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Synthesis and Structural Studies of Lithium and Sodium Complexes with OOO-Tridentate Bis(phenolate) Ligands: Effective Catalysts for the Ring-Opening Polymerization of L-Lactide

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A series of lithium and sodium complexes with OOO-tridentate bis(phenolate) ligands have been synthesized and fully characterized. The reaction of 2,2′-dihydroxy-3,3′,5,5′-tetrakis[(1-methyl-1-phenyl)ethyl]dibenzyl ether (L^1-H_2) with different ratios of ^{n}BuLi in toluene or tetrahydrofuran (THF) gave $[Li_2(L^1\text{-}H)_2]$ (**1**), $[Li_4L^1{}_2]$ (**2**), and $[Li_2L^1(THF)_3]$ (**3**), respectively. Similarly, $[Na(L^1\text{-}H)(THF)]$ (**4**), $[Na_2(L^1\text{-}H)]_2$ (**5**), and $[Na_4L^1{}_2]$ (**6**) were prepared by the reaction of L^1-H_2 and $NaN[Si(CH_3)_3]_2$ or sodium metal. In addition, the reaction of 2,2′-dihydroxy-3,3′,5,5′-tetra-*tert*-butyldibenzyl ether (L^2-H_2) with ^{n}BuLi in toluene or THF yields $Li_2(L^2\text{-}H)_2]$ (**7**) and $[Li_2(L^2\text{-}H)_2(THF)_2]$ (**8**), respectively. Further treatment of **7** with 2 mol equiv of benzyl alcohol provides $[Li_2(L^2\text{-}H)_2(BnOH)_2]$ (**9**). Complexes **1**−**4** and **6**−**9** have been structurally characterized by single-crystal X-ray analysis. The dinuclear nature of complexes **1** and **3** was confirmed from their molecular structure. Complexes **2** and **6** illustrate tetranuclear species; however, complex **4** shows a mononuclear feature. A p−π interaction exists from the phenyl ring of the 2-(methyl-1-phenylethyl) groups to the central metal in complexes **2**, **4**, and **6**, which could effectively stabilize the metal center. Among them, complexes **1**, **2**, and **5**−**9** displayed efficient catalytic behavior for the ring-opening polymerization of L-lactide in the presence of benzyl alcohol. Experimental results indicate that among these alkali-metal complexes, the sodium compound **6** displays a rapid catalytic polymerization of L-lactide in "living" fashion, yielding poly(L-lactide) with a controlled molecular weight and narrow polydispersity indices for a wide range of monomer-to-initiator ratios.

Introduction

Over the past 3 decades, poly(lactides) (PLAs) are of great interest for their potential applications in the medical field because of their biodegradable, biocompatible, and permeable properties.[1] The major polymerization method employed to prepare PLAs has been the ring-opening polymerization (ROP) of L-lactides in the presence of a metal catalyst.[2] A number of metal complexes, such as aluminum,[3] tin,[4] trivalent lanthanide,[5] iron,[6] magnesium,[7] zinc,[3f,7c−e,8]

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and titanium[9] derivatives, have been reported to be effective catalysts/initiators that catalyze the ROP of lactides, producing polymers with both high and controlled molecular weights. Recently, there have been increasing initiatives in the development of efficient and nontoxic catalysts that eliminate difficulties in the removal of the catalyst from the resulting PLAs that are targeted for biomedical applications.

Alkali-metal compounds, such as butyllithium, lithium *tert*-butoxide, and potassium *tert*-butoxide, have gained interest in catalytic transformations and were introduced for the polymerization of lactides.[10] In the past, a series of lithium and sodium complexes and multinuclear aggregates of lithium with bulky diol ligands have been developed, which demonstrated great potential toward the ROP of L-lactide at ambient temperature.[11] It was realized that the bulky ligands are indispensable for such metal complexes to provide a steric barrier around an alkali-metal center for minimizing the intra- and intermolecular transesterification side reactions in a polymerization.[11a,h]

We describe herein the synthesis and characterization of a series of novel lithium and sodium complexes **1**−**9** supported by OOO-tridentate bis(phenolate) ligands. X-ray structural studies of complexes **1**−**4** and **6**−**9** are also presented. Included in these studies are the experimental results of the polymerization of L-lactide in the presence of the alkali-metal complexes **1**, **2**, and **5**−**9** and benzyl alcohol (BnOH). We also describe how the catalytic performances of the complexes toward the ROP of L-lactide are related to their molecular structures.

Results and Discussion

Synthesis and Characterization. As shown in Scheme 1, the reaction of a OOO-tridentate bis(phenolate) ligand, 2,2′-dihydroxy-3,3′,5,5′-tetrakis[(1-methyl-1-phenyl)ethyl]-dibenzyl ether (L^1-H_2), with a stoichiometric amount of ^{n}BuLi in toluene provides the lithium complex $[Li_2(L^1\text{-}H)_2]$ (**1**) in good yield. The other lithium derivatives, $[Li_4L^1_2]$ (**2**) and $[Li_2L^1(THF)_3]$ (**3**; THF = tetrahydrofuran), were obtained from the reaction of complex **1** with a stoichiometric amount of ^{n}BuLi in toluene or in THF, respectively. When complex **2** is dissolved in THF, it further reacts with THF at ambient temperature, giving complex **3**. Alternatively, complexes **2** and **3** can also be prepared directly by the reaction of L^1-H_2 with 2 stoichiometric equiv of ^{n}BuLi in toluene or in THF, respectively.

Meanwhile, complex $[Na(L^1\text{-}H)(THF)]$ (**4**) can be prepared by the reaction of L^1-H_2 with a stoichiometric amount of $NaN[Si(CH_3)_3]_2$ in THF in 58% yield. When complex **4** is dissolved in toluene, it loses THF, forming a dinuclear species, $[Na_2(L^1\text{-}H)_2]$ (**5**), which can also be prepared directly by the reaction of L^1-H_2 with a stoichiometric amount of $NaN[Si(CH_3)_3]_2$ in toluene. Further reaction of complex **5** with a stoichiometric amount of $NaN[Si(CH_3)_3]_2$ in toluene results a tetranuclear complex, $[Na_4L^1_2]$ (**6**). In addition, the reaction of L^1-H_2 with excess sodium metal in Et_2O can also furnish compound **6** in high yield (81%).

Similarly, the reaction of 2,2′-dihydroxy-3,3′,5,5′-tetra-*tert*-butyldibenzyl ether (L^2-H_2) with a stoichiometric amount of ^{n}BuLi in toluene produces the lithium complex $[Li_2(L^2\text{-}H)_2]$ (**7**; Scheme 2). However, when L^2-H_2 reacts with ^{n}BuLi in THF, it yields a THF-coordinated product, $[Li_2(L^2\text{-}H)_2(THF)_2]$ (**8**). Further reaction of **7** with 2 mol equiv of BnOH gives $[Li_2(L^2\text{-}H)_2(BnOH)_2]$ (**9**). Alternately,

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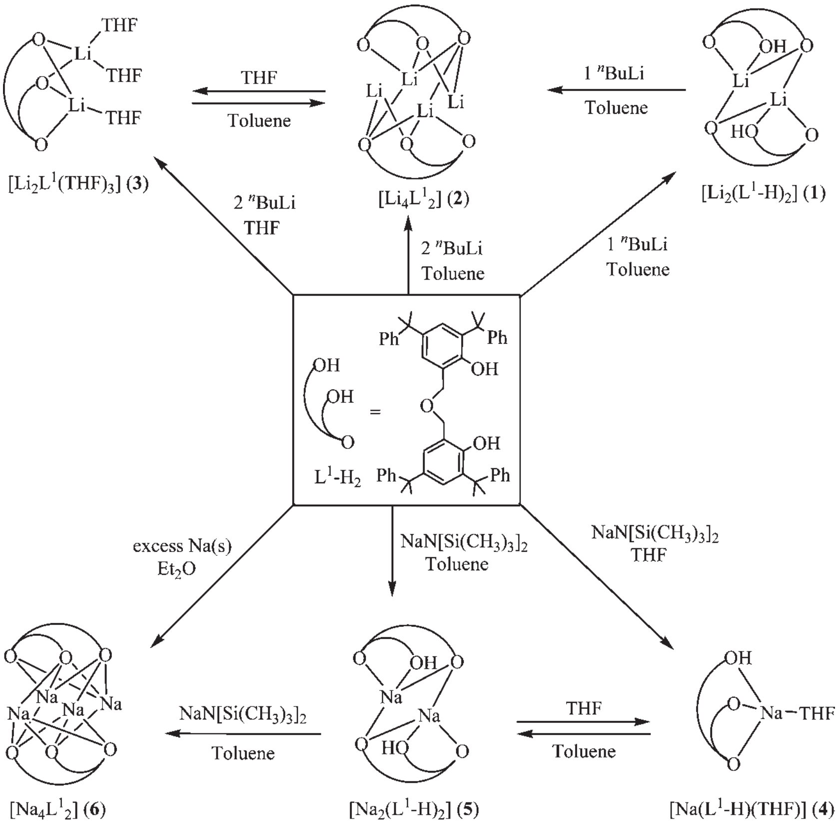
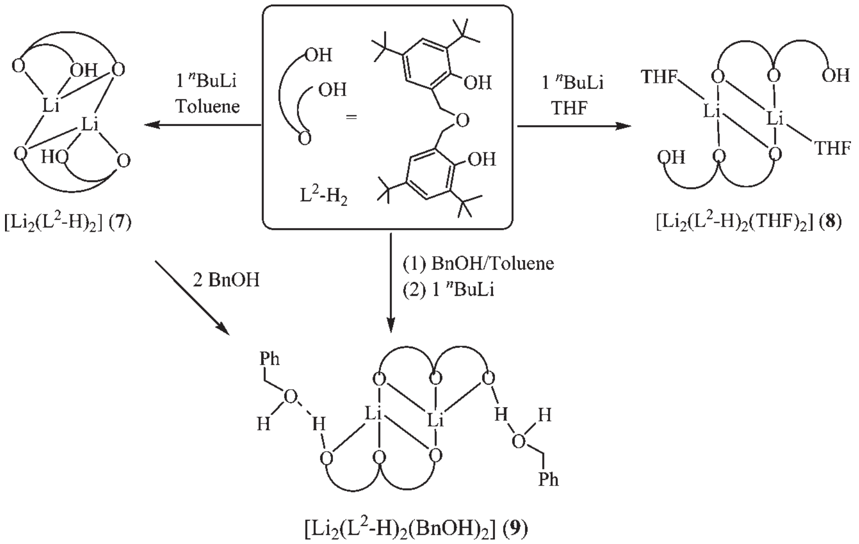
Scheme 1. Preparation of Lithium and Sodium Complexes **1**−**6**



Scheme 2. Preparation of Lithium Complexes **7**−**9**



compound **9** can be obtained by the reaction of ^{n}BuLi with a mixture of L^2-H_2/BnOH in toluene. All of these metal complexes have been characterized on the basis of ^{1}H and ^{13}C NMR spectroscopic studies, as well as by elemental analysis. The molecular structures of complexes **1**−**4** and **6**−**9** were confirmed by the X-ray structure determination of suitable single crystals.

Single crystals suitable for structural characterization of compounds **1** and **2** were obtained from slow cooling of a warm toluene solution, and the molecular structures of complexes **1** and **2** are shown in Figures 1 and 2, respectively. The molecular structure of **1** reveals a dinuclear feature in which lithium centers are tetracoordinated with the oxygen atoms of the OOO-tridentate ligand and the bridging oxygen atom of one phenolate group of the other ligand. The coordination geometry around lithium is a distorted tetrahedral, and the bridging phenolate binds to lithium asymmetrically, with Li−O(1) and LiA−O(1) bond distances of 1.919(4) and 1.839(4) Å, respectively. These three oxygen atoms of the OOO-tridentate ligand show a slight difference in coordination strength, with Li−O(1), Li−O(2), and Li−O(3) bond distances of 1.919(4), 1.984(4), and 2.096(4) Å, respectively. The Li−LiA separation of 2.449(7) Å is in good agreement with that of the previously described dilithium complex, bearing μ-O(phenolate) bridges.[11c,f] The molecular structure of complex **2** reveals a tetranuclear feature, in which two lithium centers, Li(1) and Li(1A), are tetracoordinated similarly to the structure of complex **1** and the other two lithium centers, Li(2) and Li(2A), are coordinated with the oxygen atoms of the phenolate groups of the ligands. With the presence of two other lithium centers, the bonds of the Li_2O_2 core become a little longer but the O(1)−Li(1)−O(3) angle has a dramatic decrease from 123.31(18)° to 96.44(13)°. It is worth noting that the phenyl ring of the 2-(methyl-1-phenylethyl) groups have p−π interaction to Li(2), with Li(2)−C(45), Li(2)−C(46), and Li(2)−C(50) bond distances of 2.474(3), 2.533(4), and 2.552(3) Å, respectively, which could effectively stabilize the lithium centers. The Li(1)−Li(1A) and Li(1)−Li(2) separations of 2.534(5) and 2.482(4) Å, respectively, are also in good agreement with those of the dilithium complex **1**.

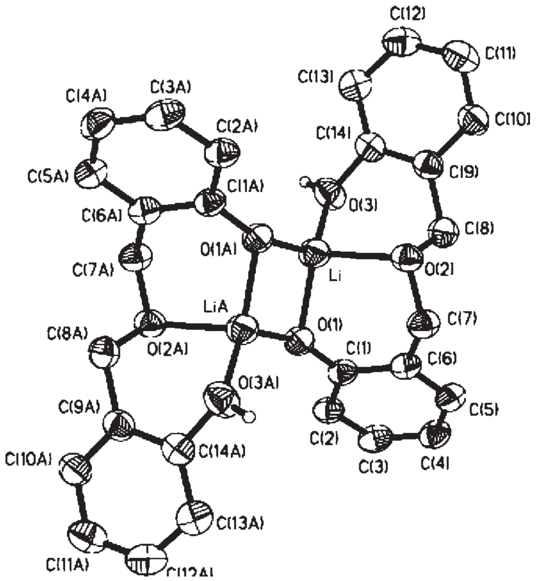


Figure 1. Molecular structure of complex **1** as 50% ellipsoids [the carbon atoms of the dimethylphenyl groups and all of the hydrogen atoms except H(3A) and H(3AA) were omitted for clarity].

Crystals suitable for the X-ray structure determination of complex **3** were obtained from a mixed hexane/THF (1:2) solution. With coordination of THF, the molecular structure of complex **3** illustrates a dinuclear mode in the solid state (Figure 3). The coordination geometry around each lithium center is a distorted tetrahedral. Li(1) is coordinated with the oxygen atoms of the OOO-tridentate ligand and one THF molecule, and Li(2) is coordinated with the oxygen atoms of the phenolate groups of the ligand and two other THF molecules. Crystals suitable for the X-ray structure determination of complex **4** were obtained from a mixed hexane/THF (1:2) solution. With coordination of THF, the molecular structure of complex **4** illustrates a mononuclear mode in the solid state (Figure 4). The sodium center is coordinated with the oxygen atoms of the OOO-tridentate ligand and one THF molecule. These four oxygen atoms show different coordination strengths, with Na−O(1), Na−O(2), Na−O(3), and Na−O(4) bond distances of 2.299(3), 2.366(2), 2.283(3), and 2.385(3) Å, respectively. Also, the phenyl rings of the ligand display p−π interaction to the sodium center, with Na−C(1), Na−C(14), and Na−C(19) bond distances of 2.871(4), 2.897(4), and 2.994(4) Å, respectively.

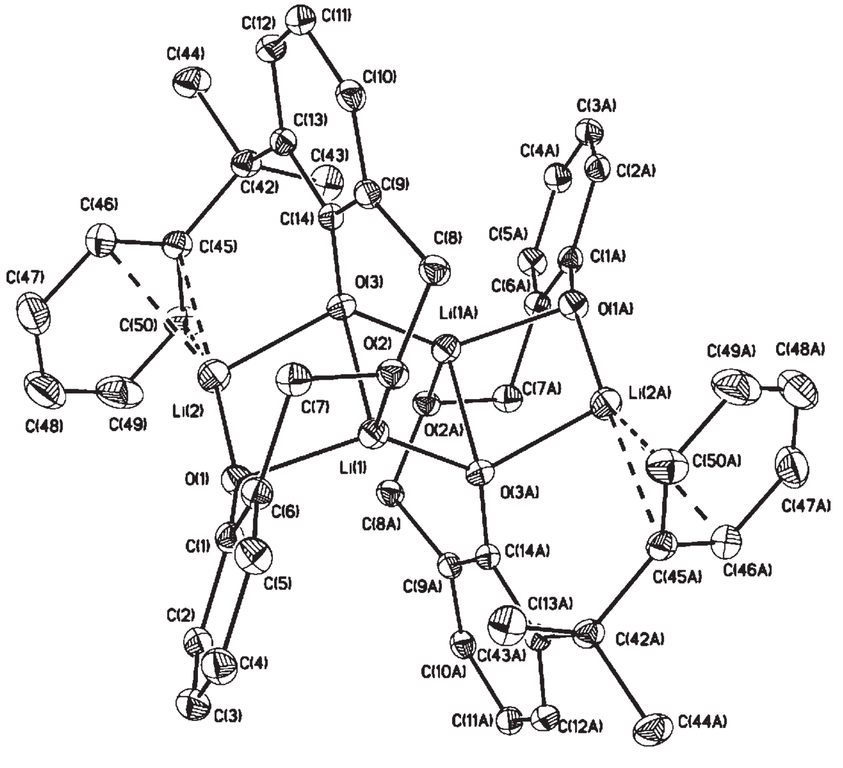


Figure 2. Molecular structure of complex **2** as 20% ellipsoids (the carbon atoms of some of the methyl-1-phenylethyl groups and all of the hydrogen atoms were omitted for clarity).

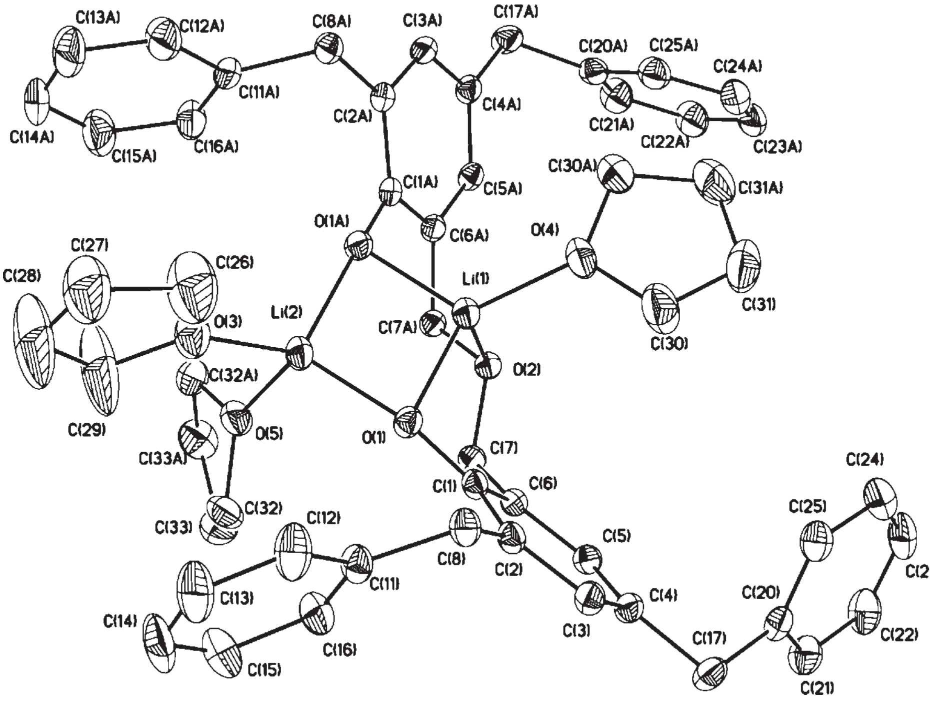


Figure 3. Molecular structure of complex **3** as 20% ellipsoids (the methyl carbon atoms of the methyl-1-phenylethyl groups and all of the hydrogen atoms were omitted for clarity).

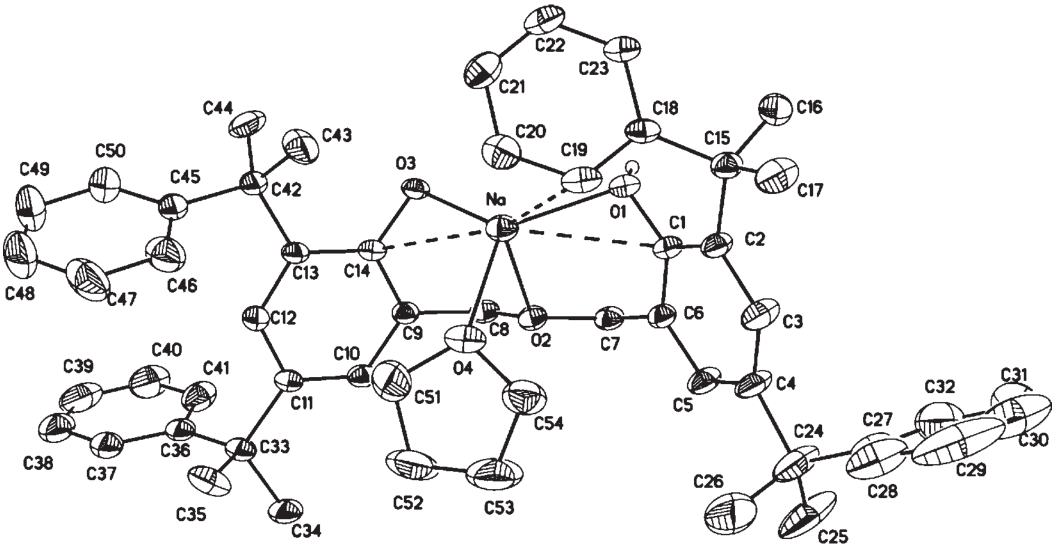


Figure 4. Molecular structure of complex **4** as 20% ellipsoids [all of the hydrogen atoms except phenol H(1A) were omitted for clarity].

The molecular structure of **6** illustrates an aggregation mode in the solid state with four sodium atoms (Figure 5) and a tetranuclear mode as in the case of complex **4**. There exists a significant difference as well between the structures of complexes **4** and **6** because of the larger size and more ionic character of the sodium ions compared with the lithium ions. Three oxygen atoms of the OOO-tridentate ligand are coordinated with two sodium centers, and each oxygen atom of the phenolate groups of the ligand acts as a bridging ligand coordinated to another sodium center, forming a Na_4O_6 core. It is interesting to note that each sodium ion is six-coordinated to four oxygen atoms and three carbon atoms of the phenyl rings of the OOO-tridentate ligand, with p−π interaction to the sodium center proven by the short distance between the sodium and carbon atoms, with Na(1)−C(45A), Na(1)−C(46A), and Na(1)−C(50A) distances of 2.788(3), 2.792(3), and 3.037(3) Å and Na(2)−C(18A), Na(2)−C(19A), and Na(2)−C(23A) distances of 2.721(2), 2.902(3), and 2.994(3) Å, respectively.

Single crystals suitable for the X-ray structure determination of complexes **7** and **8** were obtained from slow cooling of a warm toluene solution, and the molecular structures of complexes **7** and **8** are shown in Figures 6 and 7, respectively. The molecular structure of **7** is similar to that of compound **1**, revealing a dinuclear Li_2O_2 core in which lithium centers are tetracoordinated with the three donor oxygen atoms and the bridging oxygen atom of one phenolate group of the other bis(phenolate) ligand. Apart from binding of the bridging phenolate to lithium in an

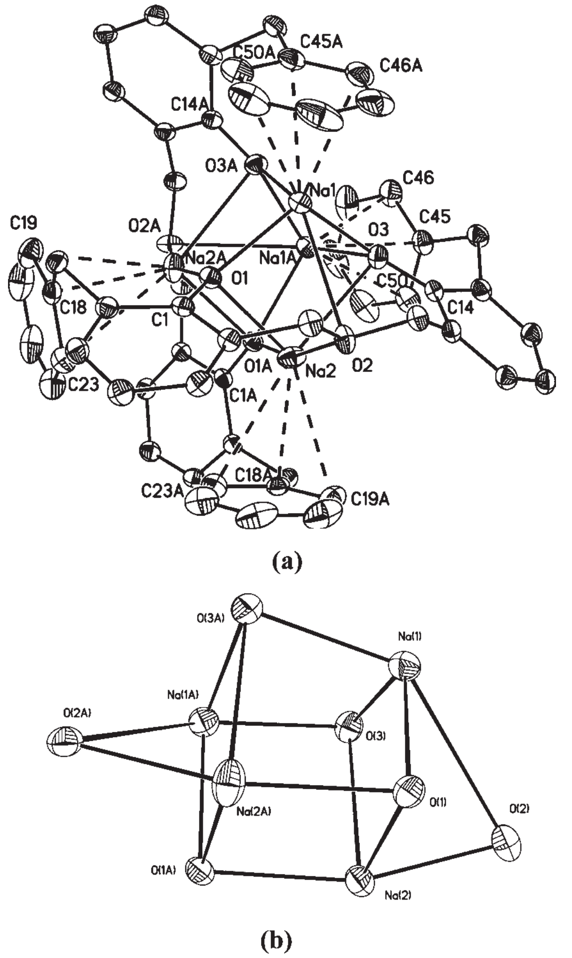


Figure 5. (a) Molecular structure of complex **6** as 20% ellipsoids (the carbon atoms of some of the methyl-1-phenylethyl groups and all of the hydrogen atoms were omitted for clarity). (b) Phenolate oxygen-bridged Na_4O_6 core.

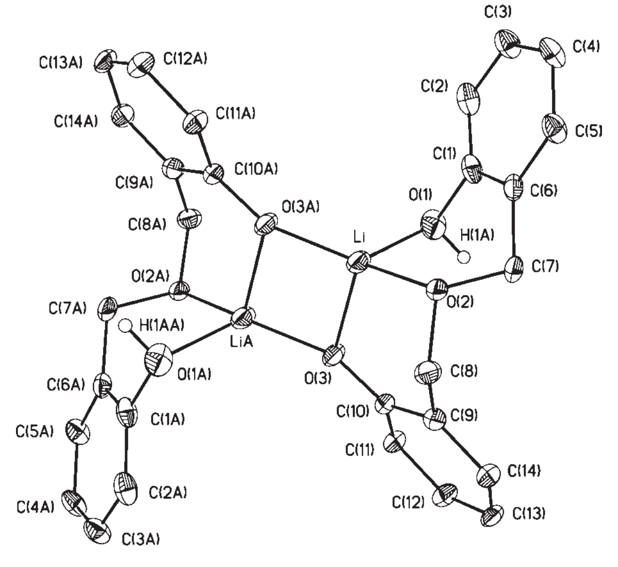


Figure 6. Molecular structure of complex **7** as 20% ellipsoids [the carbon atoms of some of the methyl-1-phenylethyl groups and all of the hydrogen atoms except phenol H(1A) and H(1AA) were omitted for clarity].

asymmetric pattern, the Li−O(3) and Li−O(3A) distances are 1.862(4) and 1.814(4) Å, respectively. Again in this case, the oxygen atoms of the OOO-tridentate donor ligand display slight differences in coordination strength, with Li−O(1), Li−O(2), and Li−O(3) bond distances of 2.027(5), 1.979(4), and 1.862(4) Å, respectively.

The molecular structure of complex **8**, as shown in Figure 7, reveals a dimeric Li_2O_2 arrangement with a OO coordination to the lithium center and a noncoordinating −OH arm of the bis(phenolate) ligand. A similar Li_2O_2 dimeric structure constructed with OOO-tridentate phenolate donor ligand is observed in the molecular structure of complex **9**, as shown in Figure 8. The molecular structure of complex **9** also discloses that two BnOH molecules are weakly bonded to the Li_2O_2 unit via O···H bonding between the oxygen atoms of the alcohol and the hydrogen atoms of the phenolate ligand.

Polymerization of L-Lactide. The ROP of L-lactide in CH_2Cl_2 employing complexes **1**, **2**, and **5**−**7** (2.5 mM) as catalysts in the presence of BnOH was systematically studied, as shown in Table 1. The experimental results indicate that complexes **1**, **2**, and **5**−**7** are all active toward the ROP of L-lactide, producing PLAs with expected molecular weights and low polydispersity indices (PDIs). The reactivity in the order of $\mathbf{6} > \mathbf{5} \gg \mathbf{2} > \mathbf{1} < \mathbf{7}$ reflects that sodium complexes have much higher activities than their lithium analogous because of the higher electropositive property of sodium than lithium. It is also noteworthy that the dinuclear complexes display lower ROP activity than the tetranuclear complexes. For instance, the dinuclear lithium complex **1** (entry 1) is less reactive than the tetranuclear lithium complex **2** (entry 2). Similarly, the polymerization time required for the dinuclear sodium complex **5** (entry 3) is longer than that for the tetranuclear sodium complex **6** (entry 5), respectively. Furthermore, the steric bulkier ligand decreases the activity of the complex ($\mathbf{1} < \mathbf{7}$).

The polymerization can reach completion within about 8 min at 0 °C in the monomer-to-initiator ratio ($[M]_0/[BnOH]_0$) range of 50−200 when using the tetranuclear sodium complex **6** as a catalyst. The linear increase in M_n with conversion and the low PDI (M_w/M_n) of the polymers revealed that the level of polymerization control was high. The ^1H NMR spectrum of PLA prepared confirms that the polymer chain is capped with a benzyl ester group on one end and a hydroxyl group on the other end with the integration ratio close to 5:1, suggesting that the benzyloxy alcohol acts as an initiator in the process. By using two equivalent ratios of BnOH as the initiator (entries 8 and 9), the polymerization requires a shorter time and M_n of the resulting polymers was half of those found in the reactions when one equivalent ratio of BnOH was used, indicating that both of the complexes have "immortal" character. It is also worth noting that compound **6** retains catalytic efficiency when using 1,2-ethanediol to replace BnOH as an initiator and the ROP of L-lactide is well-controlled with a narrow PDI (Table 1, entry 10).

On the basis of the solid-state structures of the mononuclear complex **4**, the dinuclear complexes **1** and **3**, and the tetranuclear complexes **2** and **6**, the reaction mechanism was proposed such that, by coordination of L-lactide, the tetranuclear complex $[M_4(L^1)_2]$ cleaved onto a dinuclear intermediate, $[M_2L^1(LA)_n]$. In the presence of BnOH, the dunuclear intermediate $[M_2L^1(LA)_n]$ further resulted in a monometallic intermediate, $[M(L^1\text{-}H)(OBn)(LA)]$.

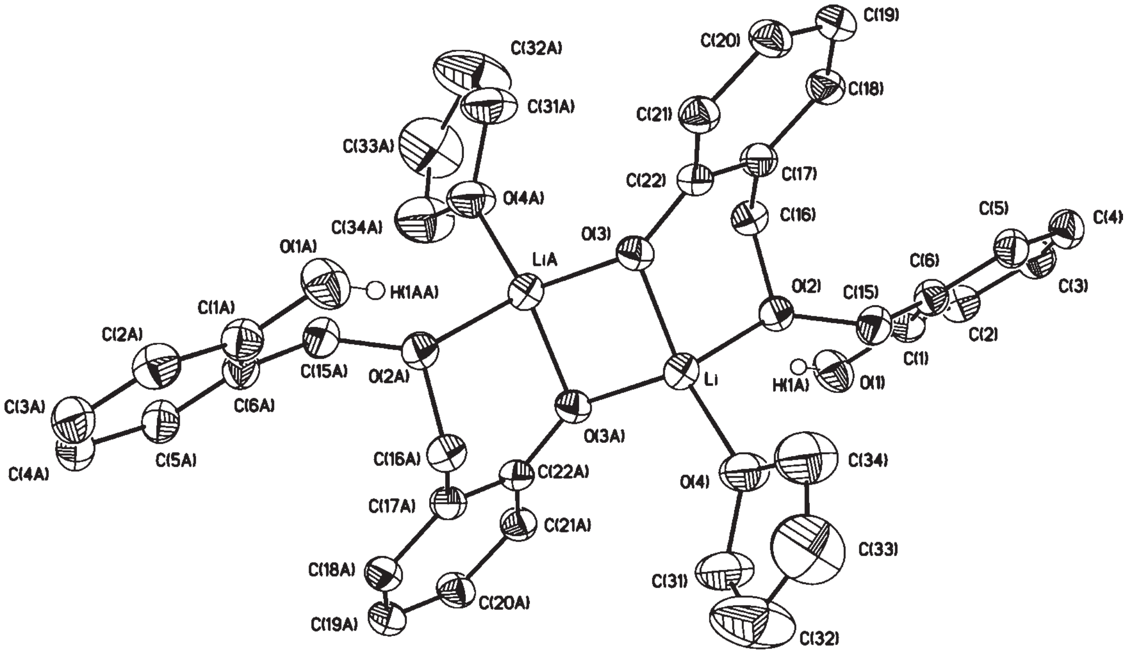


Figure 7. Molecular structure of complex **8** as 20% ellipsoids [the carbon atoms of some of the methyl-1-phenylethyl groups and all of the hydrogen atoms except phenol H(1A) and H(1AA) were omitted for clarity].

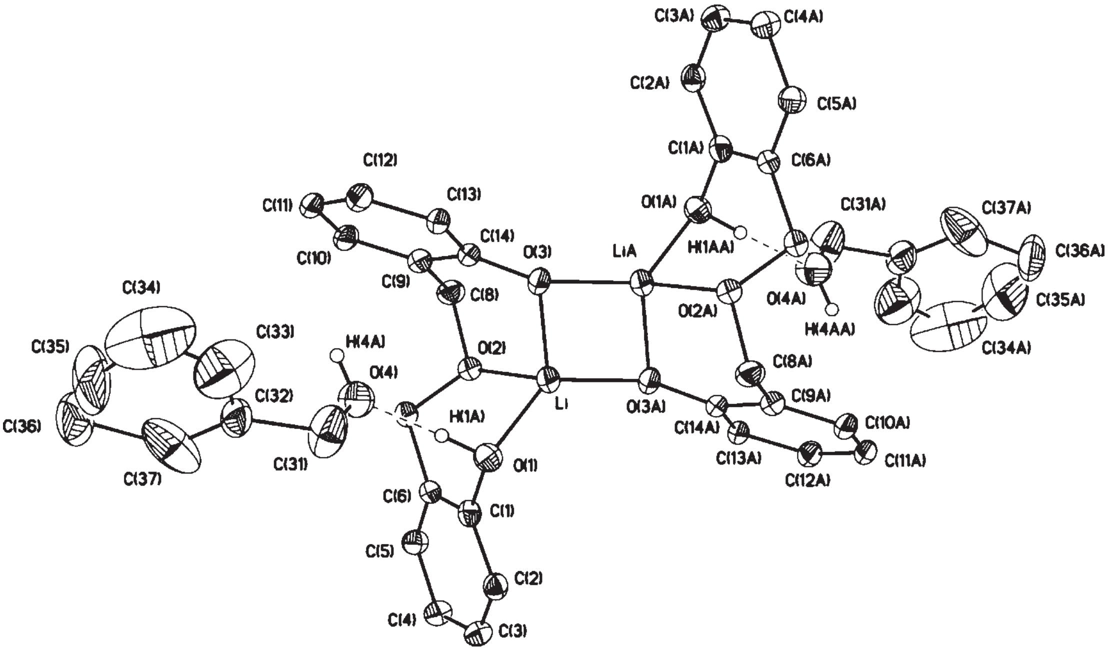


Figure 8. Molecular structure of complex **9** as 20% ellipsoids [the carbon atoms of some of the methyl-1-phenylethyl groups and all of the hydrogen atoms except phenol H(1A), H(1AA), H(4A), and H(4AA) were omitted for clarity].

Followed by the reaction of benzyl alkoxide with the activated L-lactide, a new initiator was produced.

The polymerization of L-lactide in toluene, employing complexes **7**–**9** as catalysts in the presence of BnOH, was investigated, as shown in Table 2. The polymerization results using complexes **7**–**9** as initiators reveal that they all act effectively in forming PLA with moderate-to-high molecular weights and PDIs ranging from 1.08 to 1.28. It is rather surprising to note that, in spite of the attachment of the two benzyloxy groups in complex **9** through the phenolic oxygen atoms, the time required for significant conversion (80–90%) is more (entries 4–11) than that required for complexes **7** and **8**. This is probably due to the fact that it is structurally more flexible, leading to a more active initiator when BnOH is not bound to a metal or diol ligand through hydrogen bonds. However, the role of such an OH group in the ROP is still not clearly understood.

Conclusion

Herein we have reported of a series of well-characterized lithium and sodium complexes of OOO-tridentate bis(phenolate)

Table 1. ROP of L-Lactide Catalyzed by Complexes **1**, **2**, and **5**−**7** in Dichloromethane[a]

entry	catalyst	$[LA]_0/[cat]_0/[BnOH]_0$	temp (°C)	time (min)	conv (%)[b]	M_n(calcd)[c]	M_n(obsd)[d]	M_n(NMR)[b]	PDI
1	**1**	200:1:2	20	120	91	13 200	26 200 (15 200)	14 600	1.09
2	**2**	200:1:2	20	50	93	13 500	25 900 (15 000)	14 000	1.06
3	**5**	200:1:2	0	35	96	13 900	25 000 (14 500)	13 400	1.08
4	**5**	200:1:4	0	10	95	6 900	12 500 (7300)	7 300	1.07
5	**6**	200:1:2	0	8	96	13 900	23 700 (13 700)	14 200	1.07
6	**6**	100:1:2	0	7	94	6 900	9400 (5500)	7 300	1.07
7	**6**	300:1:2	0	8	97	21 100	40 400 (23 400)	21 000	1.06
8	**6**	400:1:2	0	8	98	28 300	53 800 (31 200)	29 300	1.04
9	**6**	200:1:4	0	5	100	7 300	12 900 (7500)	7 400	1.07
10[e]	**6**	200:1:2	0	8	97	14 000	28 000 (16 200)	14 100	1.05
11	**7**	200:1:2	20	60	83	12 100	18 000 (10 300)	12 000	1.10
12	**7**	200:1:2	20	90	95	14 000	23 000 (13 200)	15 000	1.23

[a] Reaction conditions: $[cat]_0 = 0.25$ mM, dichloromethane (10 mL). [b] Obtained from ^{1}H NMR analysis. [c] Calculated from $M_w(LA) \times ([LA]_0/[BnOH]_0) \times \text{conversion} + M_w(BnOH)$. [d] Obtained from GPC analysis and calibrated by a polystyrene standard. Values in parentheses are the values obtained from GPC times 0.58.[12] [e] 1,2-Ethanediol acts as the initiator replacing BnOH.

Table 2. ROP of L-Lactide Catalyzed/Initiated by Complexes **7**−**9** in Toluene[a]

entry	catalyst	$[LA]_0/[cat]_0/BnOH]_0$	time (min)	conv (%)[b]	M_n(calcd)[c]	M_n(obsd)[d]	M_n(NMR)[b]	PDI
1	**7**	100:1:2	10	78	5700	10 000 (5900)	5900	1.10
2	**8**	100:1:2	10	79	5800	9600 (5600)	6000	1.11
3	**9**	100:1:0	10	80	6000	11 800 (6800)	6300	1.09
4	**9**	100:1:0	12	87	6400	13 300 (7600)	7200	1.10
5	**9**	100:1:0	16	91	6700	14 200 (8300)	7600	1.17
6	**9**	100:1:0	20	95	7000	13 500 (7800)	7500	1.30
7	**9**[e]	100:1:0	30	75	5500	10 400 (6100)	6200	1.11
8	**9**[e]	100:1:0	60	95	7000	12 400 (7200)	7500	1.28
9	**9**	50:1:0	12	88	3300	6800 (3900)	3700	1.12
10	**9**	150:1:0	15	85	9300	20 600 (11 900)	10000	1.08
11	**9**	200:1:0	18	85	12300	26 500 (15 300)	13800	1.08

[a] Reaction conditions: $[cat]_0 = 0.25$ mM, toluene (10 mL), temp = 30 °C. [b] Obtained from ^{1}H NMR analysis. [c] Calculated from $M_w(LA) \times ([LA]_0/[BnOH]_0) \times \text{conversion} + M_w(BnOH)$. [d] Obtained from GPC analysis and calibrated by a polystyrene standard. Values in parentheses are the values obtained from GPC times 0.58.[12] [e] CH_2Cl_2 (10 mL) was used as the solvent.

ligands. Rigorous X-ray structural studies of the single crystals of the complexes have confirmed their dimeric and tetrameric structures, and only in one case was the monomeric structure determined. Structural studies also revealed that the existing p−π interaction from the phenyl ring of the 2-(methyl-1-phenylethyl) groups to the metal center may effectively stabilize the metal center by preserving it for monomer interaction in complexes **2**, **4**, and **6**. Most of these dinuclear and tetranuclear alkali-metal complexes are shown to be active toward the ROP of L-lactide in the presence of BnOH. In connection to this, a unique comparison of the ROP activity of the tetranuclear and dinuclear initiators is derived. The polymerization processes appear to possess "immortal" character by a faster reaction using 2 equiv of BnOH with half of the molecular weight of the polymer found in the reactions compared with those when 1 equiv of BnOH is used. A low PDI of the PLAs also indicates a controlled polymerization behavior of these complexes. However, tetranuclear lithium and sodium complexes have been more active in the ROP of L-lactide than in the ROP for dinuclear complexes.

Experimental Section

General Procedures. All manipulations were carried out under a dry nitrogen atmosphere. Hexane (99%, ACS reagent, TEDIA), toluene (99%, ACS reagent, TEDIA), tetrahydrofuran (99%, ACS reagent, TEDIA), and diethyl ether (99%, ACS reagent, TEDIA) were distilled from sodium/benzophenone under nitrogen. CH_2Cl_2 was dried by refluxing at least 24 h over phosphorus pentaoxide, and benzyl alcohol (99%, Aldrich) was pretreated with CaH_2 powder (95%, Aldrich) overnight to remove dissolved water, followed by vacuum distillation. ^{n}BuLi (2.5 M in hexane), $NaN[Si(CH_3)_3]_2$ (1.0 M in THF), $NaN[Si(CH_3)_3]_2$ (0.6 M in toluene), metal sodium, and other reagents were purchased from Acros or Aldrich and used without further purification. L-Lactide was purchased from Bio Invigor Corp. and recrystallized from a toluene solution prior to use. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) spectrometer with chemical shifts given in parts per million from the internal tetramethylsilane. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument. The gel permeation chromatography (GPC) measurements were performed on a Waters 1515 Isotratic HPLC pump system equipped with a differential Waters 2414 refractive index detector using THF (HPLC grade) as the eluent. The chromatographic column was a Water Styragel Column (HR4E), and the calibration curve was made by polystyrene standards to calculate M_n(GPC).

$[Li_2(L^1\text{-}H)_2]$ (1). To an ice-cold solution (0 °C) of L^1-H_2 (1.41 g, 2.0 mmol) in toluene (20 mL) was slowly added a 2.5 M solution of ^{n}BuLi in hexane (0.8 mL, 2.0 mmol). The mixture was stirred for 4 h and concentrated in vacuo. The residue was extracted with hot toluene (30 mL), and the extract was then concentrated to ca. 15 mL. Colorless block crystals were obtained upon cooling to room temperature overnight. Yield: 1.12 g (79%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.35−6.66 (48H, m, *Ph*), 4.54 (2H, b, CH_2), 4.19 (2H, s, CH_2), 4.16 (2H, s, CH_2), 3.59 (2H, b, CH_2), 1.67−1.14 (48H, m, CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 152.23, 135.52, 129.34, 128.53, 128.06, 127.06, 126.20, 125.60, 125.51 (Ph), 71.01 (OCH_2), 42.64 ($PhC(CH_3)_2$), 42.13 ($PhC(CH_3)_2$), 31.37 ($C(CH_3)_2$), 29.91 ($C(CH_3)_2$). Anal. Calcd for $C_{100}H_{106}Li_2O_6$: C, 84.71; H, 7.54. Found: C, 84.61; H, 7.47. Mp: 190−192 °C.

[Li$_4$L$^1_2$] (2). ^{n}BuLi (1.68 mL, 2.5 M solution in hexane, 4.2 mmol) was added slowly to an ice-cold (0 °C) solution of L^1-H$_2$ (1.41 g, 2.0 mmol) in toluene (40 mL). The mixture was stirred for 12 h at 0 °C, and the volatile materials were removed under vacuum. The residue was extracted with warm toluene (30 mL), and the extract was concentrated to ca. 20 mL. Colorless crystals were obtained upon cooling at −18 °C. Yield: 1.28 g (84%). ^{1}H NMR (CDCl$_3$, ppm): δ 7.27−6.66 (53H, m, *Ph* and *Ph*CH$_3$), 4.53 (2H, b, CH_2), 4.19 (2H, s, CH_2), 4.16 (2H, s, CH_2), 3.59 (2H, b, CH_2), 2.35 (3H, s, PhCH_3), 1.67−1.08 (48H, m, CH_3). ^{13}C NMR (CDCl$_3$, ppm): δ 152.51, 136.92, 129.35, 128.54, 128.07, 127.95, 127.11, 125.61, 125.40 (Ph), 70.92 (OCH$_2$), 42.46, 42.09 (PhC(CH$_3$)$_2$), 31.43 (C(CH$_3$)$_2$). Anal. Calcd for [Li$_4$L$_2$]·C$_6$H$_5$CH$_3$ (C$_{107}$H$_{112}$Li$_4$O$_6$): C, 84.45; H, 7.42. Found: C, 84.65; H, 7.21. Mp: 172−174 °C.

[Li$_2$L^1(THF)$_3$] (3). ^{n}BuLi (1.68 mL, 2.5 M solution in hexane, 4.2 mmol) was added slowly to an ice-cold (0 °C) solution of L^1-H$_2$ (1.41 g, 2.0 mmol) in THF (40 mL). The mixture was stirred for 4 h at 0 °C, and the volatile materials were removed under vacuum. The residue was extracted with warm THF (30 mL), and the extract was concentrated to ca. 20 mL. Colorless crystals were obtained upon cooling at −18 °C. Yield: 1.32 g (66%). ^{1}H NMR (CDCl$_3$, ppm): δ 7.32−6.76 (24H, m, *Ph*), 4.56 (1H, b, CH_2), 4.19 (1H, s, CH_2), 4.16 (1H, s, CH_2), 3.59 (1H, b, CH_2), 3.71 (12H, m, OCH_2CH$_2$), 1.84 (12H, m, OCH$_2$CH_2), 1.67−1.15 (24H, m, CH_3). ^{13}C NMR (CDCl$_3$, ppm): δ 163.51, 151.78, 150.46, 135.66, 132.65, 128.49, 128.13, 127.06, 126.11, 125.66, 124.12 (Ph), 70.95 (OCH$_2$), 68.25(OCH$_2$CH$_2$), 42.72 (PhC(CH$_3$)$_2$), 42.23 (PhC(CH$_3$)$_2$), 31.36 (C(CH$_3$)$_2$), 29.93 (C(CH$_3$)$_2$), 25.91 (OCH$_2$$CH_2$). Anal. Calcd for [Li$_2$L(THF)$_3$]·THF (C$_{66}H_{84}Li_2O_7$): C, 79.01; H, 8.44. Found: C, 79.29; H, 8.59. Mp: 174−176 °C (dec).

[Na(L^1-H)(THF)] (4). To an ice-cold solution (0 °C) of L^1-H$_2$ (1.41 g, 2.0 mmol) in THF (40 mL) was slowly added a 1.0 M solution of NaN[Si(CH$_3$)$_3$]$_2$ in THF (2.0 mL, 2.0 mmol). The mixture was stirred for 12 h, and the volatile materials were removed under vacuum. The residue was extracted with a mixture of hexane (15 mL) and THF (15 mL), and the extract was concentrated to ca. 15 mL. Colorless crystals were obtained upon cooling at −20 °C for 1 week. Yield: 1.09 g (68%). ^{1}H NMR (CDCl$_3$, ppm): δ 7.41−6.80 (24H, m, *Ph*), 4.15 (2H, s, OCH_2), 4.04 (2H, b, OCH_2), 3.72 (4H, t, *J* = 6.4 Hz, OCH_2CH$_2$), 1.84 (4H, m, OCH$_2$CH_2), 1.69−1.29 (24H, m, CH_3). ^{13}C NMR (CDCl$_3$, ppm): δ 165.73, 154.26, 151.84, 135.72, 131.43, 128.63, 128.37, 128.09, 127.06, 125.94, 125.61, 125.05, 124.61, 123.48 (Ph), 74.94 (OCH$_2$), 68.21 (OCH$_2$CH$_2$), 42.65 (PhC(CH$_3$)$_2$), 42.23 (PhC(CH$_3$)$_2$), 31.41 (C(CH$_3$)$_2$), 29.92 (C(CH$_3$)$_2$), 25.87 (OCH$_2$$CH_2$). Anal. Calcd for [Na(L-H)(THF)] (C$_{54}$H$_{61}$NaO$_4$): C, 81.37; H, 7.71. Found: C, 80.93; H, 7.33. Mp: 168−170 °C (dec).

[Na$_2$(L^1-H)$_2$] (5). To an ice-cold solution (0 °C) of L^1-H$_2$ (1.41 g, 2.0 mmol) in toluene (40 mL) was slowly added a 0.6 M solution of NaN[Si(CH$_3$)$_3$]$_2$ in toluene (3.33 mL, 2.0 mmol). The mixture was stirred for 12 h, and the volatile materials were removed under vacuum. The residue was redissolved in toluene (10 mL), and 40.0 mL of hexane was added into the toluene solution. White turbidity was observed while the mixture was stirred. The resulting white powder was collected by filtration, washed with hexane three times, and then dried under vacuum. Yield: 0.844 g (58%). ^{1}H NMR (CDCl$_3$, ppm): δ 7.26−6.81 (48H, m, *Ph*), 3.93 (8H, b, CH_2), 1.67 (24H, s, CCH_3), 1.18 (24H, s, CCH_3). ^{13}C NMR (CDCl$_3$, ppm): δ 164.31, 152.35, 135.47, 131.84, 128.16, 128.04, 127.05, 126.18, 125.56, 125.44 (Ph), 70.39 (OCH$_2$), 42.54, 42.13 (PhC(CH$_3$)$_2$), 31.40, 31.35 (C(CH$_3$)$_2$). Anal. Calcd for [Na$_2$(L-H)$_2$] (C$_{100}$H$_{106}$Na$_2$O$_6$): C, 82.84; H, 7.37. Found: C, 82.47; H, 7.12. Mp: 131−132 °C.

[Na$_4$L$^1_2$] (6). An iced-cold solution (0 °C) of L^1-H$_2$ (1.41 g, 2.0 mmol) in diether ether (30 mL) was added slowly to excess sodium metal (0.46 g, 20 mmol). The mixture was stirred for 12 h until hydrogen gas evolution ceased and then concentrated in vacuo. The white residue was extracted with hot toluene (30 mL), and the extract was then concentrated to ca. 15 mL. Colorless crystals were obtained upon cooling to room temperature overnight. Yield: 1.21 g (81%). ^{1}H NMR (CDCl$_3$, ppm): δ 7.44 (8H, d, *J* = 8.0 Hz, *Ph*), 7.31 (8H, t, *J* = 8.0 Hz, *Ph*), 7.19−7.15 (8H, m, *Ph*), 6.96 (8H, d, *J* = 7.2 Hz, *Ph*), 6.90−6.75 (12H, m, *Ph*), 6.73 (4H, t, *J* = 7.2 Hz, *Ph*), 4.04 (8H, s, CH_2), 1.76 (24H, s, CH_3), 1.22 (24H, s, CH_3). ^{13}C NMR (CDCl$_3$, ppm): δ 165.72, 154.20, 152.50, 135.99, 131.38, 128.37, 128.31, 128.02, 127.08, 126.52, 125.39, 125.02, 124.97, 123.52 (Ph), 74.92 (OCH$_2$), 42.25, 42.20 (PhC(CH$_3$)$_2$), 31.53, 30.24 (C(CH$_3$)$_2$). Anal. Calcd for [Na$_4$L$_2$] (C$_{100}$H$_{106}$Na$_4$O$_6$): C, 80.40; H, 7.02. Found: C, 80.56; H, 6.86. Mp: 206−208 °C.

[(L^2-H)Li] $_2$ (7). *n*-BuLi (0.88 mL, 2.50 M in hexane, 2.20 mmol) was added slowly to an iced-cold solution of L^2-H$_2$ (0.908 g, 2.00 mmol) in hexane (30 mL). The mixture was stirred at 0 °C for 30 min, then warmed to 25 °C, and stirred for another 1.5 h. Volatile materials were removed under vacuum, giving a white solid. The solid was washed with hexane (30 mL) and then dried again to yield a white powder. Yield: 1.30 g (70.5%). ^{1}H NMR (CDCl$_3$, ppm): δ 7.21 (2H, s, ArH), 6.89 (2H, s, ArH), 4.59 (4H, s, CH_2), 1.25 (36H, s, C(CH_3)$_3$). ^{13}C NMR (CDCl$_3$, ppm): δ 138.95, 136.48, 125.25, 124.61, 123.27 (*Ar*), 71.63 (CH$_2$OCH$_2$), 34.60, 33.85, 31.50, 30.01 (C(CH$_3$)$_3$). Anal. Calcd for C$_{60}$H$_{90}$Li$_2$O$_6$: C, 78.23; H, 9.85. Found: C, 78.80; H, 9.77. IR (KBr, cm^{-1}): 1317 ($\nu_{\mathrm{CH_2OCH_2}}$, C−O stretching). Mp: 157−158 °C.

[(L^2-H)Li(THF)]$_2$ (8). *n*-BuLi (0.88 mL, 2.50 M in hexane, 2.20 mmol) was added slowly to an iced-cold solution of L^2-H$_2$ (0.908 g, 2.00 mmol) in THF (30 mL). The mixture was stirred at 0 °C for 20 min, then warmed to 25 °C, and stirred for another 1.5 h. Hexane (30 mL) was added to the mixture, giving a white solid. The solid was filtered and washed with hexane (30 mL) and then dried under vacuum. Yield: 1.60 g (78%). ^{1}H NMR (CDCl$_3$, ppm): δ 7.24 (2H, s, ArH), 6.89 (2H, s, ArH), 4.65 (4H, s, CH_2), 3.41 (4H, s, CH_2), 1.68 (4H, s, CH_2), 1.35 (18H, s, C(CH_3)$_3$), 1.24 (18H, s, C(CH_3)$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm): δ 136.61, 124.74, 124.51, 122.03 (*Ar*), 71.43 (CH$_2$OCH$_2$), 67.74 (OCH$_2$CH$_2$), 34.91 (C(CH$_3$)$_3$), 34.03 (OCH$_2$$CH_2$), 31.70, 29.78, 25.31 (C(CH$_3$)$_3$). Anal. Calcd for C$_{68}$H$_{106}$Li$_2$O$_8$: C, 76.66; H, 10.03. Found: C, 76.07; H, 9.85. IR (KBr, cm^{-1}): 1129 ($\nu_{\mathrm{CH_2OCH_2}}$, C−O stretching). Mp: 140−141 °C.

[(L^2-H)Li(BnOH)]$_2$ (9). *n*-BuLi (0.88 mL, 2.50 M in hexane, 2.20 mmol) was added slowly to an iced-cold solution of L^2-H$_2$ (0.908 g, 2.00 mmol) in diethyl ether (30 mL). The mixture was stirred at 0 °C for 20 min, then warmed to 25 °C, and stirred for another 1.5 h. Volatile materials were removed under vacuum, yielding a white powder. Diethyl ether (30 mL) was added, the solution was cooled to 0 °C, and BnOH (0.21 mL, 2.00 mmol) was added. The mixture was stirred for 10 min while the temperature was warmed to 25 °C and stirred for another 50 min. Hexane (30 mL) was added to the mixture, giving a white solid. The solid was filtered and washed with hexane (30 mL) and then dried again to yield a white powder. Yield: 1.60 g (73%). ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): δ 6.91−7.28 (ArH), 4.62 (2H, s, CH_2), 4.30 (2H, s, ArCH_2OH), 1.32 (18H, s, C(CH_3)$_3$), 1.24 (18H, s, C(CH_3)$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm): δ 139.76, 137.08, 128.44, 127.71, 127.03, 125.00, 124.54 (*Ar*), 71.83 (CH$_2$OCH$_2$), 65.27 (ArCH$_2$OH), 34.03, 34.87, 31.72, 29.85 (C(CH$_3$)$_3$). Elem. anal. Calcd for C$_{74}$H$_{106}$Li$_2$O$_8$: C, 78.13; H, 9.39. Found: C, 78.18; H, 9.32. IR (cm^{-1}): 1037 ($\nu_{\mathrm{ArCH_2OH}}$, C−O stretching). Mp: 130−131 °C.

Polymerization of L-Lactide Catalyzed by Complex 1, 2, and 5−7 in CH$_2$Cl$_2$. A typical polymerization procedure can be illustrated by the synthesis of PLA-100 (the number 100

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(12) The M_n(GPC) is multiplied by a factor of 0.58, giving the actual M_n of PLA. (a) Baran, J.; Duda, A.; Kowalski, A.; Szymanski, R.; Penczek, S. *Macromol. Rapid Commun.* **1997**, *18*, 325. (b) Biela, T.; Duda, A.; Penczek, S. *Macromol. Symp.* **2002**, *183*, 1. (c) Save, M.; Schappacher, M.; Soum, A. *Macromol. Chem. Phys.* **2002**, *203*, 889.

indicates the designed $[LA]_0/[BnOH]_0$; Table 1, entry 4). To a rapidly stirred solution of **6** (0.038 g, 0.025 mmol) and BnOH (0.038 g, 0.050 mmol) in CH_2Cl_2 (10 mL) was added L-lactide (0.72 mL, 5.0 mmol) at 0 °C. The reaction mixture was stirred for 8 min and then quenched by the addition of methanol (50 mL) to give white crystalline solids. Yield: 0.65 g (90%).

Polymerization of L-Lactide Catalyzed by Complexes 7 and 8 in Toluene. A typical polymerization procedure can be illustrated by the synthesis of PLA-100 (the number 100 indicates the designed $[LA]_0/[BnOH]_0$, Table 1, entry 4). To a rapidly stirred solution of **7** (0.038 g, 0.025 mmol) and BnOH (0.038 g, 0.050 mmol) in toluene (10 mL) was added L-lactide (0.72 mL, 5.0 mmol) at 30 °C. The reaction mixture was stirred for 8 min and then quenched by the addition of methanol (50 mL) to give white crystalline solids. Yield: 0.65 g (90%).

Polymerization of L-Lactide Initiated by Complex 9. A typical polymerization procedure can be illustrated by the synthesis of PLA-100 (the number 100 indicates the designed $[LA]_0/[\mathbf{9}]_0$; Table 2, entry 4). To a rapidly stirred solution of **9** (0.028 g, 0.025 mmol) in toluene (5.0 mL) was added L-lactide (0.36 g, 2.5 mmol) in toluene (5 mL) at 30 °C. The reaction mixture was stirred for 12 min and then quenched by the addition of H_2O (5.0 mL). Followed by the addition of hexane (50 mL), a white crystalline solid was obtained. Yield: 0.26 g (72%).

X-ray Crystallographic Studies. Suitable crystals of complexes **1**−**4** and **6**−**9** 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 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 the *SHELXTL* package. All non-hydrogen atoms were located by successive Fourier maps. All hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-hydrogen atoms, and fixed isotropic parameters were used for hydrogen atoms. Crystallographic data for complexes **1**−**4** and **6**−**9** are listed in in the Supporting Information.

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Supporting Information Available: Full details of the crystal structure determination of complexes **1**−**4** and **6**−**9** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.