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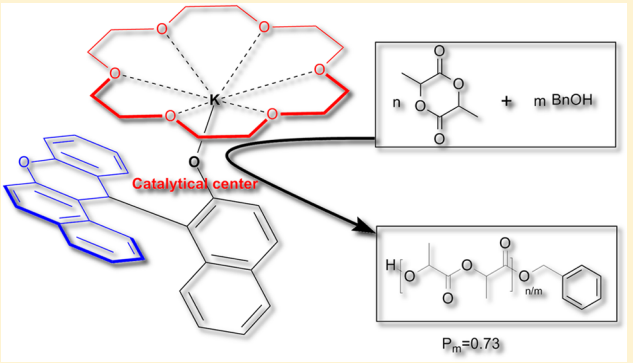
Iso-Selective Ring-Opening Polymerization of *rac*-Lactide Catalyzed by Crown Ether Complexes of Sodium and Potassium Naphthalenolates

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Supporting Information

ABSTRACT: Two crown ether complexes of sodium and potassium naphthalenolates were synthesized and entirely characterized. The two complexes can iso-selectively catalyze the ring-opening polymerization (ROP) of *rac*-lactide at room temperature and afford polylactides with desired molecular weights and narrow PDIs; the best isotacticity (P_m) achieved was 0.73.



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INTRODUCTION

During the past decades, polylactides (PLAs) have attracted considerable attention because of their biodegradable and biocompatible properties and ability to partially replace petrochemical thermoplastics due to their attractive performance characteristics. The ring-opening polymerization (ROP) of lactides catalyzed/initiated by metal complexes is a most effective method for synthesizing polylactide due to its advantages of a well-controlled molecular weight and low polydispersity (PDI).[1] Because the physical and chemical properties of polylactide are highly dependent on its stereochemistry,[2] the stereocontrolled ROP of *rac*-lactide is currently a challenging and valuable research goal that can afford PLA with various desired stereo microstructures. Many highly iso-selective aluminum complexes supported by Salen or Salan ligands have been reported,[3] but most of these complexes suffered from their low activities. To overcome this problem, some highly active zinc,[4] lanthanide,[5] indium,[6] and magnesium complexes[7,4a] have been reported recently to exhibit good heterotactic or isotactic selectivities.[8] Lithium *tert*-butoxide as an alkali metal complex can initiate the ROP of *rac*-lactide giving a heterotactic-enriched PLA (P_r = 0.76).[9] However, to our knowledge, highly iso-selective alkali metal complexes, especially sodium or potassium metal complexes, have not been explored widely for the ROP of *rac*-latide so far. Sodium and potassium are innocuous elements, and are definitely suitable for the catalytic synthesis of polylactides for use in medical-related fields.[10] Recently, we reported two crown ether complexes of sodium/potassium monophenoxide which can highly iso-selectively catalyze the ROP of *rac*-lactide giving a best P_m value of 0.86.[11] But the molecular weight of the final polymer cannot reach a high value in that system because a high $[\text{co-initiator}]_0$:$[\text{cat.}]_0$ ratio and low temperature are necessary for a controllable polymerization reaction. Hence, we reported here two new sodium and potassium complexes as catalysts which can iso-selectively catalyze the ROP of *rac*-lactide with a low $[\text{co-initiator}]_0$:$[\text{cat.}]_0$ ratio at room temperature.

RESULTS AND DISCUSSION

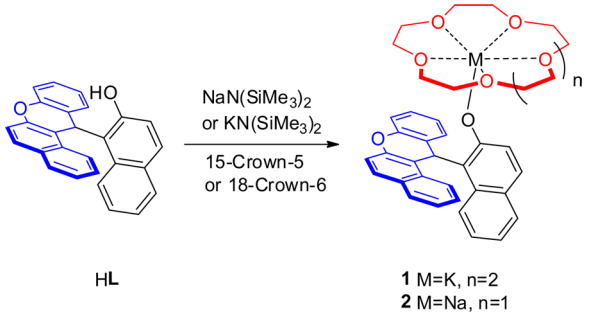
A bulky ligand of 1-(benzo[*j*]xanthen-12-yl)naphthalen-2-ol (**HL**) was synthesized by heating a mixture of naphthalen-2-ol and salicylaldehyde in a 58% yield. The structure of this ligand was confirmed by NMR, mass spectrum, elemental analysis, and the X-ray crystallography of the following two metal complexes. Complexes **1** and **2** can be obtained in 51% and 46% yields, respectively, from the reactions of **HL**, 18-crown-6/15-crown-5, and $KN(SiMe_3)_2$/$NaN(SiMe_3)_2$ in toluene (Scheme 1). Crystals of **1** and **2** suitable for X-ray structural analysis were obtained at room temperature from a saturated solution in THF and CH_3CN respectively. The molecular structure of complex **1** showed that K1 is coordinated by six oxygen atoms of the 18-crown-6 and one oxygen atom of the naphthalenoxy (Figure 1). There is a chiral carbon of C11 in this complex, and both *R* and *S* enantiomers exist in this crystal. The active K1−O1 (naphthalenoxy) center is partially sandwiched between the planar benzo[*j*]xanthenyl group at the ortho position of naphthalenoxy and the huge 18-

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Scheme 1. Synthesis of Sodium and Potassium Naphthalenolates



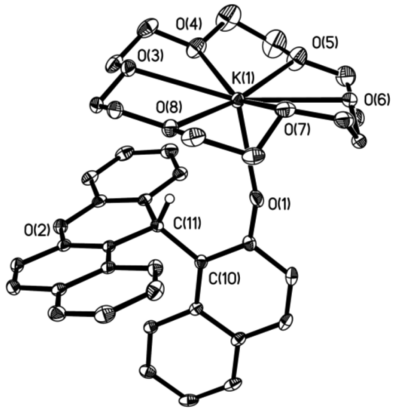


Figure 1. Molecular structure of **1** as 30% ellipsoids (all of the hydrogen atoms are omitted for clarity (except H11)). Selected bond lengths (Å): K1−O1 2.6141(14), K1−O3 2.9390(13), K1−O4 2.8100(14), K1−O5 2.7406(14), K1−O6 2.8683(13), K1−O7 2.8219(13), and K1−O8 2.6695(12).

crown-6, only an orientation at another ortho position of naphthalenoxy seems open to substrates for a catalytic reaction. The molecular structure of complex **2** is similar to complex **1** (Figure S1, Supporting Information). The Na1−O1 bond distance of 2.202(3) Å is shorter than the K1−O1 bond distance of 2.6141(14) Å in complex **1** due to the smaller ionic radius of sodium; the different bond distances may affect their catalytic behaviors in the ROP of *rac*-lactide.

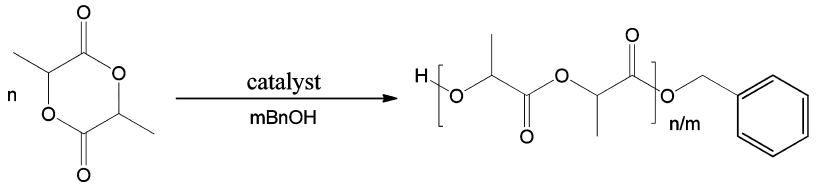
The ROP of *rac*-lactide with **1** and **2** as catalysts was systematically examined. Representative results are listed in Table 1. The polymerization of *rac*-lactide was nearly complete in 3 min for complex **1**, when a 100:1:1 ratio of $[rac\text{-LA}]_0$:$[\mathbf{1}]_0$:$[\text{BnOH}]_0$ was used (Table 1, entry 1) with a complex concentration of 2.5 mM in 10 mL of toluene at room temperature, while the same reaction consumed 4 h in CH_2Cl_2 to reach a 49% yield (Table 1, entry 2), and only 24% lactide can be converted to polymer in THF (Table 1, entry 3). First, the remarkable solvent effect puzzled us; however, the experimental facts were confirmed by repeated tries. The real reason is still unknown. But we think the different reaction rates possibly associate with the different solvent polarities and the special structure factors of this complex, for example, the rotation of the single bond of C10−C11 and the alternating polarity of this complex in the rotating progress due to the enlarged K^+/Na^+−O^-(naphthalenoxy) bond distance. For the solvent of THF, the decreased polymerization rate may also be attributed to the competitive coordination of THF which can inhibit the coordination of lactide to K^+/Na^+.[13] Compared to complex **1**, the activity of complex **2** is slightly lower because only 57% *rac*-lactide was converted to polymer under the same conditions (Table 1, entry 4), which may result from the shorter Na^+−O^- (naphthalenoxy) bond. The shorter Na^+−O^- (naphthalenoxy) bond will give rise to a shorter distance between the planar xanthenyl group and 15-crown-5; thus the surrounding of the active Na^+−O^- (naphthalenoxy) center may become more crowded, consequently the transport of lactide or BnOH to the active center will be slightly hindered. The sodium and potassium monophenolate catalysts reported by us recently exhibit some anti-Arrhenius behaviors in ROP of *rac*-lactide because the active center of these catalysts is embedded in a cavity and the polymerization rate may be affected by the oscillation of the crown ether.[11] But no anti-Arrhenius behavior can be founded in the ROP of *rac*-lactide catalyzed by complexes **1** and **2**, which may be owing to their different structures compared to the above sodium and potassium monophenolates. In complexes **1** and **2**, the active center is open to substances of the polymerization, so the polymerization rate will not be affected seriously by the oscillation of the crown ether. The polymerization catalyzed by complex **1** is living because the molecular weights of polymers are desired as calculated and increase linearly with the ratio of $[rac\text{-LA}]_0$:$[\text{BnOH}]_0$ (Table 1, entries 7−11, Figure S2, Supporting Information), which was further confirmed by second feed experiments (Table 1, entry 13) in which another portion of *rac*-lactide monomer was added after the polymerization of the first addition of *rac*-LA had gone to completion. To address the possibility of achieving immortal polymerization with complex **1** by introducing several equivalents of chain-transfer agent, polymerizations were conducted in the presence of 5 or 10 equiv of benzyl alcohol toward complex **1** (Table 1, entries 14−16). The molecular weights of polymers also agree well with the calculated M_n based on one chain growing per BnOH; the PDIs of the polymers are also narrow. It should be note that the molecular weight of the polymer is lower than the calculated one when the ratio of $[rac\text{-LA}]_0$:$[\mathbf{1}]_0$:$[\text{BnOH}]_0$ is 1000:1:1 (Table 1, entry 12), which may result from some transesterification reactions.

End-group analysis by ^{1}H NMR spectroscopy revealed that the polymer chains were end-capped by one benzyl ester and a hydroxyl (Table 1, entry 7, Figure S3, Supporting Information). Therefore, as the monomer activated mechanism supposed for most alkali metal phenoxides, the lactide can be activated after coordinating to K^+ or Na^+, and consequently BnOH can attack the carbonyl group to initiate the ROP reaction.[14] The ESI mass spectrum of a final polymer (Figure 2) confirmed it further by a series of peaks at $144m + 108 + 23$ with a charge of +1, which can be assigned to $m(C_6H_8O_4)$ + BnOH + Na^+. It is to be noted that there is another series of peaks at $0.5 \times (144m + 108 + 23 + 19)$ with a charge of +2, which can be attributed to $m(C_6H_8O_4)$ + BnOH + Na^+ + H_3O^+ (Figure 2 was enlarged in Figures S4 and S5, Supporting Information). Both series of peaks with a difference in molecular mass of ∼144 Da hint that no serious transesterification reaction happens during this polymerization process. But after a careful analysis of this ESI mass spectrum (Figure S5, Supporting Information), two very weak peaks at 1643.4989 and 1787.5382 among the three peaks of 1571.4745, 1715.5173, and 1859.5599 can be founded, which indicates the existence of a very small amount of transesterification reactions. And the transesterification reaction cannot be ignored when the $[rac\text{-LA}]_0$:$[\text{cat.}]_0$:$[\text{BnOH}]_0$ ratio is high (Table 1, entry 12).

The stereo microstructure of the poly(*rac*-lactide) was evaluated by the homonuclear-decoupled ^{1}H NMR spectra,

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Table 1. ***rac*-Lactide Polymerization Catalyzed by 1, 2, and KL−DME**[a]



entry	cat.	$[LA]_0/[cat.]_0/[BnOH]_0$	t	convn[b] (%)	M_n(calcd)[c] (g/mol)	M_n(obsd)[d] (g/mol)	M_w/M_n	P_m[e]
1	**1**	100:1:1	3 min	97	14100	14000	1.04	0.71
2[f]	**1**	100:1:1	4 h	49	7200	4900	1.27	0.67
3[g]	**1**	100:1:1	4 h	24	3600	3600	1.25	0.69
4	**2**	100:1:1	3 min	57	8300	4500	1.09	0.65
5	KL−DME	100:1:1	3 min	77	11000	8400	1.10	0.57
6[h]	**1**	100:1:1	4 h	99	14500	13300	1.07	0.74
7	**1**	20:1:1	2 min	92	2700	2100	1.09	0.65
8	**1**	200:1:1	4 min	96	27700	20900	1.02	0.73
9	**1**	300:1:1	6 min	99	42900	32500	1.06	0.72
10	**1**	400:1:1	8 min	98	56500	39000	1.07	0.71
11	**1**	500:1:1	10 min	99	71400	59200	1.07	0.70
12	**1**	1000:1:1	30 min	98	141200	70400	1.17	0.75
13	**1**	100(100):1:1	3(3) min	99	28600	24600	1.05	0.70
14	**1**	500:1:5	5 min	99	14400	14400	1.08	0.70
15	**1**	500:1:10	5 min	100	7300	8900	1.08	0.71
16	**1**	1000:1:10	5 min	95	13800	13300	1.07	0.69
17[i]	**1**	100:1:1	3 min	89	12800	10800	1.09	>0.99
18[j]	**1**	100:1:1	3 min	86	12400	12100	1.02	>0.99

[a]Reactions were performed in 10 mL of toluene, $[cat.]_0$ = 2.5 mM, at room temperature in addition to the annotated. [b]Determined by ^{1}H NMR spectroscopy. [c]Calculated from the molecular weight of *rac*-LA × $[LA]_0/[BnOH]_0$ × conversion yield + M_{BnOH}. [d]Measured by GPC in THF calibrated with standard polystyrene samples and corrected using the Mark−Houwink factor of 0.58.[12] [e]Determined by analysis of all of the tetrad signals in the methine region of the homonuclear-decoupled ^{1}H NMR spectrum. [f]In 10 mL of CH_2Cl_2. [g]In 10 mL of THF. [h]0 °C. [i]L-Lactide was used. [j]D-Lactide was used

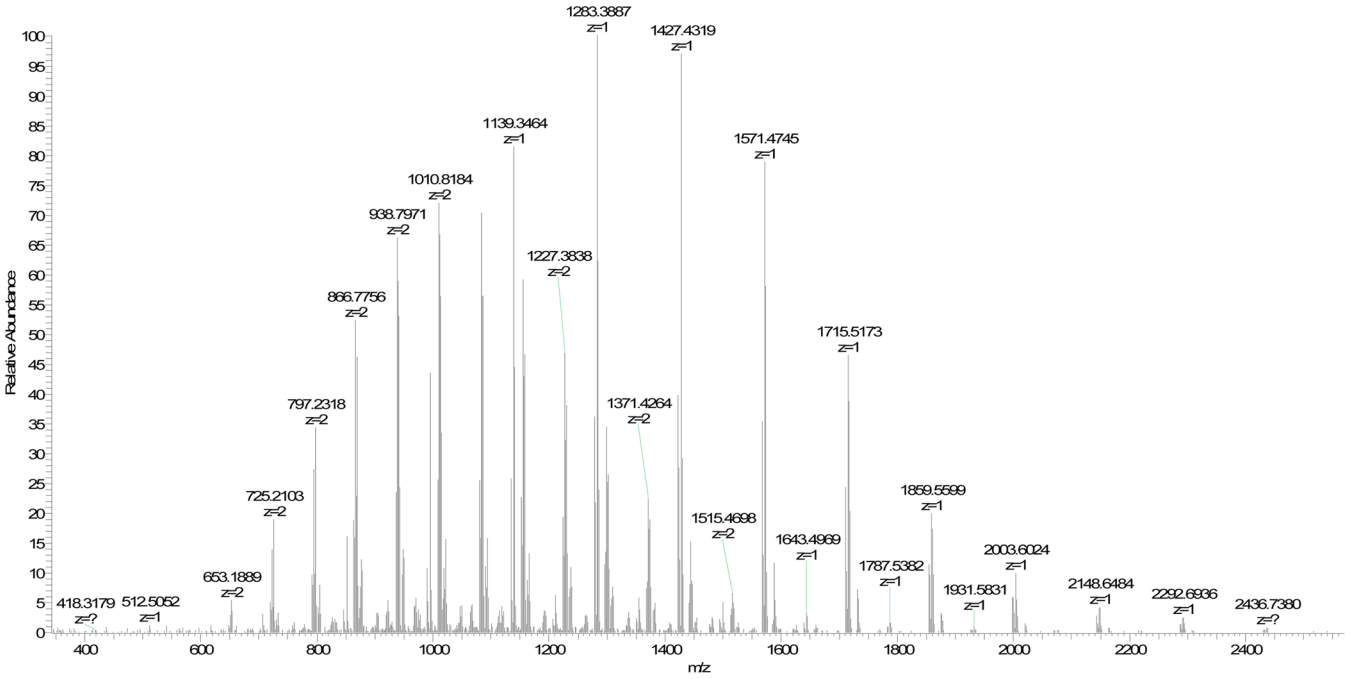


Figure 2. ESI-MS spectrum of poly(*rac*-LA) prepared by the ROP of *rac*-LA (Table 1, entry 7).

and the tetrad peaks were assigned according to the literature.[15] The iso-selectivity in toluene is slightly better than in CH_2Cl_2 and THF when the ratio of $[LA]_0$:$[cat.]_0$:$[BnOH]_0$ is 100:1:1 (Table 1, entries 1−3). The iso-selectivity of complex **1** is better than that of complex **2** under the same conditions (Table 1, entries 1 and 4). A best P_m value of 0.73 was achieved (Table 1, entry 8) for complex **1** when the ratio of $[rac\text{-}LA]_0$:$[\mathbf{1}]_0$:$[BnOH]_0$ is 200:1:1 (Figures 3 and S6, Supporting Information). All other polymers

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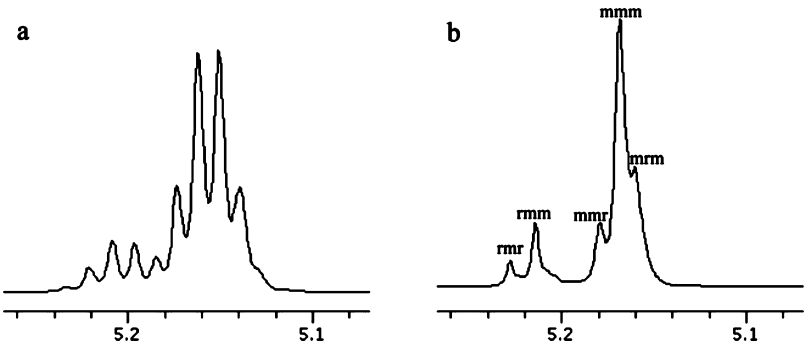


Figure 3. Methine region of the (a) ^{1}H NMR spectrum and (b) homonuclear decoupled ^{1}H NMR spectrum of the PLA generated using complex **1** (Table 1, entry 8).

are also isotactic-enriched with similar P_m values of 0.65−0.73. When the temperature decreases to 0 °C, the iso-selectivity does not improve significantly (Table 1, entry 6, P_m = 0.74, Figure S7, Supporting Information). In order to study the role of 18-crown-6, the reaction of the ligand and $KN(SiMe_3)_2$ in dimethoxyethane (DME) was performed to give a complex of K**L**−DME. K**L**−DME also can catalyze the ROP of *rac*-lactide giving a low iso-selectivity of P_m = 0.57 (Table 1, entry 5), which indicates that the crown ether is important for the highly iso-selective ROP of *rac*-lactide. Compared to other alkali-metal systems, the iso-selectivities of complexes **1** and **2** are higher.[14] The higher selectivities may result from the special configurations of these two complexes, in which the active M^+-O^- center of sodium/potassium naphthalenolate is partially sandwiched in the two layers that are constructed by the huge 18-crown-6/15-crown-5 and the planar benzo[*j*]xanthenyl group. Therefore, the stereo interactions among the chain end of polymer, incoming lactide, and the ligand will be stronger than in an open environment. For a metal-catalyzed ROP of cyclic ester, two mechanisms are often invoked to explain the steroselectivity: chain end control and enantiomorphic site control. In order to verify the iso-selective mechanism belonging to which one, the stereoerrors of a high molecular weight polymer sample (Table 1, entry 12, $[rac\text{-LA}]_0$:$[\mathbf{1}]_0$:$[BnOH]_0$ = 1000:1:1) obtained with complex **1** as a catalyst were analyzed.[3o,4a,d] Usually, a high molecular weight polymer will contain a larger number of stereoerrors which will allow us to do a creditable analysis of the iso-selective mechanism. As depicted in Figure S8, Supporting Information, the integrals of four rmr, rmm, mmr, and mrm tetrad peaks give an approximate ratio of 1:4:4:9. Because a stereoerror sequence of −*RRRRSSSS*− (−mmmrmmm−) arising from the chain end control will give a ratio of 0:1:1:1 for rmr:mmr:rmm:mrm and the singe insertion stereoerror sequence of −*RRRRSSRRRR*−/−*SSSSRRSSSS*− (−mmmrmrmmm−) arising from the enantiomorphic site control will give a ratio of 1:1:1:2 for rmr:mmr:rmm:mrm, these two type stereoerrors with an approximate ratio of 3:1 will give a ratio of 1:4:4:5. The unusual enhancement of the mrm tetrad might correspond to the presence of stereorandom transesterification during the course of the polymerization reaction, which accounts for an increase of the intensity of the mrr, rrrr, and rrm tetrads, all of which have an analogous chemical shift to the mrm tetrad, but which should not be present in the ^{1}H NMR for the polymerization of *rac*-lactide in the absence of transesterification and/or epimerization side reactions.[3o,14f,16,17] Because no serious epimerization reaction was found in the polymerization of L-lactide and D-lactide (Table 1, entries 17 and 18, Figure S9, Supporting Information) in this system, epimerization reaction should contribute very little to the enhancement of the mrm tetrad. As the ESI mass spectrum of a final polymer (Figure S5, Supporting Information) has confirmed the existence of the transesterification reaction, the slight enhancement of the mrm tetrad might result from the transesterification reaction. The peak at 5.215 ppm attributable to mmmrr/rrmmm hexads in the homonuclear-decoupled ^{1}H NMR spectrum (Figure S8, Supporting Information) also can confirm the existence of the transesterification reaction.[18] The transesterification reaction may destroy the stereomicrostructure of the polymer and make the iso-selective mechanism more complicated to understand. Therefore, at the present stage, we cannot definitively assign it to any one iso-selective mechanism. However, we think a chain end control mechanism may be predominant due to the more corresponding stereoerrors; complex **1** or **2** just affords a site for the polymerization of *rac*-lactide in which the interaction between the *rac*-lactide and the end of polymer chain is important for the high iso-selectivity. But the cooperation of enantiomorphic site control cannot be ruled out due to the chirality of the ligand. Using an enantiopure catalyst to distinguish the chain end control and enantiomorphic site control mechanisms is another normal way because different polymerization reaction rates will be observed for L-lactide, D-lactide, and *rac*-lactide. Although the ligand has a chiral ethane center which bridges naphthalenol and xanthenyl group in this system, the separation of enantiomers has not succeeded in our lab until now. Some new enantiopure ligands were designed and synthesized in our lab for further mechanism research.

CONCLUSION

In summary, efficient and iso-selective sodium and potassium naphthalenolate catalysts for the ROP of *rac*-lactide are reported in this study giving polylactides with desired molecular weights and narrow PDIs; the best isotacticity (P_m) achieved was 0.73 in this system at room temperature. Because sodium and potassium are innocuous, abundant elements in the human body and are suitable for the catalytic synthesis of medical polylactide, it is valuable to improve the iso-selectivity for the ROP of *rac*-lactide catalyzed by sodium/potassium complexes. It is also important to understand the origin of iso-selectivity and reaction mechanisms in these similar systems. Further efforts in these directions are in progress in our laboratory.

EXPERIMENTAL SECTION

General Considerations. All syntheses and manipulations of air- and moisture-sensitive materials were performed under a dry nitrogen atmosphere or in a glovebox using standard Schlenk techniques. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL ECS-400 MHz spectrometer or a Varian Mercury Plus 300 or 600 MHz spectrometer.

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The elemental compositions of the complexes were measured using an Elemental Vario EL series CHN analyzer with the samples under a nitrogen atmosphere. The molecular weights (M_n and M_w) and the molecular mass distributions (M_w/M_n) of the polymer samples were measured by gel permeation chromatography (GPC) at 25 °C using THF as a solvent, an eluent flow rate of 1 mL/min, and narrow polystyrene standards as reference samples. The measurements were performed using a Waters 1525 binary system that was equipped with a Waters 2414 RI detector using two Styragel columns (10^2−10^6 kg/mol). Each reported value was corrected using a factor of 0.58 for polylactide according to the literature.[12] The mass spectroscopic data were obtained using a Thermo Scientific Orbitrap Elite MS (LTQ Orbitrap Elit).

Materials. Toluene, THF, and hexane were dried by refluxing with sodium and benzophenone ketyl, the latter serving as an indicator. CH_2Cl_2 was distilled from P_2O_5; *rac*-LA, L-LA, and D-LA were purchased from Daigang BIO Engineer Ltd. of China and were recrystallized from toluene three times. $CDCl_3$ was purchased from J&K Scientific, Ltd., in Beijing and was dried over activated molecular sieves. $KN(SiMe_3)_2$ and $NaN(SiMe_3)_2$ were purchased from J&K Scientific Ltd. and used as received. 18-Crown-6 and 15-crown-5 were purchased from local companies and were used as received.

Synthesis of 1-(Benzo[*J*]xanthen-12-yl)naphthalen-2-ol (HL). To a nicely ground mixture of 2-naphthol (0.28 g, 2.0 mmol) and salicylaldehyde (0.12 g, 1.0 mmol) was added P_2O_5 (0.03 g, 20.0 mol %). The reaction mixture was heated at 80 °C for 12 h. After completion (monitored by TLC), the reaction mixture was cooled to room temperature, and then water (50 mL) was added. The mixture was extracted with ethyl acetate three times (3 × 25 mL). The combined extract was then washed with brine and dried over anhydrous $MgSO_4$; then the solvent was evaporated under vacuum to give a crude product, which was purified by column chromatography over silica gel (CH_2Cl_2/hexane = 2:1). A desired white product was obtained. Yield: 0.21 g (58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.84 (d, J = 8.0 Hz, Ar-*H*, 1H), 8.08 (d, J = 8.0 Hz, Ar-*H*, 1H), 7.97 (d, J = 8.0 Hz,, Ar-*H*, 1H), 7.65−7.85 (m, Ar-*H*, 3H), 7.60 (d, J = 8.0 Hz, Ar-*H*, 2H), 7.37−7.50 (m, Ar-*H*, 3H), 7.07−7.16 (m, Ar-*H*, 2H), 6.85−6.90 (m, Ar-*H*, 2H), 6.75 (d, J = 8.0 Hz, Ar-*H*, 1H), 5.43 (b, O*H*, 1H), 5.06 (s, C*H*, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 150.2, 149.4, 132.6, 130.1, 129.6, 129.4, 129.0, 128.6, 127.9, 126.8, 126.4, 124.1, 123.5, 123.4, 122.5, 121.8, 119.7, 117.7, 116.9, 116.1 (Ph), 31.9 (−*C*H−). MS (m/z): HRMS (ESI) calcd for $C_{27}H_{18}O_2$ ([M-H]$^-$), 373.1229; found, 373.1153. Anal. Calcd for $C_{27}H_{18}O_2$: C 86.61, H 4.85. Found: C 86.89, H 4.79.

Synthesis of Complex KL−DME. A solution of HL (0.37 g, 1.00 mmol) and $KN(SiMe_3)_2$ (1.1 mL, 1.1 mmol, 1.00 M in hexane) was stirred in 1,2-dimethoxyethane (50 mL) at room temperature under a N_2 atmosphere for 12 h, and a laurel-green liquid was obtained. The solvent was removed under vacuum, and the laurel-green solid residue was recrystallized using a mixture solvent of dichloromethane and *n*-hexane. A laurel-green powder was obtained. Yield: 0.26 g (63%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.48 (d, J = 9.0 Hz, Ar-*H*, 1H), 7.81 (d, J = 9.0 Hz, Ar-*H*, 1H), 7.73 (d, J = 9.0 Hz, Ar-*H*, 1H), 7.60 (t, J = 9.0 Hz, Ar-*H*, 1H), 7.42−7.57 (br, Ar-*H*, 2H), 7.17 (t, J = 9.0 Hz, Ar-*H*, 2H), 7.01−7.09 (m, Ar-*H*, 4H), 6.56−6.79 (m, Ar-*H*, 3H), 6.33 (s, Ar-*H*, 1H), 3.47 (s, −CH_2−, 4H), 3.30 (s, −CH_3, 6H), 3.23 (s, −C*H*−, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1, 148.7, 134.6, 131.9, 129.7, 129.3, 129.1, 128.3, 128.1, 127.6, 126.8, 126.1, 125.9, 124.9, 124.8, 124.1, 123.9, 123.8, 123.0, 119.3, 118.5, 118.3, 116.1, 114.4 (Ph), 71.6 (−CH_2-), 58.9 (−CH_3), 32.8 (−CH−). Anal. Calcd for $C_{31}H_{27}KO_4$: C 74.07, H 5.41. Found: C 73.91, H 5.36.

Synthesis of Complex 1. A solution of HL (0.37 g, 1.00 mmol), $KN(SiMe_3)_2$ (1.1 mL, 1.1 mmol, 1.00 M in hexane), and 18-crown-6 (0.29 g, 1.1 mmol) in toluene (50 mL) was stirred at room temperature under a N_2 atmosphere for 12 h. The mixture changed into a laurel-green turbid liquid. A green solid settled after standing still for a while; then the green solid was separated and recrystallized with a mixture solvent of dichloromethane and *n*-hexane. A dry laurel-green solid could be obtained after the solvent was removed completely under vacuum. Yield: 0.34 g (51%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (d, J = 8.0 Hz, Ar-*H*, 1H), 7.80 (d, J = 8.0 Hz, Ar-*H*, 1H), 7.72 (d, J = 8.0 Hz, Ar-*H*, 1H), 7.66 (s, −C*H*−, 1H), 7.63 (d, J = 8.0 Hz, Ar-*H*, 1H), 7.59 (d, J = 8.0 Hz, Ar-*H*, 2H), 7.43 (t, J = 8.0 Hz, Ar-*H*, 2H), 7.34 (d, J = 8.0 Hz, Ar-*H*, 1H), 7.25 (d, J = 8.0 Hz, Ar-*H*, 1H), 7.15 (t, J = 8.0 Hz, Ar-*H*, 1H), 7.09 (d, J = 8.0 Hz, Ar-*H*, 1H), 7.04 (d, J = 8.0 Hz, Ar-*H*, 1H), 6.94 (t, J = 8.0 Hz, Ar-*H*, 1H), 6.76−6.81 (m, Ar-*H*, 2H), 3.48 (s, −CH_2−, 24H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.2, 148.9, 133.4, 132.8, 130.3, 130.2, 128.1, 127.9, 127.8, 127.5, 127.4, 126.4, 126.3, 126.1, 125.3, 124.5, 124.4, 123.6, 123.0, 121.9, 121.7, 119.3, 118.4, 117.1, 115.0 (Ph), 69.6 (−CH_2−), 31.4 (−CH−). Anal. Calcd for $C_{39}H_{41}KO_8$: C 69.21, H 6.11. Found: C 68.99, H 6.23.

Synthesis of Complex 2. A solution of HL (0.37 g, 1.0 mmol) with $NaN(SiMe_3)_2$ (0.55 mL, 1.1 mmol, 2.00 M in hexane) and 15-crown-5 (0.24 g, 1.1 mmol) in toluene (50 mL) was stirred at room temperature under a N_2 atmosphere for 12 h; then the mixture changed into a laurel-green turbid liquid. A green solid settled after standing still for a while; then the laurel-green solid was separated and recrystallized with a mixture solvent of dichloromethane and *n*-hexane. The solid was dried under vacuum. Yield: 0.28 g (46%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (m, Ar-*H*, 1H), 7.68 (d, J = 8.0 Hz, Ar-*H*, 1H), 7.63 (d, J = 8.0 Hz, Ar-*H*, 1H), 7.59 (m, Ar-*H*, 1H), 7.37−7.42 (m, Ar-*H*, 2H), 7.41 (s, −C*H*-, 1H), 7.33 (t, J = 8.0 Hz, Ar-*H*, 1H), 7.26 (m, Ar-*H*, 2H), 7.11 (m, Ar-*H*, 2H), 7.07 (d, J = 8.0 Hz Ar-*H*, 1H), 7.01 (t, J = 8.0 Hz, Ar-*H*, 1H), 6.88 (t, J = 8.0 Hz, Ar-*H*, 1H), 6.71−6.76 (m, Ar-*H*, 2H), 3.59 (s, −CH_2−, 20H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4, 148.9, 133.8, 133.0, 130.4, 130.3, 128.2, 128.0, 127.5, 126.5, 126.2, 125.6, 124.8, 124.5, 123.6, 122.9, 121.8, 118.9, 117.3, 115.2 (Ph), 69.3 (−CH_2−), 31.6 (−CH−). Anal. Calcd for $C_{37}H_{37}NaO_7$: C 72.06, H 6.05. Found: C 72.51, H 6.13.

General Procedure for Polymerization of *rac*-Lactide. A typical polymerization procedure is illustrated by the synthesis of PLA-($[LA]_0$/$[cat.]_0$/$[BnOH]_0$ = 200:1:1; Table 1, entry 8). A solution of **1** (0.0169 g, 0.025 mmol), BnOH (0.025 mmol, 1 M in toluene), and *rac*-lactide (0.72 g, 5.0 mmol) in toluene (10 mL) was rapidly stirred at room temperature for 3 min; then the reaction was quenched by a few drops of water. The polymer was precipitated by adding hexane (20 mL). A white crystalline solid was obtained by recrystallization from a CH_2Cl_2/hexane mixed solvent and dried under vacuum.

Crystallographic Studies. The data were collected using a SuperNova (Dual) X-ray diffractometer equipped with a graphite-monochromated Cu/Mo Kα radiation source (λ = 1.54184/0.71073 Å). The structures were solved by direct methods using the Siemens SHELXTL PLUS program. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. All hydrogen atoms were placed by geometrical considerations and were added to the structure-factor calculations. The crystal data and refinement result are summarized in Table S1, Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra of the two complexes, the polymerization studies, and CIF files that provide the crystallographic data for complexes **1** and **2** with CCDC reference numbers of 1029548 and 1038538. 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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