H NMR spectroscopic studies. To a rapidly stirred solution of $[(EDBP)Mg(Et_2O)]_2$ (**2**) (0.054 g, 0.05 mmol) in 1,2-dichloroethane (4 mL) was added a mixture solution of L-lactide (0.72 g, 5 mmol) and benzyl alcohol (0.01 mL, 0.1 mmol). The reaction mixture was refluxed for 2 h, during which time an increase in viscosity was observed. The reaction was then quenched by the addition of an aqueous acetic acid solution (0.35 N, 10 mL), and the polymer was precipitated on pouring the mixture into *n*-hexane (40 mL) to give white crystalline solids. Yield: 0.59 g (82%).

Synthesis of Diblock Copolymer MPEG-*b*-PLA. To a rapidly stirred solution of $[(MCIMP)_2Mg_2(THF)]_2$ (**1**) (0.088 g, 0.05 mmol) in toluene (7 mL) was added a mixture of poly(ethylene glycol) methyl ether (M_w = 5000, PDI = 1.04) (0.5 g, 0.1 mmol) and L-LA (0.72 g, 5 mmol) in toluene (8 mL). The reaction mixture was refluxed for 8 h, during which time 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 (50 mL). The white solid was precipitated from a mixed hexane/MeOH (5:1) solvent twice and was dried under vacuum, giving a white solid. Yield: 0.77 g (63%).

Synthesis of 4-Hydroxy-TEMPO-Terminated Polystyrene. A typical free radical polymerization procedure was exemplified by the synthesis of PS−OH. A mixture of styrene (69 mL, 600 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 purified by a CH_2Cl_2 (40 mL)/MeOH (200 mL) mixture solution twice and collected by vacuum filtration to give white solids. The final solid was washed with 100 mL of MeOH and dried in vacuo overnight to yield 31.22 g of PS−OH (yield 76%). M_n

= 28900 and PDI = 1.13. ^{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*-PLA. To a rapidly stirred solution of $[(EDBP)Mg(Et_2O)]_2$ (**2**) (0.054 g, 0.05 mmol) in 1,2-dichloroethane (15 mL) was added a mixture of 4-hydroxy-TEMPO-terminated polystyrene (M_w = 28900, PDI = 1.13) (2.89 g, 0.1 mmol) and L-LA (0.72 g, 5 mmol) in 1,2-dichloroethane (15 mL). The reaction mixture was refluxed for 5 h, during which time 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 (100 mL). The white solid was precipitated from a mixed hexane/MeOH (5:1) solvent twice and was dried under vacuum, giving a white solid. Yield: 2.92 g (81%).

X-ray Crystallographic Studies. Suitable crystals of **1**−**3** were sealed in thin-walled glass capillaries under a nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. Intensity data were collected in 1350 frames with increasing *w* (width of 0.3° per frame). The absorption correction was based on the symmetry-equivalent reflections using SADABS program. The space group determination was based on a check of the Laue symmetry and systematic absences, and was confirmed using the structure solution. The structure was solved by direct methods using a SHELXTL package. All non-H atoms were located from successive Fourier maps, and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms.

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Supporting Information Available: For **1**−**3**, 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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