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Alkali-Metal Monophenolates with a Sandwich-Type Catalytic Center as Catalysts for Highly Isoselective Polymerization of *rac*-Lactide

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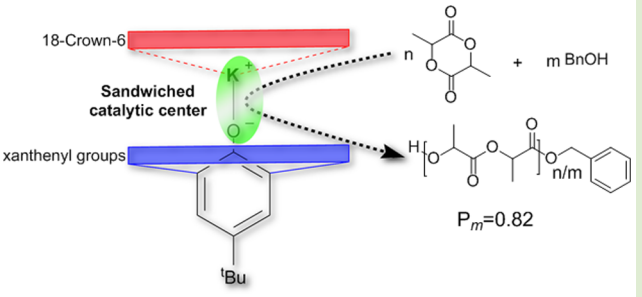
Supporting Information

ABSTRACT: Highly isoselective ring-opening polymerization (ROP) of *rac*-lactide is a challenge for sodium and potassium complexes under mild conditions. In this work, three sodium and potassium complexes with a sandwich-type catalytic center are highly active catalysts for the polymerization of *rac*-lactide and show high isoselectivities with P_m values of 0.72−0.82. The best isoselectivity of P_m = 0.82 is the highest value for alkali-metal complexes under mild conditions. The molecular weights of the obtained PLA are close to the theoretical values, and the molecular weight distributions are narrow.



Polylactide (PLA), an important biorenewable, biocompatible, and biodegradable polymer, can partially replace biologically inert polymeric materials to resolve some environmental problems originated from discarding large quantities of slowly degrading polymeric materials.[1] For its properties, PLA can be applied in packaging, agricultural materials, drug delivery, medical devices, and so on.[2] The ring-opening polymerization (ROP) 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). The physical and chemical properties of polylactide highly associate with its stereoregularity; thus, the catalytically stereocontrolled ROP of *rac*-lactide has gained considerable attention that enables the production of PLAs with various desired stereomicrostructures. Despite many heterotactic systems that have been studied well in this field, the isoselective ring-opening polymerization of *rac*-lactide remains a challenging and valuable goal. Many isoselective aluminum-Salen or aluminum-Salan initiators have been reported,[3] but most of these complexes suffered from their low activities. It seems that this problem can be overcome because some highly active zinc,[4] lanthanides,[5] indium,[6] and magnesium complexes[7] have been explored recently to exhibit good isotactic selectivities. For example, Williams's group reported highly active yttrium phosphasalen alkoxide complexes have a best isoselectivity of P_m = 0.84;[8] a chiral zinc amido-oxazolinate complexes with a high isoselectivity of P_m = 0.91 were reported by Du's group recently;[9] some achiral heteroscorpionate zwitterionic zinc complexes as catalysts could also achieve a high isoselectivity (P_m = 0.85).[10] Nevertheless, it is still rewarding to achieve highly active and highly isoselective catalysts for the ROP of *rac*-lactide.

Because the metal residues are difficult to remove from the polymer, nontoxic metal catalysts are welcomed. Sodium and potassium are innocuous and cheap elements, and definitely suitable for the catalytic synthesis of polylactides, especially in medical-related fields. In the past several years, some sodium and potassium complexes have been applied to catalyze the ROP of lactide.[11] However, to our best knowledge, sodium and potassium metal complexes have not been explored widely for the highly isoselective ROP of *rac*-lactide due to the low Lewis acidity of sodium or potassium ion. Recently, two crown ether complexes of sodium/potassium monophenoxide were reported in our group, which can highly isoselectively catalyze the ROP of *rac*-lactide giving a P_m value of 0.86.[12] However, a low temperature of −60 °C is a critical condition and indispensably high $[\text{co-initiator}]_0/[\text{Cat.}]_0$ ratios also lead to low polymer molecular weights. Another example of potassium naphthalenolate crown ether complex reported in our group, too, just shows a modest isoselectivity of P_m = 0.73.[13]

With an attempt to obtain highly isoselective sodium and potassium catalysts under mild conditions, here, we used a strategy of sandwiching an active center of sodium/potassium phenoxide into two planes, a confined space, for increasing the interaction between the incoming lactide and the active end of a polylactide chain. A new phenol ligand (**HL**) was designed and obtained by a condensation reaction of 4-*t*-butylphenol and xanthydrol at 128 °C, the predominant feature is the two planar xanthenyl groups at the two ortho positions of the hydroxyl group. Complexes **1a**−**1c** can be obtained in 61, 57, and 52% yields, respectively, from the reactions of **HL**, 18-crown-6/15-crown-5, and $KN(SiMe_3)_2/NaN(SiMe_3)_2$ in THF at room temperature (Scheme 1).

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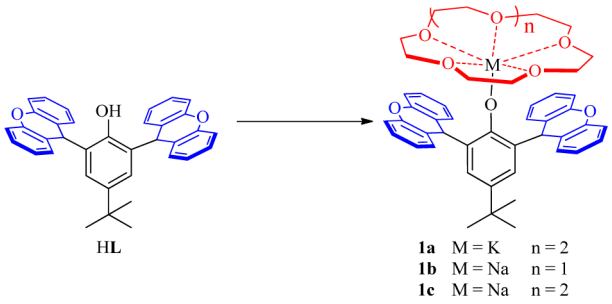
Scheme 1. Synthesis of 1a−1c



All single crystals of **HL** and complexes **1a−1c** were obtained (Figures 1, S9, S10, and S11). As the ORTEP drawing of **HL**

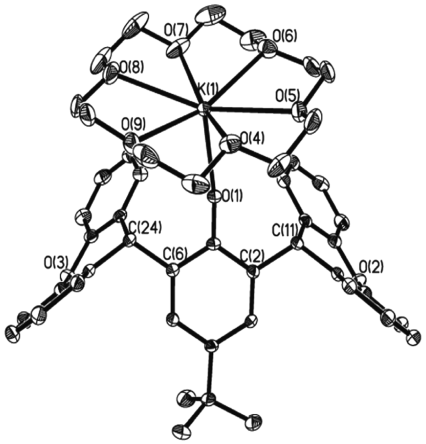


Figure 1. ORTEP drawing of complex **1a** with probability ellipsoids at the 30%, hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): K1−O1 2.4975(17), K1−O4 2.807(2), K1−O5 2.808(2), K1−O6 2.814(2), K1−O7 2.874(2), K1−O8 2.871(2), K1−O9 2.811(2), O1−K1−O4 90.74(6), O1−K1−O5 87.40(6).

shows (Figure S9), the two xanthenyl groups can rotate freely around the single C−C bonds between xanthenyl group and phenolic ring, the two xanthenyl groups own two different orientations denoted as an up one and a down one. In the molecular structure of complex **1a** (Figure 1), K1 is coordinated by six oxygen atoms of the 18-crown-6 and one oxygen atom of phenol. For the repulsion of 18-crown-6, both xanthenyl groups have a same down direction. As our design, the active K^+-O^- center is sandwiched successfully by the plane of 18-crown-6 and the plane formed by two xanthenyl groups. During the progress of polymerization of lactide, the stereointeraction between the incoming lactide and alcohol (polymer chain end) may increase due to a big steric hindrance of this special environment. The solid structures of complexes **1b** and **1c** are similar to complex **1a** (Figures S10 and S11).

It is surprising that the signal of the *t*-butyl group in complex **1a** appears at four chemical shifts in a $CDCl_3$ solution (Figures 2a and S12), the NMR spectra of complexes **1b** and **1c** are similar (Figures S13 and S14). However, the signal of the *t*-butyl group in complex **1a** does not split in a deutero benzene-d_6 or toluene-d_8 solution, even the temperature decreases to −70 °C (Figure S15). The above experiments mean complex **1a** will have different components in different solvents. Although we still do not know the real reason until now, we think the polarity of solvent may be an important factor. In order to check this, we changed the volume ratio of benzene-

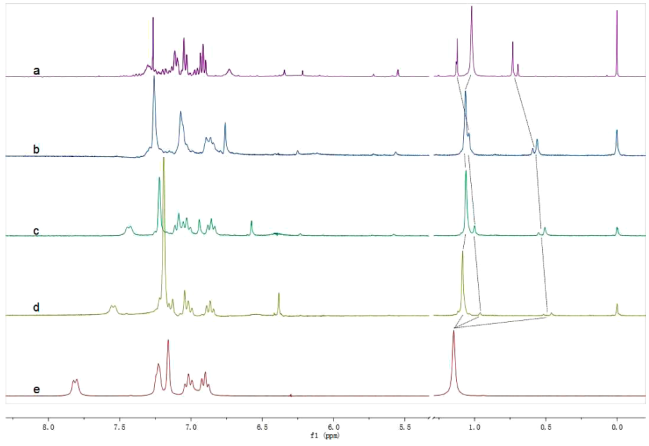


Figure 2. ^{1}H NMR spectra of **1a** in different polarity of solvents: (a) chloroform-*d*; (b) chloroform-*d*/benzene-d_6 = 2:1; (c) chloroform-*d*/benzene-d_6 = 1:1; (d) chloroform-*d*/benzene-d_6 = 1:2; (e) benzene-d_6 (more details in Figure S15).

d_6/chloroform-*d* to adjust the solvent polarity and a series of NMR spectra of complex **1a** were recorded (Figure 2, more details in Figure S16). When increasing the proportion of benzene-d_6, three peaks at 1.12, 1.01, and 0.73 ppm assigned to the *t*-butyl group decrease and finally vanish in pure benzene-d_6. The complicated proton peaks of aromatic region in $CDCl_3$ also become simple and clear in pure benzene-d_6. Furthermore, only two peaks of *t*-butyl at 0.98 and 0.88 ppm can be found in a pure low polar CD_2Cl_2 solution, the high peak at 0.88 ppm should be assigned to a primary component (Figure S17). Based on the different orientations of two xanthenyl groups in the solid structure of **HL** (Figure S9), different isomers can be expected for the different combinations of the different orientations of two xanthenyl groups (Figure S18). To distinguish the isomers of **HL** in solution via the NMR spectrum is difficult because the steric hindrance is small and the rotational barrier is low; the rotational barrier should increase in complex **1a** due to the repulsion interaction between the crown ether and xanthenyl groups, thus transformations between these different isomers will proceed slowly and these isomers can be detected via NMR in a suitable deuterium solvent. For the easy spatial adjustment of the crown ether and the long distance between the crown ether and xanthenyl group, NOESY experiments did not suggest the interaction between crown ether and xanthenyl groups, but this experiment cannot rule out the existence of rotamers. Besides the three isomers araising from the rotation of two xanthenyl groups, there should be another isomer because there are four peaks attributed to t-butyl groups in $CDCl_3$. The extra fourth peak possibly results from the dissociation of complex **1a** to a potassium crown ether cation and a phenoxide anion in $CDCl_3$ (Figure S18). This hypothesis can be supported by the DOSY spectra of complex **1a** in $CDCl_3$ (Figure S19), because there are two diffusion coefficients belonging to crown ether. The DOSY spectrum of complex **1a** in benzene-d_6 show one diffusion coefficient (Figure S20), which hints only one most stable component existing in a low polar solvent as the solid structure (Figure 1). Anyhow, these NMR spectra indicate these complexes have different components in different solvents, which definitely will affect their catalytic behaviors in the ROP of *rac*-lactide. The following catalytic experiment results also confirmed this.

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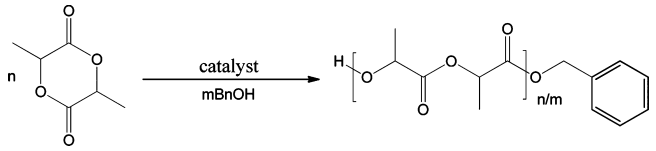
Table 1. ROP of *rac*-Lactide Catalyzed by Complexes of 1a−1c[a]



entry	complex	$[LA]_0/[M]_0/[BnOH]_0$	solvent	t (min)	conv.[b] (%)	$M_{n,calc}$[c] (g/mol)	$M_{n,obsd}$[d] (g/mol)	PDI	P_m[e]
1	**1a**	100:1:1	$CHCl_3$	10	48	7000	5200	1.07	0.67
2	**1a**	100:1:1	CH_2Cl_2	10	55	8000	3400	1.05	0.64
3	**1a**	100:1:1	THF	10	86	12500	8400	1.09	0.65
4	**1a**	100:1:1	benzene	10	92	13400	12600	1.08	0.76
5	**1a**	100:1:1	toluene	10	95	13800	13100	1.07	0.77
6	**1b**	100:1:1	toluene	10	98	14200	13500	1.21	0.72
7	**1c**	100:1:1	toluene	10	89	12800	9500	1.19	0.62
8	**1a**	200:1:1	toluene	30	95	27500	21200	1.06	0.77
9	**1a**	500:1:10	toluene	10	94	6800	6100	1.04	0.73
10[f]	**1a**	500:1:1	toluene	30	91	65700	42100	1.07	0.77
11[f]	**1a**	1000:1:1	toluene	60	95	136900	70200	1.06	0.75
12[g]	**1a**	100:1:1	toluene	120	99	14400	14000	1.08	0.82

[a] $[LA]_0$ = 0.4 mol L^{-1}, reactions were conducted in 5 mL solvent under 25 °C. [b] Lactide conversion determined by ^1H NMR. [c] Calculated from $[M_{lactide} \times [LA]_0/[BnOH]_0 \times$ conversion yield + $M_{BnOH}]$. [d] Obtained from GPC analysis and calibrated by polystyrene standard and corrected using the Mark−Houwink factor of 0.58.[20] [e] Determined by analysis of all of the tetrad signals in the methine region of the homonuclear-decoupled ^1H NMR spectra.[8] [f] Catalyst, 10 μmol; toluene, 10 mL. [g] At 0 °C.

The ROP of *rac*-lactide with **1a−1c** as catalysts was systematically examined. Representative results are listed in Table 1. When a 100:1:1 ratio of $[rac\text{-}LA]_0/[M]_0/[BnOH]_0$ was used with a complex concentration of 4.0 mM at room temperature, the polymerization of *rac*-lactide can accomplish in 48, 55, and 86% yields within 10 min for complex **1a** in $CHCl_3$, CH_2Cl_2, and THF respectively (Table 1, entries 1−3), giving modest iso-slectivities of P_m = 0.67, 0.64, and 0.65. The polymerization becomes quicker in benzene or toluene because 92 and 95% monomer can convert to polymer at the same conditions respectively, giving isoselectivities of P_m = 0.76 and 0.77 (Table 1, entries 4−5). As the NMR spectra of complex **1a** shown, there are several isomers in $CDCl_3$ and CD_2Cl_2, some low active isomers will decrease the whole reaction rate; solvent effects are very complicated, other factors, for example, the polarity of solvents, can also affect the reaction rate; the PDIs keep narrow in different solvents which can be attributed to the quick polymer chain transfer reaction between different catalyst molecules. Different isomers of one catalyst should have different stereo selectivities, the low stereoselective isomers in $CHCl_3$, CH_2Cl_2, and THF also will decrease the whole isoselectivity of the catalyst. In THF, another possible reason for the decreased polymerization rate is the competitive coordination of THF to inhibit the coordination of lactide to K^+.[14] In toluene, the isoselectivity of P_m = 0.72 for complex **1b** is similar to **1a** (Table 1, entry 6). By contrast, the isoselectivity of P_m = 0.62 for complex **1c** is lower, possibly due to the slightly weak interaction between Na^+ and 18-crown-6 evidenced by the longer average Na−O (crown) bond of 2.728(4) Å than the average Na−O (crown) bond of 2.412(4) Å in complex **1b** (Table 1, entry 7). The polymerization catalyzed by complex **1a** is living because the molecular weights of polymers are desired as calculated and increased linearly with the conversion when a ratio of $[rac\text{-}LA]_0/[M]_0/[BnOH]_0$ = 200:1:1 is used (Table 1, entry 8, Figure 3). To address the possibility of achieving immortal polymerization with complex **1a**, the polymerizations were performed in the presence of 10 equiv benzyl alcohol toward complex **1a** (Table 1, entry 9).

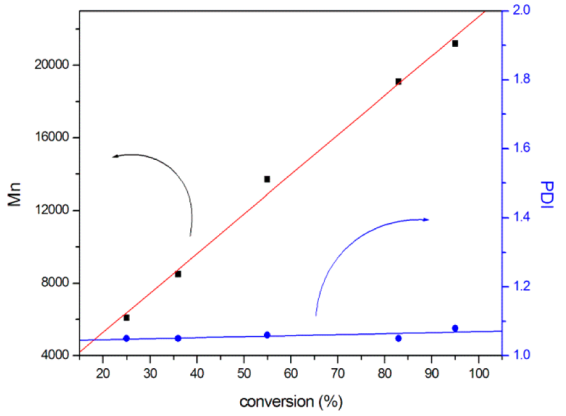


Figure 3. Relationship between the M_n (■) or the PDI value (●) of the polymer and the *rac*-LA conversion is shown ($[LA]_0/[M]_0/[BnOH]_0$ = 200:1:1, toluene, 25 °C, entry 8).

The molecular weight of polymer also agrees well with the calculated M_n based on one chain growing per BnOH; the PDIs of the polymers are narrow and the isoselectivity can also be maintained at P_m = 0.73. End-group analysis by ^1H NMR spectroscopy revealed that the polymer chains were end-capped by one benzyl ester and one hydroxyl group (Figure. S21). Therefore, the monomer activated mechanism is reasonable for this ring-opening polymerization reaction, which was supposed for most alkali metal catalyst:[15] the lactide can be activated after coordination to K atom, and consequently, BnOH as a co-initiator can nucleophilically attack the carbonyl group to initiate the ROP reaction. The ESI and MALDI-TOF mass spectrum of a final polymer (Figures S22 and S23) confirmed it further by a series of peaks at $(72.0211m + 108.0575 + 4.0313)/4$ with a charge of +4, which can be assigned to $m(C_3H_4O_2)$ + BnOH + $4H^+$. The series of peaks with a difference in molecular mass of ∼72 Da hint some trans-esterification reactions happen during this polymerization process. The side reaction becomes serious when the ratio of

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[*rac*-LA]$_0$/ [BnOH]$_0$ is high (up to 500 or 1000, Table 1, entries 10 and 11). In the homonuclear-decoupled ^{1}H NMR spectrum of a final polymer obtained at room temperature, a small peak at 5.215 ppm can be found (Table 1, entry 5, Figure S24), which also indicates the existence of a side reaction of transesterification as the SI mass spectrum shows.[16] It is nice that the side reaction can be suppressed when the reaction temperature dropped to 0 °C (Table 1, entry 12), evidenced by the decreasing of this small peak (Figures 4 and S25). Although

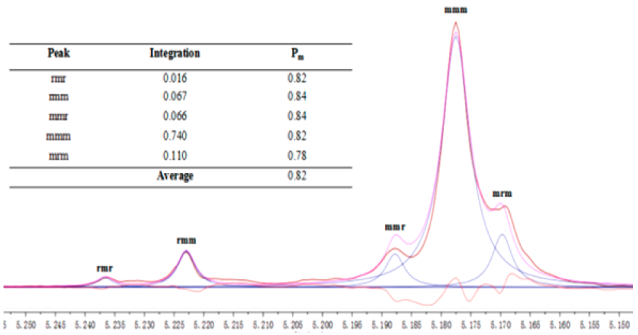

Figure 4. Homonuclear-decoupled ^{1}H NMR spectrum of PLA ([LA]$_0$/[M]$_0$/[BnOH]$_0$ = 100:1:1, 0 °C, entry 12, P_m = 0.82). The P_m values were determined for all tetrads based on Bernoulli statistics, and their average value was used. The resolution of the integrals for the peaks corresponding to the *rmr*, *rmm*, *mmr*, *mmm*, and *mrm* tetrads was improved using peak deconvolution methods.

a long time of 2 h is needed for a completion of polymerization at 0 °C when the ratio of [*rac*-LA]$_0$/[M]$_0$/[BnOH]$_0$ is 100:1:1, a good isoselectivity can be achieved with a P_m value up to 0.82. To our knowledge, this is a best value at or above 0 °C for alkali metal catalysts in this area. Compared to our previous work, the isoselectivity has some relationships with both the crown ether and the substituted group of phenol ligand;[12,13] thus, the very possible catalytic site is between the plane of 18-crown-6 and the plane formed by two xanthenyl groups. The high isoselectivity can also be confirmed by a high T_m of 166 °C (Figure S26), which is similar to the optically pure poly(L-LA) and agrees well with the highly isotactic polymer structure. The value of T_m is similar to the sample with a similar isotacticity reported in the literature.[17]

In order to get more insight into the stereoselective mechanism of these catalysts, the stereoerrors in the microscopic structure of a final polymer (Table 1, entry 12) have been studied by the tetrad signals in the homonuclear-decoupled ^{1}H NMR spectrum.[18] As shown in Figure 4, the four *rmr*/*rmm*/*mmr*/*mrm* tetrad peaks show an approximate ratio of 1:4:4:7, the characteristic stereoerrors sequence of −*RRRRSSSS*− will give a ratio of 0:1:1:1 for *rmr*/*rmm*/*mmr*/*mrm* tetrad peaks, and the ratio will change to 1:1:1:2 for the characteristic stereoerrors sequence of −*RRRRSSRRRR*−/−*SSSSRRSSSS*−. The sum of the two errors sequence at a 3:1 ratio will give a ratio of 1:4:4:5 which is similar to the experimental value. The latter stereoerror sequence usually is ascribed to enantiomorphic site control errors, but another possibility cannot be negelected that the consecutive chain end control errors can also lead to this stereoerror sequence. After careful calculation and considering no persistent enantiomorphic structure in these catalysts, a chain-end control mechanism is believed to be suitable for this system. Based on the isoselectivity, the probability of consecutive stereo errors is 18% × 18% = 3.24%, which is close to the experimental value of 18% × 1/4 = 4.5% for consecutive chain end control errors (Figure S27). The enhancement of this consecutive error probability may results from a transesterification reaction, which also can be confirmed by the small peak at 5.215 ppm attributable to *mmmrr*/*rrmmm* hexads (Figure 4).[16,19] The transesterification reaction also gives rise to the increase of *mrm* tetrad peaks because the tetrad peaks of *mrr*, *rrr*, and *rrm* have similar chemical shifts. Therefore, at this stage, the chain-end control mechanism is suitable for the stereoselective mechanism of this system.

In summary, three new crown ether complexes sodium and potassium monophenolates with a sandwiched active M$^+$-O$^-$ (phenoxy) center were synthesized. All of these complexes exhibit high activities, high iso-selectivities, and good control for the ring-opening polymerization of *rac*-lactide. The best isoselectivity of P_m = 0.82 is a highest recorded value at or above 0 °C for alkali-metal complexes, which also is comparable to those observed in indium-, zinc-, and lanthanide-based systems. Sodium and potassium complexes are potentially good choice for the catalytic synthesis of medical polylactides owing to their nontoxicity and abundance properties; the work to further improve the stereocontrollability of this system via adjusting the phenol ligands is in progress in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Full experimental details, representative NMR spectra, ESI-MS spectrum and DSC traces of polymers, and CIF files that provide the crystallographic data for compounds of **HL**, **1a**, **1b**, and **1c** with CCDC reference numbers of 1034435, 1034436, 1034437, and 1034438. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00209.

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Notes

The authors declare no competing financial interest.

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