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Ring-opening polymerization of *rac*-lactide catalyzed by crown ether complexes of sodium and potassium iminophenoxides†

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A series of iminophenoxide ligand precursors [2-(RN=CH)C₆H₄OH] (HL¹: R = C₆H₅; HL²: R = 2,6-ⁱPr₂C₆H₃) and [2-(RN=CH)-4,6-^tBu₂C₆H₂OH] (HL³: R = C₆H₅; HL⁴: R = 2,6-ⁱPr₂C₆H₃) were synthesized. These compounds reacted with NaN(SiMe₃)₂/15-crown-5 or KN(SiMe₃)₂/18-crown-6 to afford corresponding crown ether complexes of sodium and potassium iminophenoxides (1, (15-C-5)NaL²; 2, (15-C-5)NaL³; 3, (15-C-5)NaL⁴; 4, (18-C-6)KL¹; 5, (18-C-6)KL²; 6, (18-C-6)KL³; 7, (18-C-6)KL⁴). Catalysis of the complexes toward the ring-opening polymerization of *rac*-lactide was studied. Each of the complexes exhibited high catalytic activity at room temperature. Complexes 2, 3, 6 and 7 showed poor isotactic selectivity and relatively broad molecular weight distributions. Complexes 1 and 5 resulted in more stereoregular polymers with P_m values of 0.58 and 0.66, respectively. Complex 4 led to the best selectivity for isotacticity (P_m = 0.75) when the polymerization was performed in toluene at 0 °C.

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Introduction

Polylactide (PLA), an important biodegradable and biocompatible polymer, has been used in a wide variety of applications such as drug delivery systems, resorbable sutures, and medical implants.^{1–11} The ring-opening polymerization (ROP) of lactides catalyzed by metal complexes is a major method for the synthesis of PLA with controlled molecular weights, low polydispersity indices (PDIs), and specific stereo-microstructures.^{12–14} A lot of metal complexes such as Zn,^{15–24} Mg,^{25–27} Al,^{38–45} Sn,^{46–57} and rare earth metal complexes^{58–74} have been proven to be effective for the ROP of lactides. In recent years alkali metal complexes also attracted great interest owing to their high catalytic activity and cheapness, wide availability and nontoxic nature of alkali metals.^{75–101} Several alkali metal complexes supported by iminophenoxide ligands have been reported to efficiently initiate the ROP of lactides. In 2012 Chen *et al.* reported the synthesis and catalysis of lithium and sodium iminophenoxide complexes toward the ROP of L-lactide.⁹¹ In 2015 Cano *et al.* synthesized a series of lithium, sodium, and potassium iminophenoxide complexes, and found that the lithium complexes resulted in heterorich-PLA (P_r = 0.75),¹⁰²

while sodium and potassium complexes presented poor stereoselectivity in the polymerization of *rac*-lactide.⁹² Chakraborty *et al.* reported similar complexes which catalyzed solvent free ROP of *rac*-lactide with high catalytic activity and led to heterorich-PLA.⁹³ Recently Wu and co-workers reported that crown ether complexes of sodium and potassium mono-phenoxides exhibited high catalytic activity and high iso-selectivity for the ROP of *rac*-lactide.^{94–101} However, the phenoxide ligands are required to have very bulky *ortho*-substituents on the aromatic rings to achieve good selectivity.^{94–101} It is interesting to design simpler ligands to get high catalytic selectivity of complexes. A strategy is to use chelate ligands to restrict rotation of M–O_{Ar} bonds of alkali metal complexes. In a earlier work we demonstrated that crown ether complex of potassium quinolin-8-olate did initiate iso-selective ROP of *rac*-lactide. The P_m value¹⁰³ reached 0.75 when the polymerization of 100 equiv. of *rac*-lactide was performed in toluene at 0 °C.¹⁰⁴ We intended to examine more chelate ligands to improve catalytic selectivity of the chelate alkali metal complexes. Herein we report synthesis and catalytic study of crown ether complexes of sodium and potassium iminophenoxides with different substituents on the aromatic rings.

Results and discussion

Iminophenols 2-(PhN=CH)C₆H₄OH (HL¹), 2-(2,6-ⁱPr₂C₆H₃N=CH)-C₆H₄OH (HL²), 2-(PhN=CH)-3,5-^tBu₂C₆H₂OH (HL³) and 2-(2,6-ⁱPr₂C₆H₃N=CH)-3,5-^tBu₂C₆H₂OH (HL⁴) were synthesized according to reported procedures.⁹² Treatment of the iminophenols with NaN(SiMe₃)₂/15-crown-5 or KN(SiMe₃)₂/18-crown-6 in toluene at room temperature afforded corresponding

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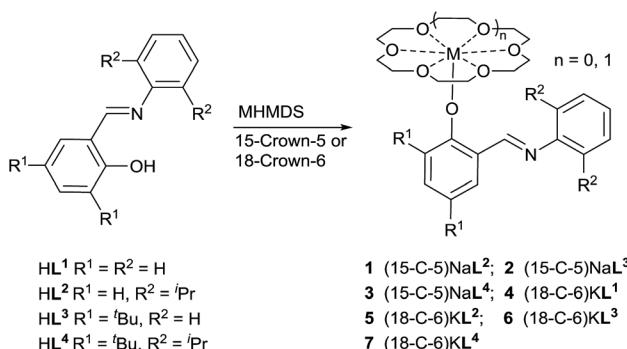
crown ether complexes of sodium and potassium iminophenoxydes **1–7** respectively (Scheme 1). However, treatment of HL^1 with $\text{NaN}(\text{SiMe}_3)_2$ in toluene or THF in the presence of 15-crown-5 could not generate expected crown ether sodium complex.

Complexes **1–7** are yellow solids, soluble in DMSO, THF, and slightly soluble in toluene. They were characterized by elemental analyses, ^1H and $^{13}\text{C}\{\text{H}\}$ NMR spectroscopy. Complexes **3** and **4** were further characterized by single crystal X-ray diffraction techniques. The ORTEP drawing of complex **3** is presented in Fig. 1, along with selected bond lengths and angles. The structure shows that the phenoxy ligand coordinates to the central sodium cation in a monodentate mode, rather than an O,N-chelate mode. This might be due to steric repulsion between the *N*-arylimino group and the crown ether ligand which combines with Na^+ through coordination of the five oxygen atoms. The $\text{C}(13)-\text{O}(6)-\text{Na}(1)$ angle of $159.67(17)^\circ$ reveals approximately linear arrangement of $\text{C}(13)$, $\text{O}(6)$ and $\text{Na}(1)$ atoms. The $\text{O}(6)-\text{Na}(1)$ distance of $2.1393(18)$ Å is slightly

shorter than corresponding one in sodium 2-(anthracen-9-yl)-4,6-di-*tert*-butylphenolate crown ether complex ($2.1478(18)$ Å). The $\text{O}(6)-\text{C}(13)$ distance of $1.277(2)$ Å is also slightly shorter than corresponding that in the above-mentioned complex ($1.287(3)$ Å).⁹⁸

The ORTEP drawing of complex **4** is presented in Fig. 2, along with selected bond lengths and angles. In the structure the phenoxy ligand also coordinates to the central metal in a monodentate mode. However, the $\text{C}(15)-\text{O}(7)-\text{K}(1)$ angle of $130.8(3)^\circ$ shows that the connectivity of $\text{C}(15)$, $\text{O}(7)$ and $\text{K}(1)$ atoms is not linear. The $\text{C}(15)-\text{O}(7)-\text{K}(1)$ plane is almost perpendicular to the adjacent aromatic ring plane, the torsion angle of $\text{K}(1)-\text{O}(7)-\text{C}(15)-\text{C}(14)$ being 96° . The $\text{K}(1)-\text{C}(7)$ distance of $2.623(3)$ Å is within a normal range compared with the reported crown ether potassium phenoxide complexes.^{94–100} The $\text{O}(7)-\text{C}(15)$ distance of $1.289(5)$ Å is comparable with those in crown ether potassium complex bearing 2-(anthracen-9-yl) phenolate ligands.⁹⁸

In the presence of benzyl alcohol, catalysis of complexes **1–7** in the ROP of *rac*-lactide was tested, and the results are summarized in Table 1. Each of the complexes showed high catalytic activity in toluene at room temperature (Table 1, entries 1–7). When using a molar ratio of $100 : 1 : 1$ for $[\text{LA}]_0/[\text{M}]_0/[\text{BnOH}]_0$, complex **1** led to faster polymerization of *rac*-lactide than complexes **2** and **3** for the three similar sodium complexes (Table 1, entries 1–3). Potassium complexes **4–7** exhibited same activity order. Thus, the complexes without *ortho*-*tert*-butyl group on the phenoxy rings led to faster ROP of *rac*-lactide than the other ones with *ortho*-*tert*-butyl groups on the phenoxy rings. It seems that the stereo hindrance of *ortho*-*tert*-butyl groups on the phenoxy rings decreases the ROP rate (Table 1, entries 4–7). But we cannot rule out influence of electron effect of the *ortho*- and *para*-position *tert*-butyl groups.



Scheme 1 Synthesis of crown ether complexes of sodium and potassium iminophenoxydes.

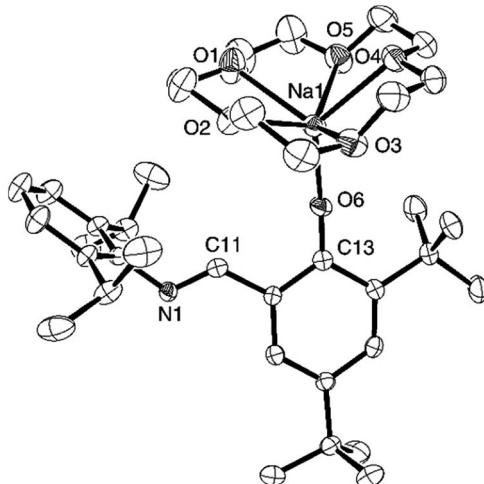


Fig. 1 ORTEP drawing of complex **3** with 20% probability thermal ellipsoids. Selected bond lengths (Å) and angles (deg): $\text{Na}(1)-\text{O}(6)$ $2.1393(18)$, $\text{Na}(1)-\text{O}(1)$ $2.450(3)$, $\text{Na}(1)-\text{O}(2)$ $2.431(2)$, $\text{Na}(1)-\text{O}(3)$ $2.495(2)$, $\text{Na}(1)-\text{O}(4)$ $2.402(2)$, $\text{Na}(1)-\text{O}(5)$ $2.492(2)$, $\text{N}(1)-\text{C}(11)$ $1.267(2)$, $\text{O}(6)-\text{C}(13)$ $1.277(2)$; $\text{C}(13)-\text{O}(6)-\text{Na}(1)$ $159.67(17)$.

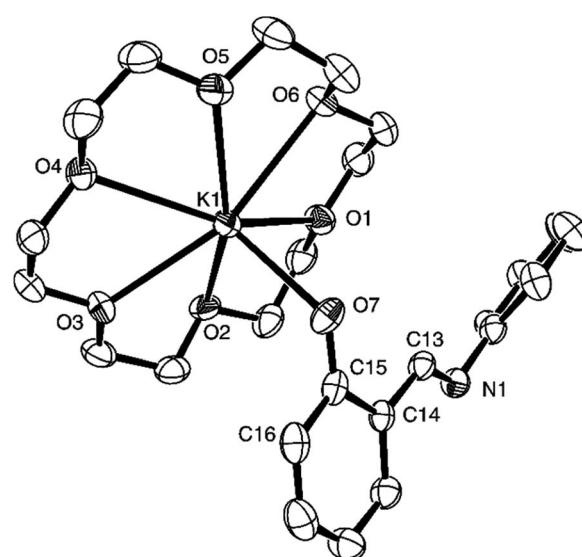


Fig. 2 ORTEP drawing of complex **4** with 20% probability thermal ellipsoids. Selected bond lengths (Å) and angles (deg): $\text{K}(1)-\text{O}(7)$ $2.623(3)$, $\text{K}(1)-\text{O}(3)$ $2.758(3)$, $\text{K}(1)-\text{O}(5)$ $2.833(3)$, $\text{K}(1)-\text{O}(1)$ $2.856(3)$, $\text{K}(1)-\text{O}(6)$ $2.868(3)$, $\text{K}(1)-\text{O}(2)$ $2.890(3)$, $\text{K}(1)-\text{O}(4)$ $2.913(3)$, $\text{N}(1)-\text{C}(13)$ $1.288(4)$, $\text{O}(7)-\text{C}(15)$ $1.289(5)$; $\text{C}(15)-\text{O}(7)-\text{K}(1)$ $130.8(3)$.



Table 1 ROP of *rac*-LA catalyzed by complexes 1–7^a

Entry	Cat.	[LA] ₀ :[Cat.] ₀ :[BnOH] ₀	Time (min)	Conv. ^b (%)	<i>M</i> _{n,calc} ^c (g mol ⁻¹)	<i>M</i> _{n,GPC} ^d (g mol ⁻¹)	PDI	<i>P</i> _m ^e
1	1	100 : 1 : 1	1	99	14 400	10 100	1.32	0.58
2	2	100 : 1 : 1	5	97	14 100	9200	1.25	0.52
3	3	100 : 1 : 1	5	97	14 100	8600	1.30	0.52
4	4	100 : 1 : 1	3	98	14 200	7400	1.18	0.69
5	5	100 : 1 : 1	3	98	14 200	10 400	1.39	0.66
6	6	100 : 1 : 1	7	98	14 200	8900	1.27	0.53
7	7	100 : 1 : 1	10	97	14 100	7800	1.28	0.52
8	1	200 : 1 : 1	3	99	28 600	25 400	1.36	0.60
9	1	300 : 1 : 1	5	99	42 900	30 800	1.39	0.59
10	1	400 : 1 : 1	10	99	57 200	43 000	1.36	0.62
11	1	500 : 1 : 1	15	99	71 500	56 400	1.37	0.63
12	1	500 : 1 : 10	2	99	7200	8500	1.34	0.61
13 ^f	1	100 : 1 : 1	15	99	14 400	9500	1.16	0.71
14	4	200 : 1 : 1	5	97	28 100	12 500	1.11	0.70
15	4	300 : 1 : 1	10	99	42 900	21 000	1.28	0.69
16	4	400 : 1 : 1	15	96	55 500	25 800	1.25	0.69
17	4	500 : 1 : 1	30	89	64 200	29 400	1.18	0.66
18	4	500 : 1 : 10	3	99	7200	8100	1.37	0.70
19 ^g	4	100 : 1 : 1	30	19	2800	400	1.21	—
20 ^h	4	100 : 1 : 1	30	15	2300	400	1.19	—
21 ^f	4	100 : 1 : 1	20	97	14 100	5600	1.06	0.75

^a [Cat.]₀ = 5 mmol L⁻¹, reactions were conducted in 4 cm³ solvent under 25 °C. ^b *rac*-LA conversion was determined by ¹H NMR spectra. ^c *M*_{n,calc} = 144.13 × [LA]₀/[BnOH]₀ × conv. (%) + 108.14. ^d Obtained from GPC analysis and calibrated against the polystyrene standard, multiplied by 0.58.¹⁰⁵

^e Determined by analysis of all of the tetrad signals in the methine region of the homonuclear-decoupled ¹H NMR spectra.^f Polymerization reaction was run at 0 °C. ^g Polymerization reaction was carried out in CH₂Cl₂. ^h Polymerization reaction was carried out in THF.

The *ortho*-position substituents on the *N*-aryl rings exhibited less effect on the catalytic activity of the complexes, which might be because the aromatic rings are far from the metal centers. In addition, the potassium complexes are less active than corresponding sodium complexes (5 vs. 1, 6 vs. 2, and 7 vs. 3), which is different from the previous report results.^{95,98} The molecular weights of the final polymers generated by those catalysis are lower than expected. A plausible reason could be the presence of transesterification side reaction in the process of polymerization.^{94–101} The relatively wide molecular weight distributions (1.18 to 1.39) and MALDI-TOF MS analysis (Fig. 3) of the polymers support this explanation. For example, the MS analysis of the polymer showed two main series of peaks. A series of peaks at 144 m + 108 + 23, which can be assigned to m(C₆H₈O₄) + BnOH + Na⁺. Another series of peaks at 72 m + 108 + 23, which can be ascribed to m(C₃H₄O₂) + BnOH + Na⁺. The series of peaks separated by *m/z* = 72 Da is indicative of transesterification occurring in the process of polymerization.

The sodium and potassium complexes **1** and **4** were selected for a more detailed study on their catalysis. At first, higher monomer loadings were tested using **1**/BnOH and **4**/BnOH, respectively (Table 1, entries 8–11 and 14–17). **1**/BnOH showed higher activity than **4**/BnOH. For example, **1**/BnOH drove 500

equiv. of *rac*-lactide to PLA in 15 min in 99% conversion, whereas **4**/BnOH drove 89% conversion of 500 equiv. of *rac*-lactide to spend 30 min. Each of **1**- and **4**-catalyzed ROP gave a linear relationship of the molecular weights of polymers to the ratio of monomer to catalyst (Fig. 4 and 5), implying that the polymerizations are controlled. Complexes **1** and **4** were demonstrated to catalyze the immortal ROP of 500 equiv. of *rac*-LA in the presence of 10 equiv. of BnOH, resulting in polymers with controlled molecular weights (Table 1, entries 12 and 18). We also examined the catalytic reaction by **4**/BnOH in CH₂Cl₂ and THF, respectively (Table 1, entries 19 and 20). Both CH₂Cl₂ and THF were less effective than toluene. In these solvents the catalyst exhibited lower activity than in toluene and the molecular weight of the polymers were markedly lower than the theoretical values.

The reactions in toluene exhibited isoselectivity (e.g. Fig. 6). Potassium complex **4**/BnOH showed the highest selectivity when using a ratio of 100 : 1 : 1 for [LA]₀/[**4**]₀/[BnOH]₀, producing isotactic PLA with a *P*_m value of 0.69 at room temperature. Among the three sodium complexes, **1** exhibited better catalytic selectivity. These experimental facts demonstrated that the complexes with less sterically hindered ligands had better catalytic selectivity. Based on this



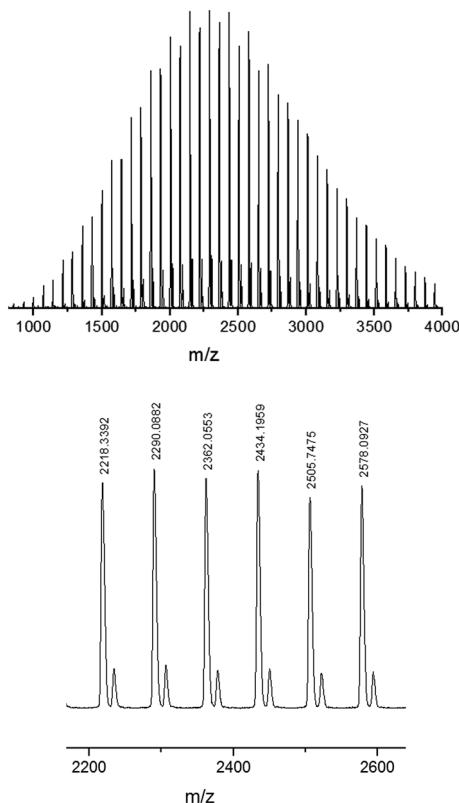


Fig. 3 The MALDI-TOF MS analysis of the polymer prepared by using 4/BnOH as catalyst in toluene at room temperature, ratio of $[LA]_0/[M]_0/[BnOH]_0 = 20 : 1 : 1$.

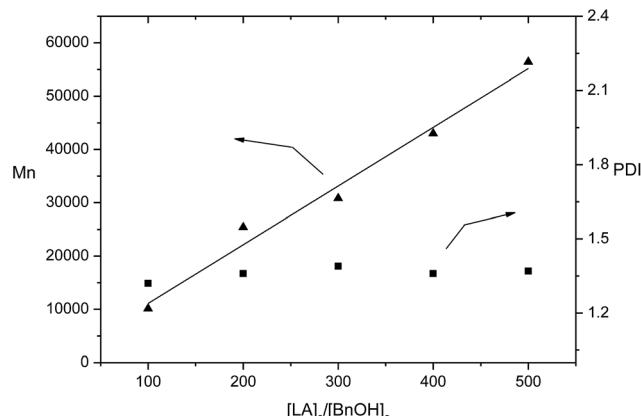


Fig. 4 Polymerization of *rac*-LA catalyzed by 1/BnOH in toluene at room temperature. The relationships between M_n (▲), PDI (■) of the polymer and the initial mole ratios $[LA]_0/[BnOH]_0$ is shown (Table 1, entries 1 and 8–11).

experimental result, we speculate that the phenoxide ligands might coordinate to alkali metal center in a *O,N*-chelate mode during the process of catalysis, which improved the catalytic selectivity of the complexes through restricting rotation of the M–O_{aryl} single bond. A less sterically hindered phenoxo group and *N*-aryl group would benefit formation of *O,N*-chelate complexes.

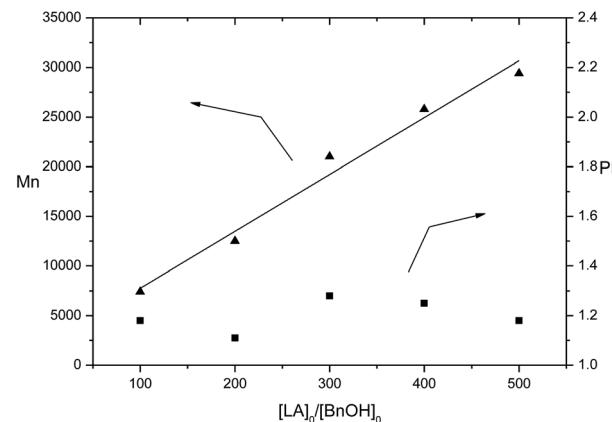


Fig. 5 Polymerization of *rac*-LA catalyzed by 4/BnOH in toluene at room temperature. The relationships between M_n (▲), PDI (■) of the polymer and the initial mole ratios $[LA]_0/[BnOH]_0$ is shown (Table 1, entries 4 and 14–17).

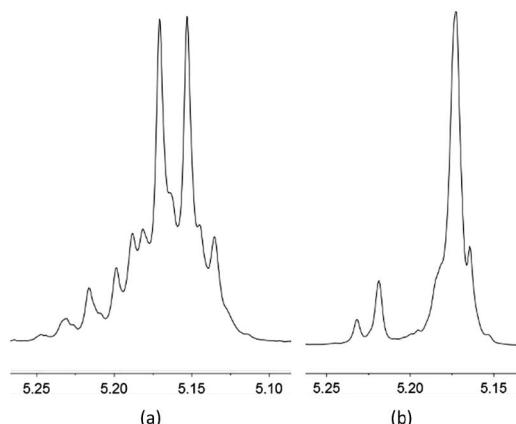


Fig. 6 Methine region of the (a) normal ^1H NMR spectrum and (b) homonuclear decoupled ^1H NMR spectrum of the PLA prepared by complex 4/BnOH catalysis (Table 1, entry 21).

We also noticed that the P_m values of the polymers catalyzed by 1/BnOH slightly increased with the increase of the ratio of *rac*-LA to catalyst (Table 1, entries 1 and 8–11). However, the P_m values of the polymers catalyzed by 4/BnOH were approximately unchanged when the ratio of monomer to catalyst varied from 100 to 400 and slightly decreased when the ratio of monomer to catalyst was 500 (Table 1, entries 4 and 14–17). Reduction of polymerization temperature led to increase of selectivity whether the catalyst was 1 or 4. The P_m value of the PLA was 0.71 when 100 equiv. of *rac*-LA was catalytically polymerized by 1/BnOH at 0 °C and the P_m value of the PLA reached 0.75 when 100 equiv. of *rac*-LA was catalytically polymerized by 4/BnOH at 0 °C (Table 1, entries 13 and 21). The end group analysis of the PLA proved that the polymer chain was capped with one benzyl ester end and one hydroxyl end (Fig. 7), which are consistent with an insertion mechanism of a benzyloxy group into the lactide as supposed for most alkali metal phenoxides.^{94–100}



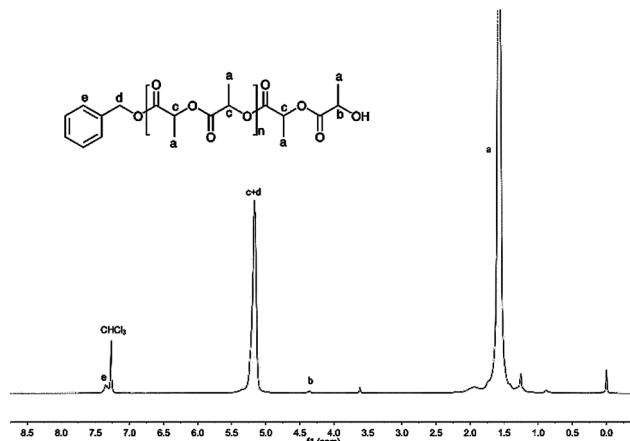


Fig. 7 The ^1H NMR spectrum of PLA initiated by 4/BnOH (Table 1, entry 4) (NMR: 400 MHz, solvent: CDCl_3 , reference: TMS).

Conclusions

In summary, we have synthesized and characterized a series of sodium and potassium iminophenoxydes bearing 15-crown-5 or 18-crown-6 as the auxiliary ligand. In the presence of benzyl alcohol, all the complexes can efficiently catalyze the ROP of *rac*-lactide. The catalysts with bulky substituents on the aromatic rings of phenoxy and *N*-aryl groups are unfavored for the selectivity of the polymers. The potassium complex without any substituents except imino group on the aromatic rings, $[(18\text{-crown-6})\text{KOC}_6\text{H}_4\{2\text{-}(\text{PhN}=\text{CH})\}]$ (4), exhibited the best selectivity of isotacticity ($P_m = 0.75$) when the ROP was carried out at 0°C . During the catalytic process, the iminophenoxy ligands might coordinate to the alkali metal center in a *O,N*-chelate mode which improved the catalytic selectivity of the complexes through restricting rotation of the $\text{M}-\text{O}_{\text{aryl}}$ single bond.

Experimental

All air or moisture sensitive manipulations were performed under dry N_2 using standard Schlenk techniques. Solvents were distilled under nitrogen over sodium (toluene), sodium/benzophenone (*n*-hexane and tetrahydrofuran), or CaH_2 (dichloromethane) and degassed prior to use. $\text{NaN}(\text{SiMe}_3)_2$, $\text{KN}(\text{SiMe}_3)_2$ and other reagents were purchased from local chemical companies and used as received. BnOH was distilled from CaO . *rac*-Lactide was purchased from Daigang Biomaterial Co. and recrystallized three times from toluene prior to use. DMSO-d6, purchased from EMD Millipore Corporation, was degassed, and stored over 4 Å molecular sieves. CDCl_3 was purchased from Cambridge Isotope Laboratories and used as received. NMR spectra were recorded on a Bruker AVANCE III 400 spectrometer at ambient temperature. The chemical shifts of ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were referenced to internal solvent resonances. Elemental analyses were performed on an Elementar Vario EL III analyzer. Gel permeation chromatography (GPC) was recorded on a Waters 150C instrument equipped with UltraStyragel columns (103, 104, and 105 Å) and

a 410 refractive index detector, using monodispersed polystyrene as the calibration standard. THF (HPLC grade) was used as an eluent at a flow rate of $1\text{ cm}^3\text{ min}^{-1}$.

Synthesis of complex 1

To a stirred solution of HL^2 (0.28 g, 1.00 mmol) and 15-crown-5 (0.22 g, 1.00 mmol) in toluene (10 cm^3) was slowly added $\text{NaN}(\text{SiMe}_3)_2$ (0.55 cm^3 , 2 M solution in THF, 1.1 mmol) at room temperature. The mixture was stirred for 10 h to generate a yellow solution. The resulting solution was concentrated *in vacuo*. *n*-Hexane (20 cm^3) was added to the solution to afford complex 1 as a yellow solid (0.30 g, 57%). ^1H NMR (400 MHz, DMSO-d6): δ 8.44 (s, 1H), 7.59 (dd, $J = 7.7, 2.0\text{ Hz}$, 1H), 7.04 (d, $J = 7.6\text{ Hz}$, 2H), 6.98–6.91 (m, 1H), 6.89–6.81 (m, 1H), 6.17 (d, $J = 8.4\text{ Hz}$, 1H), 5.93 (t, $J = 7.2\text{ Hz}$, 1H), 3.56 (s, 20H), 3.02–2.91 (m, 2H), 1.09 (d, $J = 6.9\text{ Hz}$, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO-d6): δ 174.06, 161.93, 152.06, 137.66, 132.25, 126.78, 123.05, 122.87, 122.28, 122.18, 106.98, 69.34, 27.16, 23.39. Anal. calcd for $\text{C}_{29}\text{H}_{42}\text{NNaO}_6$: C 66.52, H 8.08, N 2.67; found: C 66.23, H 8.22, N 2.70.

Synthesis of complex 2

To a stirred solution of HL^3 (0.30 g, 1.00 mmol) and 15-crown-5 (0.22 g, 1.00 mmol) in toluene (10 cm^3) was slowly added $\text{NaN}(\text{SiMe}_3)_2$ (0.55 cm^3 , 2 M solution in THF, 1.1 mmol) at room temperature. The mixture was stirred for 10 h and yellow precipitates were formed. The precipitates were collected by filtration, washed with toluene, and dried *in vacuo* to give yellow solids (0.25 g, 45%). ^1H NMR (400 MHz, DMSO-d6): δ 8.79 (s, 1H), 7.38 (d, $J = 2.9\text{ Hz}$, 1H), 7.31–7.24 (m, 2H), 7.07–6.97 (m, 3H), 6.95 (d, $J = 2.9\text{ Hz}$, 1H), 3.55 (s, 20H), 1.33 (s, 9H), 1.19 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO-d6): δ 173.23, 162.37, 155.59, 139.89, 128.71, 126.24, 126.04, 122.50, 120.82, 120.28, 69.46, 34.90, 33.37, 31.79, 29.52. Anal. calcd for $\text{C}_{31}\text{H}_{46}\text{NNaO}_6$: C 67.49, H 8.40, N 2.54. Found: C 67.02, H 8.57, N 2.66.

Synthesis of complex 3

To a stirred solution of HL^4 (0.39 g, 1.00 mmol) and 15-crown-5 (0.22 g, 1.00 mmol) in toluene (10 cm^3) was slowly added $\text{NaN}(\text{SiMe}_3)_2$ (0.55 cm^3 , 2 M solution in THF, 1.1 mmol) at room temperature. The mixture was stirred for 10 h and yellow precipitates were formed. The precipitates were collected by filtration, washed with toluene, and dried *in vacuo* to give yellow solids (0.32 g, 50%). ^1H NMR (400 MHz, DMSO-d6): δ 8.46 (s, 1H), 7.50 (d, $J = 2.7\text{ Hz}$, 1H), 7.02 (d, $J = 7.6\text{ Hz}$, 2H), 6.96 (d, $J = 2.8\text{ Hz}$, 1H), 6.90 (t, $J = 7.6\text{ Hz}$, 1H), 3.54 (s, 20H), 3.05–2.93 (m, 2H), 1.33 (s, 9H), 1.21 (s, 9H), 1.09 (d, $J = 6.9\text{ Hz}$, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO-d6): δ 172.41, 163.01, 152.59, 139.42, 137.74, 125.98, 125.67, 122.13, 121.69, 120.92, 119.87, 69.20, 34.87, 33.33, 31.86, 29.64, 27.09, 23.40. Anal. calcd for $\text{C}_{37}\text{H}_{58}\text{NNaO}_6 \cdot 0.4\text{C}_7\text{H}_8$: C 71.06, H 9.17, N 2.08. Found: C 71.06, H 9.19, N 2.15.

Single crystals of complex 3 suitable for X-ray diffraction analysis were obtained from a saturated toluene solution.



Synthesis of complex 4

To a stirred solution of **HL**¹ (0.19 g, 1.00 mmol) and 18-crown-6 (0.27 g, 1.00 mmol) in toluene (10 cm³) was slowly added KN(SiMe₃)₂ (1.1 cm³, 1 M solution in THF, 1.1 mmol) at room temperature. The resultant mixture was stirred at room temperature for 10 h and yellow precipitates were formed. The precipitates were collected by filtration, washed with toluene, and dried *in vacuo* to give yellow solids (0.21 g, 42%). ¹H NMR (400 MHz, DMSO-d6): δ 8.78 (s, 1H), 7.51 (dd, J = 7.8, 2.1 Hz, 1H), 7.29 (t, J = 7.8 Hz, 2H), 7.09–6.96 (m, 3H), 6.83–6.75 (m, 1H), 6.09 (dd, J = 8.6, 0.7 Hz, 1H), 5.82 (t, J = 7.2 Hz, 1H), 3.53 (s, 24H). ¹³C{¹H} NMR (101 MHz, DMSO-d6): δ 175.39, 160.70, 154.95, 132.55, 128.82, 126.85, 123.57, 123.08, 122.89, 120.76, 106.30, 69.44. Anal. calcd for C₂₅H₃₄KNO₇·0.15C₇H₈: C 60.94, H 6.91, N 2.73; found: C 61.15, H 6.68, N 2.96.

Single crystals of complex **4** suitable for X-ray diffraction analysis were obtained from a THF/toluene solution.

Synthesis of complex 5

To a stirred solution of **HL**² (0.28 g, 1.00 mmol) and 18-crown-6 (0.27 g, 1.00 mmol) in toluene (10 cm³) was slowly added KN(SiMe₃)₂ (1.1 cm³, 1 M solution in THF, 1.1 mmol) at room temperature. The resultant mixture was stirred at room temperature for 10 h to generate a yellow solution. The solution was concentrated *in vacuo*. Then *n*-hexane (20 cm³) was added to the concentrated solution to afford complex **5** as a yellow solid (0.28 g, 48%). ¹H NMR (400 MHz, DMSO-d6): δ 8.40 (s, 1H), 7.56 (dd, J = 7.6, 1.9 Hz, 1H), 7.02 (d, J = 7.6 Hz, 2H), 6.96–6.87 (m, 1H), 6.83–6.75 (m, 1H), 6.05 (d, J = 8.6 Hz, 1H), 5.82 (t, J = 7.1 Hz, 1H), 3.54 (s, 24H), 3.04–2.89 (m, 2H), 1.07 (d, J = 6.9 Hz, 12H). ¹³C{¹H} NMR (101 MHz, DMSO-d6): δ 174.88, 161.91, 152.26, 137.68, 132.20, 126.44, 123.30, 122.80, 122.23, 122.01, 105.92, 69.44, 27.13, 23.37. Anal. calcd for C₃₁H₄₆KNO₇·0.15C₆H₁₄: C 64.21, H 8.12, N 2.35; found: C 63.83, H 8.58, N 2.67.

Synthesis of complex 6

To a stirred solution of **HL**³ (0.30 g, 1.00 mmol) and 18-crown-6 (0.27 g, 1.00 mmol) in toluene (10 cm³) was slowly added KN(SiMe₃)₂ (1.1 cm³, 1 M solution in THF, 1.1 mmol) at room temperature. The resultant mixture was stirred at room temperature for 10 h and yellow precipitates were formed. The precipitates were collected by filtration, washed with toluene, and dried *in vacuo* to give yellow solids (0.39 g, 64%). ¹H NMR (400 MHz, DMSO-d6): δ 8.83 (s, 1H), 7.40 (d, J = 2.8 Hz, 1H), 7.27 (t, J = 7.7 Hz, 2H), 7.02–6.96 (m, 3H), 6.95 (d, J = 2.9 Hz, 1H), 3.52 (s, 24H), 1.33 (s, 9H), 1.20 (s, 9H). ¹³C{¹H} NMR (101 MHz, DMSO-d6): δ 173.51, 162.32, 155.71, 139.94, 128.69, 126.00, 125.93, 122.37, 120.76, 119.88, 69.42, 34.89, 33.36, 31.79, 29.48. Anal. calcd for C₃₃H₅₀KNO₇: C 64.78, H 8.24, N 2.29; found: C 64.60, H 8.39, N 2.42.

Synthesis of complex 7

To a stirred solution of **HL**⁴ (0.39 g, 1.00 mmol) and 18-crown-6 (0.27 g, 1.00 mmol) in toluene (10 cm³) was slowly added KN(SiMe₃)₂ (1.1 cm³, 1 M solution in THF, 1.1 mmol) at room

temperature. The resultant mixture was stirred at room temperature for 10 h and yellow precipitates were formed. The precipitates were collected by filtration, washed with toluene, and dried *in vacuo* to give yellow solids (0.32 g, 46%). ¹H NMR (400 MHz, DMSO-d6): δ 8.48 (s, 1H), 7.51 (s, 1H), 7.02 (d, J = 7.6 Hz, 2H), 6.95 (s, 1H), 6.90 (t, J = 7.6 Hz, 1H), 3.52 (s, 24H), 3.07–2.94 (m, 2H), 1.34 (s, 9H), 1.21 (s, 9H), 1.10 (d, J = 6.8 Hz, 12H). ¹³C{¹H} NMR (101 MHz, DMSO-d6): δ 172.81, 162.99, 152.70, 139.49, 137.72, 125.59, 125.46, 122.10, 121.59, 120.77, 119.63, 69.41, 34.87, 33.30, 31.86, 29.57, 27.09, 23.37. Anal. calcd for C₃₉H₆₂KNO₇: C 67.30, H 8.98, N 2.01; found: C 67.30, H 8.87, N 2.06.

X-ray crystallography

Single crystals of complexes **3** and **4** were respectively mounted in Lindemann capillaries under nitrogen. Diffraction data were collected at 298(2) K on a Bruker Smart CCD area detector with graphite-monochromated Mo K α radiation (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS-97 (ref. 106) and refined against F^2 by full-matrix least squares using SHELXL-97.¹⁰⁷ Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determination are listed in Table 2.

Polymerization of *rac*-LA

A typical polymerization procedure was exemplified using **1**/BnOH as the catalyst. Complex **1** (10.94 mg, 0.02 mmol) and

Table 2 Details of the X-ray structure determinations of complex **3** and **4**

Complex	3	4
Empirical formula	C ₃₇ H ₅₈ NNaO ₆	C ₂₅ H ₃₄ KNO ₇
f_w	635.83	499.63
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2/n	<i>C</i> 2/c
<i>a</i> (Å)	15.9289(13)	24.817(2)
<i>b</i> (Å)	11.4741(9)	17.2980(15)
<i>c</i> (Å)	21.5944(18)	17.5045(16)
β (deg)	102.398(2)	133.796(3)
<i>V</i> (Å ³)	3854.8(5)	5424.0(8)
<i>Z</i>	4	8
D_{calcd} (g cm ⁻³)	1.096	1.224
<i>F</i> (000)	1384	2128
μ (mm ⁻¹)	0.082	0.237
θ Range for data collecn (deg)	2.21 to 25.02	2.33 to 25.02
No. of reflns collected	19 317	13 632
No. of indep reflns (<i>R</i> _{int})	6798 (0.0635)	4778 (0.1302)
Restraints/params	0/416	0/307
Goodness of fit on F^2	1.052	1.011
Final <i>R</i> indices ^a [$I > 2\sigma(I)$]	R_1 = 0.0492; wR_2 = 0.0526	R_1 = 0.0715, wR_2 = 0.1323
<i>R</i> indices (all data)	R_1 = 0.1527, wR_2 = 0.0597	R_1 = 0.1586, wR_2 = 0.1517
Largest diff peak and hole [e Å ⁻³]	0.189 and -0.187	0.618 and -0.225

^a $R_1 = \sum ||F_o|| - |F_c|| / \sum |F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$.



BnOH (0.20 cm³, 0.1 M in toluene, 0.02 mmol) were added in sequence to toluene (1.8 cm³). The resultant mixture was stirred at room temperature for 10 min and then added to a stirred mixture of *rac*-LA (0.2883 g, 2.00 mmol) and toluene (2.0 cm³) at the same temperature. The polymerization reaction was terminated after 1 min by adding a drop of water. White precipitates were filtered under reduced pressure and washed with hexane. Drying the wet cake under vacuum gave the polymer as white solid. For GPC analysis, the sample was dissolved in THF, passed through a short neutral aluminum oxide column, precipitated in methanol, and dried under vacuum.

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103 P_m is the probability of meso linkages between monomer units. $[mmm] = P_m^2 + (1 - P_m)P_m/2$, $[mmr] = [rmm] = (1 - P_m)P_m/2$, $[rmr] = (1 - P_m)^2/2$, $[mrm] = [(1 - P_m)^2 + P_m(1 - P_m)]/2$.

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