Synthesis, Characterization, and Catalytic Studies of Lithium Complexes: Efficient Initiators for Ring-Opening Polymerization of L-Lactide

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ABSTRACT: The reaction of 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) (EDBP-H_2) with ^{n}BuLi in tetrahydrofuran (THF), giving [(EDBP-H)Li(THF)$_3$] (**1**) in high yield. However, the reaction of EDBP-H_2 with ^{n}BuLi in the presence of benzyl alcohol (BnOH) in diethyl ether or tetrahydrofuran produces compounds [(EDBP-H)Li(BnOH)]$_2$ (**2**) and [(EDBP-H)Li(BnOH)(THF)$_2$] (**3**), respectively. Further reaction of **2** with excess of THF produces **3**. Alternatively, **3** can also be prepared by the reaction of benzyl alcohol with **1** in toluene. Experimental results show that **2** and **3** efficiently initiate the ring-opening polymerization (ROP) of L-lactide in a controlled fashion, yielding polymers with very narrow polydispersity indexes in a wide range of monomer-to-initiator ratios. Block copolymers, polystyrene-*b*-poly(L-lactide), have also been prepared from the ring-opening polymerization of L-latide catalyzed by **3** using polystyrene as a macroinitiator.

Introduction

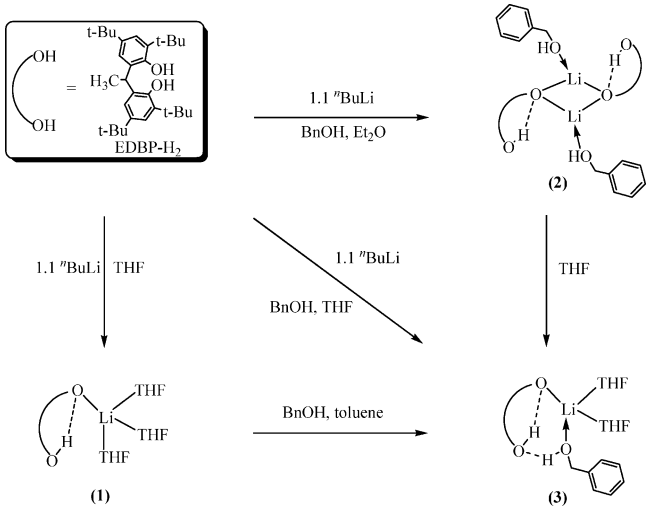
In recent years polylactides (PLAs) are of great interest for their applications in the medical field due to the biodegradable, biocompatible, and permeable properties.[1] The major polymerization method employed to synthesize these polymers has been the ring-opening polymerization (ROP) of lactides.[2] Aluminum alkoxides,[3] stannous,[4] yttrium,[5] and trivalent lanthanide derivatives[6] are effective initiators for ROP of lactones/lactides. It is important for developing new catalytic systems to obtain more compatible catalysts with the purpose of biomedical applications. Therefore, there has been increasing interest in the development of efficient and lower cytotoxic catalyts systems for the preparation of poly(ϵ-caprolactone) (PCL) and PLA. As a result, several alkali metal compounds such as butyllithium, lithium *tert*-butoxide, and potassium *tert*-butoxide have been used to polymerize L-lactide and *rac*-lactide.[7] In addition, many magnesium, zinc,[8] and lithium alkoxides have also been prepared and shown to be active toward the ROP of lactides.[9]

Most recently, a series of novel lithium aggregates with a bulky ligand, 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) (EDBP-H_2), have been synthesized and have shown great reactivity toward ROP of L-lactide in our laboratory.[10] This bulky ligand is designed to provide a steric barrier around active lithium ions for minimizing the side reaction. We report herein the synthesis, characterization, and catalytic studies of several novel lithium species. The catalytic activities of [(EDBP-H)Li(BnOH)]$_2$ toward ROP of L-lactide was also presented. Experimental results show that the lithium compound catalyzes the polymerization of L-lactide in "living" characterization, yielding PLA with very narrow polydispersity indexes (PDIs) in a wide range of monomer-to-initiator ratios.

Results and Discussion

Synthesis and Characterization. The reaction of 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) (EDBP-H_2) with ^{n}BuLi in tetrahydrofuran (THF) produces [(EDBP-H)Li(THF)$_3$] (**1**), as shown in Scheme 1. However, the reaction of EDBP-H_2 with ^{n}BuLi in the presence of benzyl alcohol (BnOH) in diethyl ether afforded [(EDBP-H)Li(BnOH)]$_2$ (**2**), a highly efficient initiator for ROP of L-lactide. When the dinuclear species **2** dissolves in tetrahydrofuran, it further reacts with THF at ambient temperature, giving a mononuclear [(EDBP-H)Li(BnOH)(THF)$_2$] (**3**). Alternatively, **3** can also be prepared directly by the reaction of EDBP-H_2 with ^{n}BuLi in the presence of benzyl alcohol in THF or by the reaction of compound **1** with benzyl alcohol in toluene. Formation of these complexes has been confirmed by ^{1}H and ^{13}C NMR spectroscopy as well as X-ray structural determination. For instance, in the ^{1}H NMR spectrum of **1**, a quartet resonance for methine proton (C(7)-hydrogen, Figure 1) locates at 5.35 ppm (1 H), and a triplet resonance for THF (OCH_2CH$_2$−) locates at 3.42 ppm. The ratio between these two peaks is 1:12,

Scheme 1. Preparation of Compounds 1−3[a]



[a] Abbreviations: ^{n}BuLi (*n*-butyllithium), BnOH (benzyl alcohol), Et_2O (diethyl ether), THF (tetrahydrofuran).

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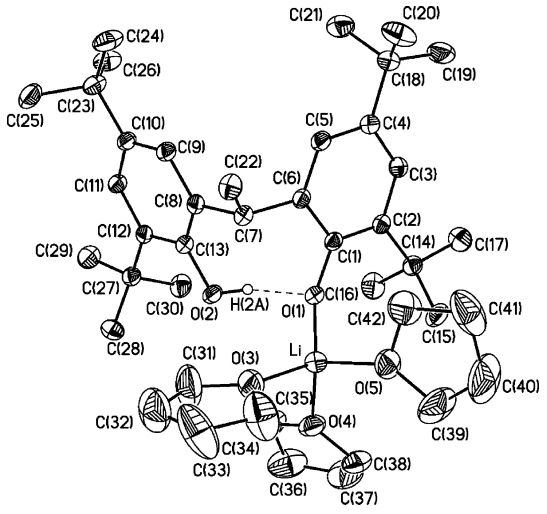


Figure 1. Molecular structure of [(EDBP-H)Li(THF)$_3$] **(1)** as 20% ellipsoids (all of the hydrogen atoms cxcept H(2A) are omitted for clarity). Selected bond lengths (Å): Li−O(1) 1.855(5), Li−O(3) 2.018(6), Li−O(4) 1.988(5), Li−O(5) 1.989-(5), H(2A)−O(1) 1.631.

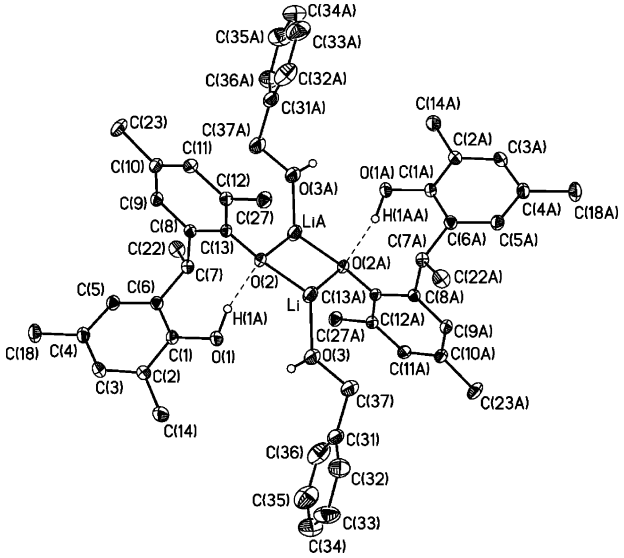


Figure 2. Molecular structure of [(EDBP-H)Li(BnOH)]$_2$ **(2)** as 20% ellipsoids (methyl carbons of the *tert*-butyl groups and all of the hydrogen atoms except H(1A) and H(3A) are omitted for clarity). Selected bond lengths (Å): Li−O(2) 1.819(4), Li−O(3) 1.897(4), Li−O(2A) 1.910(4), O(2)−Li(A) 1.910(4), H(1A)−O(2) 1.762.

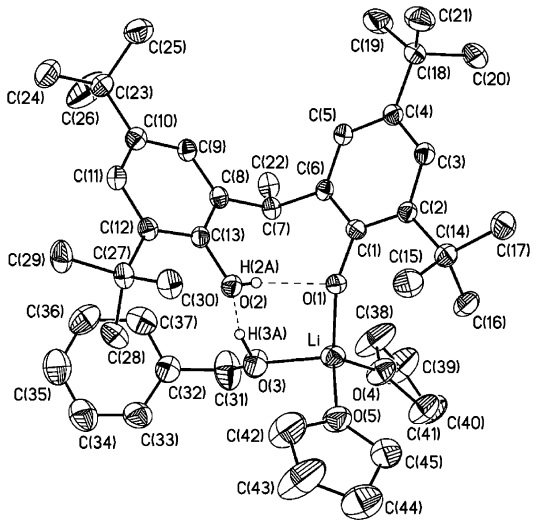
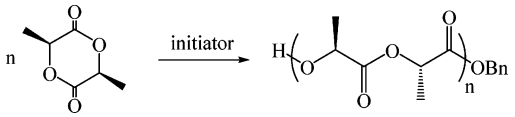


Figure 3. Molecular structure of [(EDBP-H)Li(BnOH)(THF)$_2$] **(3)** as 20% ellipsoids (all of the hydrogen atoms except H(2A) and H(3A) are omitted for clarity). Selected bond lengths (Å): Li−O(1) 1.888(7), Li−O(3) 1.981(8), Li−O(4) 1.919(8), Li−O(5) 1.972(8), H(2A)−O(1) 1.889, H(3A)−O(2) 1.757.

demonstrating a EDBP-H/THF ratio of 1:3 in compound **1**. In the ^{1}H NMR of **2**, a broad resonance for methine proton (C(7)-hydrogen, Figure 2) locates at 5.06 ppm (1 H), and a singlet resonance for benzyl alkoxy (OCH_2Ph) locates at 3.99 ppm. The ratio between these two peaks is 1:2, illustrating a EDBP-H/BnOH ratio of 1:1 in compound **2**. The ^{1}H NMR of compound **3** is similar to those of compounds **1** and **2**, as supported by the presence of a quartet resonance for methine proton (C(7)-hydrogen, Figure 3) at 5.57 ppm (1 H), a singlet resonance for benzyl alkoxy (OCH_2Ph) at 4.15 ppm, and a triplet resonance for THF (OCH_2CH$_2$−) at 3.41 ppm. The ratio between these three peaks is 1:2:8, consistent with an EDBP-H/BnOH/THF ratio of 1:1:2 in compound **3**.

Single crystals suitable for X-ray structural determination of compound **1** are obtained from slow cooling of a hexane solution, and its molecular structure is shown in Figure 1. Compound **1** is monomeric in which the lithium atom is four-coordinated bonded to the phenoxy oxygen of the EDBP-H ligand and oxygen of three tetrahydrofuran molecules. The phenol oxygen does not coordinate to lithium. However, an intramolecular hydrogen bond was observed between the phenoxy

Table 1. Ring-Opening Polymerization of L-Lactide Initiated by Compounds 2 and 3 in CH_2Cl_2



entry	$[M]_0/[I]_0/[ROH]$	initiator	time (h)	temp (°C)	PDI	M_n(obsd)[a]	M_n(calcd)[b]	M_n(NMR)[c]	conv (%)[c]	yield (%)
1	50/1/0	**2**	1	25	1.16	15900 (9200)	7300	7500	>99	73
2	25/1/0	**2**	2	0	1.07	5500 (3200)	3500	3100	93	79
3	50/1/0	**2**	2	0	1.04	10300 (6000)	6700	5900	91	76
4	100/1/0	**2**	2	0	1.08	22800 (13200)	13400	11100	92	85
5	200/1/0	**2**	2	0	1.05	41100 (23800)	26500	22100	92	88
6	25(25)/1/0	**2**	2 (2)[d]	0	1.04	10800 (6300)	6800	6200	93	82
7	200/1/8	**2**	1	0	1.14	6500 (3800)	3200	3600	98	88
8	400/1/32	**2**	1	0	1.11	3800 (2200)	1800	1800	99	83
9	25/1/0	**3**	3	0	1.05	6300 (3700)	3400	3600	92	71

[a] Obtained from GPC analysis and calibrated by polystyrene standard. Values in parentheses are the values obtained from GPC times 0.58.[14] [b] Calculated from the molecular weight of L-LA times $[M]_0/[I]_0$ times conversion yield. [c] Obtained from ^{1}H NMR analysis. [d] Prepolymerization of L-LA with **2** for 2 h, followed by the addition of another portion of L-LA.

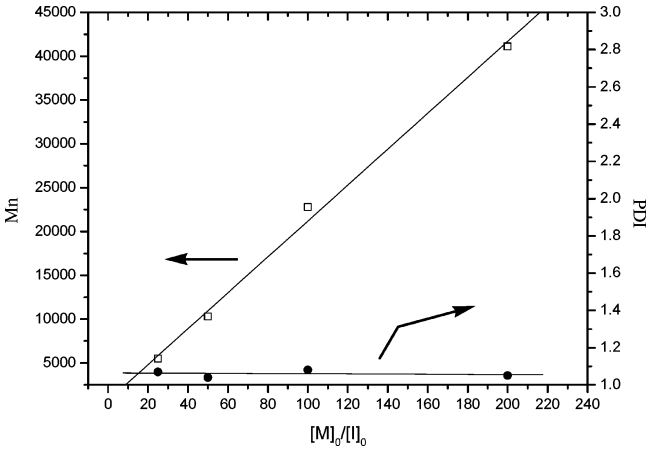


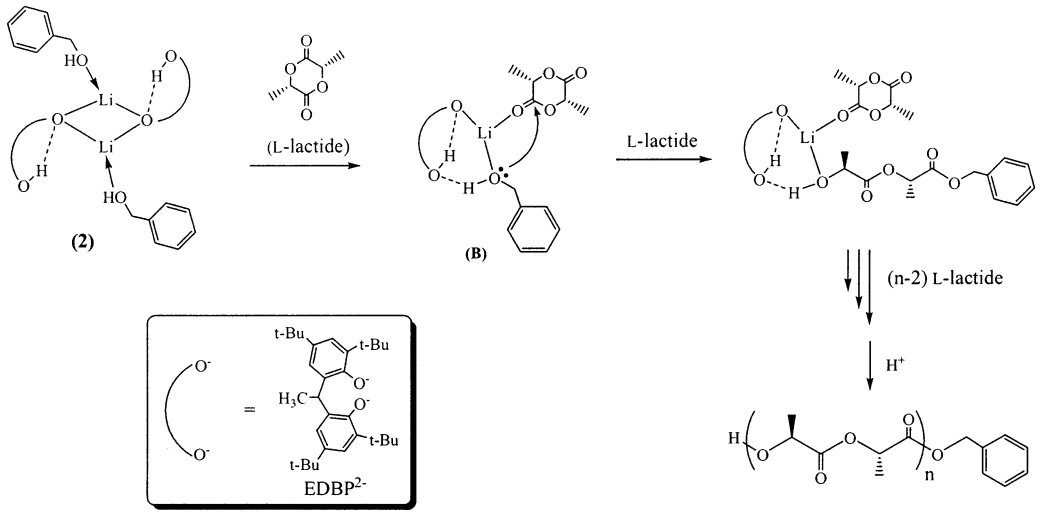
Figure 4. Polymerization of L-lactide initiated by [(EDBP-H)Li(BnOH)]$_2$ (**2**) in CH_2Cl_2 at 0 °C. The relationship between molecular weight (M_n (□), GPC) and polydispersity index (PDI (●)) of the polymer vs the initial molar ratio $[M]_0/[I]_0$ ($[M]_0$: the initial concentration of L-LA, $[I]_0$: the initial concentration of **2**).

oxygen and phenol group of the EDBP with H (2A)···O (1) of 1.618 Å and the nearly linear O(2)−H(2A)···O(1) angle at 166.9°. The crystal structure of **2** consists of two equivalent Li atoms, and each Li is three-coordinated bonded by two-bridged phenoxy oxygen atoms of two EDBP-H ligands and the oxygen atom of benzyl alcohol (Figure 2). There is an intramolecular hydrogen bond between the phenol group and the phenoxy oxygen atom of the EDBP-H ligand with H(1A)···O(2) distances of 1.762 Å and the nearly linear O(1)−H(1A)···O(2) angle at 165.0°. The molecular structure of compound **3** consists of one four-coordinated Li atom, where the Li atom is bonded to the phenoxy oxygen atom of the EDBP-H ligand and two THF oxygens and one benzyl alcohol with Li−O(1) 1.885(6), Li−O(3) 1.985(7), Li−O(4) 1.922(7), and Li−O(5) 1.967(7) Å, as illustrated in Figure 3. Similar to compounds **1** and **2**, an intermolecular hydrogen between two oxygen atoms of the EDBP-H group is observed in compound **3** with an H(2A)···O(1) distance of 1.724 Å and the nearly linear O(2)−H(2A)···O(1) angle at 169.7°. It is worth noting that a hydrogen bond between benzyl alcohol and phenol oxygen atom of EDBP-H$^-$ ligand exists with an H(3A)···O(2) distance of 1.902 Å along with O(3)−H(3A)···O(2) angle at 156.4°.

Ring-Opening Polymerization of L-Lactide. Recently, we have found that lithium alkoxide coordinated with sterically bulky ligands can effectively catalyze ring-opening polymerization of L-lactide at low temperature, giving PLA with very narrow molecular weight distribution.[10] In this context, ROP of L-lactide employing **2** as an initiator is systematically examined in CH_2Cl_2 at 0 and 25 °C, as shown in Table 1. Experimental results show that compound **2** is an efficient catalyst for the ROP of L-lactide. Coversion of L-lactide goes to >91% within 2 h at ambient temperature (entries 1−5) with very narrow polydispersity indexes (PDI), and the reaction rate decreases with the decrease in temperature (entries 1 and 3). A linear relationship between the number-average molecular weight (M_n) and the monomer-to-initiator ratio ($[M_0]/[I_0]$) existed (Figure 4), implying the controlled characterization of the polymerization process that is further confirmed by the polymerization resumption experiment (entry 6). Compound **2** catalyzes ROP of L-lactide with a number of polymer molecules exceeding the number of initiator molecules (entries 7 and 8). The polymerization of L-lactide was initiated with **2** in the presence of benzyl alcohol as the chain transfer agent. Preliminary results show that as much as 32-fold of BnOH can be added, resulting in a polymer with very low polydispersity and a molecular weight (M_n) of only 1/33 of that without the addition of BnOH.

The ^{1}H NMR spectrum of PLA was obtained in order to determine the molecular weight and chain end of PLA. Peaks at 7.32 ppm ($C_6H_5CH_2$−) and 4.38 ppm (HOC*H*Me−) with an integral ratio of 5:1 between H_e and H_c (see Supporting Information) indicate the polymer chain should be capped with one benzyl ester and one hydroxy end, suggesting that the polymerization occurs through the insertion of benzyl alkoxy group into the lactide. The molecular weight of PLA, M_n(NMR), is calculated on the basis of the ratio between the integration of peak at 7.32 ($C_6H_5CH_2$−) and 1.58 ($CHCH_3$). Furthermore, epimerization of the chiral centers in PLA does not occur as observed by the homonuclear-decoupled ^{1}H NMR studies in the methine region. Compound **3** has also shown excellent activity toward the ROP of L-lactide (entry 9). However, the reaction rate is somewhat slower than that of **2**, probably due to the existence of THF retarding the coordination of LLA to lithium.

Scheme 2. Proposed Mechanism for Ring-Opening Polymerization of L-Lactide Initiated by Compound 2



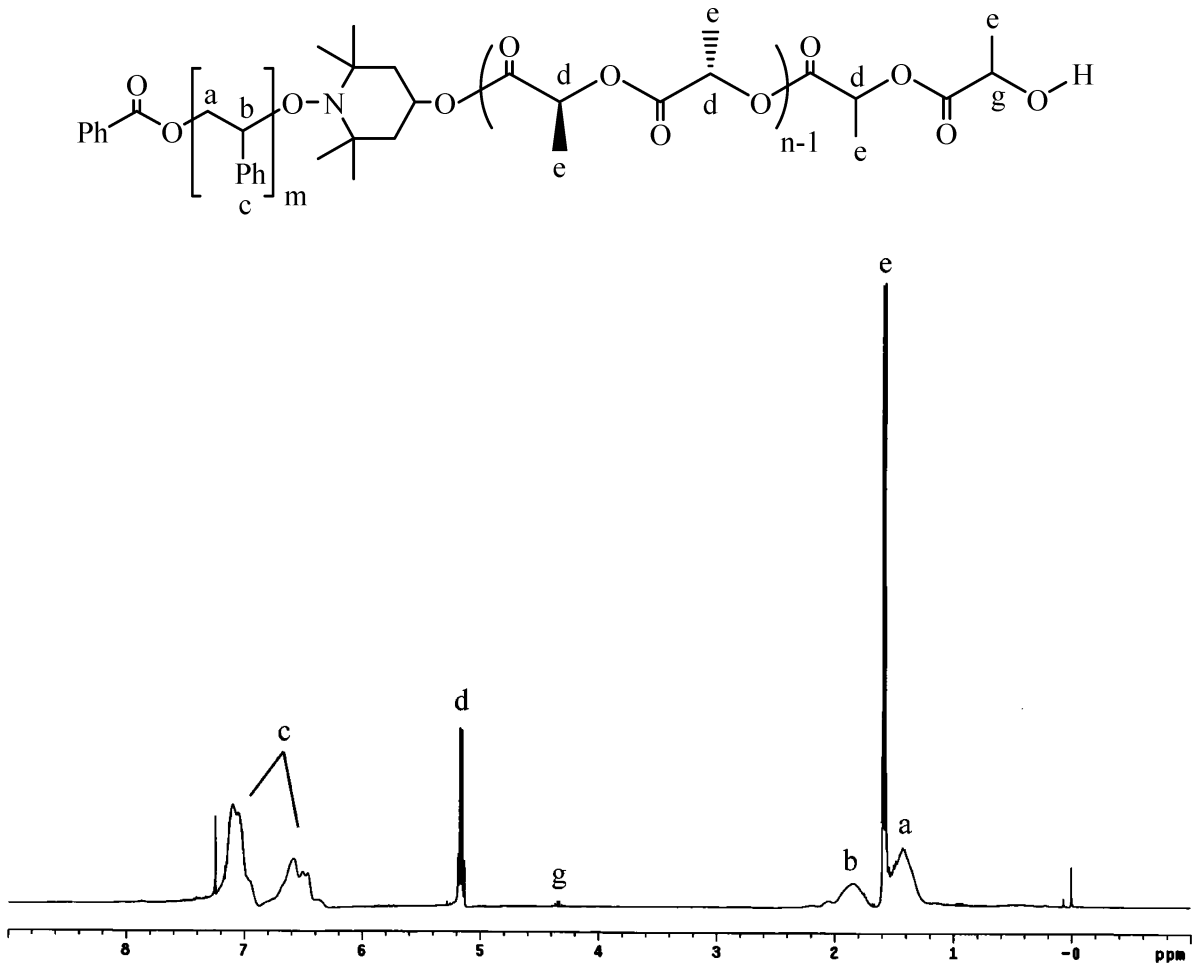


Figure 5. ^{1}H NMR spectrum of PS-*b*-PLA diblock copolymer in $CDCl_3$ catalyzed by [(EDBP-H)Li(THF)$_3$] (**1**) (see Experimental Section). The *m*/*n* ratio of PS and PLLA can be calculated from the integration ratio between peaks c and peak d.

On the basis of the catalytic and structural studies of compounds **2** and **3**, we believe that, during polymerization of L-LA, the coordination of L-LA to the dimeric compound **2** gives the monomeric intermediate (**B**). Followed by the insertion of a benzyl alkoxy group, in which benzyl alcohol is activated by the formation of a hydrogen bond through the terminal oxygen atom of EDBP-H, to the carbonyl group of L-LA leads to the ring-opening polymerization, as shown in Scheme 2. Activation of benzyl alcohol by the formation of hydrogen bond has been observed and verified by theoretical studies of a magnesium complex.[11]

Synthesis of Diblock Copolymer PS-*b*-PLA. Mesoporous polystyrene monoliths have been prepared from the hydrolysis of PS-*b*-PLA block copolymer.[12] These morphologies may provide new applications of block copolymers in the field of nanotechnologies. However, developing a convenient synthetic route to copolymers with control over molecular weight is a challenging task in material chemistry research. Most recently, we have prepared PS-*b*-PLA block copolymers through the controlled ring-opening polymerization of L-lactide using a lithium complex in the presence of PS as a macroinitiator. We reported here a new catalyst for the preparation of PS-*b*-PLA copolymer.

Polystyrene with 4-hydroxy-TEMPO terminal was synthesized by a free radical polymerization approach similar to the method reported by Georges et al.[13] 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 = 12 500) with low polydispersity (PDI = 1.12). Block copolymer of PS and PLA was further prepared by the ring-opening polymerization of L-lactide catalyzed by **1** using PS as a macroinitiator. In the ^{1}H NMR spectrum of PS-*b*-PLA (Figure 5), a broad signal in the aromatic region and the typical triplets at 1.84 and 5.18 ppm shows the block nature of the PS-*b*-PLA copolymer. Moreover, in the GPC profile (Figure 6) peak A corresponds to polystyrene (M_n = 12 500, PDI = 1.12), and peak B corresponding to PS-*b*-PLA after polymerization with 100 equiv of L-LA increase in molecular weight (M_n = 34 200, PDI = 1.12) was observed (peak B) to confirm the formation of block copolymer.

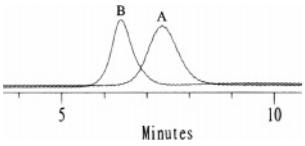


Figure 6. GPC profiles of copolymerization of PS-*b*-PLA diblock copolymer: (peak A) the prepolymer, PS-OH (M_n = 12 500, PDI = 1.12); (peak B) after block copolymerization of PS-*b*-PLA (M_n = 34 200, PDI = 1.12).

In conclusion, several novel lithium compounds (**1**−**3**) have been synthesized and structurally characterized. Among them, compound **1** is an efficiently catalyst for the preparation of PS-*b*-PLA copolymer, and

compounds **2** and **3** have demonstrated to efficiently initiate the "controlled" ROP of L-lactide.

Experimental Section

General Considerations. All manipulations were carried out under a dry nitrogen atmosphere. ^{1}H spectra were recorded on a Varian Mercury-400 (400 MHz) spectrometer with chemical shifts given in ppm from the internal TMS. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument. The gel permeation chromatography (GPC) measurements were performed on a Hitachi L-7100 system equipped with a differential Bischoff 8120 RI detector and 5 μm PL gel columns (Phenomenex; 100 Å) in series. The GPC columns were eluted with tetrahydrofuran at 30 °C at 1 mL/min and were calibrated using a polynomial fit to 10 monodisperse polystyrene standards.

Materials. Hexane (99%, A.C.S. reagent, TEDIA), toluene (99%, A.C.S. reagent, TEDIA), diethyl ether (99%, A.C.S. reagent, TEDIA), and tetrahydrofuran (99%, A.C.S. reagent, SHOWA) were distilled from sodium/benzophenone under nitrogen, while methylene chloride (99%, A.C.S. reagent, SHOWA) was distilled from P_2O_5 under nitrogen. Styrene monomer (99%, Lancaster) and benzyl alcohol (99%, Aldrich) were first treated with CaH_2 powder (95%, Aldrich) for a few days to remove dissolved water and then distilled under vacuum. 2,2′-Ethylidenebis(4,6-di-*tert*-butylphenol) and ^{n}BuLi (2.5 M in hexane) were purchased and used as such without further purification. L-Lactide (98%, Aldrich) was recrystallized from toluene twice and stored in a drybox.

[(EDBP-H)Li(THF)$_3$] (1). ^{n}BuLi (0.88 mL, 2.5 M in hexane, 2.2 mmol) was added slowly to an ice cold (0 °C) solution of 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) (0.88 g, 2.0 mmol) in tetrahydrofuran (20 mL). The mixture was stirred for 1 h, and the volatile materials were removed under vacuum. The residue was extracted with warm hexane (20 mL), and the extract was then concentrated to ca. 10 mL. Colorless crystals were obtained on cooling to −20 °C overnight. Yield: 1.2 g (88%). Anal. Calcd for $C_{42}H_{69}LiO_5$: C, 76.32; H, 10.52. Found: C, 76.29; H, 10.42%. ^{1}H NMR (C_6D_6, ppm): δ 7.55, 7.33 (s, 4H, *Ph*); 5.35 (br, 1H, −C*H*(CH$_3$)); 3.42 (t, 12H, −OC*H*$_2$CH$_2$−, J = 6.0 Hz); 1.68 (br, 3H, −CH(C*H*$_3$)); 1.52 (s, 18H, −CH(C*H*$_3$)$_3$); 1.35−1.29 (m, 30H, −C(C*H*$_3$)$_3$, −OCH$_2$C*H*$_2$−).

[(EDBP-H)Li(BnOH)]$_2$ (2). ^{n}BuLi (0.88 mL, 2.5 M in hexane, 2.2 mmol) was added slowly to an ice cold (0 °C) mixed solution of 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) (0.88 g, 2.0 mmol) and benzyl alcohol (0.21 mL, 2.0 mmol) in diethyl ether (20 mL). The mixture was stirred for 1 h, and the volatile materials were removed under vacuum. The residue was extracted with warm toluene (20 mL), and the extract was then concentrated to ca. 10 mL. Colorless crystals were obtained on cooling to −20 °C overnight. Yield: 0.90 g (81%). Anal. Calcd for $C_{74}H_{106}Li_2O_6$: C, 80.40; H, 9.66. Found: C, 79.92; H, 9.53%. ^{1}H NMR (C_6D_6, ppm): δ 7.33−6.89 (m, 18H, *Ph*); 5.06 (br, 2H, −C*H*(CH$_3$)); 3.99 (s, 4H, −C*H*$_2$Ph); 1.68 (d, 6H, −C*H*(CH$_3$), J = 6.8 Hz); 1.56, 1.44, 1.32 (s, 72H, −C(C*H*$_3$)$_3$).

[(EDBP-H)Li(BnOH)(THF)$_2$] (3). Method A: [(EDBP-H)-Li(BnOH)]$_2$ (1.11 g, 1.0 mmol) was rapidly stirred in THF (20 mL) at 25 °C for 1 h, and the volatile materials were removed under vacuum. The residue was extracted with hot hexane (30 mL), and the extract was concentrated to ca. 20 mL. Colorless crystals were obtained on cooling to −20 °C overnight. Yield: 1.1 g (78%). Anal. Calcd for $C_{45}H_{69}LiO_5$: C, 77.55; H, 9.98. Found: C, 77.56; H, 9.72%. ^{1}H NMR (C_6D_6, ppm): δ 7.54−7.00 (m, 9H, *Ph*); 5.57 (q, 1H, −C*H*(CH$_3$), J = 7.2 Hz); 4.15 (s, 2H, −C*H*$_2$Ph); 3.41 (t, 8H, −OC*H*$_2$CH$_2$−, J = 6.8 Hz); 1.70 (d, 3H, −C*H*(CH$_3$), J = 7.2 Hz); 1.47−1.30 (m, 48H, −C(C*H*$_3$)$_3$, −OCH$_2$C*H*$_2$−).

Method B: ^{n}BuLi (0.88 mL, 2.5 M in hexane, 2.2 mmol) was added slowly to an ice cold (0 °C) mixed solution of 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) (0.88 g, 2.0 mmol) and benzyl alcohol (0.21 mL, 2.0 mmol) in THF (20 mL). The mixture was stirred for 1 h, and the volatile materials were removed under vacuum. The residue was extracted with warm hot hexane (30 mL), and the extract was then concentrated to ca. 20 mL. Colorless crystals were obtained on cooling to −20 °C overnight. Yield: 1.0 g (73%).

Method C: Benzyl alcohol (0.21 mL, 2.0 mmol) was added to a rapidly stirred solution of [(EDBP-H)Li(THF)$_3$] (1.35 g, 2.0 mmol) in toluene (20 mL) at 25 °C. The mixture was stirred for 1 h, and the volatile materials were removed under vacuum. The residue was extracted with hot hexane (30 mL), and the extract was then concentrated to ca. 20 mL. Colorless crystals were obtained on cooling to −20 °C overnight. Yield: 1.05 g (75%).

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 0 °C. The conversion yield (91%) of PLA-50 was analyzed by ^{1}H NMR spectroscopic studies. To a rapidly stirred solution of [(EDBP-H)Li(BnOH)]$_2$ (**2**) (0.055 g, 0.05 mmol) in dichloromethane (4 mL) was added a mixture solution of L-lactide (0.72 g, 5.0 mmol) in dichloromethane (6 mL). The reaction mixture was stirred for 2 h, during which an increase in viscosity was observed. The mixture was then quenched by the addition of an aqueous acetic acid solution (0.35 N, 10 mL), and the polymer was precipitated on pouring into *n*-hexane (50 mL) to give white crystalline solids. Yield: 0.55 g (76%).

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 (29 mL, 250 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 an 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 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 by 100 mL of MeOH and dried in vacuo overnight to yield 19.51 g of PS-TEMPO-OH (yield: 74%). M_n = 12 500 and PDI = 1.12. ^{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-H)Li(THF)$_3$] (**1**) (0.066 g, 0.1 mmol) in dichloromethane (15 mL) was added a mixture of 4-hydroxy-TEMPO-terminated polystyrene (M_w = 12 500, PDI = 1.12) (1.25 g, 0.1 mmol) and l-LA (1.44 g, 10 mmol) in dichloromethane (15 mL). The reaction mixture was reacted for 3 h, during which an increase in viscosity was observed. After the reaction was quenched by the addition of an excess acetic acid aqueous solution (10 mL, 0.35 N), the polymer was precipitated into *n*-hexane (100 mL). The white solid was precipitated from a mixed *n*-hexane/CH_2Cl_2 (5:1) solvent twice and was dried under vacuum, giving a white solid. Yield: 2.07 g (77%). M_n = 34 200 and PDI = 1.12. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.46−7.09 (br, 5H, ArH); 5.16 (q, 1H, CH(CH$_3$), J = 7.2 Hz); 1.84 (br, 1H, CH); 1.58 (d, 1H, CH(CH$_3$), J = 7.2 Hz); 1.42 (br, 2H, CH_2).

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 ω (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: Tables giving full details of the crystal data **1**−**3** and ^{1}H NMR spectrum of PLA-50. This material is available free of charge via the Internet at http://pubs.acs.org.

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