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Mononuclear Salen−Sodium Ion Pairs as Catalysts for Isoselective Polymerization of *rac*-Lactide

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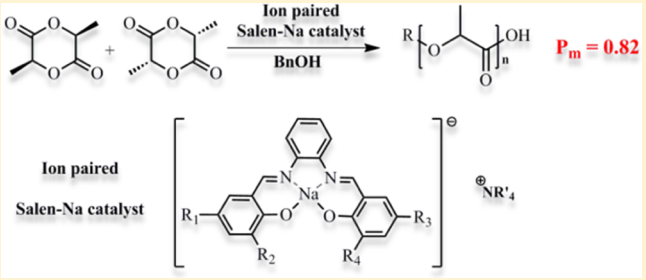
Supporting Information

ABSTRACT: A series of mononuclear salen−sodium anions, as the first examples, were synthesized with tetra-alkyl ammonium as a counterpart cation. These complexes are efficient catalysts for the isoselective ring-opening polymerization of *rac*-lactide; the molecular weights of polymers are under control and molecular weight distributions are narrow when five equivalents of BnOH is used as an initiator. The best isoselectivity value of P_m = 0.82 was achieved at −70 °C. The experimental results together with a density functional theory calculation show that a ligand-assisted activated monomer mechanism is more reasonable than an activated monomer mechanism for this system.



INTRODUCTION

Polymers as important materials have been infiltrating into every aspect of human being's daily life for the low cost, durability, safeness, and easy processability. The global production of polymers has reached 322 million metric tons in 2015 and an accumulative total of 8.3 billion metric tons as of 2017.[1] However, rapid growth in demand and production, combined with the typically outstanding durability of some petroleum-based polymers, had created a dire pollution prediction that there would be more plastic in the sea than fish.[2] Polylactide as one of the bio-derived polymers becomes a judicious choice to replace partial petroleum-based polymers in some fields such as packaging, fiber technology, and medicine because of its biodegradability and biocompatibility. The ring-opening polymerization (ROP) is an efficient approach to synthesize polylactide because of the controllable molecular weight, adjustable tacticity, and narrow molecular weight distribution (*Đ*). The tacticity of polylactide can greatly affect its chemical and physical properties, for example, its melting point.[3−5] Thus, it is of great importance to control the tacticity of polylactide, and the catalysts play a crucial role in polymerization progress for this purpose. In the past four years, some sodium/potassium complexes supported with crown ether were explored by us[6−12] and Wu and Wang,[13,14] which can isoselectively catalyze the ROP of *rac*-lactide (A and B in Chart 1); the isoselectivity even can reach P_m = 0.94 at −70 °C.[9] The isoselectivities of sodium/potassium complexes seem to be comparable to some good aluminum,[15−34] indium,[35−40] lanthanides,[35,41−46] zinc,[29,47−54] and other complexes[32,55−64] which have been extensively investigated. To develop sodium/potassium stereoselective catalysts is valuable for the ROP of *rac*-lactide because of nontoxicity and low price. During the study, it attracts our curiosity as to why crown ether is important in these sodium/potassium complex systems? Can crown ether be replaced by other auxiliary ligands in sodium/potassium complexes for the isoselective polymerization of *rac*-lactide? Although the adjustments of bulky-substituted groups in phenol ligands can increase the stereoselectivity, we speculate that the multiple-chelate effect and the flexible plane feature of crown ether sodium/potassium cation are important because no outstanding stereoselectivity can be achieved in the absence of crown ether in these systems. The multiple-chelate crown ether can inhibit the dissociation of sodium crown ether cation and lead to crown ether sodium cation very stably. As we know the spatial angle between the initiator and the lactide monomer can be compressed by the flexible plane of crown ether sodium/potassium cation, the interaction between the initiator and lactide monomer increases and consequently stereoselectivity can increase in the chain propagation progress.

To replace crown ether in sodium/potassium catalysts using other type ligands with multiple-chelate effect and flexible plane structure factor for the isoselective polymerization of *rac*-lactide, salen ligands with benzyl diamine as precursors seem to be a good option because of their flexible plane feature of ligands, a tetra chelate coordination site, simple synthesis, and adjustable steric and electronic effects. Although some more easily synthesized and monocharged Schiff base sodium complexes have been explored for the ROP of lactide,[65−67]

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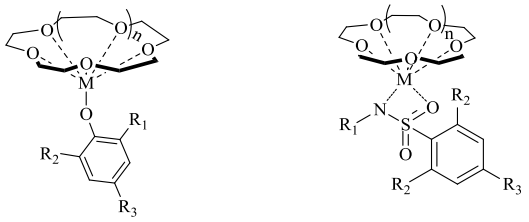
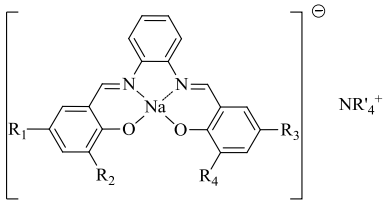
Chart 1. Alkali Metal Crown Ether Complexes and Mononuclear Salen−Na Complexes



A
M= Na, K; n=1, 2

B
M= Na, K; n=1, 2



C
This work

1 $R_1 = R_2 = R_3 = R_4 = {}^tBu$, $NR'_4{}^+ = NBu_4{}^+$
2 $R_1 = R_2 = R_3 = R_4 = Cumyl$, $NR'_4{}^+ = NBu_4{}^+$
3 $R_1 = R_3 = NO_2$, $R_2 = R_4 = {}^tBu$, $NR'_4{}^+ = NBu_4{}^+$
4 $R_1 = NO_2$, $R_3 = R_2 = R_4 = {}^tBu$, $NR'_4{}^+ = NBu_4{}^+$
5 $R_1 = R_2 = R_3 = R_4 = {}^tBu$, $NR'_4{}^+ = NMe_4{}^+$
6 $R_1 = R_2 = R_3 = R_4 = {}^tBu$, $NR'_4{}^+ = NEt_4{}^+$

these complexes are binuclear or tetranuclear complexes and the surroundings around metal center are not planar; some Schiff base sodium complexes show heteroselectivities for the ROP of *rac*-lactide reported by Tabernero and Cano et al.,[66] however, to our knowledge, no isoselective Schiff base sodium complexes have been reported for the ROP of *rac*-lactide so far. Inspired by some good stereoselective salen catalysis systems for the ROP of cyclic esters, for example, salen aluminum,[15−26] gallium,[55,56] lanthanum,[35,41] and other complexes,[17,35,37,58,68] mononuclear sodium salen complexes may be envisioned to show some isoselectivities to the ROP of *rac*-lactide. However, a considerable hindrance of salen ligands for the synthesis of mononuclear sodium/potassium complexes is that salen ligands normally are bicharged after deprotonation; the metal charge of mononuclear salen complexes normally is equal or greater than +2. Therefore, among various salen metal complexes, mononuclear salen complexes of one positively charged sodium ion have not been explored widely in stereoselective organic or polymerization reactions so far. In this work, some first examples of mononuclear salen−sodium complexes were synthesized and applied in the isoselective polymerization of *rac*-lactide.

RESULTS AND DISCUSSION

With an aim to get mononuclear salen−sodium complexes in mind, salen−sodium ion-paired complexes **1**−**6** were synthesized readily by consecutive treatments of salen ligands with NaH and tetra-alkyl ammonium chloride (C in Chart 1, Scheme S1). Crystals of complex **4** suitable for diffraction data collection were obtained from a mixed solution of tetrahydrofuran (THF) and *n*-hexane. Similar to other mononuclear salen metal complexes, Na1 is coordinated by two N atoms and two oxygen atoms of salen ligand and one oxygen atom of THF. Although the ligand partially twists, the surrounding of Na1 is almost a square pyramid (SP) (τ = 0.19) (Figure 1), and the salen ligand can be considered as an almost planar ligand toward the metal center. τ is a geometric parameter of a five-coordinated metal ion that distinguishes an SP from a trigonal bipyramid (TBP) (τ = 0 for SP and τ = 1 for TBP).[69] The coordinated THF can be removed under vacuum for a

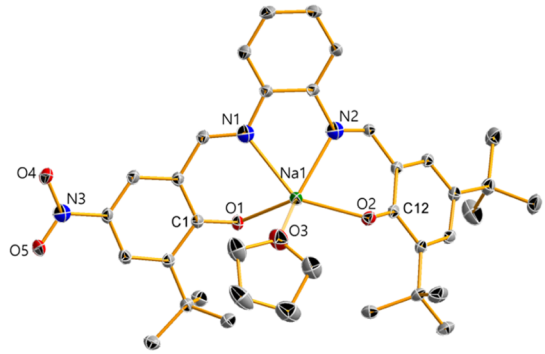


Figure 1. ORTEP drawing of anion part of complex **4** as 30% ellipsoids (all of the hydrogen atoms and tetra-*n*-butyl ammonium cation are omitted for clarity). Selected bond lengths (Å) and angles (°): Na1−O1 2.2572(12), Na1−O2 2.2435(12), Na1−N1 2.4625(14), Na1−N2 2.3845(13), Na1−O3 2.3501(15); O1−Na1−N1 74.85(5), O2−Na1−N1 143.08(5), O2−Na1−O1 131.65(5), O1−Na1−N2 121.32(5), O1−Na1−O3 96.99(5), O2−Na1−N2 75.93(4), O2−Na1−O3 94.51(5), N2−Na1−N1 67.44(4), O3−Na1−N1 108.55(6), and O3−Na1−N2 136.46(6).

long time (Figure S9), which suggests that THF just weakly coordinates to sodium atom and can be replaced by lactide monomer in the ROP progress. The hydrodynamic radii of complexes **1**, **2**, and **4** based on translational diffusion coefficients from diffusion-ordered spectroscopic (DOSY) spectra also support that they are mononuclear complexes (Figures S15−17, see related calculations in Table S1). The solubility of complex **3** is low in C_6D_6, and its DOSY spectrum was not obtained.

The ROP proceeds quickly using complex **1** as a catalyst with a ratio of $[LA]_0/[Cat.]_0/[BnOH]_0$ = 100:1:1 in toluene at room temperature. However, the molecular weight of the polymer is lower than the calculated value and molecular weight distribution is broad (Table 1, entry 1). Both chain end groups of benzyl and hydroxyl can be found clearly in ^1H NMR spectrum of the obtained polymer (Figure 2a). However, the amount of benzyl group is less than that of hydroxyl because the ratio between the integrals at 7.30−7.40

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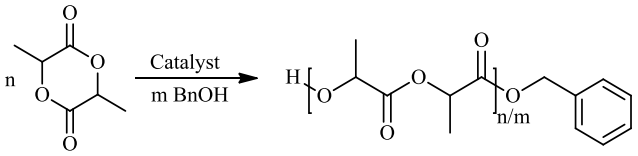
Table 1. Polymerization of *rac*-Lactide Catalyzed by Complexes 1−6[a]



entry	T (°C)	Cat.	$[LA]_0/[Cat.]_0/[BnOH]_0$	time (min)	Conv. (%)[b]	$M_{n,obs}$ (g/mol)[c]	$M_{n,calcd}$ (g/mol)[d]	$M_{n,nmr}$ (g/mol)[e]	$Đ$[c]	P_m[f]
1	rt	**1**	100:1:1	4	90	4500	13 100	4600(9800)	1.75	0.51
2	rt	**1**	100:1:0	17	93	7400			2.87	0.50
3	rt	**1**	100:1:5	1	90	1900	2700	3100	1.19	0.57
4	0	**1**	100:1:5	2	94	2000	2800	2500	1.14	0.67
5	−40	**1**	500:1:5	15	74	11 200	10 800	13 000	1.05	0.78
6[g]	−40	**1**	500:1:5	55	99	10 800	14 400	15 500	1.20	0.63
7[h]	−40	**1**	500:1:5	400	79	8300	11 500	9200	1.58	0.67
8	−40	**1**	250:1:5	11	85	5400	6200	5900	1.06	0.75
9	−40	**1**	500:1:5	20	97	13 600	14 100	15 400	1.28	0.78
10	−40	**1**	750:1:5	30	90	15 900	19 500	17 300	1.12	0.78
11	−40	**1**	1000:1:5	30	78	20 200	22 600	22 900	1.03	0.77
12	−40	**1**	1500:1:5	35	73	24 400	31 600	34 800	1.13	0.75
13	−40	**1**	500(500):1:5	16(16)	72	18 100	20 800	14 900	1.08	0.76
14	−70	**1**	500:1:5	465	94	11 700	13 600	13 900	1.05	0.78
15	−70	**2**	500:1:5	1080	90	10 800	13 100	12 900	1.06	0.79
16	−70	**5**	500:1:5	210	90	14 100	13 100	13 100	1.03	0.77
17	−70	**6**	500:1:5	300	94	15 600	13 600	14 100	1.11	0.76
18	rt	**3**	100:1:1	2880	<5					
19	rt	**4**	100:1:1	20	93	7900	13 500	4100(9500)	1.93	0.59
20	−70	**4**	500:1:5	2220	87	9200	12 600	11 100	1.06	0.82

[a]Conditions unless specified otherwise: reactions were performed in 10 mL of toluene, with 0.01 mmol of catalyst. [b]Determined by ^{1}H NMR spectroscopy. [c]Experimental M_n and $Đ$ values determined by gel permeation chromatography (GPC) in THF against polystyrene standards and corrected using the factor 0.58.[70] [d]Calculated from the molecular weight of $M_{n,rac\text{-LA}} \times [LA]_0/[BnOH]_0 \times$ conversion + $M_{n,BnOH}$. [e]Determined by the end group analysis, $M_n = N_{\text{repeated number of methine}} \times 72 + 108$ based on the end group of hydroxyl, the values in brackets are calculated based on end group of benzyl when the ratio between hydroxyl and benzyl groups are not close to 1:1. [f]Determined by the analysis of all of the tetrad signals in the methine region of the homonuclear-decoupled ^{1}H NMR spectrum. [g]The solvent is CH_2Cl_2. [h]The solvent is THF.

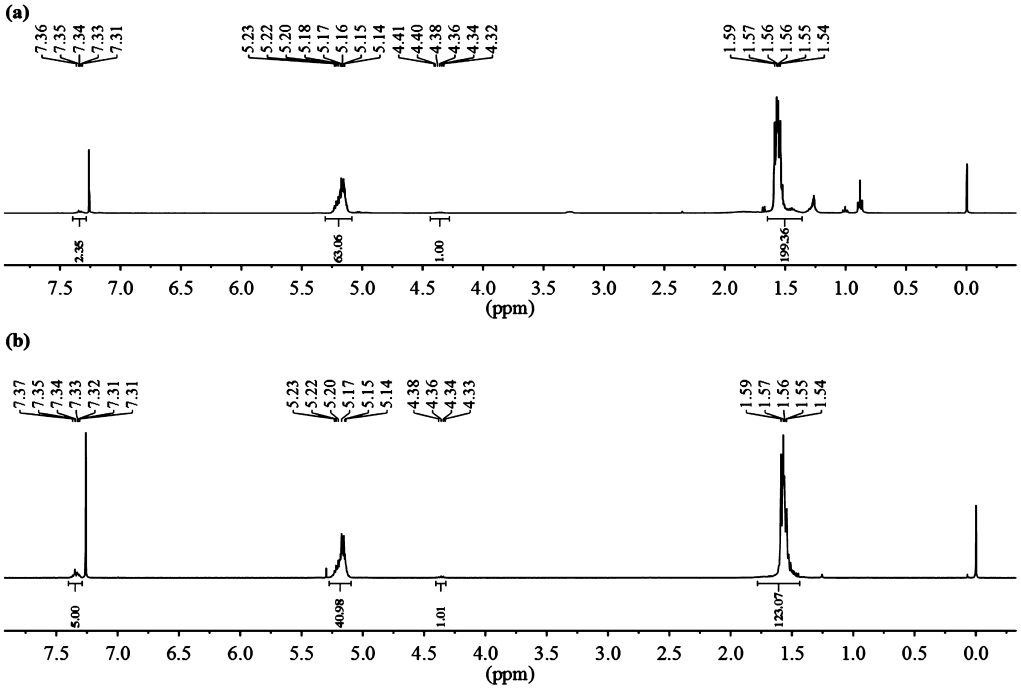


Figure 2. ^{1}H NMR spectra of poly(*rac*-LA) prepared by complex **1**: (a) $[rac\text{-LA}]_0/[Cat.\mathbf{1}]_0/[BnOH]_0$ = 100/1/1, $[rac\text{-LA}]_0$ = 0.1 M, at room temperature (Table 1, entry 1) and (b) $[rac\text{-LA}]_0/[Cat.\mathbf{1}]_0/[BnOH]_0$ = 100/1/5, $[rac\text{-LA}]_0$ = 0.1 M, at room temperature (Table 1, entry 3).

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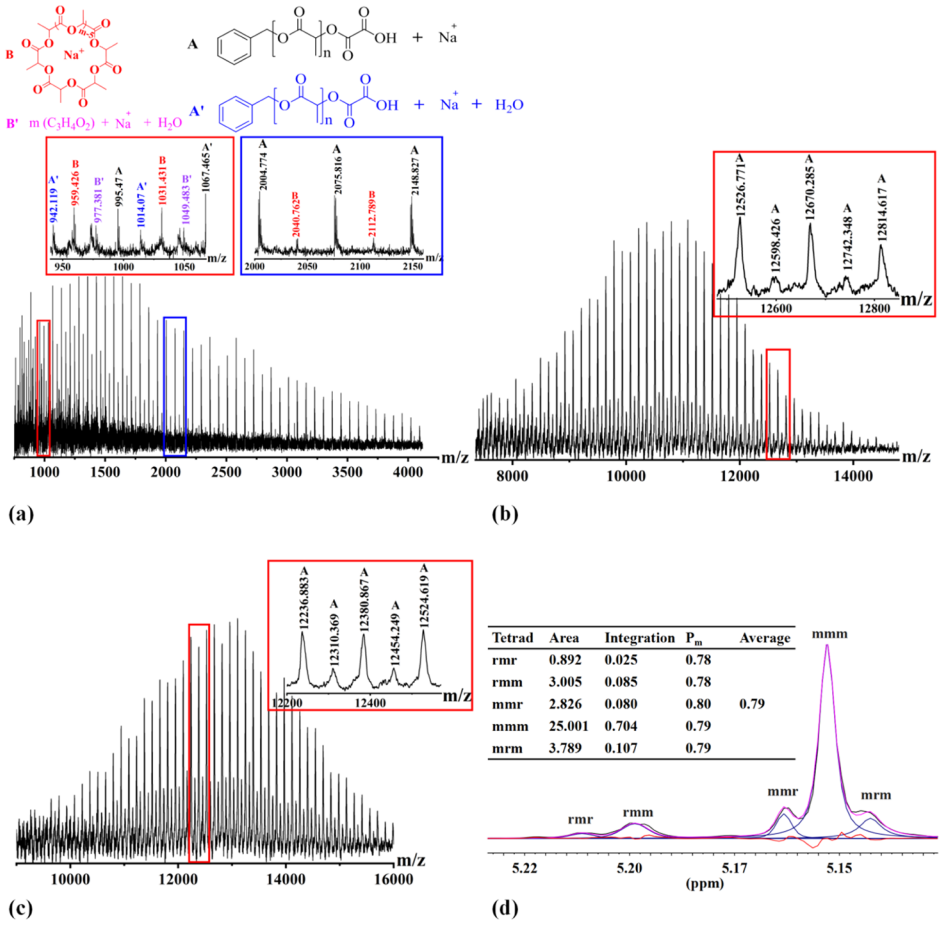

Figure 3. MALDI-TOF mass spectra of poly (*rac*-LA) prepared by complex **1**: (a) $[rac\text{-LA}]_0/[\text{Cat.}\mathbf{1}]_0/[\text{BnOH}]_0$ = 100/1/5, $[rac\text{-LA}]_0$ = 0.1 M, at room temperature (Table 1, entry 3); (b) $[rac\text{-LA}]_0/[\text{Cat.}\mathbf{1}]_0/[\text{BnOH}]_0$ = 500/1/5, $[rac\text{-LA}]_0$ = 0.5 M, at −40 °C (Table 1, entry 5); (c) $[rac\text{-LA}]_0/[\text{Cat.}\mathbf{1}]_0/[\text{BnOH}]_0$ = 500/1/5, $[rac\text{-LA}]_0$ = 0.5 M, at −70 °C (Table 1, entry 14); and (d) deconvolution of the homonuclear-decoupled ^{1}H NMR spectrum of PLA with a low deviation (red line) P_m = 0.79 (Table 1, entry 15).

ppm (Ar-*H* of benzyl) and 4.30−4.40 ppm (C*H* linked to end hydroxyl) is just about 2.35, which indicates BnOH was not the exclusive initiator in this condition. In the absence of BnOH, the polymerization also can happen (Table 1, entry 2) and the molecular weight distribution (*Đ*) of 2.85 is very broad. The MALDI-TOF mass spectrum of the resulting polymer showed a main series of peaks at 72*m* + 23(*m* ($C_3H_4O_2$) + Na^+) with a positive charge and a weak series of peaks with a positive charge at 72*n* + 540 + 23 (*m*($C_3H_4O_2$) + salen ligand + Na^+), which proved that ligand anion itself can initiate the ROP reaction as one side reaction (Figure S18). There are two weak peaks at 4.30 and 4.90 ppm in the ^{1}H NMR of the obtained polymer after recrystallization (Figure S19), which hints another side polymerization reaction also can be initiated by lactide anion because of the deprotonation of monomer by salen anion at room temperature as in our previous work.[6] To suppress these two kinds of side polymerizations, the addition of multiple equivalents of alcohol sometimes is helpful; because there are potential hydrogen bond interactions between alcohol and phenoxy groups within these salen−sodium anions, the concentration of the adduct of alcohol and salen−sodium anion will increase; thereafter, the concentration of free salen−sodium anion without the coordination of alcohol will decrease, and the related side reaction initiated by ligand anion itself and deprotonation of monomer should decrease. As expected, upon addition of 5 equivalents of BnOH as a coinitiator in this system, the molecular weight distribution of the resulting polymer becomes narrow (Table 1, entry 3), and the ratio between the integral at 7.30−7.40 ppm (Ar-*H*) and the integral 4.30−4.40 ppm (C*H*) is close to 5 (Figure 2b). A complicated MALDI-TOF spectrum of the polymerization showed (Table 1, entry 3, Figure 3a) a series of primary peaks at 72*n* + 108 + 23 with a positive charge, which can be assigned to *n*($C_3H_4O_2$) + BnOH +Na^+ for the resulting linear polymers end-capped with benzyl and hydroxyl groups; a series of peaks with a positive charge at 72*m* + 23 (*m*($C_3H_4O_2$) + Na^+) can be assigned to cyclic polymer, which agrees with the lower GPC value of molecular weight than that of NMR value; traces of a positive charge at 72*m* + 23 +18 and 72*n* + 108 + 23 + 18 can be assigned to m ($C_3H_4O_2$) + Na^+ + H_2O and n ($C_3H_4O_2$) + BnOH + Na^+ + H_2O, respectively. These series of peaks with a difference of molar mass of ∼72 Da suggest that trans-esterification reactions happen seriously during the polymerization process in this condition. The ^{1}H NMR spectra of the residues of polymerization reactions at room temperature (Table 1, entries 1 and 3, Figure 4a,b) show a weak quartet peak at 5.07 ppm and a doublet peak at 1.72 ppm, which can be ascribed to meso-lactide because of an epimerization reaction,[6,71] and about 14.8 and 9.6% *rac*-lactide can be converted to meso-lactide in the presence of one and five equivalents of BnOH, respectively. Decreasing the temperature

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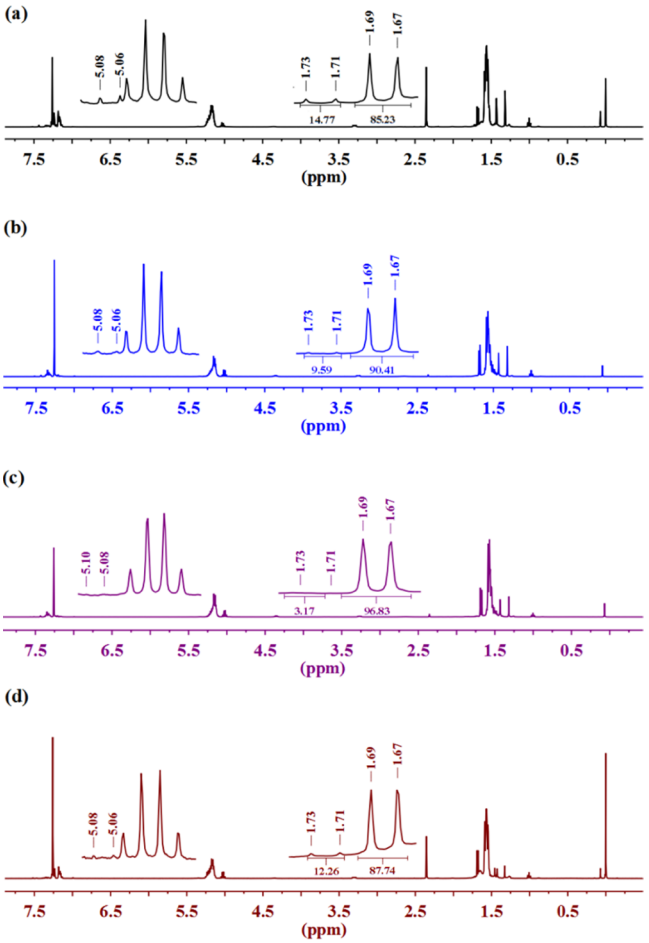

Figure 4. ^{1}H NMR spectra of the residue of polymerization reaction: (a) [*rac*-LA]$_0$/[Cat.**1**]$_0$/[BnOH]$_0$ = 100/1/1, [*rac*-LA]$_0$ = 0.1 M, at room temperature (Table 1, entry 1); (b) [*rac*-LA]$_0$/[Cat.**1**]$_0$/[BnOH]$_0$ = 100/1/5, [*rac*-LA]$_0$ = 0.1 M, at room temperature (Table 1, entry 3); (c) [*rac*-LA]$_0$/[Cat.**1**]$_0$/[BnOH]$_0$ = 100/1/5, [*rac*-LA]$_0$ = 0.1 M, at 0 °C (Table 1, entry 4); and (d) [*rac*-LA]$_0$/[Cat.**4**]$_0$/[BnOH]$_0$ = 100/1/1, [*rac*-LA]$_0$ = 0.1 M, at room temperature (Table 1, entry 19).

to 0 °C, the peaks at 5.07 and 1.72 ppm (Table 1, entry 4, Figure 4c) seem to be not obvious in ^{1}H NMR (meso-lactide ~ 3.2%). The ROP of L-LA also can show the inhibition of epimerization clearly when the temperature decreases from room temperature to −40 and −70 °C because the tetrads of mmm peak of methine of the resulting poly(L-lactide) increase to about 93 and 95%, respectively (Figure S20). When the temperature was kept at −40 or −70 °C, the molecular weights of polymers are close to the calculated values and increase linearly with the ratio of [*rac*-LA]$_0$/[BnOH]$_0$ (Table 1, entries 5, 8 and 10−12, Figure 5a), which can be further supported by a second feed experiment in which another portion of *rac*-LA was added after the polymerization of the first portion *rac*-LA had gone to completion (Table 1, entry 13). It is to note that at such a low temperature, lactide monomer does not totally be dissolved but the molecular distributions of obtained polymers are still narrow possibly because the dissolving rate of monomer is quicker than the rate of ROP; and a reverse phenomenon, where the dissolving rate of monomer is slower than the rate of ROP, was reported in our previous work.[6] Importantly, complex **1** shows a modest isoselectivity to the ROP of *rac*-lactide, and isoselectivity increases from 0.57 to 0.67 further to more than 0.75 when the temperature decreases from R.T. to 0 °C and further to −40 °C. MALDI-TOF spectrum of the polymer obtained at −40 °C shows (Table 1, entry 5, Figure 3b) a series of primary peaks with a positive charge at 144*n* + 108 + 23 and a series of weak peaks with a difference in molecular mass of ~72 Da; compared to the polymer obtained at room temperature, the transesterification reactions decrease obviously. When the solvent changes to THF or CH_2Cl_2, the isoselectivities do not change to be better (Table 1, entries 5 vs 6 and 7). When the conversion is high to 97% (Table 1, entry 9), the *Đ* value of the resulting polymer becomes larger, and the GPC traces even show an obvious shoulder peak (Figure 5b), which indicates that the back-biting side reaction becomes serious because of no enough monomer supply. It is also to be noted that when the ratios of [*rac*-LA]$_0$/[Cat.]/[BnOH]$_0$ increase to 1000/1/5 and 1500/1/5, a peak should appear clearly too, which suggests the side reaction exists in the whole polymerization progress but becomes slightly serious and visible in GPC traces for high-molecular-weight polylactides. That is to say, when polymer chains are long, the coordination possibility of a carbonyl group to sodium atom increases, and then the side reaction of transesterification including the back-biting reaction becomes serious in this system. Further decreasing the temperature to −70 °C, the P_m value does not increase obviously (Table 1, entry 14); however, MALDI-TOF spectrum of the obtained polymer (Table 1, entry 14, Figure 3c) clearly shows a series of primary peaks with a positive charge at 144*n* + 108 + 23 (*n*LA + BnOH + Na^+) and a weak series of peaks with a positive charge at 72*n* + 108 + 23 ($n(C_3H_4O_2)$ + BnOH + Na^+); compared to −40 °C, the transesterification reaction can

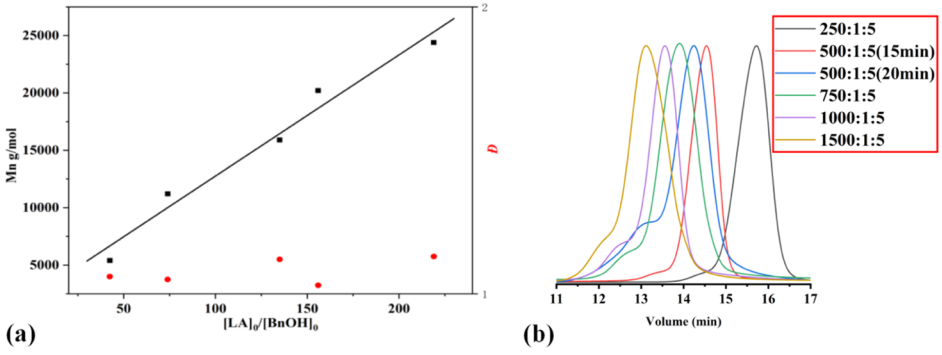

Figure 5. (a) Plots of the relationship between Mn (■) and *Đ* (●) of the polymer catalyzed by complex **1** and the initial mole ratio [*rac*-LA]$_0$/[BnOH]$_0$ (Table 1, entry 5, 8, 10−12); (b) representative GPC traces of the poly(*rac*-LA) prepared by complex **1** (Table 1, entries 5, 8−12).

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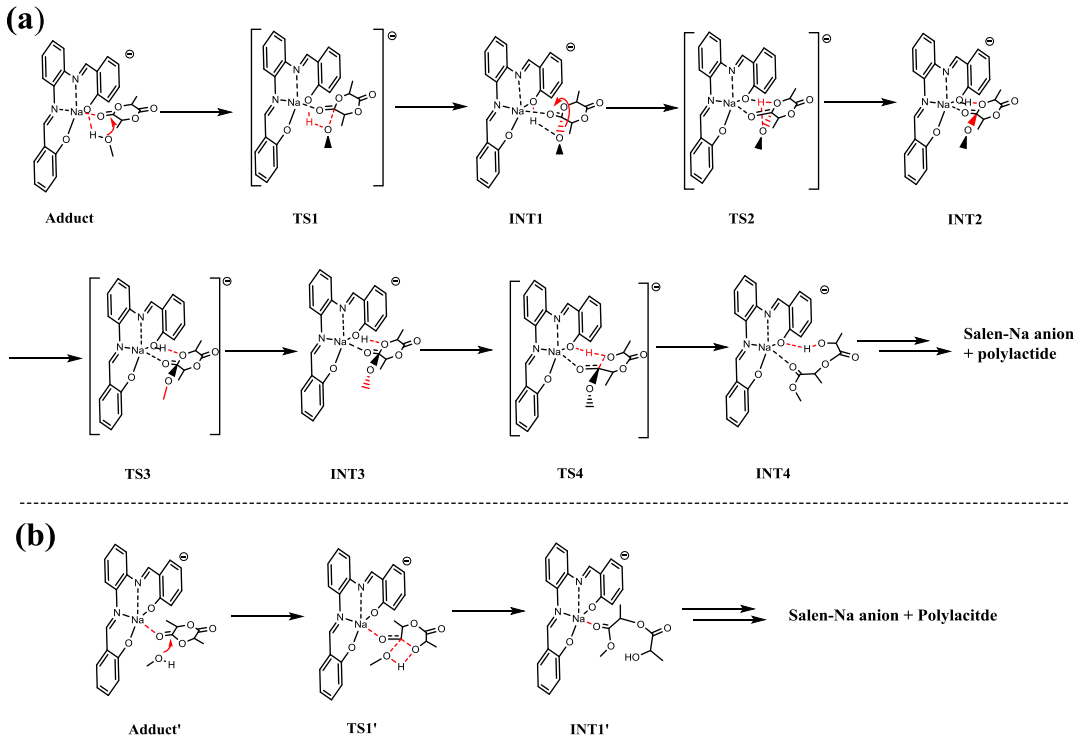
Scheme 1. Two Proposed Mechanisms for the Ring-Opening Polymerization of Lactide-Catalyzed by Salen−Na Anion in the Presence of Alcohol: (a) Ligand-Assisted Activated Monomer Mechanism; (b) Activated Monomer Mechanism without a Hydrogen Bond Interaction between Methanol and Salen−Na Anion; Note Methanol Was Used as a Model Alcohol in DFT Calculation and the Optimized Geometries of These Complexes Can be Found in the Supporting Information



decrease further. When complex **2**, with more bulky-substituted groups of cumyl, was used as a catalyst, the isoselectivity was similar to complex **1** (Table 1, entry 15) which exhibits that *t*-butyl groups in complex **1** are bulky enough. Further increase of the hindrance of substituted groups just slows down the polymerization rate because the serious steric hindrance can impede the monomer to approach the active metal center (Table 1, entries 14 vs 15). When different cations of NMe_4^+ and NEt_4^+ in complexes **5** and **6** were utilized to replace $N^nBu_4^+$ in complex **1**, no clear differences of isoselectivities were found for the ROP of *rac*-lactide (Table 1, entries 14 vs 16 and 17), which suggests that the environment close to sodium atom is similar. However, their ROP rates are slightly different. The DOSY spectra can prove these complexes are tight ion-paired complexes in nonpolar solvents because of electronic interactions (Figure S21), and they are loose ion pairs in the polar solvent of $CDCl_3$ (Figure S22); thus, the surrounding of big salen anions in toluene were partially occupied by different size cations, respectively, and the approach of monomer to sodium atom center was partially hindered at different levels.

To decrease the side polymerization initiated by salen−sodium anion itself, complex **3** with two electron-withdrawing nitro groups was synthesized. However, the ROP polymerizations in toluene, CH_2Cl_2, and THF are very slow (Table 1, entry 18). The possible reason is that the base strength of the phenoxy group of complex **3** is not strong enough to activate BnOH to initiate the ROP reaction, and another reason is also possible that the solubility of complex **3** in toluene and CH_2Cl_2 is low, and coordinated solvent molecules of THF can restrain monomers to be activated. Thus, asymmetric complex **4** with just one nitro group was synthesized with an aim to increase solubility and retain the base strength of salen−Na anion. Using complex **4** as a catalyst, the obtained polymer with a ratio of $[rac\text{-LA}]_0/[\mathbf{4}]_0/[\text{BnOH}]_0$ = 100/1/1 shows a weak quartet peak at 5.07 ppm in the ^{1}H NMR spectrum at room temperature (Table 1, entry 19, Figure 4d). Therefore, compared to complex **1**, the epimerization is somewhat suppressed using complex **4** as a catalyst because the basicity of salen ligand anion decreases (Table 1, entries 1 vs 19, Figure 4a vs 4d). The P_m value of 0.59 of complex **4** also is slightly better than complex **1** at room temperature possibly because of the suppression of epimerization reaction. However, the molecular weight also is lower than the expected polymer solely initiated by BnOH. When the temperature is −70 °C and 5 equivalents of BnOH is used as initiator, the P_m value increases to 0.82 for complex **4** (Table 1, entry 20), and the molecular weight becomes close to the theoretic value and the molecular weight distribution becomes narrow. To understand the stereo sequence of the polymer, the stereo microstructure of a polymer sample (P_m = 0.79, Table 1, entry 15, Figure 3d) obtained with complex **2** as a catalyst was analyzed. In the homo-decoupled ^{1}H NMR spectrum of this sample, a good deconvolution of the peaks of methine (Figure 3d) shows that the integral ratio of mmr, mrm, and rmm peaks is close to 1/1/1, which can be attributed to the main sequence errors of *RRRRSSSS*/*SSSSRRRR*. Thus, the obtained isotactic-enriched polylactides are stereo multiblock polymers. The actual ratio of 1/3.4/3.2/4.3 for rmr, rmm, mmr, and mrm peaks agree with the Bernoullian statistics of these tetrads for the stereoselective ROP of *rac*-lactide via a chain-end control mechanism, for example, the experimental value of [mrm]/[mmm] = 15.2% is similar to the calculated value of [mrm]/[mmm] = $P_r/(2\ P_m^2 + P_rP_m)$ = 14.9% based on P_m value of

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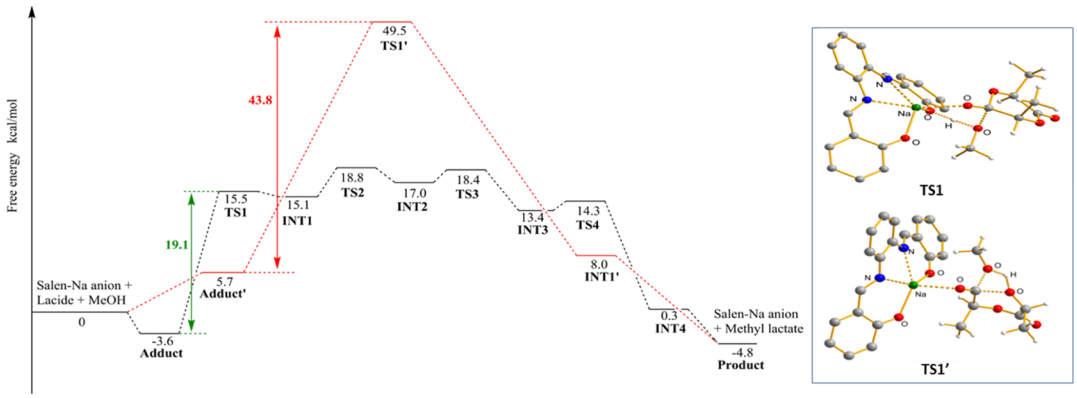

Figure 6. Free-energy profiles calculated for the ROP of L-lactide catalyzed by salen−Na anion model complex through a ligand-assisted activated monomer mechanism (black color) and activated monomer mechanism (red color), respectively, including an inset of key intermediates of TS1 and TS1′.

0.79. Although salen−Na complex **4** is asymmetric, the stereo sequence error distribution of the resulting polymer is similar to the sample obtained with complex **2** as a catalyst, indicating that the stereoselective mechanism is similar (Table 1, entry 20, Figure S23).

To get more insight into the ROP mechanism of this system, the reaction of complex **1** and BnOH was conducted in a ^{1}H NMR tube with deuterated benzene as a solvent (Figure S24); the methene protons of BnOH downshifts from 4.30 to 4.36 ppm; one proton of the ligand shifts to a high field from 8.60 to 8.57 ppm. These shift values prove that there are some interactions between BnOH and complex **1**, which may be a hydrogen bond interaction between the oxygen atom of salen−sodium anion and the hydroxyl group of BnOH. The NOESY spectrum of the adduct of complex **1** and BnOH in deuterated benzene (Figure S25) shows an obvious cross-peak between the protons; methene of BnOH and ortho-position *tert*-butyl group of hydroxyl in salen ligand hints that BnOH is close to the butyl group of the salen ligand. Accordingly, the existence of a hydrogen-bond interaction between BnOH and the oxygen atom of salen ligand can be confirmed further. Thus, a ligand-assisted activated monomer mechanism was proposed as the polymerization mechanism of the ROP of *rac*-LA catalyzed by these catalysts (Scheme 1a), which also was verified by density functional theory (DFT) calculations at the M06l/6-31+G(d, p) level. To reduce the time for the calculation work, simple salen ligand without substituted group was used as a model ligand, and methanol was used to replace BnOH or the growing macro-alcohol; tetra-alkyl group was omitted. The calculated reaction energy profile for the proposed mechanism encapsulates that the key species is shown in Figure 6. In the catalytic system, the catalyst interacts with the initiator MeOH and lactide monomer to form an adduct, where the lactide monomer is activated by the coordination to sodium ion, and methanol is activated via a hydrogen bond to the oxygen atom of salen anion. The nucleophilic attack of methoxy to the carbonyl group of lactide leads to the tetrahedral intermediate INT1 via a transition state TS1 with an activation energy of 19.1 kcal/mol; concomitantly, the proton of methanol transfers to the oxygen atom of phenoxy group of salen anion. After a rotation of lactide segment with an energy barrier of 3.7 kcal/mol, the oxygen atom of the C−O bond of lactide can replace methoxy to interact with the phenol group through the hydrogen-bonding interaction and then intermediate INT2 forms. After a very easy rotation of the end group of methoxy with an energy barrier of 1.4 kcal/mol (TS3), the C−O single bond of lactide breaks to give an intermediate (INT4) via a transition state TS4 with an activation energy of 0.9 kcal/mol and at the same time the H atom transfers to the oxygen atom of the C−O single bond of lactide. Finally, the ring-opening polymer product leaves away and salen−sodium anion is regenerated. In contrast, when the ROP reaction proceeds via an activated monomer mechanism (Scheme 1b), the alcohol is not activated via a hydrogen bond interaction with ligand anion. This energy barrier for a four-member-ring transition state TS1′ is very high (43.8 kcal/mol), which is not in line with the fact that the reaction can happen at room temperature quickly. In this ligand-assisted activated monomer mechanism, the hydrogen bond interaction between ligand anion and alcohol is important because the first step is a rate-determining step. Compared with complex **1**, the lower activity of complex **4** with an electron-withdrawing group also agrees with this ligand-assisted activated monomer mechanism too.

CONCLUSIONS

In summary, six salen−sodium ion pairs were first synthesized and owned mononuclear structures evidenced by DOSY spectra and one single-crystal structure. These complexes can catalyze the ROP of *rac*-LA efficiently. Some side reactions including epimerization and transesterification can be suppressed upon addition of multiple equivalents of alcohol at a low temperature, and the molecular weights of obtained polylactide can increase linearly with the ratio of $[rac\text{-LA}]_0/[\text{BnOH}]_0$ upon addition of 5 equivalents of alcohols. These salen−sodium anion complexes can stereo-selectively catalyze the ROP of *rac*-lactide with a best P_m value of 0.82 at −70 °C, which possibly is attributed to the subtle planar feature of salen ligand around the sodium metal center. The DFT calculation showed a ligand-assisted activated monomer mechanism that is more reasonable than an activated monomer mechanism for this system, in which both activations of monomer and alcohol are important.

ASSOCIATED CONTENT

Supporting Information

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Experimental details, ^{1}H NMR and ^{13}C NMR spectra of complexes **1**−**6**, polymerization studies, and computational details. X-ray crystallographic data of complex **4** with CCDC reference number of 1860889 (PDF)

Accession Codes

CCDC 1860889 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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