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Synthesis, Characterization, and Catalysis of Mixed-Ligand Lithium Aggregates, Excellent Initiators for the Ring-Opening Polymerization of L-Lactide

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Abstract: Three novel mixed-ligand lithium aggregates, $[(\mu_3\text{-EDBP})Li_2]_2[(\mu_3\text{-}^nBu)Li(0.5Et_2O)]_2$ (**1**), $[(\mu_3\text{-EDBP})Li_2]_2[(\mu_3\text{-OBn})Li]_2$ (**2**), and $[(\mu_3\text{-EDBP})Li_2]_2[(\mu_3\text{-OCH}_2CH_2OCH_2CH_3)Li]_2$ (**3**), have been synthesized and structurally characterized. The reaction of 2,2′-ethylidene-bis(4,6-di-*tert*-butylphenol) (EDBP-H$_2$) with 3.6 molar equiv of ^nBuLi gives **1** in high yield. **1** further reacts with benzyl alcohol and 2-ethoxyethanol respectively to yield the corresponding products **2** and **3**. Experimental results show that **2** and **3** efficiently initiate the ring-opening polymerization of L-lactide in a controlled fashion, yielding polymers with very narrow polydispersity indexes in a wide range of monomer-to-initiator ratios.

Introduction

Alkyllithiums and lithium alkoxides play an important role in organic syntheses due to their applications as alkylating and deprotonating reagents and also as catalysts in polymerization.[1] In particular, the complexes derived from RLi and MOR named as superbases such as $^nBuLi\cdot KO^tBu$ have been shown to be extremely useful in organic syntheses.[2] It is well known that complexes [RLi·LiOR] are prepared from the reactions of organolithium compounds with alcohols and have the tendency to form oligomeric structures in the solid state.[3] The first crystal structure of RLi·LiOR, $[CH_3(CH_2)_3Li\cdot LiOC(CH_3)_3]_4$, was reported by Boche et al. in 1990.[4] Since then, only a few of RLi· LiOR aggregates have been structurally characterized.[5]

Because of its biodegradable, biocompatible, and permeable properties, polylactide (PLA) is of great interest for many applications in the medical field.[6] The major polymerization method employed to synthesize these polymers has been the ring-opening polymerization (ROP) of lactides. Aluminum alkoxides[7] are often used for the controlled polymerization of lactones; however, they exhibit low activity in lactide polym-

erization. Zinc,[8] stannous,[9] yttrium[10] and trivalent lanthanide derivatives[11] have been reported to be effective initiators of ROP of lactones/lactides giving polymers with both high molecular weights and high yields. However, the cytotoxicity and difficulties in removal of the catalyst from the resulting polymer have limited their utilization when a medical-grade polymer is required. Recently, magnesium alkoxides have also been reported to be active toward the ROP of lactides.[12]

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Scheme 1
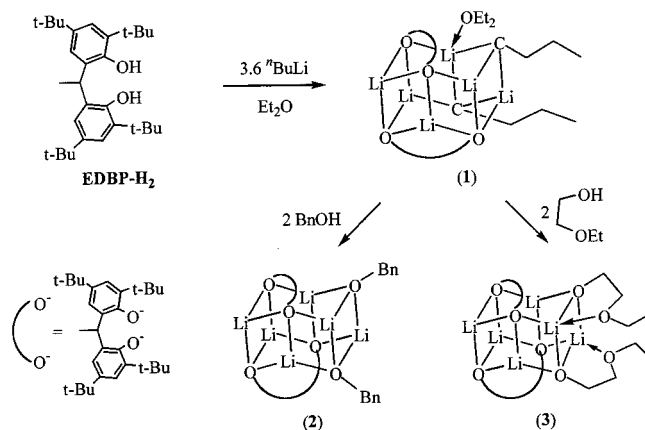
Recently, we became interested in understanding the role of lithium alkoxide addition to alkyllithium as well as its reactivity, and as a result we report herein the synthesis, characterization, and catalytic studies of novel lithium derivatives $[(\mu_3\text{-EDBP})\text{Li}_2]_2[(\mu_3\text{-}^n\text{Bu})\text{Li}(0.5\text{Et}_2\text{O})]_2$ (**1**), $[(\mu_3\text{-EDBP})\text{Li}_2]_2[(\mu_3\text{-OBn})\text{Li}]_2$ (**2**), and $[(\mu_3\text{-EDBP})\text{Li}_2]_2[(\mu_3\text{-OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_3)\text{Li}]_2$ (**3**).

Results and Discussion

Syntheses and Crystal Structure Studies. The unusual lithium aggregate, $[(\mu_3\text{-EDBP})\text{Li}_2]_2[(\mu_3\text{-}^n\text{Bu})\text{Li}(0.5\text{Et}_2\text{O})]_2$ (**1**), is obtained as a white crystalline solid in 89% yield from the reaction of 2,2′-ethylidene-bis(4,6-di-*tert*-butylphenol) (EDBP−H$_2$) with 3.6 molar equiv of ^{n}BuLi in diethyl ether, followed by the removal of solvent and crystallization from hexane as shown in Scheme 1. Compound **1** stands as the first example in which ^{n}BuLi forms an aggregate in the presence of lithium biphenoxides and has been characterized by spectroscopic studies as well as by X-ray structure determination. Although many syntheses of lithium alkoxides have been reported, their structural characterization is greatly limited in the literature when it comes to lithium phenoxides.[13] The crystal structure of **1** consists of two six-membered, Li$_3$O$_2$C, rings linked by three Li$_2$O$_2$, two Li$_2$OC, and Li$_2$C$_2$ cores as displayed in Figure 1. Both of the oxygen atoms of two EDBP ligands are bridged to three lithium atoms. It is interesting to note that two ^{n}Bu groups are unequally coordinated to two lithium atoms with average distances of Li(3)−C 2.146(10) Å and Li(4)−C 2.306(10) Å. The asymmetric coordination of these two ^{n}Bu groups is compensated by the coordination of an excess diethyl ether on Li(4), thereby making Li(4) four-coordinated.

The ^{n}Bu groups coordinated to lithium in compound **1** can be replaced by almost any alkoxy group without any dramatic changes in its skeleton. The reaction of compound **1** with 2 molar equiv of benzyl alcohol (BnOH) at ambient temperature yields $[(\mu_3\text{-EDBP})\text{Li}_2]_2[(\mu_3\text{-OBn})\text{Li}]_2$ (**2**) in 75% yield. As depicted in Figure 2, the hexanuclear species **2** consists of three different kinds of three-coordinated Li atoms, where Li(1) and Li(6) are bonded to the two oxygen atoms of two EDBP ligands. Li(2) and Li(5) are each bonded to one oxygen atom of two
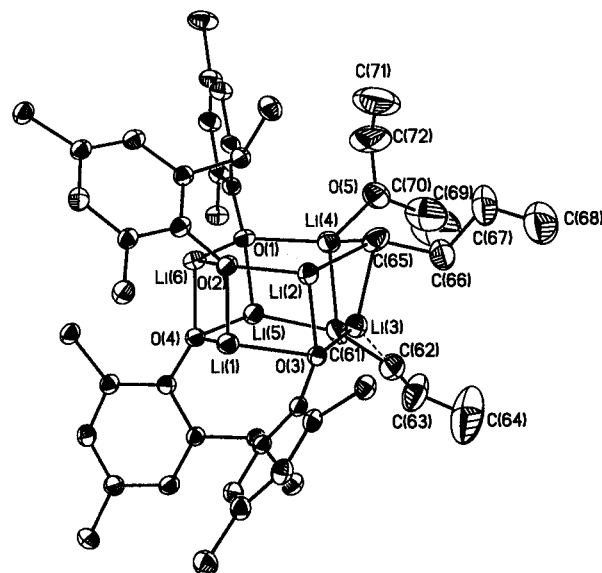
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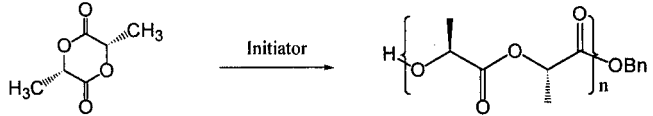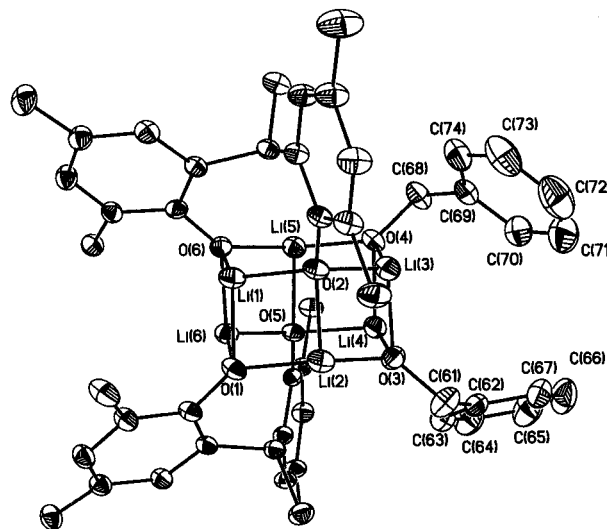

Figure 1. Molecular structure of **1** as 10% ellipsoids (methyl carbons of the *tert*-butyl groups and all of the hydrogen atoms are omitted for clarity). Selected bond lengths (Å): Li(1)−O(2) 1.885(7), Li(1)−O(3) 2.045(7), Li(1)−O(4) 1.900(7), Li(2)−O(2) 1.825(7), Li(2)−O(3) 1.927(7), Li(2)−C(65) 2.135(10), Li(3)−O(3) 1.849(8), Li(3)−C(61) 2.128(9), Li(3)−C(65) 2.164(10), Li(3)−C(62) 2.353(8), Li(4)−O(1) 2.043(8), Li(4)−O(5) 2.064(8), Li(4)−C(61) 2.318(10), Li(4)−C(65) 2.293(10), Li(5)−O(1) 1.876(7), Li(5)−O(4) 1.944(7), Li(5)−C(61) 2.131(9), Li(6)−O(1) 1.909(7), Li(6)−O(2) 2.177(7), Li(6)−O(4) 1.865(7).

Figure 2. Molecular structure of **2** as 20% ellipsoids (methyl carbons of the *tert*-butyl groups and all of the hydrogen atoms are omitted for clarity). Selected bond lengths (Å): Li(1)−O(1) 1.891(5), Li(1)−O(2) 1.877(6), Li(1)−O(6) 2.077(6), Li(2)−O(1) 1.862(6), Li(2)−O(2) 1.920(6), Li(2)−O(3) 1.867(6), Li(3)−O(2) 1.930(6), Li(3)−O(3) 1.896(6), Li(3)−O(4) 1.947(6), Li(4)−O(3) 1.918(6), Li(4)−O(4) 1.911(6), Li(4)−O(5) 1.964(6), Li(5)−O(4) 1.836(6), Li(5)−O(5) 1.943(5), Li(5)−O(6) 1.865(6), Li(6)−O(1) 2.075(5), Li(6)−O(5) 1.876(5), Li(6)−O(6) 1.891(5).

EDBP groups and one OBn group, and Li(3) and Li(4) are each bonded to one EDBP oxygen and two OBn groups. All of the six oxygen atoms are triply bridged. It is worth noting that Li(1), Li(2), Li(5), and Li(6) atoms are surrounded by the sterically bulky EDBP ligands, but Li(3) and Li(4) are rather sterically less hindered; therefore, these two Li atoms attain the ability to act as Lewis acids. Indeed, the reaction of compound **1** with 2 molar equiv of 2-ethoxyethanol yields $[(\mu_3\text{-EDBP})$-

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Table 1. Ring-Opening Polymerization of L-Lactide Initiated by Complex **2** or **3**

entry	initiator	$[M]_o/[I]_o$	CH_2Cl_2 (mL)	temp (°C)	time (h)	M_w/M_n	M_n (GPC)[a]	M_n (calcd)[b]	M_n (NMR)[c]	conv (%)[c]
1	**2**	150	10	25	1	1.43	22100 (12800)	10800		>99
2	**2**	150	20	25	1	1.24	15200 (8800)	10300		95
3	**2**	50	10	0	6	1.06	6300 (3700)	3500	3600	98
4	**2**	100	10	0	6	1.07	12000 (7000)	6900	7200	96
5	**2**	150	10	0	6	1.11	16700 (9700)	10400		98
6	**2**	200	10	0	6	1.12	23900 (13900)	14100		98
7	**2**	50 (50)[d]	10	0	6 (6)	1.11	11200 (6500)	7200	7400	99
8	**3**	100	10	0	6	1.06	12400 (7200)	6800	6800	95

[a] Obtained from GPC analysis and calibrated by polystyrene standard. Values in parentheses are the values obtained from GPC times 0.58.[18] [b] Calculated from the molecular weight of L-lactide times $[M]_o/2[I]_o$ times conversion yield. [c] Obtained from ¹H NMR analysis. [d] Prepolymerization of LA with **2** for 6 h, followed by the addition of another portion of LA.
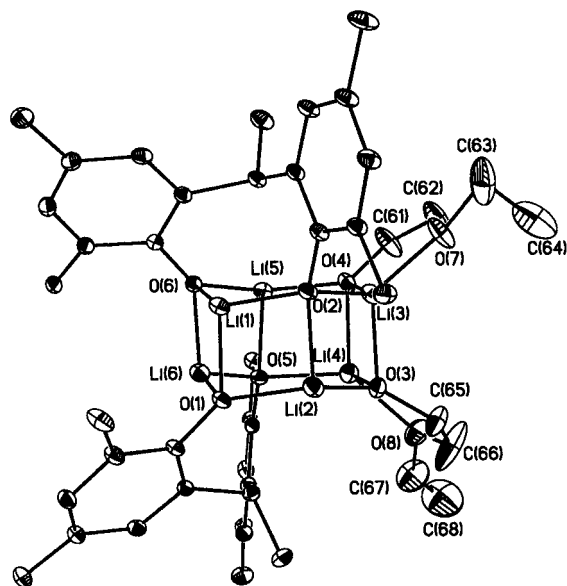

Figure 3. Molecular structure of **3** as 10% ellipsoids (methyl carbons of the *tert*-butyl groups and all of the hydrogen atoms are omitted for clarity). Selected bond lengths (Å): Li(1)−O(2) 1.869(8), Li(1)−O(1) 1.892(7),Li(1)−O(6) 2.146(8), Li(2)−O(3) 1.818(9), Li(2)−O(1) 1.881(8), Li(2)−O(2) 1.943(8), Li(3)−O(2) 2.034(9), Li(3)−O(7) 1.931(9), Li(3)−O(3) 1.933(9), Li(3)−O(4) 1.949(10), Li(4)−O(3) 1.951(9), Li(4)−O(4) 1.961(8), Li(4)−O(5) 2.024(9), Li(4)−O(8) 2.026(9), Li(5)−O(4) 1.836(8), Li(5)−O(6) 1.859(8), Li(5)−O(5) 1.914(7), Li(6)−O(5) 1.870(7), Li(6)−O(6) 1.882(8), Li(6)−O(1) 2.064(9).

$Li_2]_2[(\mu_3\text{-}OCH_2CH_2OCH_2CH_3)Li]_2$ (**3**). The X-ray structure determination of **3** reveals that its structure is similar to that of **2**, except that the oxygen atoms of two ethoxy groups are further coordinated to the sterically less hindered lithium atoms, Li(3) and Li(4) (Figure 3). This bonding makes Li(3) and Li(4) four-coordinated, whereas Li(1), Li(2), Li(5), and Li(6) are three-coordinated.

Ring-Opening Polymerization of L-Lactide. Though many lithium alkoxides have shown excellent catalytic activity toward ROP of lactones and lactides,[14] this process is often accompanied by backing reactions, leading to the formation of macrocycles and thereby resulting in very broad or multimodal molecular weight distribution. To solve this problem, several strategies have been designed. One successful approach is to use suitable
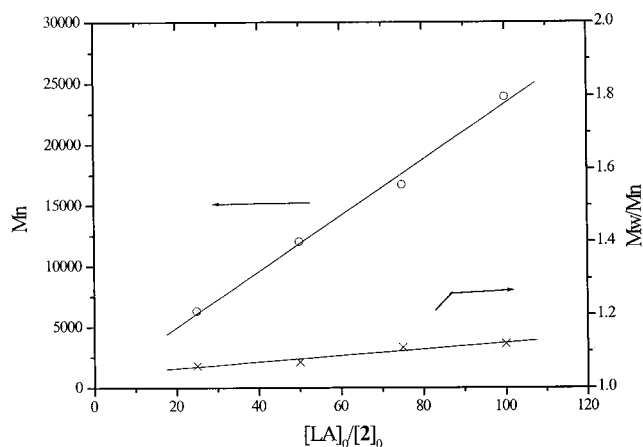

Figure 4. Polymerizatin of L-lactide initiated by **2** in CH_2Cl_2 at 0 °C. The relationship between M_n (○) (M_w/M_n (×)) of the polymer and initial mole ratio $[LA]_0/[2]_0$ is shown.

bulky ligands to interact coordinatively with the active initiating ion pair and therefore provide a steric barrier to a certain extent around that ion pair to minimize the side reactions. This strategy has been successfully applied in the anionic polymerization of (meth)acrylates[15] and the ring-opening polymerization of lactones/lactides.[16]

In this context, ROP of L-lactide employing **2** (0.05 mmol) as initiator is systematically examined in CH_2Cl_2 (10 mL) at 0 and 25 °C as shown in Table 1. It was found that complex **2** is an efficient initiator for the ROP of L-lactide. ROP of lactide goes to completion within 1 h at room temperature (entries 1 and 2), and the reaction rate decreases with the decrease in temperature (entries 3−6). However, the polydispersity indexes (PDIs) of poly(L-lactide)s obtained at 0 °C are quite narrow, ranging from 1.06 to 1.12, and a linear relationship between the number-average molecular weight (M_n) and the monomer-to-initiator ratio (M/I) existed (Figure 4), implying the controlled character of the polymerization process which is further confirmed by the polymerization resumption experiment (entry 7). It is worth noting that the ¹H NMR spectrum (Figure 5) of PLA shows one benzyl ester and one hydroxy chain end

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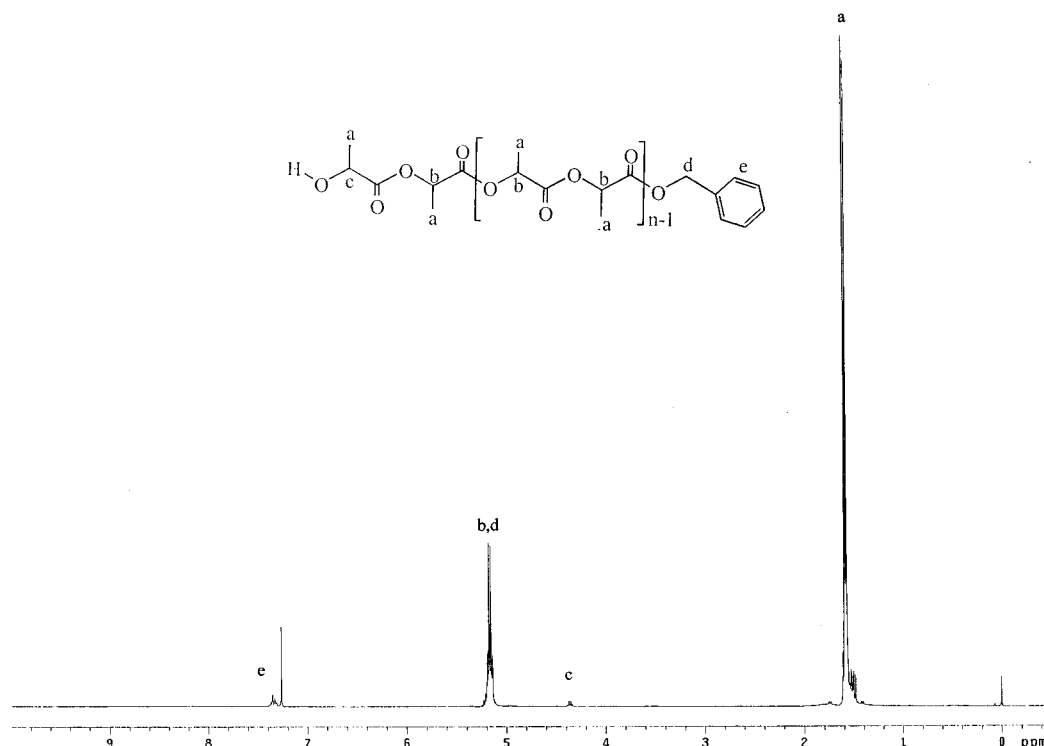
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(17) See Supporting Information.

(18) The M_n(GPC) is multiplied by a factor of 0.58, giving the actual M_n of polylactide. Baran, J.; Duda, A.; Kowalski, A.; Szymanski, R.; Penczek, S. *Macromol. Rapid Commun.* **1997**, *18*, 325.

Figure 5. ^{1}H NMR spectrum of PLA-50 initiated by complex **2**.

Scheme 2
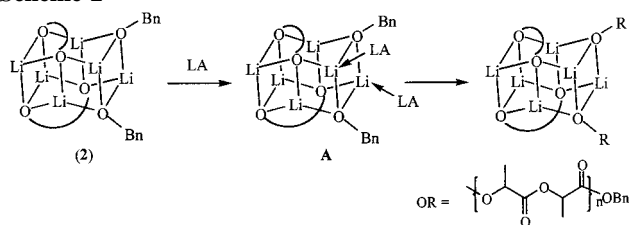
with an integral ratio of 5:1 between H_e and H_c, suggesting that the initiation occurs through the insertion of the benzyl alkoxy group from compound **2** into L-lactide and the backing reactions do not occur in our condition. This is further verified by the following experimental results. First, the homonuclear decoupled ^{1}H NMR spectrum reveals only one resonance at δ 5.16 ppm in the methine region.[17] Second, if cyclization occurs during polymerization, the PDIs of the resulting PLA will be much higher. However, the PDIs of the PLA obtained are in a very narrow range. Furthermore, epimerization of the chiral centers in PLA does not occur as observed by the homonuclear decoupled ^{1}H NMR studies in the methane region. The formation of **3** suggests that the ROP of L-lactide initiated by **2** may proceed by the coordination of L-lactide on Li(3) and Li(4), leading to intermediate **A**, followed by the attacking of the benzyl alkoxy group on the carbonyl group of lactide, as shown in Scheme 2. Additionally, compound **3** has also shown excellent activity toward the ROP of L-lactide (entry 8). Further study of its catalytic activity is currently underway.

In conclusion, we have discovered three novel lithium aggregates, and their structures have been characterized by X-ray diffraction. While these three compounds are potential catalysts toward polymerization, compounds **2** and **3** have been demonstrated to efficiently initiate the "controlled" ROP of L-lactide.

Experimental Section

General. All manipulations were carried out under a dry nitrogen atmosphere. Solvents, benzyl alcohol, 2-ethoxyethanol, L-lactide, and deuterated solvents were purified before uses. 2,2′-Ethylidene-bis(4,6-

di-*tert*-butylphenol) and *n*-BuLi (2.5 M in hexane) were purchased and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-300 (300 MHz for ^{1}H and 75 MHz for ^{13}C) or a Varian Gemini-200 (200 MHz for ^{1}H and 50 MHz for ^{13}C) spectrometer with chemical shifts given in ppm from the internal TMS or center 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 weight and molecular weight distributions were calculated using polystyrene as standard.

[(μ_3-EDBP)Li$_2$]$_2$[(μ_3-^{n}Bu)Li(0.5Et$_2$O)]$_2$ (1). To an ice cold solution (0 °C) of 2,2′-ethylidene-bis(4,6-di-*tert*-butylphenol) (0.88 g, 2.0 mmol) in diethyl ether (20 mL) was slowly added an *n*-BuLi (2.88 mL, 2.5 M in hexane, 7.2 mmol) solution. The mixture was stirred for 1 h and was then concentrated in vacuo. The residue was extracted with hot hexane (20 mL), and the extract was then concentrated to ca. 10 mL. Colorless crystals were obtained on cooling to −20 °C overnight. Yield: 0.98 g (89%). Anal. Calcd for$C_{72}H_{116}O_5Li_6$: C, 78.38; H, 10.6. Found: C, 78.03; H, 9.07. ^{1}H NMR (C_6D_6, ppm): δ 7.77, 7.64, 7.45, 7.25 (d, 8H, Ph); 5.66 (q, 2H, C*H*(CH$_3$), J = 7.2 Hz); 3.20 (q, 4H, OC*H$_2$*CH$_3$, J = 6.8 Hz); 1.71 (d, 6H, CH(C*H$_3$*), J = 7.2 Hz); 1.48−1.55 (m, 8H, C*H$_2$*CH$_2$); 0.99 (t, 6H, OCH$_2$C*H$_3$*, J = 6.8 Hz); 0.96 (t, 6H, CH$_2$C*H$_3$*); 1.51, 1.46, 1.34, 0.90 (s, 72H, C(CH$_3$)$_3$); −0.56 (m, 4H, LiC*H$_2$*).

[(μ_3-EDBP)Li$_2$]$_2$[(μ_3-OBn)Li]$_2$ (2). Benzyl alcohol (0.21 mL, 2 mmol) was added slowly to an ice cold solution (0 °C) of [(μ_3-EDBP)-Li$_2$]$_2$[(μ_3-^{n}Bu)Li(0.5Et$_2$O)]$_2$ (**1**) (1.10 g, 1.0 mmol) in toluene (20 mL). The mixture was stirred for 2 h and was then dried in vacuo. The residue was extracted with 25 mL of hot hexane, and the extract was then concentrated to ca. 10 mL and cooled to −20 °C to furnish a white crystalline solid. Yield: 0.85 g (75%). Crystals suitable for X-ray structure determination were obtained from a hot saturated toluene solution. Anal. Calcd for $C_{74}H_{102}O_6Li_6$: C, 78.71; H, 9.10. Found: C, 77.95; H, 9.01. ^{1}H NMR (C_6D_6, ppm): δ 7.83, 7.60, 7.48, 7.24 (d, 8H, Ph); 6.99−7.05 (m, 10H, Ph); 6.02 (q, 2H, C*H*(CH$_3$), J = 6.8 Hz); 4.73 (d, 2H, OC*H$_2$*Ph); 4.40 (d, 2H, OC*H$_2$*Ph); 1.75 (d, 6H, CH(C*H$_3$*), J = 6.8 Hz); 1.54, 1.42, 1.34, 0.90 (s, 72H, C(CH$_3$)$_3$).

[(μ_3-EDBP)Li$_2$]$_2$[(μ_3-OCH$_2$CH$_2$OEt)Li]$_2$ (3). 2-Ethoxyethanol (0.19 mL, 2 mmol) was added slowly to an ice cold solution (0 °C) of [(μ_3-

EDBP)Li$_2$]$_2$[(μ_3-^{n}Bu)Li(0.5Et$_2$O)]$_2$ (**1**) (1.10 g, 1.0 mmol) in toluene (20 mL). The mixture was stirred for 1 h and was then dried under vacuum. The residue was extracted with 30 mL of hot hexane, and the extract was then concentrated to ca. 15 mL and cooled to −20 °C to yield a white solid. Yield: 0.93 g (85%). Crystals suitable for X-ray diffraction were grown in a hot saturated toluene solution. Anal. Calcd for C$_{68}$H$_{106}$O$_6$Li$_6$: C, 74.71; H, 9.77. Found: C, 74.56; H, 9.70. ^{1}H NMR (C$_6$D$_6$, ppm): δ 7.75, 7.54, 7.43, 7.26 (d, 8H, Ph); 5.88 (q, 2H, C*H*(CH$_3$), J = 6.8 Hz); 3.99 (m, 4H, OC*H*$_2$CH$_2$OEt); 2.98 (m, 4H, OCH$_2$C*H*$_2$OEt); 3.29 (q, 4H, OC*H*$_2$CH$_3$); 1.70 (d, 6H, CH(C*H*$_3$), J = 6.8 Hz); 1.60, 1.54, 1.33, 0.99 (s, 72H, C(CH$_3$)$_3$); 0.61 (t, 6H, OCH$_2$C*H*$_3$).

Polymerization of L-Lactide Initiated by 2. A typical polymerization procedure was exemplified by the synthesis of PLA-100 (the number 100 indicates the designed [LA]$_0$/[**2**]$_0$) at 0 °C. The conversion yield (96%) of PLA-100 was analyzed by ^{1}H NMR spectroscopic studies. A solution of [(μ_3-EDBP)Li$_2$]$_2$[(μ_3-BnO)Li]$_2$ (**2**) (0.056 g, 0.05 mmol) in CH$_2$Cl$_2$ (4 mL) was added to a rapidly stirring solution of L-lactide (0.72 g, 5 mmol) in CH$_2$Cl$_2$ (6 mL). The reaction mixture was stirred at 0 °C for 6 h. Volatile materials were removed in vacuo, and the residue was redissoved in toluene (10 mL). 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 (40 mL) to give white crystalline solids. Yield: 0.62 g (86%).

X-ray Crystallographic Studies. Suitable crystals of **1**, **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° 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.

Supporting Information Available: Further details of the crystal structure determination of **1**, **2**, and **3** (CIF). ^{1}H NMR spectrum of PLA-100 initiated by **3** and the homonuclear decoupled ^{1}H NMR spectrum of PLA in the methine region (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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