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Synthesis and Characterization of Multi-Alkali-Metal Tetraphenolates and Application in Ring-Opening Polymerization of Lactide

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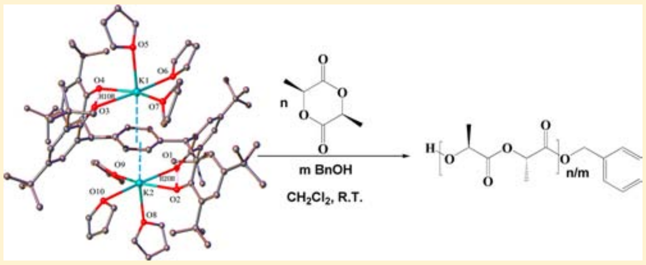
S *Supporting Information*



ABSTRACT: A series of alkali metal complexes supported by two bulky tetraphenols were synthesized and characterized. The reactions of *α,α,α′,α′*-tetra(3,5-di-*tert*-butyl-2-hydroxyphenyl)-*p*-xylene(*para*-tetraphenol) with ^{n}BuLi, sodium, and KSi(NMe$_2$)$_3$ gave bimetallic complexes **1**, **2**, and **3**, respectively. Treatments of the *α,α,α′,α′*-tetra(3,5-di-*tert*-butyl-2-hydroxyphenyl)-*m*-xylene(*meta*-tetraphenol) with 2 or 4 equiv of ^{n}BuLi afforded complexes **4** or **5**, while the reactions of *meta*-tetraphenol with sodium and KSi(NMe$_2$)$_3$ gave only trimetallic complexes **6** and **7** for the additional p−*π* interaction. Complexes **1**−**7** were all characterized by single-crystal X-ray diffraction techniques. In the presence of benzyl alcohol, all complexes are active catalysts for the ring-opening polymerization of L-lactide. Comparatively, bimetallic complexes **1**, **2**, and **3** are more efficient catalysts because of their symmetric structures, in which complex **3** presents as a rare highly active potassium catalyst for the ring-opening polymerization of lactide, leading to polymers with good molecular weight control and narrow molecular weight distributions.

■ INTRODUCTION

In the past several decades, poly(lactic acid) (PLA) has attracted wide attention for applications in packaging and medical fields due to its biorenewability, biodegradability, and biocompatibility.[1] A particularly convenient method for the synthesis of polylactide is the ring-opening polymerization (ROP) of lactide, commonly made via glucose fermentation, owning to the advantages of well-controlled molecular weight and low polydispersity (PDI);[2] many complexes including aluminum,[3] titanium,[4] zinc,[5] magnesium,[6] tin,[7] lanthanide,[8] and other metals[9] have been reported as excellent initiators/catalysts for the controlled ROP of lactides, affording polymers with both high and controlled molecular weights. Because the toxic metal residues in polymers have to be removed since it is to be used as a biomaterial, magnesium,[6] calcium,[10] iron,[11] and highly active metal-free catalysts[12] have been extensively applied in the ROP of lactides to address this issue. Recently alkali metallic complexes also have emerged as very attractive alternative catalysts in the ring-opening polymerization of lactides because of their low cost and low toxicity, especially as the seventh and ninth most abundant elements of K (0.35%) and Na (0.14%) in the human body.[13] Simple alkali metal complexes, like butyllithium,[14] lithium tert-butoxide,[15] and potassium *tert*-butoxide,[16,14a] are highly active for ROP of lactides but suffer from some undesirable side reactions, and polymerizations normally are uncontrollable. Series of bulky ligand-supported alkali metal complexes and multinuclear aggregates, for example, lithium, sodium, and potassium diphenolates reported by Lin, Chen, and our groups[17] and cage-like sodium and lithium iminophenoxides reported by Chen,[17r] demonstrated great potential toward the ROP of L-lactide at ambient temperature, which inferred that the bulky ligands are indispensable for such alkali metal complexes to provide a steric barrier around a metal center for minimizing the transesterification side reactions in a polymerization. Even some bulky polyamines as auxiliary ligands can significantly improve catalytic behavior of simple sodium aryloxides in polymerization of lactides reported by Davidson and García-Viv groups.[18]

Nevertheless, to find excellent alkali metal catalysts still remains a significant challenge to obtain polylactide with high and controlled molecular weights and even with the desirable stereostructure. Herein, we describe the synthesis and characterization of a series of novel lithium, sodium, and potassium complexes, **1**−**7**, supported by bulky tetraphenol ligands. X-ray structural studies of these complexes are also presented. The experimental results of the polymerization of L-lactide in the presence of the alkali-metal complexes and benzyl alcohol (BnOH) demonstrated that some symmetric bimetallic complexes are excellent catalysts for ROP of L-lactide. We also describe how the catalytic performances of the complexes toward the ROP of L-lactide are related to their molecular structures.

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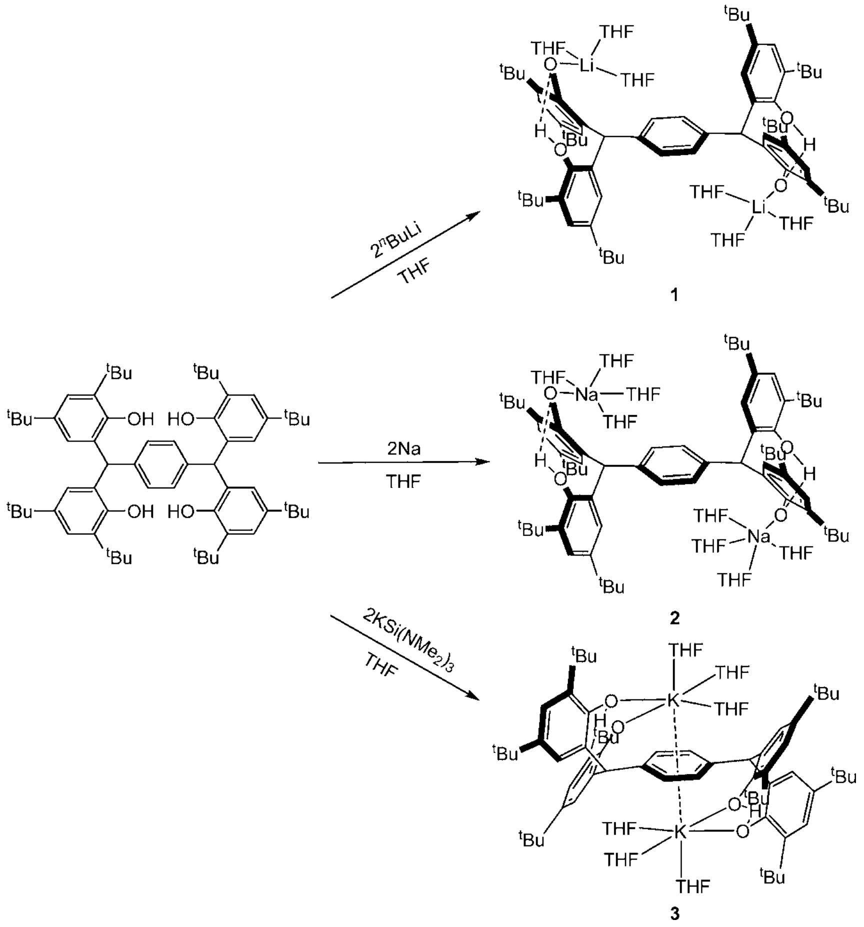
Scheme 1. Synthesis of Complexes 1, 2, and 3

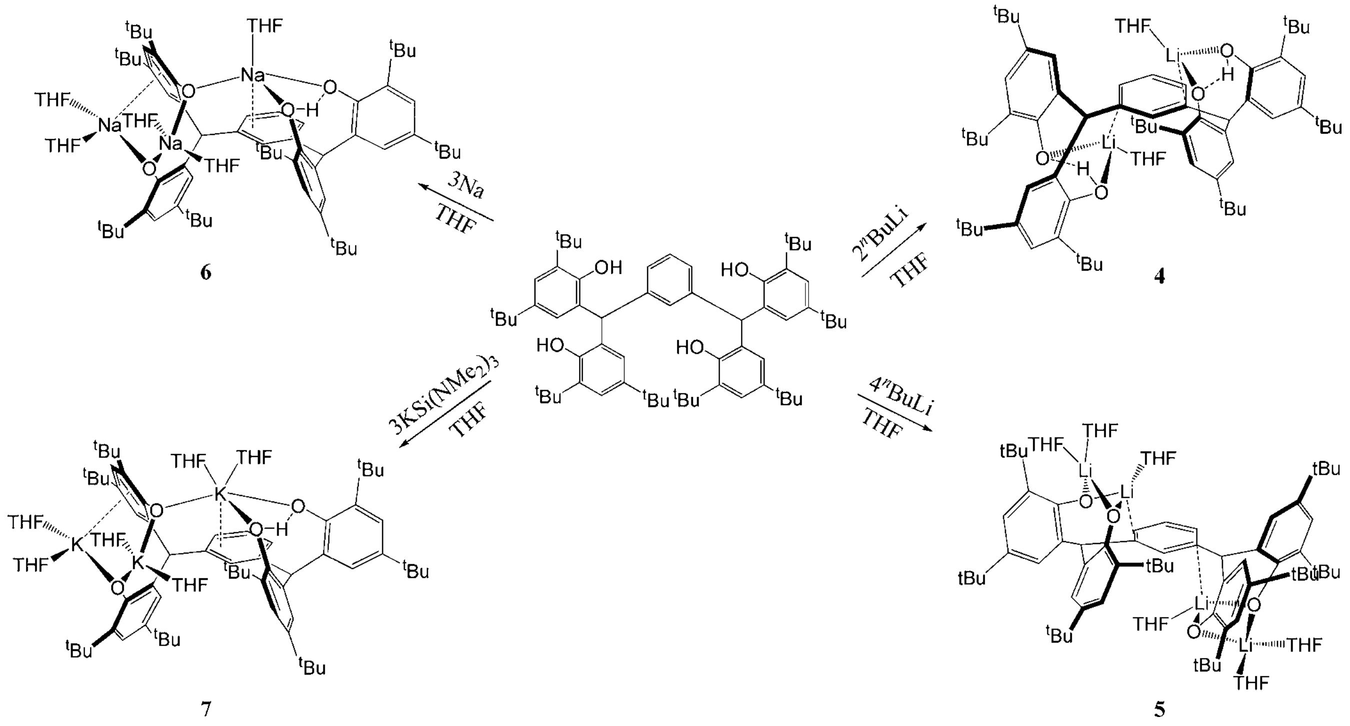


RESULTS AND DISCUSSION

Synthesis and Characterization. Because the EDBP-Na,[17h] EDBP-Li,[17d] and EDBP-K[17j] complexes showed controllable behavior in the ring-opening polymerization of lactides, two more bulky tetraphenol ligands, *α*,*α*,*α*′,*α*′-tetra(3,5-di-*tert*-butyl-2-hydroxyphenyl)-*p*-xylene(*para*-tetraphenol) and *α*,*α*,*α*′,*α*′-tetra(3,5-di-*tert*-butyl-2-hydroxyphenyl)-*m*-xylene(*meta*-tetraphenol), were chosen as the fusion of two EDBP-like biphenol ligands bridged by benzene at *meta*- or *para*-positions, and the two bulky EDBP-like biphenol fragments can mutually act as a bulky group to each other for which the related alkali metallic tetrapholates are expected to be good catalysts for the ROP of lactides. The two ligands were synthesized in high yields according to the literature[19] and are characterized by NMR spectroscopy as well as microanalyses. The reactions between the *para*-tetraphenol and 2 equiv of *n*-butyl lithium, sodium, and KSi(NMe$_2$)$_3$ give the bimetallic complexes in high yields (Scheme 1). The clear single set ^{1}H NMR spectra of complexes **1**, **2**, and **3** in CDCl$_3$ solution indicate only one principal product existing in the reaction mixtures; the stability of the bimetallic complex of **3** can be proven by the fact that the reactions between KSi(NMe$_2$)$_3$ and *para*-tetraphenol with the ratios of 1:2, 1:1, and 2:1 all give bimetallic complex **3** as the main product together with some unreacted ligands. Complexes **4** and **5** can be readily synthesized by the reactions of *n*-butyl lithium and *meta*-tetraphenol with the ratio of 2:1 and 4:1 in THF with 63%, and 40% yields, respectively. While, the reactions between *meta*-tetraphenol and sodium or KSi(NMe$_2$)$_3$ are more complicated, bimetallic sodium and potassium complexes cannot be obtained even with the exact molar ratio of 2:1 between metals and ligand. Alternatively, these reactions give unexpected trimetallic sodium and potassium complexes **6** and **7** in 38% and 41% yields possibly due to their special configuration, which will be discussed in the following structure part, and definitely the mixtures of 1 equiv of ligand and 3 equiv of sodium or KSi(NMe$_2$)$_3$ can afford trimetallic complexes in higher yields of 63% or 66% (Scheme 2).

In order to understand the different reactions between *meta*-tetraphenolates and *para*-tetraphenolates and their related catalytic performances, we grew crystals of complexes **1**, **2**, **3**, **4**, **5**, **6**, and **7**. Single crystals suitable for structural characterization of complex **1** were obtained from slow cooling of a warm THF/toluene solution, and the molecular structure of complex **1** is shown in Figure 1. The geometry around the lithium is a tetrahedron with the coordination of three oxygen atoms from THF and one oxygen atom from phenol. The average Li−O (THF) bond length of 1.958(7) Å and Li−O(Ar) bond length of 1.870(6) Å are comparable to the corresponding bond lengths in EDBP-Li complex.[17b,d] Crystals of complex **2** were obtained from slow cooling of a warm CH$_2$Cl$_2$/hexane/THF solution. The structure is similar to complex **1** except four THF are coordinated to one sodium atom (Figure 2). As shown by the ORTEP drawing in Figure 3, complex **3** is a symmetric bimetallic compound; each K$^+$ ion is coordinated by three THF molecules, two oxygen atoms of phenol, and the center benzene ring of the ligand through a strong p−*π* interaction with an average distance of 2.743(7) Å between the K$^+$ and benzene ring.[20] The hydrogen bonds of O1−H···O2 and O3−H···O4 also can be founded.

Scheme 2. Synthesis of Complexes 4, 5, 6, and 7



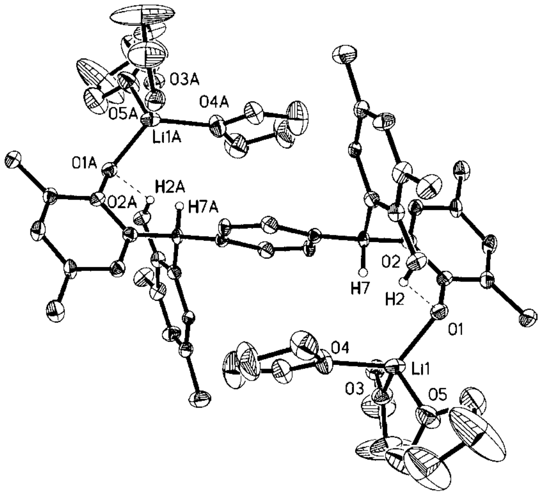


Figure 1. Molecular structure of **1** as 25% ellipsoids (the methyl carbon atoms of the *tert*-butyl groups and most of the hydrogen atoms are omitted for clarity). Selected bond lengths (Å): Li1−O1 1.870(6); Li1−O3 1.924(6); Li1−O4 1.971(7); Li1−O5 1.979(7).

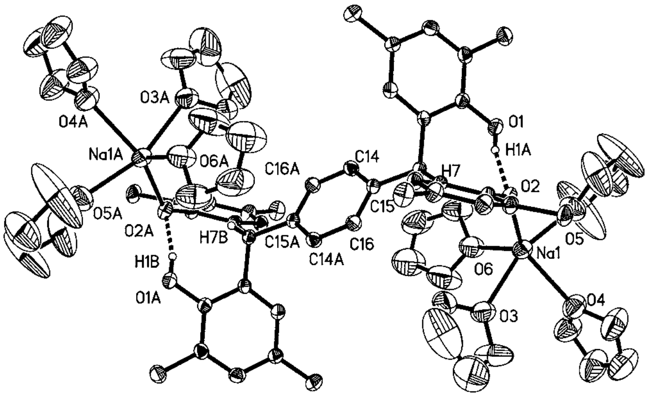


Figure 2. Molecular structure of **2** as 25% ellipsoids (the methyl carbon atoms of the *tert*-butyl groups and most of the hydrogen atoms are omitted for clarity). Selected bond lengths (Å): Na1−O2 2.238(2); Na1−O5 2.356(3); Na1−O6 2.363(3); Na1−O4 2.431(3); Na1−O3 2.439(3).

The strong p−π interaction possibly is the main factor that enables the bimetallic potassium complex **3** to be more stable than the monometallic or trimetallic complex; as a result only bimetallic complex as major product was obtained for the reactions between potassium and ligand with the ratios of 2:1, 1:1, 2:1, and even 3:1 at room temperature.

Single crystals suitable for structural characterization of complexes **4**, **5**, **6**, and **7** were obtained from slow cooling of a warm THF/toluene solution too. The molecular structure of complex **4** is depicted in Figure 4. Li1 is coordinated by one THF and two oxygen atoms of phenols; a weak cation−π interaction between Li1 and the center of the benzene ring with a distance of 2.322(9) Å can be found. Two hydrogen bonds of O1−H···O2 and O1A-H···O2A exist in this complex. The molecular structure of complex **5** is shown in Figure 5. In this structure, the environment of Li2 is similar to that of the lithium atom in complex **4**, and the Li1 is tetracoordinated by two THF and two oxygen atoms of phenols.

The structure of complex **6** is shown in Figure 6; three Na^{+} ions are located in different positions. Na1 is coordinated by one THF, O1 and O4 from phenol, and the center of the benzene ring through a p−π interaction with a distance of 2.765(10) Å.[21] Na2 is coordinated by two THF, one oxygen atom of O3 from phenol, and one peripheral benzene ring through a p−π interaction with a distance of 2.716(8) Å. Na3 is tetracoordinated by two THF and two oxygen atoms of O3 and O4 from phenols. A hydrogen bond of O1−H···O2 also can be founded. The structure of complex **7**, which is similar to that of complex **6**, is

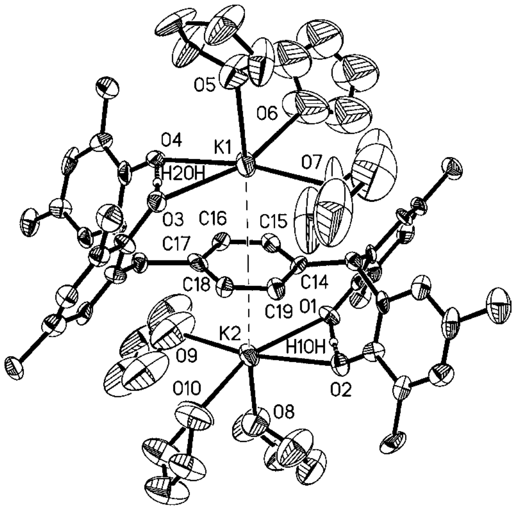


Figure 3. Molecular structure of **3** as 30% ellipsoids (the methyl carbon atoms of the *tert*-butyl groups and most of the hydrogen atoms are omitted for clarity). Selected bond lengths (Å): O6−K1 2.718(9); O7−K1 2.770(7); O8−K2 2.642(6); O9−K2 2.715(6); K1−O4 2.689(8); K1−O3 2.709(8); K1−O5 2.789(9); K2−O10 2.668(10); K2−O1 2.760(8); K2−O2 2.762(8).

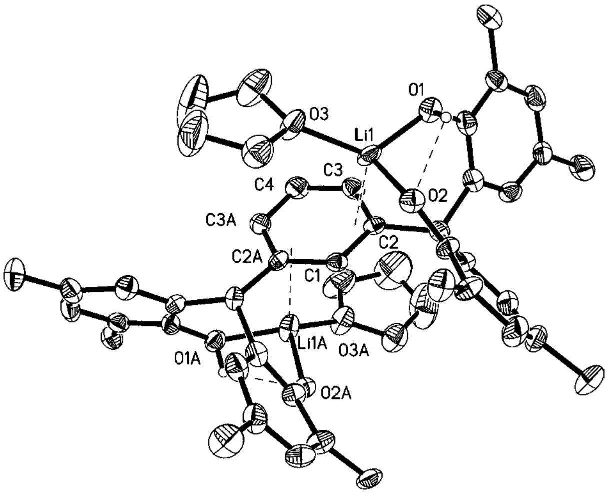


Figure 4. Molecular structure of **4** as 30% ellipsoids (the methyl carbon atoms of the *tert*-butyl groups and most of the hydrogen atoms are omitted for clarity). Selected bond lengths (Å): Li1−O1 1.858(10); Li1−O2 1.863(9); Li1−O3 1.958(10).

depicted in Figure 7. There are also two important p−π interactions to stabilize the trimetallic structure: one is the interaction between K1 and the center of the benzene ring with a distance of 3.156(8) Å, and another is between K2 and one peripheral benzene ring with a distance of 2.577(5) Å. Therefore, the ready synthesis of trimetallic sodium or potassium complexes possibly is due to the two additional strong p−π interactions, which do not exist in the *meta*-tetraphenolate lithium complexes.

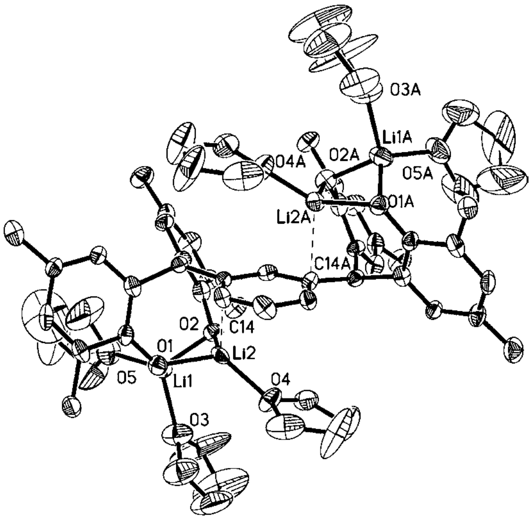


Figure 5. Molecular structure of **5** as 30% ellipsoids (the methyl carbon atoms of the *tert*-butyl groups and most of the hydrogen atoms are omitted for clarity). Selected bond lengths (Å): Li1−O2 1.909(16); Li1−O5 1.942(17); Li1−O1 1.973(17); Li1−O3 2.107(17); Li2−O2 1.860(14); Li2−O1 1.869(13); Li2−O4 1.950(15).

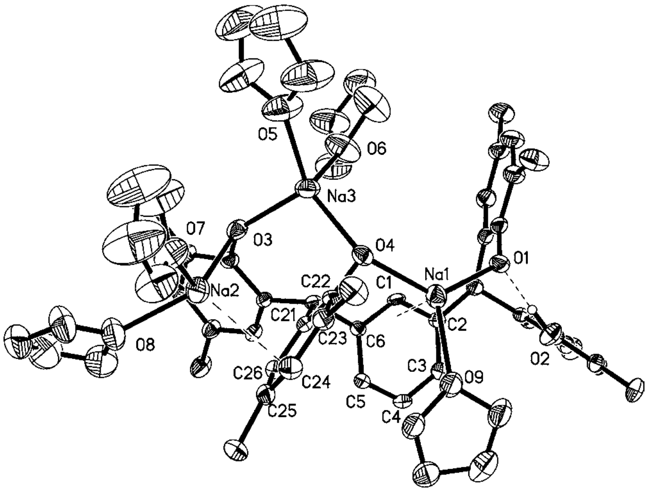


Figure 6. Molecular structure of **6** as 30% ellipsoids (the methyl carbon atoms of the *tert*-butyl groups and most of the hydrogen atoms are omitted for clarity). Selected bond lengths (Å): Na1−O3 2.199(3); Na1−O1 2.274(3); Na1−O9 2.300(4); Na2−O7 2.305(5); Na2−O2 2.323(4); Na2−O8 2.368(4); Na3−O2 2.243(3); Na3−O1 2.293(3); Na3−O6 2.302(5); Na3−O5 2.340(4).

Polymerization of L-Lactide. The ROP of L-lactide catalyzed by alkali metal complexes **1**−**7** was systematically conducted in both the absence and the presence of BnOH as a co-initiator with different monomer/initiator ratios at room temperature. Representative results are collected in Table 1. The polymerizations of L-lactide almost went to completion in 180 min, 5 min, and 2 min for complexes **1**, **2**, and **3** when a 200:1 (monomer/catalyst) ratio was used without BnOH (entries 1−3); therefore, sodium and potassium complexes **2** and **3** are more active than lithium complex **1**. It should be noted that in the polymerization catalyzed by complexes **1**, **2**, and **3**, only modest control was observed under this experimental condition as inferred from the relatively high PDIs and the slightly unpredictable molecular weights of the resulting polymers.[22] Upon addition of benzyl alcohol as the co-initiator, the PDIs of the polymers change to be narrower, especially for complex **3** with the PDIs ranging from 1.05 to 1.24 (entries 17−28). The polymerization reaction rates keep the same order of **1** < **2** < **3**, and the molecular weights are more predictable. The living polymerizations catalyzed by complexes **1**, **2**, and **3** were elucidated by the fact that the molecular weights of polymers increased linearly with the ratio of $[LA]_0/[BnOH]_0$ (entries 4−20, Figure 8, and Figures S1 and S2, Supporting Information), which

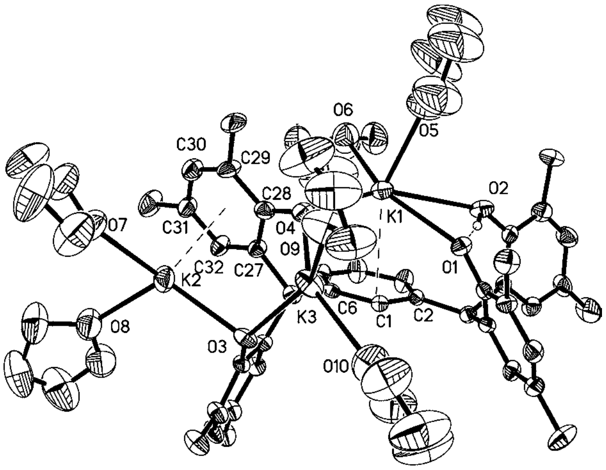


Figure 7. Molecular structure of **7** as 25% ellipsoids (the methyl carbon atoms of the *tert*-butyl groups and most of the hydrogen atoms are omitted for clarity). Selected bond lengths (Å): K1−O1 2.633(5); K1−O4 2.685(6); K1−O2 3.175(6); O5−K1 2.687(8); O6−K1 2.711(7); K2−O8 2.669(9); K2−O3 2.681(6); O7−K2 2.653(6); O7−K2 2.653(6); K3−O3 2.567(5); K3−O4 2.629(6); K3−O9 2.759(10).

was further confirmed by second feed experiments (entry 21−22) in which another portion of L-LA monomer was added after the polymerization of the first addition of L-LA had gone to completion. Analysis of PLA-100:1:2 (entry 18) produced from complex **3** at an initial $[\mathrm{LA}]_0/[\mathrm{complex}]_0/[\mathrm{BnOH}]_0$ ratio of 100:1:2 by ^{1}H NMR shows a characteristic quadruple methine peak (Figure 9) at 5.16 ppm indicating no serious epimerization of the chiral centers in the polymers, which can also be confirmed by the homonuclear-decoupled ^{1}H NMR studies in the methine region. Peaks at 7.32 ppm ($C_6H_5CH_2-$) and 4.38 ppm (HOC*H*Me−) with an integral ratio of 5:1 between He and Hc indicate that the polymer chain is capped with one benzyl ester and one hydroxy end, suggesting that the polymerization occurs through the insertion of L-lactide into the metal−benzyl alkoxy bond. To address the possibility of achieving immortal polymerization with these catalysts by introducing several equivalents of chain-transfer agent, polymerizations with complexes **2** and **3** were conducted in the presence of 2, 4, 8, 16, and 20 equiv benzyl alcohol toward complex. The number-average molar mass (M_n) of the polymers also are in good agreement with the calculated M_n based on one chain growing per BnOH; the polydispersity indexes of the polymers are also narrow. And in entry 28, the highly active catalyst of complex **3** (1 equiv) even can catalyze ROP of 1000 equiv of L-lactide in presence of 20 equiv of BnOH with contolled molecular weight and narrow PDI.

The results demonstrate that the catalytic activities of sodium and potassium complexes **2** and **3** are higher than that of lithium complex **1** for ROP of L-lactide in both the presence and absence of BnOH, which matches the results in previous studies.[17r] The general explanation is that the size of K^+ and Na^+ exceeds that of Li^+, which increases the ability of lactide coordination with the metal. Comparisons of the activities with similar alkali metal complexes supported by EDBP and MBMP ligands are listed in Table 2. Lithium complex **1** shows similar catalytic performances to $[(\mathrm{EDBP\text{-}H})\mathrm{Li}(\mathrm{BnOH})]_2$.[17d] Sodium and potassium complexes of **2** and **3** display higher activities than tetranuclear $[\mathrm{MBMPNa_2(THF)_3}]_2$ and $[(\mathrm{MBMPK_2})_2(\mathrm{THF})_5]_2$[22] but slight lower activities than $(\mathrm{EDBP\text{-}H})\mathrm{Na(MeOH)_2}$ and $[(\mathrm{EDBP\text{-}H})\mathrm{K(THF)_2}]_2$ in presence of alcohol as co-initiator possibly due to the more bulky ligand of tetraphenol, which can decrease the ability of lactide to coordinate with Na^+ or K^+. The ROP of L-lactide can proceed in a more controllable manner with predictable polymers and narrow molecular distributions, which may be also attributed to the more bulky steric hindrance in tetraphenolates than in EDBP or MBMP ligand for the reduction of side reactions. Anyway, the sodium and potassium complexes **2** and **3** can be assigned as highly active catalysts for ROP, and as far as we know, potassium complexes have seldom been reported as catalysts for the controllable ROP of lactides;[17j,o,22] complex **3** may encourage us to find more excellent nontoxic potassium catalysts for the ring-opening polymerization of lactides.

Complexes of *meta*-tetraphenolates **4**, **5**, **6**, and **7** were also employed as catalysts for the ring-opening polymerization of L-lactide with BnOH as a co-initiator. Representative results are collected in Table 1 (entries 29−43). The results show potassium complex **7** is more active than lithium complexes **4** and **5** and sodium complex **6** too. As we anticipated based on the structures of the complexes, poorly controllable polymerizations were observed for complexes **6** and **7**; we think the three asymmetric active metal centers in these complexes give rise to different initiation and propagation rates for ROP of lactide. And due to the two symmetric active centers, the polymerization of L-lactide catalyzed by complex **4** is controllable.

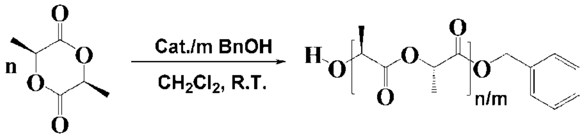
In conclusion, four dinuclear, two trinuclear, and one tetranuclear alkali-metal complexes supported by bulky tetraphenol ligands have been prepared and characterized. The molecular structures of complexes **1**, **2**, **3**, **4**, **5**, **6**, and **7** were further confirmed by single-crystal X-ray diffraction techniques. All complexes exhibited activity for the ring-opening polymerization of L-lactide, in which bimetallic alkali complexes **1**, **2**, **3**, and **4** are more efficient catalysts than the others possibly because of the symmetric bulky configuration. Especially, potassium complex **3** is a highly active catalyst for the controllable ring-opening polymerization of L-lactide, which may encourage us to find more excellent nontoxic potassium catalysts for the ring-opening polymerization of cyclic esters.

■ EXPERIMENTAL SECTION

General Procedures. All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques or a glovebox. Toluene, THF, and hexane were dried by refluxing over sodium benzophenone ketyl. CH_2Cl_2 was dried over P_2O_5. All solvents were distilled and stored in solvent reservoirs that contained 4 Å molecular sieves and were purged with nitrogen. ^{1}H and ^{13}C NMR spectra were recorded using spectrometers of the Varian Mercury Plus family. Mass spectroscopic data were obtained from a Bruker APEX II (FT-ICR MS). Commercial chemicals were purchased and used without further purification. *α*,*α*,*α*′,*α*′-Tetra(3,5-di-*tert*-butyl-2-hydroxyphenyl)-*p*-xylene(*para*-tetraphenol) and *α*,*α*,*α*′,*α*′-tetra(3,5-di-*tert*-butyl-2-hydroxyphenyl)-*m*-xylene(*meta*-tetraphenol) were prepared according to the method reported in the literature.[19]

Synthesis of Complex 1. A solution of *para*-tetraphenol (0.924 g, 1.00 mmol) and 2.20 mmol ^{n}BuLi (2.40 mol/L in hexane) was stirred in THF (25.0 mL) at room temperature under a N_2 atmosphere for 3 h. The solvent was then removed under vacuum, and then recrystallization with hexane afforded a white solid. Yield: 1.23 g (90%). Anal. Calcd for $C_{88}H_{136}O_{10}Li_2$: C 77.27, H 10.02. Found: C 77.90, H 10.11. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.16−1.19 (m, t-Bu, 36H), 1.31−1.36 (m, t-Bu, 36H), 1.73 (s, OCH_2CH_2, 24H), 3.60 (s, OCH_2CH_2, 24H), 6.66 (s, C*H*, 2H), 6.96−7.00 (m, Ar-*H*, 5H), 7.10−7.20 (m, Ar-*H*, 5H), 7.21−7.26 (m, Ar-*H*, 1H), 7.36 (m, Ar-*H*, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 25.2, 26.6, 29.9, 30.2, 30.6, 31.5, 31.7, 34.2, 34.7, 34.9, 120.9, 122.9, 124.4, 129.1, 133.8, 136.6.

Table 1. ROP of L-Lactide Catalyzed by Complexes 1−7[a]



entry	catalyst	$[LA]_0/[cat.]_0/[BnOH]_0$	t (min)	conv. (%)[b]	$M_{n,calcd}$[c]	$M_{n,obsd}$[d]	PDI
1	**1**	200:1:0	180	97	28000	35700	1.58
2	**2**	200:1:0	5	82	23700	40800	1.36
3	**3**	200:1:0	2	99	28600	24500	1.35
4	**1**	50:1:2	60	98	3600	3200	1.06
5	**1**	100:1:2	60	98	7200	7000	1.23
6	**1**	150:1:2	60	95	10400	10400	1.20
7	**1**	200:1:2	60	95	13800	14700	1.16
8	**2**	50:1:2	5	99	3700	4000	1.24
9	**2**	100:1:2	5	85	6200	5400	1.38
10	**2**	200:1:2	5	77	11200	11600	1.03
11	**2**	300:1:2	5	60	13100	14300	1.12
12	**2**	100:1:4	5	99	3700	4100	1.19
13	**2**	300:1:4	10	99	10800	11000	1.06
14[e]	**2**	400:1:4	10	87	12600	12200	1.13
15[e]	**2**	500:1:4	10	79	14300	13400	1.12
16[e]	**2**	500:1:8	10	99	9000	9300	1.14
17	**3**	50:1:2	1	84	3100	3400	1.05
18	**3**	100:1:2	1	83	6100	6500	1.10
19	**3**	200:1:2	2	81	11800	10600	1.16
20	**3**	300:1:2	2	81	17600	19600	1.06
21[f]	**3**	50 (50):1:2	1 (1)	99	7200	5300	1.07
22[f]	**3**	100 (100):1:2	1 (1)	97	14100	12900	1.24
23	**3**	100:1:4	1	83	3100	3500	1.09
24[g]	**3**	300:1:4	3	93	10200	9200	1.07
25[g]	**3**	400:1:4	5	95	13800	14000	1.07
26[g]	**3**	400:1:8	10	85	6200	6300	1.08
27[g]	**3**	400:1:16	10	97	3600	3700	1.08
28[h]	**3**	1000:1:20	30	96	7000	6300	1.07
29	**4**	100:1:2	60	99	7200	5400	1.34
30	**4**	150:1:2	60	99	10800	11100	1.25
31	**4**	200:1:2	60	97	14000	13100	1.35
32	**4**	300:1:2	60	99	21700	23160	1.12
33	**5**	100:1:4	60	98	3600	3900	1.15
34	**5**	150:1:4	60	98	5400	4600	1.28
35	**5**	250:1:4	60	94	8600	6200	1.23
36	**5**	300:1:4	60	98	10700	8900	1.28
37	**6**	150:1:3	30	99	7200	6080	1.48
38	**6**	300:1:3	30	98	14200	12800	1.50
39	**6**	450:1:3	30	98	21300	13400	1.57
40	**6**	300:1:1	30	97	42000	15200	1.52
41	**7**	450:1:3	5	99	21700	5500	1.37
42	**7**	600:1:3	5	96	27600	5300	1.22
43	**7**	250:1:1	5	99	35800	5470	1.09

[a] Reactions performed in 5 mL of dichloromethane at 30 °C, $[cat.]_0$ = 5 mM. [b] Determined by ^{1}H NMR spectroscopy. [c] Calculated from the molecular weight of L-LA times $[LA]_0/[BnOH]_0$ times conversion yield + M_{BnOH}, for entries 1−3 calculated from the molecular weight of L-LA times $[LA]_0/[cat.]_0$ times conversion yield. [d] Measured by GPC in THF calibrated with standard polystyrene samples and corrected using the Mark−Houwink factor of 0.58. [e] In 10 mL of dichloromethane. [f] Polymerization of L-LA with **3** for 1 min, followed by the addition of another portion of L-LA. [g] In 7 mL of dichloromethane. [h] In 20 mL of dichloromethane.

*Synthesis of Complex **2**.* A solution of *para*-tetraphenol (0.924 g, 1.00 mmol) and sodium (0.050 g, 2.20 mmol) was stirred in THF (25.00 mL) at 45 °C under a N_2 atmosphere for 12 h. The solvent was then removed under vacuum, and then recrystallization with hexane afforded a white solid. Yield: 1.46 g (95%). Anal. Calcd for $C_{96}H_{152}O_{12}Na_2$: C 74.67, H 9.92. Found: C 75.01, H 10.02. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.28 (m, *t*-Bu, 36H), 1.30 (m, *t*-Bu, 36H), 1.80 (s, OCH_2CH_2, 32H), 3.67 (m, OCH_2CH_2, 32H), 5.31 (s, *CH*, 2H), 7.13 (m, Ar-*H*, 4H), 7.17 (m, Ar-*H*, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): 25.4, 30.2, 31.8, 34.0, 59.1, 68.2, 122.6, 125.6, 127.7, 131.7, 138.5, 142.0, 156.0.

*Synthesis of Complex **3**.* A solution of *para*-tetraphenol (0.924 g, 1.00 mmol) and 2.20 mmol $KSi(NMe_2)_3$ (1.00 mol/L in hexane) was stirred in THF (25.00 mL) at room temperature under a N_2 atmosphere for 3 h. The solvent was then removed under vacuum, and then

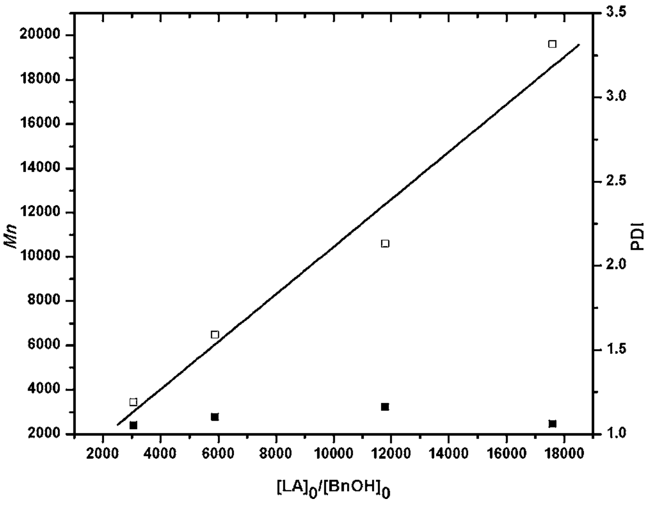


Figure 8. Polymerization of L-LA initiated by complex **3** in dichloromethane at room temperature. The relationship between M_n (□) or PDI (■) of the polymer and the initial mole ratios $[LA]_0/[BnOH]_0$ is shown in entry 17–20 in Table 1.

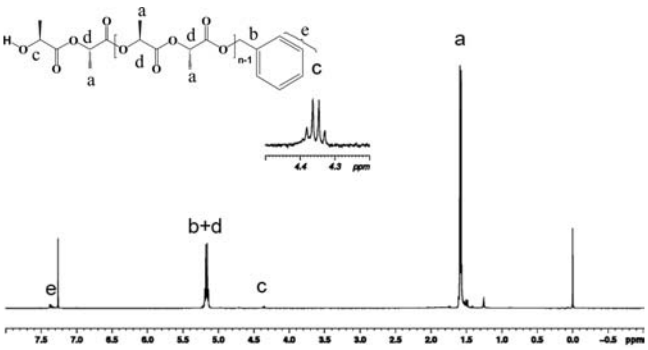


Figure 9. ^1H NMR analysis poly(L-LA) obtained from polymerization of L-LA initiated by complex **3** (entry 18 in Table 1).

recrystallization with hexane afforded a white solid. Yield: 1.38 g (94%). Anal. Calcd for $C_{88}H_{136}O_{10}K_2$: C 73.80, H 9.57. Found: C 74.18, H 9.52. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.26 (m, *t*-Bu, 36H), 1.29 (m, *t*-Bu, 36H), 1.83 (m, OCH_2CH_2, 24H), 3.69 (m, OCH_2CH_2, 24H), 5.12 (s, CH, 2H), 7.01 (m, Ar-*H*, 4H), 7.10 (m, Ar-*H*, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): 25.5, 29.8, 31.9, 33.9, 35.1, 67.8, 122.2, 126.5, 127.8, 130.3, 136.5, 137.2, 157.0.

*Synthesis of Complex **4**.* A solution of *meta*-tetraphenol (0.924 g, 1.00 mmol) and 4.40 mmol Li^nBu (2.40 mol/L in hexane) was stirred in THF (25.0 mL) at room temperature under a N_2 atmosphere for 3 h. The solvent was then removed under vacuum, and then recrystallization with hexane afforded a white solid. Yield: 0.696 g (63%). Anal. Calcd for $C_{74}H_{104}O_6Li_2$: C 80.11, H 9.71. Found: C 80.39, H 9.52. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.23 (s, *t*-Bu, 36H), 1.35 (s, *t*-Bu, 36H), 1.74–1.87 (m, OCH_2CH_2, 8H), 3.58–3.62 (m, OCH_2CH_2, 8H), 5.31 (s, CH, 2H), 6.85–7.22 (m, Ar-*H*, 11H), 7.62 (s, Ar-*H*, 1H), ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.38, 29.90, 30.08, 31.67, 33.86, 34.15, 35.06, 122.75, 125.40, 128.23, 136.85, 137.29, 143.64, 161.56, 162.39.

*Synthesis of Complex **5**.* A solution of *meta*-tetraphenol (0.924 g, 1.00 mmol) and 4.4 mmol ^nBuLi (2.40 mol/L in hexane) was stirred in THF (25.0 mL) at room temperature under a N_2 atmosphere for 3 h. The solvent was then removed under vacuum, and then recrystallization with hexane afforded a white solid. Yield: 0.561 g (40%). Anal. Calcd for $C_{88}H_{134}O_{10}Li_4$: C 76.60, H 9.79. Found: C 76.92, H 9.82. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.98–1.42 (m, *t*-Bu, 72H), 1.74 (s, OCH_2CH_2, 24H), 3.52 (m, OCH_2CH_2, 24H), 6.53–6.63 (m, CH, 2H), 6.80–7.26 (m, Ar-*H*, 12H).

*Synthesis of Complex **6**.* A solution of *meta*-tetraphenol (0.924 g, 1.00 mmol) and sodium (0.050 g, 2.20 mmol) was stirred in THF (25.0 mL) at 45 °C under a N_2 atmosphere for 12 h. The solvent was then removed under vacuum, and then recrystallization with hexane afforded a white solid. Yield: 0.912 g (63%). Anal. Calcd for $C_{88}H_{127}O_9Na_3$: C 74.74, H 9.48. Found: C 74.52, H 9.82. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.10–1.42 (m, *t*-Bu, 72H), 1.74–1.87 (m, OCH_2CH_2, 20H), 3.63–3.68 (m, OCH_2CH_2, 20H), 5.35 (s, CH, 2H), 7.15 (m, Ar-*H*, 12H).

*Synthesis of Complex **7**.* A solution of *meta*-tetraphenol (0.924 g, 1.00 mmol) and 3.30 mmol $KSi(NMe_2)_3$ (1.00 mol/L in hexane) was stirred in THF (25.0 mL) at room temperature under a N_2 atmosphere for 3 h. The solvent was then removed under vacuum, and then recrystallization with hexane afforded a white solid. Yield: 0.987 g (66%). Anal. Calcd for $C_{88}H_{135}O_{10}K_3$: C 71.89, H 9.25. Found: C 72.22, H 9.42. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.18 (m, *t*-Bu, 45H), 1.32 (s, *t*-Bu, 27H), 1.79–1.88 (m, OCH_2CH_2, 24H), 3.69–3.73 (m, OCH_2CH_2, 24H), 5.19 (s, CH, 2H), 7.05–7.211 (m, Ar-*H*, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.4, 30.1, 31.8, 33.9, 34.9, 68.1, 122.9, 124.6, 127.4, 129.0, 132.3, 136.0, 137.6, 145.7, 162.8.

General Procedure for Polymerization of L-Lactide. A typical polymerization procedure can be illustrated by the synthesis of PLLA-100 ($[LA]_0/[cat.]_0/[BnOH]_0 = 200:1:2$; Table 1, entry 19). To a rapidly stirred solution of **3** (0.036 g, 0.025 mmol) in CH_2Cl_2 (5 mL) was added L-lactide (0.72 g) at room temperature. The reaction mixture was stirred for 2 min, and then quenched with the addition of water (0.5 mL).

Table 2. Comparison of Activities of Similar Alkali Metal Complexes in ROP of L-Lactide

entry	catalyst	$[LA]_0/[cat.]_0/[ROH]_0$	*T* (°C)	*t* (min)	conv. (%)	$M_{n,calcd}$[g]	$M_{n,obsd}$[h]	PDI
1[a]	$[(EDBP\text{-}H)Li\ (BnOH)]_2$[17d]	200:1:0	0	120	92	26500	23800	1.05
2[a]	**1**	200:1:2	0	120	93	26900	23800	1.03
3[b]	$(EDBP\text{-}H)Na\ (MeOH)_2$[17h]	200:1:0	20	8	98	14100	23100	1.11
4[c]	$[MBMPNa_2(THF)_3]_2$[22]	250:0.25:1	70	30	89	32100	16000	1.38
5[d]	**2**	200:0.5:2	20	20	91	13100	13700	1.05
6[d]	$[(EDBP\text{-}H)K(THF)_2]_2$[17j]	200:0.5:2	20	10	98	14100	11400	1.02
7[e]	$[(MBMPK_2)_2(THF)_5]_2$[22]	300:0.125:1	70	120	95	41000	25600	1.33
8[d]	**3**	200:0.5:2	20	10	85	12300	12600	1.03
9[f]		200:0.5:2	30	5	95	13800	14000	1.07

[a] Reactions performed in 10 mL of dichloromethane, $[cat.]_0$ = 5 mM, $[Li^+]_0$ = 10 mM, ROH = BnOH. [b] Reactions performed in 20 mL of toluene, $[cat.]_0$ = 2.5 mM, $[Na^+]_0$ = 2.5 mM, ROH = MeOH. [c] Reactions performed in toluene, $[cat.]_0$ = 4 mM, $[Na^+]_0$ = 1 mM, ROH = ^iPrOH. [d] Reactions performed in 20 mL of dichloromethane; the solubility of complex **2** in toluene very low; $[cat.]_0$ = 1.25 mM, $[Na^+]_0$ = 2.5 mM, ROH = MeOH. [e] Reactions performed in toluene, $[cat.]_0$ = 0.42 mM, $[K^+]_0$ = 3.3 mM, ROH = ^iPrOH. [f] Reactions performed in 5 mL of dichloromethane, $[cat.]_0$ = 5 mM, $[K^+]_0$ = 10 mM, ROH = BnOH. [g] Calculated from the molecular weight of L-LA times $[LA]_0/[ROH]_0$ times conversion yield + $M_{ROH.}$ [h] Measured by GPC in THF calibrated with standard polystyrene samples and corrected using the Mark–Houwink factor of 0.58.

Table 3. Details of the X-ray Structure Determinations of Complexes **1**, **2**, **3**, **4**, **5**, **6**, and **7**

	1	**2**	**3**	**4**	**5**	**6**	**7**
formula	$C_{112}H_{184}O_{16}Li_2$	$C_{98}H_{156}O_{12}Na_2Cl_2$	$C_{88}H_{136}O_{10}K_2$	$C_{88}H_{136}O_{10}Li_2$	$C_{88}H_{134}O_{10}Li_4$	$C_{91}H_{135}O_9Na_3$	$C_{88}H_{135}O_{10}K_3$
fw	1800.47	1714.01	1432.17	1367.05	1379.71	1440.96	1467.24
temp	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)
cryst syst	triclinic	monoclinic	monoclinic	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	$P\bar{1}$	$C2/c$	Cc	$P2_12_12$	$P2_12_12$	$P2_1/n$	Cc
a, Å	12.94(4)	26.1333(9)	28.303(16)	17.390(5)	17.406(13)	16.749(2)	35.298(9)
b, Å	14.87(4)	12.6759(4)	25.160(14)	23.311(7)	23.338(17)	22.288(3)	14.342(4)
c, Å	17.42(5)	32.1125(12)	15.445(9)	11.320(3)	11.340(8)	24.722(4)	19.574(5)
α, deg	100.33 (7)	90.00	90.00	90.00	90.00	90.00	90.00
β, deg	107.34(6)	102.395(4)	120.720(6)	90.00	90.00	98.877(2)	106.594(2)
γ, deg	109.56(7)	90.00	90.00	90.00	90.00	90.00	90.00
V, Å^3	2866(15)	10389.7(6)	9455(9)	4589(2)	4607(6)	9118(2)	9497(4)
Z	2	4	4	2	2	4	4
density (calcd) g·cm^{-3}	1.043	1.096	1.006	0.988	0.995	1.050	1.026
absorb.coeff., mm^{-1}	0.067	0.175	0.149	0.062	0.062	0.078	0.192
$F(000)$	990	3720	3128	1496	1508	3140	3188
θ range	1.28−25.00	3.19−25.00	2.23−24.37	2.50−23.32	2.31- 23.49		2.23−24.37
index ranges	$-15 < h < 11$	$-31 < h < 28$	$-30 < h < 32$	$-17 < h < 19$	$-19 < h < 17$	$-19 < h < 19$	$-44 < h < 37$
	$-16 < k < 17$	$-15 < k < 13$	$-28 < k < 29$	$-25 < k < 25$	$-26 < k < 26$	$-26 < k < 25$	$-17 < k < 17$
	$-20 < l < 19$	$-32 < l < 38$	$-17 < l < 17$	$-12 < l < 12$	$-12 < l < 12$	$-29 < l < 28$	$-23 < l < 24$
data/restraints/params	8054/23/611	8562/0/529	14113/292/835	6160/64/443	6409/120/473	4705/40/942	14265/266/894
GOF	1.002	1.047	0.965	0.920	1.025	0.974	0.947
final R indices	0.0749	0.0793	0.0786	0.0774	0.0784	0.0783	0.0826
$[I > 2\sigma(I)]$	0.1376	0.1936	0.1687	0.1639	0.1678	0.1458	0.1839
peak and hole, e·Å^{-3}	0.235, −0.206	0.319, −0.301	0.965, −0.981	0.920, −0.923	0.174, −0.147	0.974, −0.981	0.947, −0.955
CCDC numbers	902967	902968	902969	902970	902971	902972	902973

The polymer was precipitated by the addition of hexane (20 mL); a white crystalline solid was obtained by recrystallization with the mixed solvents of hexane/CH_2Cl_2 and dried under a vacuum.

Crystallographic Studies. The X-ray single-crystal data collections were performed on a Bruker SMART APEX CCD diffractometer or Agilent Technologies SuperNova dual source diffractometer using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. Semi-empirical absorption corrections were applied using the SADABS program. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXS-97 and SHELXL-97 programs.[23] Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. The crystal data and refinement results are summarized in Table 3.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures showing polymerization of L-LA by complexes **1** and **2** and CIF files giving crystallographic data for **1**, **2**, **3**, **4**, **5**, **6**, and **7** with CCDC reference numbers of 902967, 902968, 902969, 902970, 902971, 902972, and 902973. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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