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Isoselective Ring-Opening Polymerization of *rac*-Lactide Catalyzed by Sodium/potassium Tetradentate Aminobisphenolate Ion-paired Complexes

Xinlei Li,[a] Zhaowei Jia,[a] Xiaobo Pan,[a] and Jincai Wu *[a]

Abstract: Two sodium/potassium tetradentate aminobisphenolate ion-paired complexes were synthesized and structurally characterized. These ion-paired complexes are efficient catalysts for the ring-opening polymerization of *rac*-lactide (*rac*-LA) in the presence of 5 equivalents BnOH as an initiator and side reaction of epimerization can be suppressed well at low temperatures. The polymerizations are controllable affording polylactides with desirable molecular weights and narrow molecular weight distributions; the highest molecular weight can reach to 50.1 kg/mol in this system; and a best isoselectivity of P_m = 0.82 was achieved which are rarely reported for isoselective sodium/potassium complexes without crown ether as an auxiliary ligand. The solid structures suggest BnOH can be activated by an interaction with the anion of sodium/potassium complex via a hydrogen bond and monomer will be activated by coordination to sodium/potassium ion.

Introduction

Over the past decades, the widespread application of polymer materials has brought a great convenience to people's production and daily lives. At the same time, unsustainable production problems and environmental pollution have strongly raised people's concerns; with the depletion of non-renewable fossil oil, it is becoming more and more urgent to find new environmentally-friendly and renewable polymer materials to replace traditional petroleum based polymer materials. Polylactide (PLA) as a typical representative of such materials has received great attention.[1-6] Because the tacticity can remarkably affect the physical properties of polylactide, the stereoselective ring-opening polymerization (ROP) of *rac*-lactide is still a current research hotspot. To date, many good metal complexes have been used for the stereoselective ROP of *rac*-lactide, such as aluminium,[7-22] indium,[23-27] zinc,[28-33] and other metal complexes.[34-37] In the past few years, we firstly reported some highly isoselective sodium/potassium complexes for the ROP of *rac*-lactide,[38-42] which is interesting because sodium/potassium metal ions are nontoxic and suitable for the synthesis of medical-related polylactide. Normally the low Lewis acidity of sodium/potassium ion will cause the interactions between substrates be weak and the stereoselectivities of organic or polymerization reactions consequently are not very high; the charm of coordination chemistry is that auxiliary ligands can construct a confined environment around active sodium/potassium ion centre and can synergistically improve the interactions between ligand, monomer, and polymer chains, then the stereoselectivities of sodium/potassium complexes can increase. In previous highly isoselective sodium/potassium complex systems, the auxiliary ligands mainly focused on crown ethers and one charged bulky phenol, and the good isoselectivity even can reach to P_m = 0.94 at - 70 °C. The crown ether ligands seem to be indispensable in previous sodium/potassium systems for high isoselectivities because of the confined space between crown ether and bulky substituted groups of phenol ligand. However, as a general principle in many stereoselective organic/polymerization reactions, when the surrounding of active metal centre is suitably crowded via subtle designs of ligand, a highly stereoselective system should be achieved too. With this intuition in mind and after many trials, we reported here a new system without crown ether as ligand to achieve isoselective ROP of *rac*-lactide.

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Results and Discussion

In order to provide a limited space around the active sodium/potassium metal centre for the ROP reaction, a claw-type aminobisphenol ligand (Figure 1, Scheme S1) was selected, which also was successfully utilized in heteroselective yttrium complexes for the ROP of *rac*-lactide.[43-45] Complex **1** was obtained with a yield of 47 % by sequent reactions of aminobisphenol ligand with $NaN(SiMe_3)_2$, tetrabutylammonium chloride, and BnOH. In the absence of BnOH, it was failed to purify the resulting oil mixture. Single crystals of complex **1** were obtained from a THF solution at room temperature. In the solid structure of complex **1** (Figure 2a), sodium ion is coordinated by two phenol oxygen atoms (O1 and O2), two nitrogen atoms (N1 and N2) of the ligand and one oxygen atom (O5) of a benzyl alcohol; this benzyl alcohol also has an interaction with the phenol oxygen atom (O2) via a hydrogen bond (O5-H5A···O2, the O-O distance is 2.587(3) Å). Another benzyl alcohol also attaches to the whole molecule only via a hydrogen bond (O3-H3A···O1) interaction with a O-O distance of 2.372(14) Å. Interestingly, there are some disorders in the crystals of complex **1** and the coordinated benzyl alcohol can be replaced partially by THF (Figure 2b, the occupancy is 77 % in the solid structure, and this disordered molecule is abbreviated as complex **1'**) because of excess amount of solvent molecules of THF in solution. This substituted reaction hints the coordinated benzyl alcohol can be replaced smoothly by lactide monomer in the ROP progress; and this structure also suggests benzyl alcohol can be activated by a hydrogen bond interaction with the negative oxygen atom of anion. Compared to free benzyl alcohol, the methylene signal of benzyl alcohol shifts obviously from 4.303 ppm to 4.464 ppm in the ^{1}H NMR spectrum of complex **1** (Figure S6), which hints the existence of a hydrogen bond between them again. The same diffusion coefficients of benzyl alcohol and complex **1** in benzene-d_6 in DOSY experiment (Figure S9) proves the two molecules of benzyl alcohol adhere to sodium aminobisphenolate anion in solution.[46] In the DOSY spectrum in benzene-d_6, tetrabutylammonium cation has a same diffusion coefficient with the whole molecule, which indicates the electronic interaction between cation and anion is strong in the nonpolar solvent, such as benzene and toluene, and complex **1** is a tight ion pared complex.

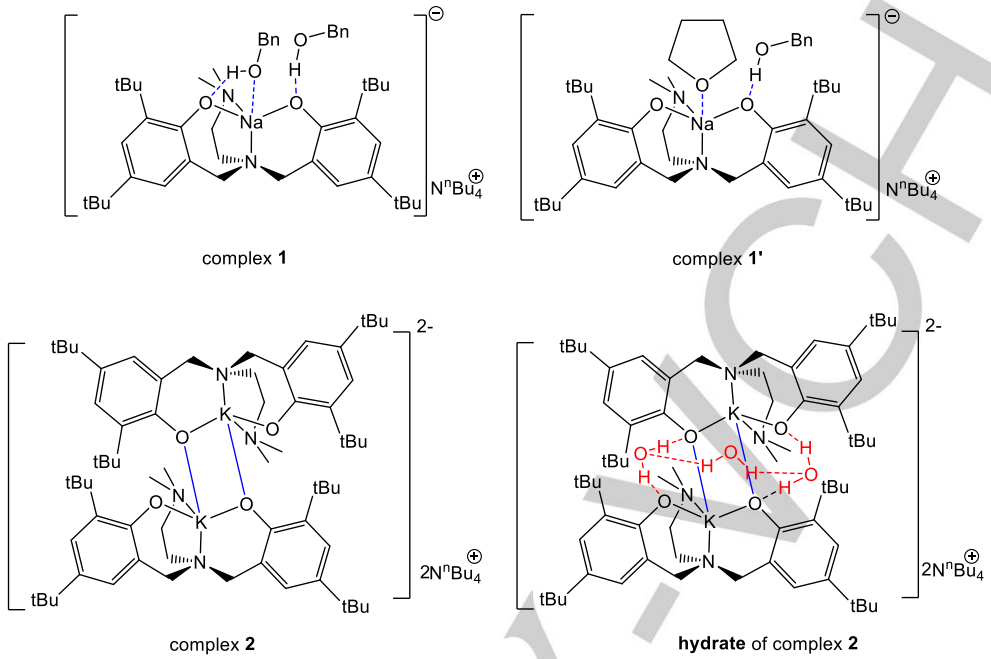


Figure 1. Sodium/potassium tetradentate aminobisphenolate ion-paired complexes.

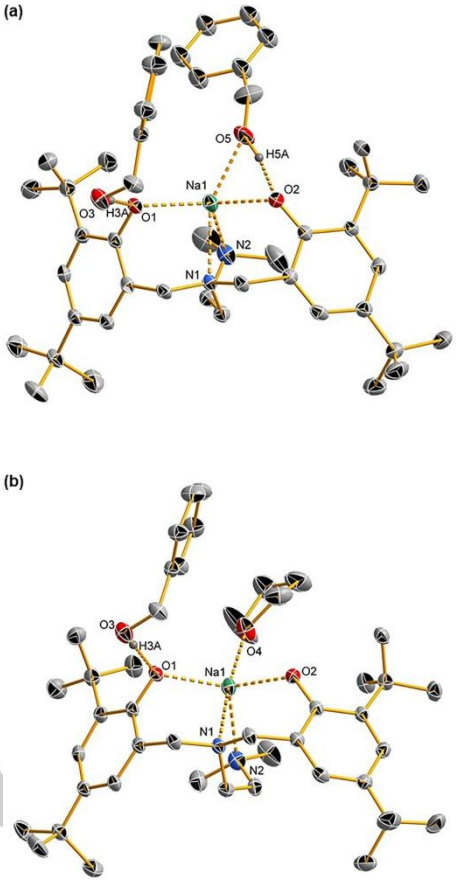


Figure 2. ORTEP drawing of complex **1** (a) and its distorted structure **1'** (b), except for hydroxyl hydrogen atoms of benzyl alcohol, other hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Na1-N1 2.498(2), Na1-N2 2.590(3), Na1-O1 2.284(2), Na1-O2 2.309(2), Na1-O3 2.257(11), Na1-O4 2.488(3); O2-H5-O5 2.587(3), O1-H3-O3 2.372(14). Symmetry code of #: -x, y, -z+1/2. CCDC number: 1882477.

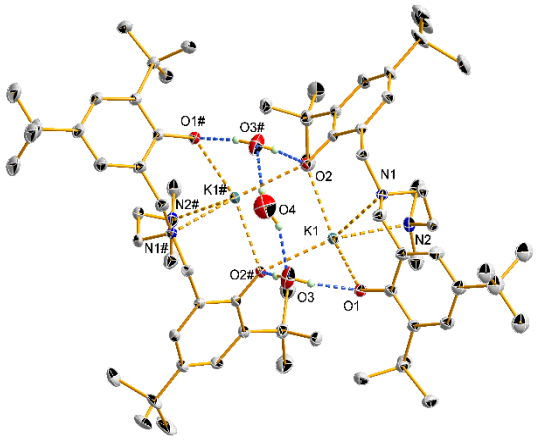


Figure 3. ORTEP drawing of the hydrates of complex **2** (some hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and bond angles (°): K1-N1 2.78464(18), K1-N2 2.8525(2), K1-O1 2.60690(16), K1-O2 2.64768(15), K1-O2# 2.72682(14), K1-O3 3.1012(2), O3-H-O1 2.6083(3), O3-H-O2# 2.7128(2), O4-H-O3 2.722; O3-H-O1 167.8, O3-H-O2# 165.5, O4-H-O3 152.7. Symmetry code of #: 1-x, y, 0.5-z. CCDC number: 1881629.

Complex **2** was obtained by the reaction of aminobisphenol ligand with $KN(SiMe_3)_2$, then with tetrabutylammonium chloride. Complex **2** without BnOH can be purified easily as a white solid with a moderate yield of 57 %. Single crystals of complex **2** were obtained from a mixture of toluene and n-hexane, the structure show it was binuclear with two respective phenol oxygen atoms of two ligands as bridges (Figure 3). Three water molecules can be found in the solid structure because small amounts of water entered the vial of solution in the slow progress of growing crystal. It is interesting that there are six hydrogen bonds in the hydrates of complex **2**, shown as the blue dash lines in Figure 3, between seven oxygen atoms of O1(O1#), O2(O2#), O3(O3#), and O4. The six hydrogen bonds may be an important factor to stabilize the binuclear structure. In fact, the DOSY spectrum of anhydrous complex **2** in benzene-d_6 showed two different diffusion coefficients which hinted a fast dissociation equilibrium reaction between mononuclear and binuclear species (Figure S10, we tried but failed to obtain precise diffusion coefficients in this DOSY experiment due to the low degree of accuracy of NMR probe (5 mm FG/RO Digital Auto Tune Switchable probe, JNM ESC400M)). Similarly to complex **1**, the interaction between complex **2** and BnOH also can be found because the methylene single of benzyl alcohol shift clearly from 4.303 ppm to 4.729 ppm in the ^{1}H NMR spectrum of a 1:1 mixture of complex **2** and BnOH (Figure S7). Thus, despite the crystals of adducts of complex **2** and BnOH were not obtained after many trials, complex **2** will be able to form a similar monomeric complex as complex **1** upon addition of excess BnOH in the following catalytic experiments.

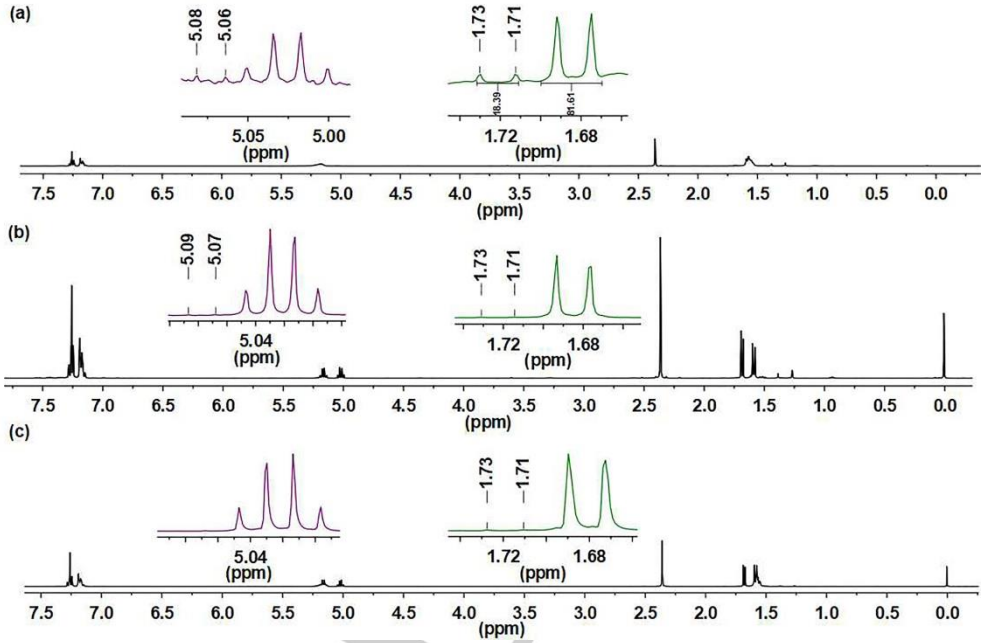
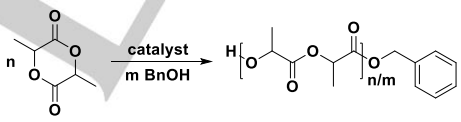


Figure 4. ^{1}H NMR spectra of the residue of polymerization reaction: (a) [*rac*-LA]$_0$/[Cat.**1**]$_0$/[BnOH]$_0$ = 100/1/0, [Cat.**1**]$_0$ = 2.0 mM, at room temperature; (b) [*rac*-LA]$_0$/[Cat.**1**]$_0$/[BnOH]$_0$ = 100/1/3, [Cat.**1**]$_0$ =2.0 mM, at room temperature; (c) [*rac*-LA]$_0$/[Cat.**1**]$_0$/[BnOH]$_0$ = 100/1/3, [Cat.**1**]$_0$ =2.0 mM, at -70 ^{o}C.

Table 1 Polymerization of *rac*-Lactide catalyzed by complexes **1** and **2**.



Entry	Cat.	Temp. (^{o}C)	[*rac*-LA]$_0$/[Cat.]$_0$ /[BnOH]$_0$	Time	[b]Conv. (%)	[c]$M_{n,obsd}$ (g/mol)	[d]$M_{n,calcd}$ (g/mol)	[e]$M_{n,NMR}$ (g/mol)	$Đ$	P_m
1	**1**	R.T.	100/1/0	30s	73	4400	5300	5500	1.46	0.53
2	**1**	R.T.	100/1/3	10s	84	2000	2400	2500	1.38	0.61
3[f]	**1**	R.T.	100/1/0	240min	91	3100	6600	4000	1.78	0.52
4[g]	**1**	R.T.	100/1/0	240min	<5	-	-	-	-	-
5	**1**	-70	100/1/3	7 min	91	2400	2600	2700	1.08	0.72
6	**1**	-70	500/1/3	90 min	84	10200	12100	11100	1.03	0.72
7[h]	**1**	-70	500/1/3	110 min	98	13700	14000	13300	1.02	0.81
8	**2**	-70	500/1/5	50 min	88	11000	13000	12100	1.05	0.75
9[h]	**2**	-70	500/1/5	50 min	84	13000	12100	12000	1.02	0.80
10[i]	**1**	-70	1000/1/3	120min	72	20000	20700	-	1.08	0.80
11[j]	**1**	-70	1000/1/3	240min	90	27700	26000	-	1.01	0.82
12[j]	**2**	-70	1000/1/5	240min	80	26000	23000	-	1.04	0.81
1c	**1**	-70	2000/1/3	360min	87	50900	50100	-	1.02	0.82

[a]Reactions were performed in 5.0 mL of toluene, [cat.]$_0$ = 2.0 mM. [b]Determined by ^{1}H NMR spectrum. [c]Experimental M_n and $Đ$ determined by GPC in THF

against polystyrene standards, and corrected using the factor 0.58 for poly(LA).[47] [d]Calculated from the molecular weight of *rac*-LA × $[LA]_0/[BnOH]_t$ × conversion yield + M_{BnOH}($[BnOH]_t$ includes BnOH molecules in complex **1** and $[BnOH]_0$ for the calculation of molecular weight). [e]Determined from the relative integration of the signals for the main-chain methine units and chain ends. [f]In 5.0 mL of THF. [g]In 5.0 mL of CH_2Cl_2. [h]Reactions were performed in 30 mL of toluene, $[cat.]_0$ = 0.17 mM. [i]Reactions were performed in 10 mL of toluene, $[cat.]_0$ = 0.50 mM. [j]Reactions were performed in 20 mL of toluene, $[cat.]_0$ = 0.25 mM.

Complex **1** can catalyze the ROP of *rac*-lactide quickly, the polymerization conversion for the 100/1/0 ratio of [*rac*-LA]$_0$/[Cat.**1**]$_0$/[BnOH]$_0$ in toluene at room temperature can reach to 73 % within 30 s (Table 1, entry 1, [cat.**1**]$_0$ = 2.0 mM). However, when the solvent was changed to THF, 4 hours was consumed to reach 91% conversion of monomer (Table 1, entry 3), the significantly decreased polymerization rate may result from the competed coordination reaction of THF. Almost no polymerization happened when dichloromethane was utilized as solvent because complex **1** will decompose in slightly acidic solvents of dichloromethane or chloroform evidenced by ^{1}H NMR spectrum of complex **1** in chloroform-*d* (Table 1, entry 4). Therefore, toluene was screened as a solvent for this catalytic system. However, the experimental molecular weight is not close to the theoretical value, the molecular weight distribution (*Đ*) of 1.46 is somewhat broad, and the stereoselectivity with P_m = 0.53 also is not obvious (Table 1, entry 1). The epimerization side reaction also occurs (Figure 4a, Table 1, entry 1) during the polymerization via exchanging proton reaction between methine of lactide monomer and anion base of complex **1**, which can be verified by a weak quartet peak at 5.07 ppm and doublet peak at 1.72 ppm in ^{1}H NMR spectrum of the reaction mixture. These two peaks can be assigned to *meso*-lactide,[48-49] which is about 18.4 % to total monomers. The epimerization side reaction may be an import reason for the low stereoselectivity of this polymerization reaction. In view of hydrogen interactions between BnOH and complex **1**, it is envisioned that the concentration of naked anion base of complex **1** (without coordinated BnOH) will decrease upon addition of large amounts of BnOH, which may be able to suppress the epimerization side reaction. As expected, when the ratio of [LA]$_0$/[Cat.**1**]$_0$/[BnOH]$_0$ changed from 100/1/0 to 100/1/3, that is to say five equivalents BnOH was used including two BnOH molecules in complex **1**, the epimerization side reaction was inhibited remarkably because the signals of *meso*-lactide were not obvious (Figure 4b, Table 1, entry 2); consequently an increased isoselectivity was observed with a P_m value of 0.63. What is more, the molecular weight become close to the theoretical value and the *Đ* value is 1.38. The MALDI-TOF of resulting poly(*rac*-lactide) (Table 1, entry 2, Figure 5a) showed a primary series of peaks at m/z = 108 + 23 + 72n corresponding to the sequences of $(C_3H_4O_2)_n$ + Na^+ + BnOH, which suggested a linear feature of the resulting polylactide but it also indicates that the transesterification reaction was serious; the weak series peaks of sequences of m/z = 23 + 72n can be attributed to a cyclic esterification. When temperature decreased to -70 ^{o}C, the conversion of monomer can quickly reach to 91 % too within 7 min (Table 1, entry 5). The molecular weight was close the calculated value, *Đ* value of resulting polymer become to be 1.08, and a better P_m value of 0.72 was obtained. The molecular weights can increase linearly with the ratio of [*rac*-LA]$_0$/[BnOH]$_t$ (Table 1, entries 5, 6, 11 and 13, Figure 6) with narrow *Đ* values (< 1.10). The 1:1 ratio between the end capped groups of benzyloxy and hydroxyl in ^{1}H NMR spectrum of obtained sample proved the obtained polylactide was linear and BnOH was an actual initiator (Figure 7, table 1, entry 5), where multiple chemical peaks at about 7.32 ppm can be assigned to protons on the benzene ring of benzyl ($C_6H_5CH_2$-) end group and a quartet peak at 4.37 ppm can be attributed to a proton of methine linked with the hydroxyl end group. The linear feature of polylactide can be further confirmed by the following facts: the molecular weight calculated with ^{1}H NMR technology was close the experimental GPC value; and the MALDI-TOF of resulting poly(*rac*-lactide) showed the molecular weight was close the GPC value (Figure 5b) with primary sequences of $(C_6H_8O_4)_n$ + Na^+ + BnOH evidenced by the main series peaks of m/z = 144n + 108 + 23. The side reactions of transesterifications almost did not happen because the series of peaks separated with a difference in molecular mass of ~72 Da was not obvious. When the ratios of [*rac*-LA]$_0$/[Cat.**1**]$_0$/[BnOH]$_0$ increased to 1000/1/3 and 2000/1/3, the catalyst concentration was changed from 2.0 mM to 0.50 mM, 0.25 mM, and 0.17 mM (Table 1, entries 10, 11 and 13) because the large molecular weight polymers at a high ratio of [*rac*-LA]$_0$/[BnOH]$_0$ will precipitate out of the polymerization system in the absence of enough amounts of toluene solvent to dissolve or gelate them. For the polymerization of 1000/1/3 ratio of [*rac*-LA]$_0$/[Cat.**1**]$_0$/[BnOH]$_0$, the isoselectivity with a P_m value of 0.82 was achieved (Figure 5d). The increased isoselectivity from 0.72 to 0.82 (Table 1, entries 5 vs 11) may be ascribed to a low concentration of the catalyst and a low polymerization rate at such a low temperature (Table 1, entries 6 vs 7). When the ratio of [*rac*-LA]$_0$/[Cat.**1**]$_0$/[BnOH]$_0$ was 2000/1/3, the desirable molecular weight of resulting poly(*rac*-lactide) can be high to 50.1 kg/mol with a narrow *Đ* value of 1.02 and high P_m value of 0.82 (Table 1, entry 13). The larger molecular weight polylactide cannot be obtained further as we continued to increase the ratio of [*rac*-LA]$_0$/[BnOH]$_0$, because the polymerization almost was quenched possibly due to the enrichment of trace water within the toluene solvent and lactide monomer. When complex **2** was applied as a catalyst with potassium ion to replace sodium ion in complex **1**, similar isoselectivity for the ROP of *rac*-lactide was achieved (Table 1, entries 8, 9, and 12) with a slightly higher activity (Table 1, entries 6 vs 8). The molecular weight of resulting polylactide was close to calculated value and the molecular weight distribution was narrow too. The ^{1}H NMR (Figure S8) and MALDI-TOF spectra (Figure 5c) also confirmed the resulting polylactide are linear and end-capped with benzyloxy and hydroxyl groups respectively. Compared to other metal complexes, for example, aluminum and zirconium complexes, [7, 8, 34, 36] the activity of this sodium/potassium complex is higher; although the very low temperature condition is a drawback of this isoselective ROP system which needs to be solved in the future, the iso-selectivities of this complex are considerably high for sodium/potassium complexes without crown ether as ligands. Anyway, to find a highly isoselective system at a high temperature with some new design of ligands for sodium/potassium complex systems are still in progress in our lab.

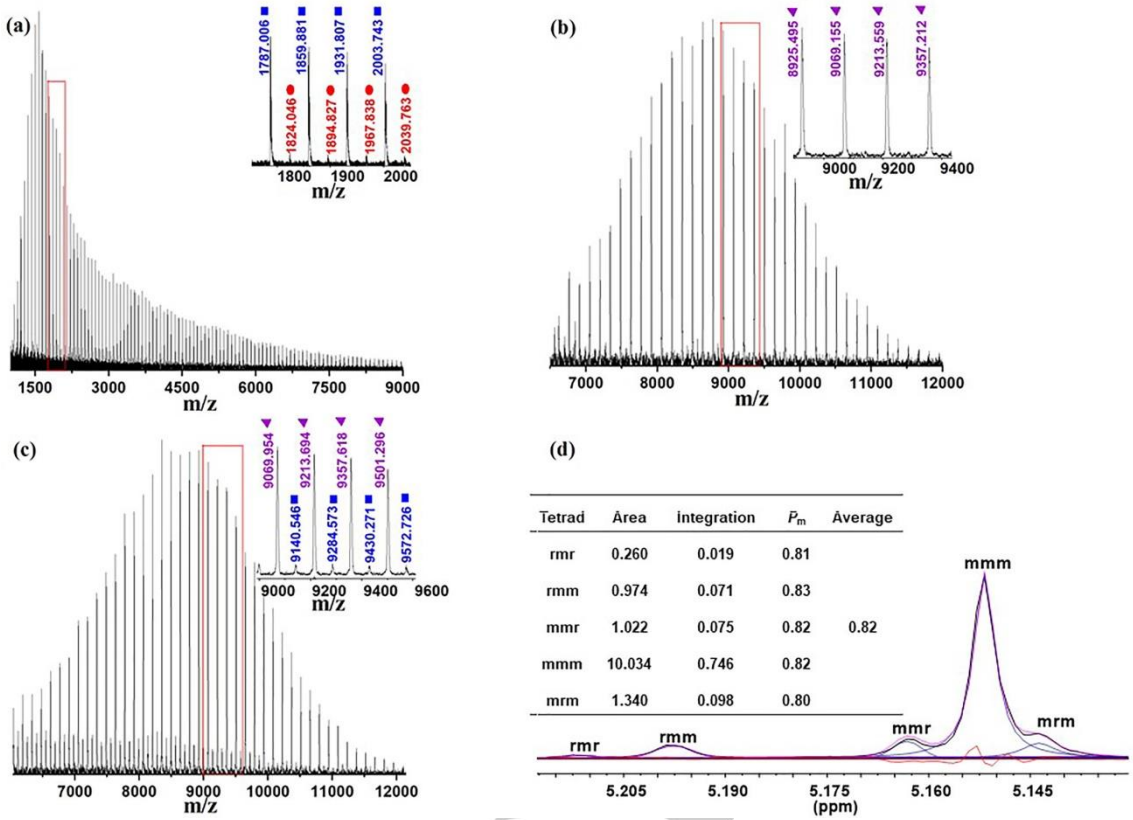


Figure 5. MALDI-TOF spectra (matrix: DCTB; ionization salt: CF_3CO_2Na; solvent: THF) of poly(*rac*-LA): (a) $[rac\text{-LA}]_0/[\text{Cat. }\mathbf{1}]_0/[\text{BnOH}]_0$ = 100/1/3, $[\text{Cat. }\mathbf{1}]_0$ = 2.0 mM, at room temperature (Table 1, entry 2); (b) $[rac\text{-LA}]_0/[\text{Cat.}\mathbf{1}]_0/[\text{BnOH}]_0$ = 500/1/3, $[\text{Cat.}\mathbf{1}]_0$ = 2.0 mM, at -70 °C (Table 1, entry 6); (c) $[rac\text{-LA}]_0$:$[\text{Cat. }\mathbf{2}]_0$:$[\text{BnOH}]_0$ = 500/1/5, $[\text{Cat.}\mathbf{2}]_0$ = 2.0 mM, at -70 °C (Table 1, entry 8) ; (d)The deconvolution of the homonuclear-decoupled ^{1}H NMR spectrum of PLA with a low deviation (red line) P_m = 0.82 (Table 1, entry 11).

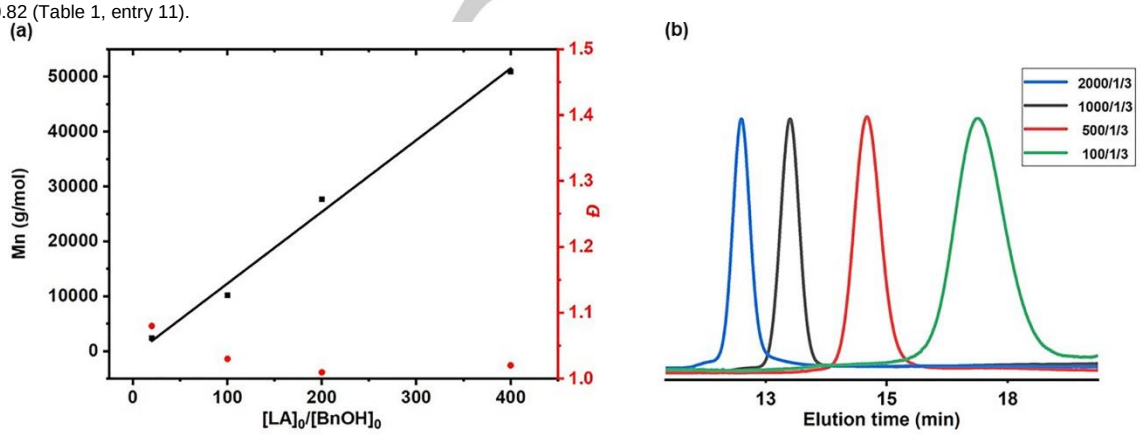


Figure 6. (a) Plots of the relationship between Mn (■) and Đ (●) of the polymer catalyzed by complex **1** and the initial mole ratio $[rac\text{-LA}]_0/[\text{BnOH}]_t$ (Table 1, entry 5, 6, 11 and 13); (b) the representative gel-permeation chromatography (GPC) traces of the poly(*rac*-LA) prepared by complex **1** (Table 1, entry 5, 6, 11 and 13).

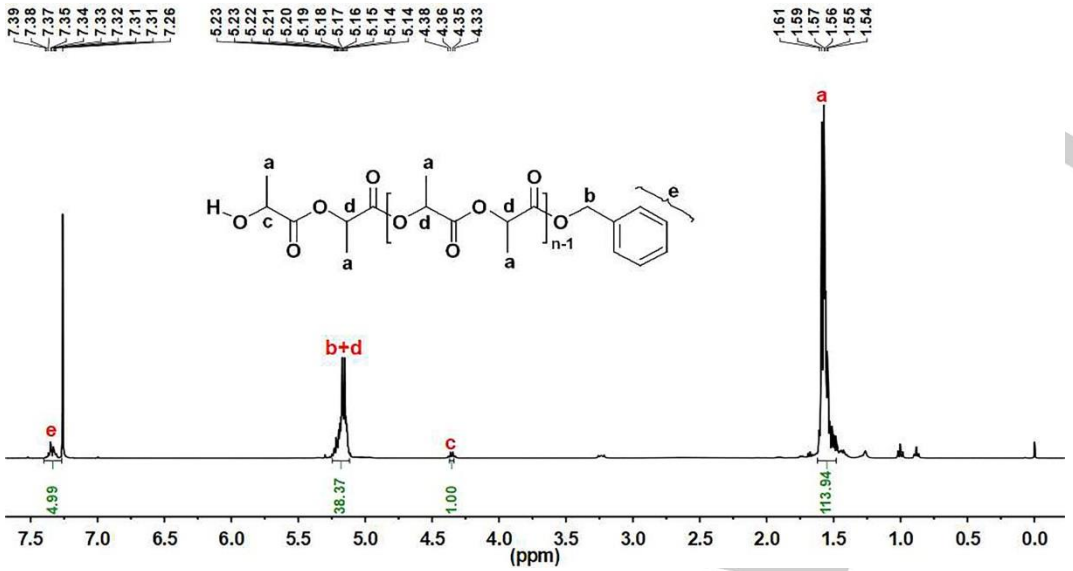


Figure 7. The ^{1}H NMR spectrum of poly(*rac*-LA) prepared by complex **1**: [*rac*-LA]$_0$/[Cat.**1**]$_0$/[BnOH]$_0$ = 100/1/3, [*rac*-LA]$_0$ = 0.2 M, at -70 ^{o}C.

In order to understand the stereoselective mechanism for this system and the details about the stereo sequence of these polymers, the stereo sequence errors of a polymer sample (P_m = 0.82, Table 1, entry 11, Figure 5d) obtained with complex **1** as a catalyst was analyzed. Except a primary mmm tetra peak, four tetra peaks of rmr, mmr, mrm, and rmm can be discovered by a good deconvolution of the signals of methine in the homo-decoupled ^{1}H NMR spectrum of this sample (Figure 5d). The integral ratio of mmr, mrm, and rmm peaks is close to 1/1/1, which suggested the main sequence errors are *RRRRSSSS*/*SSSSRRRR*. Therefore, the obtained isotactic polylactide are stereo multi-block polymers. The actual ratio of 1/3.7/3.9/5.2 for rmr, rmm, mmr, and mrm peaks was in accord with the Bernoullian statistics of these four tetrads for the isoselective ROP of *rac*-lactide via a chain-end control mechanism. For instance, the theoretical [mrm]/[mmm] (P_r/($2P_m^2$ + P_rP_m)) value is 12.1 % based on the P_m value of 0.82 which agrees with the experimental value of 13.4 %.

Conclusions

Two sodium/potassium tetradentate aminobisphenolate ion-paired complexes were synthesized without crown ether as an auxiliary ligand. The solid structures of complexes **1** and **1'** can clearly show BnOH can be activated by an interaction with the anion of sodium complex via a hydrogen bond and monomer will be activated by coordination to sodium ions. These complexes can isoselectively catalyze the ROP of *rac*-lactide with a best P_m value of 0.82 at -70 ^{o}C, which may result from the crowded surrounding around active sodium/potassium atom centre as our design. In this system, the epimerization side reactions can be suppressed well at a low temperature and upon addition multiple initiators of BnOH. The molecular weights of poly(*rac*-lactide) were controllable, the molecular weight distributions were narrow, and the highest molecular weight can reach to 50.1 kg/mol in this system.

Experimental Section

All solvents were dried by standard methods. *Rac*-lactide and *L*-lactide was purchased from Daigang BIO Engineer Limited Co. of China and recrystallized three times using dry toluene. The aminobisphenol ligand was synthesized according to a reference.[50] Other chemicals involved are commercially available and purified before use. All instruments and experimental conditions including NMR, gel permeation chromatography, and X-ray diffraction diffractometer used in the experiments are presented in supporting information.

Preparation of complex 1. NaN(SiMe$_3$)$_2$ (1.9 mL, 3.8 mmol, 2.0 M in THF) was added to a THF (20 mL) solution of aminobisphenol ligand (1.0 g, 1.9 mmol) at room temperature under a nitrogen atmosphere. After stirring overnight, anhydrous tetrabutylammonium chloride (0.53 g, 1.9 mmol) and BnOH (0.41 g, 3.8 mmol) was added into the mixture solution and continued to be stirred overnight again. After removing THF, the crude product was recrystallized using cold n-hexane with a 47 % isolated yield (0.68 g). Single crystals of complex **1** were obtained from a THF solution at room temperature with a CCDC number of 1882477. ^{1}H NMR(400 MHz, C_6D_6, ppm, 25 ^{o}C): 7.51 (d, *J* = 2.7 Hz, 2H, Ar-*H*), 7.30-7.32 (m, 4H, Ar-*H*), 7.26 (d, *J* = 2.7 Hz, 2H, Ar-*H*), 7.19-7.21 (m, 4H, Ar-*H*), 7.06-7.10 (m, 2H, Ar-*H*), 6.09 (s, 2H, Bn-O*H*), 4.70 (d, *J* = 10.6 Hz, 2H, Ar-CH_2-), 4.61(s, 4H, -CH_2- in Bn group), 3.21 (d, *J* = 10.5 Hz, 2H, Ar-CH_2-), 2.81 (m, 8H, -αCH_2- in (^{n}Bu)$_4$N$^+$), 2.72 (m, 2H, NCH_2CH$_2$NMe$_2$), 1.86 (s, 18H, ^{t}Bu-*H*), 1.68 (s, 2H, NCH$_2$CH_2NMe$_2$), 1.53 (m, 24H, ^{t}Bu-*H*+N(CH_3)$_2$), 1.11 (m, 16H, -(β+γ)-CH_2- in (^{n}Bu)$_4$N$^+$), 0.76 (t, *J* = 6.7 Hz, 12H, δCH_3-(^{n}Bu)$_4$N$^+$). ^{13}C NMR (100 MHz, C_6D_6, ppm, 25 ^{o}C): δ 168.64, 143.94, 136.61, 130.69, 127.71, 127.31, 123.21, 65.21, 64.81, 58.80, 49.33, 45.93, 36.38, 34.53, 33.11, 30.98, 24.45, 20.25, 14.23. Anal. Calcd (%) for $C_{64}H_{106}N_3NaO_4$: C 76.52, H 10.64, N 4.18. Found: C 76.61, H 10.61, N 4.10.

Preparation of complex 2. A mixture of aminobisphenol ligand (1.9 mmol, 1.0 g) and KN(SiMe$_3$)$_2$ (1.9 mL, 3.8 mmol, 2M) in 20mL THF was stirred overnight under a nitrogen atmosphere; then tetrabutylammonium chloride (0.53 g, 1.9 mmol) was added into the mixture system, which was stirred overnight again. After removing solvent under vacuum, the crude mixture was recrystallized using a mixed solvent of toluene and n-hexane, and a white solid was precipitated and dried under vacuum with an isolated yield of 57% (1.47g). ^{1}H NMR (400 MHz, C_6D_6, ppm, 25 ^{o}C): 7.50 (d, *J* = 2.8 Hz, 2H, Ar-*H*), 7.29 (d, J = 2.7 Hz, 2H, Ar-*H*), 4.64 (m, 2H, Ar-CH_2-), 3.11 (m, 2H, Ar-CH_2-), 3.05 - 2.98 (m, 8H, -αCH_2- in (^{n}Bu)$_4$N$^+$),

2.86 (m, 2H, NCH_2CH$_2$NMe$_2$), 1.86 (m, 20H, ^{t}Bu-*H* + NCH$_2$CH_2NMe$_2$), 1.54 (s, 18H, ^{t}Bu-*H*), 1.43 (s, 6H, N(CH_3)$_2$), 1.27 – 1.12 (m, 16H, -(β+γ)-CH_2- in (^{n}Bu)$_4$N$^+$), 0.77 (d, *J* = 7.2 Hz, 12H, δCH_3-(^{n}Bu)$_4$N$^+$). ^{13}C NMR (100 MHz, C_6D_6, ppm, 25 ^{o}C): δ 168.22, 145.38, 136.54, 129.46, 127.88, 126.95, 122.79, 64.93, 64.58, 58.62, 49.84, 45.14, 36.42, 34.51, 33.17, 30.99, 24.39, 20.28, 14.20. Anal. Calcd (%) for $C_{84}H_{144}N_5KO_4$: C 73.84, H 10.62, N 5.13. Found: C 73.90, H 10.53, N 5.09.

Typical polymerization of *rac*-lactide

The synthesis of poly(*rac*-LA) at room temperature is demonstrated using a typical example of polymerization procedure (Table 1, entry 1) as the following: *rac*-LA (0.144 g, 1.0 mmol) was added to a solution of complex **1** (0.008 g, 0.01 mmol) and BnOH (100 μL, 0.01 mmol, 0.1 M) in toluene (5 mL) under a nitrogen atmosphere. After the solution was stirred for 30s at room temperature, the reaction was then quenched with toluene solution of benzoic acid. Then the polymer was recrystallized from dichloromethane and n-hexane.

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Keywords: isoselective polymerization • *rac*-Lactide • sodium/potassium complex • ion-paired complex

CCDC: 1882477 and 1881629 for the crystal structures of complex **1** and hydrate of complex **2**.

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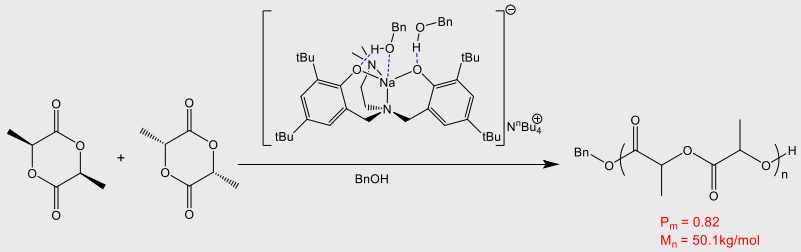

Sodium/potassium ion-paired complexes without crown ether are efficient catalysts for the isoselective ring-opening polymerization of *rac*-lactide (*rac*-LA).

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Isoselective Ring-Opening Polymerization of *rac*-Lactide Catalyzed by Sodium/potassium Tetradentate Aminobisphenolate Ion-paired Complexes