Accepted Manuscript

Metal-Size Influence of Alkali Metal Complexes for Polymerization of *rac*-Lactide

Jiao Xiong, Yangyang Sun, Jitao Jiang, Changjuan Cheng, Xiaobo Pan, Cheng Wang, Jincai Wu

PII:	S0277-5387(17)30774-X
DOI:	https://doi.org/10.1016/j.poly.2017.11.046
Reference:	POLY 12948
To appear in:	Polyhedron
Received Date:	4 October 2017
Accepted Date:	28 November 2017



Please cite this article as: J. Xiong, Y. Sun, J. Jiang, C. Cheng, X. Pan, C. Wang, J. Wu, Metal-Size Influence of Alkali Metal Complexes for Polymerization of *rac*-Lactide, *Polyhedron* (2017), doi: https://doi.org/10.1016/j.poly. 2017.11.046

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Metal-Size Influence of Alkali Metal Complexes for Polymerization of

rac-Lactide

Jiao Xiong,^a Yangyang Sun,^a Jitao Jiang,^a Changjuan Cheng,^a Xiaobo Pan,^a Cheng Wang,^b* Jincai Wu^a*

^aState Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, Lanzhou University, Lanzhou 730000, People's Republic of China.

^bThe Second Affiliated Hospital of Lanzhou University, Lanzhou 730000, China.

* Corresponding authors. Tel.: +86 931 8912552; fax: +86 931 8912582. *E-mail addresses:* wujc@lzu.edu.cn (J. Wu).

ABSTRACT

A series of alkali metal complexes with 2, 2'-ethylidenebis(4,6-di-tert-butylphenol) (EDBP-H₂) as a ligand have been synthesized. In the presence of benzyl alcohol as an initiator, all complexes exhibit good catalytic behaviors for the ring-opening polymerization (ROP) of *rac*-lactide, giving desirable molecular weights and narrow molecular weight distributions. The relative order of activities for this series of complexes is Li > Na > K > Rb, which is related to metallic ion radius; and Lewis acidity of these metal ions is also an important factor for the kinetics of the ROP. The relative order of stereoselectivities for this series of complexes is $\text{Rb} \approx \text{K} > \text{Na} >> \text{Li}$ in this system. The first example of Rb complex in the ROP of *rac*-lactide in this paper was also described, showing a modest activity and a nice polymerization control, even with a certain isoselectivity.

Keywords: polylactide; ring-opening polymerization; alkali metal complexes; isoselectivity.

1. Introduction

Polylactide (PLA), as a leading biodegradable polymer, has been widely used in daily life because of its biorenewable and biocompatible properties, and expected to be an alternative for petroleum-based products since the existence of serious pollution of the ecosystem in the nowadays world [1]. The major method employed to synthesize PLA is the ring-opening polymerization (ROP) of lactide because of well-controlled molecular weight and low molecular weight distribution (D) compared to the direct condensation of lactic acid [2]. Thus, many metal complexes have been synthesized to catalyze the ROP of lactide, including Mg [3], Ca [4], Zn [5], Al [6], Ti [7], lanthanide complexes [8] alkali metal complexes [9] and so on. Although some of these metal complexes are excellent initiators/catalysts, most of them are still suffered from some demerits. For example, Salen aluminum complexes show impressive degrees of stereocontrol but usually with low activities [2e, 6a, 6q]; lanthanide complexes also show good isoselectivity, but are cytotoxic [10]; calcium is essential element in the human body and innocuous, while good stereoselective catalysts have rarely been reported [4a]; thus, there is still a lot of room to improve the ROP of polylactide mediated by metal complexes. Alkali metal complexes, like sodium and potassium complexes, are one of our main research subject due to non-toxicity and high reactivity [11]. Recently, a series of sodium and potassium crown ether complexes were reported to efficiently catalyze the ROP of rac-lactide with high activities and high isoselectivities [12], the highest isoselectivity even can reach to $P_{\rm m} = 0.94$ at -70 °C [12e] and the molecular weight can

be high up to 107 kg/mol [12h]. The research of stereoselective synthesis of polylactide is valuable because the physical and chemical properties of polylactide are highly dependent on their stereo microstructures [13]. As pointed out in our previous work, a confined space around metal center of alkali metal complexes is important for the controllable isoselective ring-opening polymerization of *rac*-lactide. The confined space or steric effect around the metal center does not only depend on the substituted group of ligand but also the metal ionic radii. The effective ionic radii of six-coordinate Na⁺, K⁺, and Rb⁺ are 116, 152, and 166 pm, respectively [14]. Considering spherical volume, which is of a cubic function, the size ratio of these three ion radii will be 1:2.25:2.93, Rb⁺ is nearly the three times size of Na⁺. To deeply understand the effect caused by different ionic radii, herein, we explore the catalytic performance of a series of lithium, sodium, potassium, and rubidium complexes, which enables us to understand the influence of atomic size and coordination environment on the activity of metal complexes for the isoselective polymerization of rac-lactide. In addition, to our knowledge, the rubidium phenolate reported in this work is the first example of rubidium complex utilized as a catalyst for the ROP of cyclic ester.

2. Experimental Section

2.1. General Considerations

All complexes were synthesized and crystallized under a dry argon atmosphere, and all the polymerization reaction were performed in a glovebox using standard Schlenk techniques. The ¹H NMR and ¹³C NMR spectra were recorded on a Varian mercury plus

300M or JNM-ECS 400M MHz spectrometer; The elemental compositions of the four metal complexes were measured using an Elemental Vario EL series CHN analyzer under a nitrogen atmosphere. The GPC measurements were performed using a Waters 1525 binary system that was equipped with a Waters 2414 RI detector and two Styragel columns (102-106 kg/mol) by using THF (HPLC grade) as an eluent running at 1 mL min⁻¹. Molecular weights (M_n) and molecular weight distributions (D) were calculated using polystyrene as the standard. Each measuring value was corrected using a factor of 0.58 for polylactide according to the literature [15]. The mass spectroscopic data were obtained using a Thermo Scientific Orbitrap Elite MS (LTQ Orbitrap Elit).

2.2. Materials

Toluene, THF, and hexane were dried by refluxing several hours with sodium, and benzophenone serve as an indicator. CH₂Cl₂ was distilled with P₂O₅; *rac*-LA was purchased from Daigang BIO Engineer Ltd. of China and was recrystallized from toluene at least three times. CDCl₃ was purchased from J&K Scientific, Ltd. in Beijing and dried with activated molecular sieves. KN(SiMe₃)₂, NaN(SiMe₃)₂, ^{*n*}BuLi, Rb, were purchased from J&K Scientific Ltd. 18-crown-6 and 12-crown-4 were purchased from local companies and were used as received.

2.3. Synthesis

2.3.1. Synthesis of $Rb(O^{t-}Bu)$

Add element Rb (0.095 g, 1.10 mmol) to a solution of tert-butyl Alcohol (0.22 mL,

2.3 mmol) in THF and stir at room temperature under an argon atmosphere for 24 h. The light-yellow liquid formed was dried under vacuum and a white powder was obtained. Yield: 0.17 g (97 %).

2.3.2. Synthesis of complex 1

To a solution of EDBP-H₂ (0.438 g, 1.0 mmol) and 12-crown-4 (0.194 g, 1.1 mmol) in toluene (50.0 mL), ^{*n*}BuLi (1.1 mmol, 2.4 M in hexane) was added dropwise. After stir at room temperature under an argon atmosphere for 12 h, a white turbid liquid was obtained. The precipitate formed was separated by filtration, washed with 20 mL hexane and dried in vacuum to give a white powder (0.58 g, 94 %). Colorless crystals of **1** suitable for X-ray diffraction studies were obtained from a toluene solution at room temperature. ¹H NMR (400 MHz, CDCl₃): δ 7.20 (d, *J* = 2.5 Hz, Ar-*H*, 2H), 6.98 (d, *J* = 2.4 Hz, Ar-*H*, 2H), 5.14 (q, *J* = 7.5 Hz, Ar-*H*, 1H), 3.98 (b, -CH₂-, 8H), 3.64 (b, -CH₂-, 8H), 1.65 (d, *J* = 7.4 Hz, -CH₃, 3H), 1.41 (s, -C(CH₃)₃, 18H), 1.30 (s, -C(CH₃)₃, 18H). ¹³C NMR (100 MHz, CDCl₃): 157.14, 135.69, 134.75, 134.53, 120.02, 119.87 (Ph), 66.95 (-CH₂-), 35.00, 34.12 (-*C*(CH₃)₃), 31.94, 30.05 (-C(*C*H₃)₃), 29.48 (*C*HCH₃), 19.97 (CH₃). Anal. Calcd for C₃₈H₆₁O₆Li: 73.47, H 9.86. Found: C 73.52, H 9.90.

2.3.3. Synthesis of complex 2

According to the procedure described above for **1**, EDBP-H₂ (0.438 g, 1.0 mmol) and 18-crown-6 (0.290 g, 1.1 mmol) was converted to complex **2** as a white powder (0.65 g, 90 %) by reacting with NaN(SiMe₃)₂ (0.55 mL, 1.1 mmol, 2.0 M in THF) in toluene.

Colorless crystals of **2** suitable for X-ray diffraction studies were obtained from a toluene solution at room temperature. ¹H NMR (400 MHz, CDCl₃): δ 7.13 (d, *J* = 2.4 Hz, Ar-*H*, 2H), 6.93 (d, *J* = 2.5 Hz, Ar-*H*, 2H), 5.19 (q, *J* = 7.4 Hz, -CH-, 1H), 3.67 (s, -CH₂-, 24H), 1.59 (d, *J* = 7.5 Hz, -CH₃, 3H), 1.39 (s, -C(CH₃)₃ 18H), 1.28 (s, -C(CH₃)₃ 18H). ¹³C NMR (100 MHz, CDCl₃): 158.60, 135.21, 134.77, 134.55, 119.62, 119.44 (Ph), 68.98 (-CH₂-), 34.79, 34.05 (-C(CH₃)₃), 31.98, 30.06 (-C(CH₃)₃), 19.83 (CH₃). Anal. Calcd for C₄₂H₆₉O₈Na: C 69.63, H 9.61. Found: C 69.58, H 9.59.

2.3.2. Synthesis of complex 3

According to the procedure described above for **1**, EDBP-H₂ (0.438 g, 1.0 mmol) and 18-crown-6 (0.290 g, 1.1 mmol) was converted to complex **3** as a white powder (0.64 g, 86 %) by reacting with KN(SiMe₃)₂ (1.1 mL, 1.1 mmol, 1.0 M in THF) in toluene. Colorless crystals of **3** suitable for X-ray diffraction studies were obtained from a toluene solution at room temperature. ¹H NMR (400 MHz, CDCl₃): δ 7.19 (d, *J* = 2.5 Hz, Ar-*H*, 2H), 6.94 (d, *J* = 2.6 Hz, Ar-*H*, 2H), 5.23 (q, *J* = 7.4 Hz, -CH-, 1H), 3.66 (s, -CH₂-, 24H), 1.66 (d, *J* = 7.5 Hz, -CH₃, 3H), 1.39 (s, -C(CH₃)₃ 18H), 1.27 (s, -C(CH₃)₃) 18H). ¹³C NMR (100 MHz, CDCl₃): 158.89, 135.28, 134.46, 134.23, 119.64, 119.59 (Ph), 69.74 (-CH₂-), 35.02, 34.03 (-C(CH₃)₃), 31.97 (-C(CH₃)₃), 30.24 (CHCH₃), 29.99 (-C(CH₃)₃), 19.68 (CH₃). Anal. Calcd for C₄₂H₆₉O₈K: C 68.01, H 9.48. Found: C 68.07, H 9.38.

2.3.4. Synthesis of complex 4

To a solution of EDBP-H₂ (0.438 g, 1.0 mmol) and 18-crown-6 (0.290 g, 1.1 mmol) in toluene (50.0 mL), Rb(Ot-Bu) (0.158 g, 1.1 mmol in toluene) was added dropwise. After stir at room temperature under an argon atmosphere for 12 h, a white turbid liquid was obtained. The precipitate formed was separated by filtration, washed with 20 mL hexane and dried in vacuum to give a white powder (0.65 g, 83%). Colorless crystals of **4** suitable for X-ray diffraction studies were obtained from a CDCl₃ solution at room temperature. ¹H NMR (400 MHz, CDCl₃): δ 7.23 (d, *J* = 2.2 Hz, Ar-*H*, 2H), 6.99 (d, *J* = 2.4 Hz, Ar-*H*, 2H), 5.19 (q, *J* = 7.5 Hz, -C*H*-, 1H), 3.67 (s, -C*H*₂-, 24H), 1.71 (d, *J* = 7.4 Hz, -C*H*₃, 3H), 1.46 (s, -C(C*H*₃)₃ 18H), 1.34 (s, -C(C*H*₃)₃, 18H). ¹³C NMR (100 MHz, CDCl₃): 158.95, 135.41, 134.58, 134.44, 119.74, 119.66 (Ph), 69.84 (-CH₂-), 35.05, 34.06 (-*C*(CH₃)₃), 31.98 (-C(*C*H₃)₃), 30.71 (*C*HCH₃), 30.01 (-C(*C*H₃)₃), 19.64 (*C*H₃). Anal. Calcd for C₄₂H₆₉O₈Rb; C 64.02, H 8.81. Found: C 64.06, H 8.83.

2.3.5. General procedure for polymerization of rac-lactide

A typical polymerization procedure is illustrated by the synthesis of PLA $([LA]_0/[cat.]_0/[BnOH]_0 = 100:1:1, Table 1, entry 1)$. In a glove box, to a solution of **3** (7.4 mg, 0.01 mmol) and BnOH (100 µL, 0.1 M in toluene) in 5 mL toluene, *rac*-lactide (0.144 g, 1.0 mmol) was added. The mixture was then rapidly stirred at ambient temperature for 10 h. The reaction was quenched by one drop of water. Resulting polymers were precipitated in hexane and dried to give final products.

2.4. Crystallographic studies

The data were collected using a SuperNova (Dual) X-ray diffractometer equipped with a graphite-monochromated Cu/Mo K α radiation source ($\lambda = 1.54184/0.71073$ Å). The structure was solved by direct methods using the Siemens SHELXTL PLUS program [16]. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. All hydrogen atoms were placed by geometrical considerations and were added to the structure-factor calculations. No. CCDC 1533900-1533903 contain the supplementary crystallographic data for this paper.

3. Results and Discussion

3.1. Synthesis and Structures of alkali metal complexes 1-4.



Scheme 1. Preparation of compounds 1-4.

2,2'-ethylidenebis(4,6-di-tert-butylphenol) (EDBP-H₂) was applied as a ligand in this work due to its non-toxicity, which had been approved by the U.S. Food and Drug Administration as an indirect food additive. So stereoselective researches utilizing EDBP complexes in ROP reactions seem to be of potential values. Thus, four alkali metal complexes, **1** (EDBP-H)Li(12-crown-4), **2** (EDBP-H)Na(18-crown-6), **3**

(EDBP-H)K(18-crown-6), and **4** (EDBP-H)Rb(18-crown-6) were prepared by treatment of EDBP-H₂ with the same equivalents of 12-crown-4/18-crown-6 and ⁿBu-Li/NaN(SiMe₃)₂/KN(SiMe₃)₂/^tBu-ORb in toluene at ambient temperature (Scheme 1), all these four complexes were isolated as white solids in high yields (> 80%), and were confirmed by the elemental analysis, NMR spectra, and single crystal X-ray diffraction.



Fig. 1. Molecular structures of complexes 1-4 with probability ellipsoids at 30% (most of the hydrogen atoms are omitted for clarity). Selected bond lengths (Å): complex 1, Li1–O1 = 1.833(4), Li1--O2 = 3.512(42), O2---O1 = 2.594(21); complex 2, Na1-O1 = 2.266(19), Na1---O2 = 3.549(19), O2---O1 = 2.528(21); complex 3, K1–O1 = 2.677(19), K1---O2 = 3.942(20); O2---O1 = 2.513(26); complex 4, Rb1–O1 = 2.871(5), Rb1---O2 = 3.233(6), O2---O1 = 2.433(81).

Crystals suitable for single-crystal X-ray diffraction were isolated from toluene solution for complexes 2, 3, and 4, and from CDCl₃ solution for complex 1, respectively. The molecular structures of 1-4 are monomeric species wherein the metal center is coordinated by one EDBP-H anion ligand and one crown ether auxiliary ligand (Fig. 1). Compared to complexes 3 and 4, the crown ether auxiliary ligand in complex 2 shows a severely distorted geometry, which is inconsistent with our previously work [12d]. We think the shorter Na1-O1 bond distance (2.266 Å versus 2.677 Å (K1-O1) and 2.871 Å (Rb1-O1)) leads to a closer distance and a stronger repulsion between crown ether and tert-butyl on EDBP-H ligand, and this repulsion force the crown ether to adjust its configuration with a distorted geometry to give a whole stable structure. Unlike Li1, Na1, and K1 atoms, Rb1 atom in complex 4 almost locates in the middle of the two oxygen atoms (O1 and O2) of EDBP-H with a shortest distance of 3.233 Å between Rb1 and O2 of hydroxyl group despite the longest ionic radius of Rb. While Li1, Na1, K1 atoms are strongly biased towards one side and cause longer M-O2 distances of 3.516, 3.549 and 3.942 Å, respectively. Therefore, the shortest distance of M(Rb)-O2 may suggest this repulsion between crown ether and tert-butyl on EDBP-H is the smallest in complex 4 because the radius of Rb is large enough to separate crown ether auxiliary ligand and EDBP-H ligand; the coordination of Rb to O2 can make complex 4 more stable. Since Li has the shortest ionic radii, we change 18-crown-6 to 12-crown-4 to avoid seriously distorted configuration. As showed in Fig. 1, the 1.833 Å bond distance of Li1-O1 is comparable to other Li-O bind in phenolate lithium complexes

which indicate there is no remarkable repulsion between crown ether and the tert-butyl groups of EDBP-H [17].

3.2. Controllability of Catalysts 1-4 in the ROP of rac-Lactide.

The ring-opening polymerizations of *rac*-lactide catalyzed by 1-4 were systematically examined under room temperature with the reaction concentration of 1-4 was 2.0 mM (Table 1). It was found that complexes 1-4 were efficient catalysts for the ROP of rac-lactide in toluene solution. 86% of rac-LA was converted into PLA in toluene within 10 hours when complex 3 was used (Table 1, entry 1). However, less than 30% of rac-LA can be converted into polymer within the same time when CH₂Cl₂ or THF was applied as a solvent (Table 1, entries 2 and 3), which may be caused by solvent polarities to form loose or tight ion paired complexes [12d] or competitive coordination of THF as we reported in our previous works [12d,12e]. However, the polymerization catalysed by complex 3 with just one equivalent of alcohol as initiator showed only modest controllability as inferred from the relatively lower molecular weight of polymer than calculated value (Table 1, entry 1). In alkali metal phenolate system, an uncontrollable ROP reaction of lactide giving cyclic polylactide can happens sometimes via a coordination-insertion mechanism with phenoxy as initiator directly, which has been reported by Cano and us [9h, 12e]. Upon addition of excess benzyl alcohol as the co-initiator (two, three, and four equivalents, respectively) to suppress this side reaction, the molecular weights become to agree with the calculated values (Table 1, entries 4-6). The polymerizations catalyzed by complexes 1, 2 and 4 are also living, which can be

proved by the controllable molecular weights and low molecular weight distributions (D < 1.17, Table 1, entries 7–13) and can be confirmed further by the fact that the molecular weights of polymers with complex **4** as a catalyst increase linearly with the ratio of [*rac*-LA]₀:[BnOH]₀ (Table 1, entries 9-13, Fig. 2). Particularly, it is worth to note that this is the first example of rubidium phenolate complex used for catalyzing the ROP reaction of lactide. And the large radius of rubidium ion provides more diversity to design alkali metal complexes for the ROP of cyclic esters, as well as potential different catalytic characteristic.

Tuble 10 fue Euclide I off mentauton Cutury 200 of 1										
Ent	Cat.	$[LA]_0/[Cat.]_0$	t/h	$\operatorname{Conv.}^{b}(\%)$	$M_{\rm n}({\rm calcd})^c$	$M_{\rm n}({\rm obsd})^d($	D^d	$P_{\rm m}^{\ e}$		
ry		/[BnOH] ₀			g/mol)	g/mol)				
1	3	100:1:1	10	86	12500	8500	1.06	0.64		
2^{f}	3	100:1:1	10	23	3700	3400	1.05	0.60		
3 ^{<i>g</i>}	3	100:1:1	10	28	4500	4100	1.10	0.61		
4	3	100:1:2	8	85	6200	6100	1.05	0.70		
5	3	100:1:3	5.5	93	4600	4700	1.05	0.71		
6	3	100:1:4	4	90	3300	3200	1.06	0.71		
7	1	100:1:4	1	90	3300	3100	1.12	0.55		
8	2	100:1:4	1.5	91	3400	3800	1.17	0.60		
9	4	100:1:4	5.5	82	3100	3300	1.04	0.71		
10	4	200:1:4	6.5	90	6600	6500	1.03	0.71		
11	4	300:1:4	9	92	10000	9700	1.03	0.72		
12	4	400:1:4	10	97	14100	13900	1.03	0.72		
13	4	500:1:4	11.5	98	17700	17000	1.03	0.71		
14	4	20:1:1	6	76	2300	2300	1.05	0.67		

Table 1. rac-Lactide Polymerization Catalyzed by 1 - 4^a.

^{*a*}Reactions were performed in 5 mL of toluene at room temperature, $[Cat.]_0 = 2.0$ mM. ^{*b*}Determined by ¹H NMR spectroscopy. ^{*c*}Calculated from the molecular weight of *rac*-LA × $[LA]_0/[BnOH]_0$ × conversion yield + M_{BnOH} . ^{*d*}Experimental molecular weight (M_n) and molecular weight distribution (D) were measured by gel permeation chromatography (GPC) at 40 °C using THF as a solvent, an eluent flow rate of 1 mL/min, and calibrated with standard polystyrene samples and corrected using the Mark–Houwink factor of 0.58.[15]. ^{*e*}Determined by analysis of all of the tetrad signals in the methine region of the homonuclear-decoupled ¹H NMR spectrum [8e, 18]. ^{*f*}In 5 mL CH₂Cl₂. ^{*g*}In 5 mL THF.



Fig. 2. Polymerization of *rac*-LA catalyzed by 4 in toluene at room temperature. The relationships between $M_n(\blacksquare)$, B (•) of the polymer and the initial mole ratios $[LA]_0/[BnOH]_0$ (Table 1, entries 9-13) is shown.

3.3 Activity of Catalysts 1-4 in the ROP of rac-Lactide.

Based on the time consumed to convert *rac*-LA into PLA with similar conversions (Table 1, entries 6-9), we got the order of activities is 1 > 2 > 3 > 4, which is coincide with the Lewis acidities of alkali metals. Generally, the metal centers with higher Lewis acidity are postulated to result in stronger binding to activation of monomer and give higher polymerization rates in a ligand-assisted monomer-activated mechanism for alkali metal phenolate complex system in the presence of alcohol. However, increased Lewis acidity of the metal center may also induce stronger binding of the phenoxy to the metal, retarding the ability of phenoxy group to activate alcohol [9d]. But in this system, the shortest distance of O1---O2 of EDBP-H in rubidium complex 4 illustrates the intramolecular hydrogen bond of O1---H-O2 is stronger than that in lithium, sodium and potassium complexes 1-3 (O2---O1, 2.594 Å (Li) > O2---O1, 2.528 Å (Na) >

O2---O1, 2.513 Å (K) > O2---O1, 2.433 Å (Rb)). The stronger intramolecular hydrogen bond can lead the negative charge on O1 decrease. Thus, the basicity of oxygen atom O1 in rubidium complex 4 is slightly weaker than that in complexes 1-3. DFT at M062X level with 6311+g(d) basis set for C, H, O, Li, Na, K, and ADZP for Rb [19] were performed and natural bond orbital (NBO) analysis showed the negative charges of O1 atoms in these four complexes are -0.95, -0.922, -0.914, and -0.865 respectively, which confirms that the basicity order of EDBP-H anions is 1 > 2 > 3 > 4. And NBO analysis results also confirm the hydrogen bond becomes stronger when metal ion changes from Li⁺ to Rb⁺ because the hydrogen bond order between O1---H-O2 is 0.0989, 0.1421, 0.1548, and 0.2251 in complexes 1-4 respectively; as a result, the strong hydrogen bond can reduce the negative charge on oxygen atom of O1. Therefore, the Lewis acidity of the cation in complex 1 is the strongest, and the Lewis basicity of anion in complex 1 also is strongest. Both the activations of monomer and alcohol in complex 1 are easier than that in complexes 2-4, and the activity order of these four complexes seems to be reasonable (Figure 3). It is worth mentioning that, besides the Lewis acidities, the steric hindrance of the active center sometimes may be another factor for the order of rates. Usually the less crowdedness around the metal center can facilitate the ROP reaction because the monomer of lactide can reach the metal center easier to be activated. As we initially designed, rubidium complex 4 should be less crowded because of its large ion radius compared with sodium and potassium complexes with the same EDBP-H and 18-crown-6 ligands. But herein, this situation becomes more complicated

because the EDBP-H should adjust its configuration to adapt different alkali metal ions. The surrounding of rubidium ion seem to be more crowded than that in complexes 2 and 3 when we compared the O1---O2 distances in these four complexes (O2---O1, 2.594 Å (Li) > O2--O1, 2.528 Å (Na) > O2--O1, 2.513 Å (K) > O2--O1, 2.433 Å (Rb)), butconsidering the large radius of the rubidium ion and flexible shift of crown ether on rubidium ion, we believe the surrounding of rubidium ion should not be more crowded remarkably than that of sodium and potassium complexes 2 and 3. It is interesting that this activity order is contrast to similar sodium and potassium monophenolates previously reported by us which are more active than complex 1-4. The intramolecular hydrogen bond should be a reason for this remarkably different activity order. Possibly, the intramolecular hydrogen bond in this system make the Lewis basicity of O1 weak and lead the activation of alcohol at a low level; consequently, the Lewis acidities of metal ions with different abilities to activation of monomer become a unique important factor for the ROP reaction rate.



Fig. 3. The activations of monomer and alcohol mechanism for complexes 1-4.

3.4. Stereoselectivity of Catalysts 1-4 in the ROP of rac-Lactide.

The stereo microstructures of resulting poly(rac-lactide)s were evaluated by homonuclear-decoupled ¹H NMR spectra [18c, 20]. Compared to previous works of us, Wang, and Ma [12], all of the complexes 1-4 based on EDBP-H ligand also show isoselectivities which proves again the crown ether is important for this isoselective system because no isoselective catalysts of EDBP-H-alkali metal complexes without crown ether auxiliary ligand was reported for the ROP of rac-lactide [21]. Complexes 3 and 4 show a similar $P_{\rm m}$ value of 0.71 when the ratio of $[rac-LA]_0:[1]_0:[BnOH]_0$ is 100:1:4, (Fig. 4; Table 1, entries 6, 9), which are better than that of complexes 1 ($P_m =$ 0.55) and 2 ($P_{\rm m} = 0.60$) under the same reaction conditions (Table 1, entries 7 and 8). It is worth noting that when complex 3 was used as a catalyst and just one equivalent of benzyl alcohol was used as initiator, the $P_{\rm m}$ value decreased from 0.71 to 0.64. But when the amounts of benzyl alcohol are more than two equivalents, the $P_{\rm m}$ values almost do not change (Table 1, entries 4-6). The low isoselectivity of complex 3 at low equivalents of BnOH may results from the side cyclization reaction initiated by phenoxy directly via a coordination-insertion mechanism as mentioned in the above discussion. The low isoselectivity also may result from transesterification, because transesterification can increase the stereo errors. The transesterification in the presence of just one equivalent of BnOH is more serious than that in a large amount of alcohol can be proved by the noticeable stronger peak at 5.215 ppm in homonuclear decoupled ¹H NMR spectrum (Fig. S1), which was resulting from the overlap of *mrm* tetrad with

rrr, *rrm* and *mrr* tetrads, the later tetrads were enhanced by transesterification side reaction. The isoselectivity of lithium complex **1** is low can be attribute to the shortest radius of lithium and the shortest Li-O1 bond which will give a small confined space between EDBP-H ligand and crown ether. We believe that only a suitable confined space can give a high isoselectivity.



Fig. 4. $P_{\rm m}$ values determined for all tetrads based on Bernoulli statistics. Their average values were used (Table 1, entry 6) [8e, 18].

The ESI mass spectrum of low molecular weight polymer obtained with complex **4** as catalyst and 4 equivalent of benzyl alcohol as initiator (Table 1, entry 9) shows a series of main peaks at 144n + 108 + 23 + 23 with charge of +2 and a series of main peaks at 144n + 108 + 23 + 23 + 19 with charge of +3 (Fig. 5), which can be assigned to $n(C_6H_8O_4) + BnOH + 2Na^+$ and $n(C_6H_8O_4) + BnOH + 2Na^+ + H_3O^+$ separately, demonstrating the existence of benzyl alcohol on the polymer chain. Some

intermolecular transesterification may occur during reaction, as a cluster of weak peaks with a molecular mass interval of ~72 Da were observed in both series of peaks. When complex **4** and 1 equivalent of benzyl alcohol was used (Table 1, entry 1), the ESI mass spectrum of resulting polymer only shows a series of main peaks at 72n + 108 + 23 + 18with charge of +2 and a series of peaks at 72n + 108 + 18 with charge of +1 (Fig. S3), which can be assigned to $n(C_3H_4O_2) + BnOH + Na^+ + NH_4^+$ and $n(C_3H_4O_2) + BnOH +$ NH_4^+ , respectively. Those main peaks with a molecular mass interval of ~72 Da demonstrate the existence of serious transesterification reaction during this ROP reaction, which can explain the reason for molecular weights of polymer are small and selectivity was low when 1 equivalent of benzyl alcohol was used as initiator.



Fig. 5. ESI-MS spectrum of poly (*rac*-LA) prepared by catalyst **4** when [*rac*-LA]₀:[**4**]₀:[BnOH]₀ is 100:1:4 (Table 1, entry 9, Z stand for the charge of polymer chain).

4. Conclusions

In summary, a series of lithium, sodium, potassium, and rubidium complexes for the ROP of rac-lactide are reported in this study. In the presence of multiple equivalents of benzyl alcohol, all complexes can exhibit good behaviors for the ROP of rac-lactide and give desired molecular weights and narrow molecular weight distributions. Both the order of rates and the degree of stereoselectvities show a correlation with the metallic covalent radius and corresponding structures. A smaller metal ion causes a higher polymerization rate resulting in a relative order of rates: Li > Na > K > Rb, which agrees well with the activation of monomer and the activation of alcohol by EDBP-H anion. The lithium and sodium complexes with smaller metal center show low steroselectivities comparing to potassium and rubidium complexes; this may result from the steric hindrance surrounding of the active center, which is indirectly influenced by the metallic atomic radius. Rubidium complex shows a medium activity and a nice polymerization control for the ROP of *rac*-lactide, offering more diversity for the design of excellent metal catalysts for the stereoselective ROP of cyclic esters.

Acknowledgments

Financial support from the National Natural Science Foundation of China (No. 21671087, 21771094 and 21401161), the Science Foundation of Gansu Province of China (No. 1308RJ2A121 and 1506RJZA213), the Fundamental Research Funds for the Central Universities (lzujbky-2017-k07), the project for the National Basic Science Personnel Training Fund (J1103307), and the ScGrid of the Supercomputing Center of the Chinese Academy of Sciences are gratefully acknowledged.

References

[1] (a) E. Chiellini, R. Solaro, Adv. Mater. 8 (1996) 305-313; (b) K.E. Uhrich, S.M. Cannizzaro,
R.S. Langer, K.M. Shakesheff, Chem. Rev. 99 (1999) 3181-3198; (c) A.-C. Albertsson, I.K.
Varma, Biomacromolecules 4 (2003) 1466-1486; (d) E.S. Place, J.H. George, C.K. Williams,
M.M. Stevens, Chem. Soc. Rev. 38 (2009) 1139-1151.

[2] (a) O. Dechy-Cabaret, B. Martin-Vaca, D. Bourissou, Chem. Rev. 104 (2004) 6147-6176; (b)
R. Platel, L. Hodgson, C. Williams, Polym. Rev. 48 (2008) 11-63; (c) M.J. Stanford, A.P. Dove,
Chem. Soc. Rev. 39 (2010) 486-494; (d) C.M. Thomas, Chem. Soc. Rev. 39 (2010) 165-173; (e)
P.J. Dijkstra, H. Du, J. Feijen, Polym. Chem. 2 (2011) 520-527.

[3] (a) B.M. Chamberlain, M. Cheng, D.R. Moore, T.M. Ovitt, E.B. Lobkovsky, G.W. Coates, J. Am. Chem. Soc. 123 (2001) 3229-3238; (b) L.E. Breyfogle, C.K. Williams, J.V.G. Young, M.A. Hillmyer, W.B. Tolman, Dalton Trans. (2006) 928-936; (c) H.-Y. Tang, H.-Y. Chen, J.-H. Huang, C.-C. Lin, Macromolecules 40 (2007) 8855-8860; (d) M.-Y. Shen, Y.-L. Peng, W.-C. Hung, C.-C. Lin, Dalton Trans. (2009) 9906-9913; (e) M.-T. Chen, P.-J. Chang, C.-A. Huang, K.-F. Peng, C.-T. Chen, Dalton Trans. (2009) 9068-9074; (f) W.-C. Hung, C.-C. Lin, Inorg. Chem. 48 (2009) 728-734; (g) L. Wang, H. Ma, Macromolecules 43 (2010) 6535-6537; (h) Y. Wang, W. Zhao, X. Liu, D. Cui, E.Y.X. Chen, Macromolecules 45 (2012) 6957-6965; (i) Y. Huang, W. Wang, C.-C. Lin, M.P. Blake, L. Clark, A.D. Schwarz, P. Mountford, Dalton Trans. 42 (2013) 9313-9324; (j) H. Xie, Z. Mou, B. Liu, P. Li, W. Rong, S. Li, D. Cui, Organometallics 33 (2014) 722-730; (k) H. Wang, Y. Yang, H. Ma, Macromolecules 47 (2014) 7750-7764; (l) Y. Gao, Z. Dai, J. Zhang, X. Ma, N. Tang, J. Wu, Inorg. Chem. 53 (2014) 716-726; (m) Y. Sun, Y. Cui, J. Xiong, Z. Dai, N. Tang, J. Wu, Dalton Trans. (2015); (n) B. Gao, D. Zhao, X. Li, Y. Cui, R. Duan, X. Pang, RSC Adv. 5 (2015) 440-447.

[4] (a) M.H. Chisholm, J. Gallucci, K. Phomphrai, Chem. Commun. (2003) 48-49; (b) D.J. Darensbourg, W. Choi, O. Karroonnirun, N. Bhuvanesh, Macromolecules 41 (2008) 3493-3502;
(c) M.H. Chisholm, J.C. Gallucci, G. Yaman, T. Young, Chem. Commun. (2009) 1828-1830; (d) N. Ajellal, J.F. Carpentier, C. Guillaume, S.M. Guillaume, M. Helou, V. Poirier, Y. Sarazin, A. Trifonov, Dalton Trans. 39 (2010) 8363-8376; (e) M. Bouyhayi, Y. Sarazin, O.L. Casagrande, J.F. Carpentier, Appl. Organomet. Chem. 26 (2012) 681-688; (f) J.P. Davin, J.-C. Buffet, T.P. Spaniol, J. Okuda, Dalton Trans. 41 (2012) 12612-12618; (g) J.B.L. Gallaway, J.R.K. McRae, A. Decken, M.P. Shaver, Can. J. Chem. Rev. Can. Chim. 90 (2012) 419-426; (h) J. Wojtaszak, K. Mierzwicki, S. Szafert, N. Gulia, J. Ejfler, Dalton Trans 43 (2014) 2424-2436.

[5] (a) M. Cheng, A.B. Attygalle, E.B. Lobkovsky, G.W. Coates, J. Am. Chem. Soc. 121 (1999) 11583-11584; (b) C.K. Williams, L.E. Breyfogle, S.K. Choi, W. Nam, V.G. Young, M.A. Hillmyer, W.B. Tolman, J. Am. Chem. Soc. 125 (2003) 11350-11359; (c) J. Wu, Y.-Z. Chen, W.-C. Hung, C.-C. Lin, Organometallics 27 (2008) 4970-4978; (d) D.J. Darensbourg, O. Karroonnirun, Inorg. Chem. 49 (2010) 2360-2371; (e) C.A. Wheaton, P.G. Hayes, Chem. Commun. 46 (2010) 8404-8406; (f) Y. Sarazin, B. Liu, T. Roisnel, L. Maron, J.-F. Carpentier, J. Am. Chem. Soc. 133 (2011) 9069-9087; (g) C.C. Roberts, B.R. Barnett, D.B. Green, J.M. Fritsch, Organometallics 31 (2012) 4133-4141; (h) S. Song, X. Zhang, H. Ma, Y. Yang, Dalton

Trans. 41 (2012) 3266-3277; (i) H. Sun, J.S. Ritch, P.G. Hayes, Dalton Trans. 41 (2012) 3701-3713; (j) C.-Y. Sung, C.-Y. Li, J.-K. Su, T.-Y. Chen, C.-H. Lin, B.-T. Ko, Dalton Trans. 41 (2012) 953-961; (k) Z. Dai, J. Zhang, Y. Gao, N. Tang, Y. Huang, J. Wu, Catal. Sci. Technol. 3 (2013) 3268-3277; (l) Z. Mou, B. Liu, M. Wang, H. Xie, P. Li, L. Li, S. Li, D. Cui, Chem. Commun. 50 (2014) 11411-11414.

[6] (a) T.M. Ovitt, G.W. Coates, J. Am. Chem. Soc. 124 (2002) 1316-1326; (b) Z. Zhong, P.J. Dijkstra, J. Feijen, J. Am. Chem. Soc. 125 (2003) 11291-11298; (c) P. Hormnirun, E.L. Marshall, V.C. Gibson, A.J.P. White, D.J. Williams, J. Am. Chem. Soc. 126 (2004) 2688-2689; (d) H. Du, X. Pang, H. Yu, X. Zhuang, X. Chen, D. Cui, X. Wang, X. Jing, Macromolecules 40 (2007) 1904-1913; (e) A. Alaaeddine, C.M. Thomas, T. Roisnel, J.-F.o. Carpentier, Organometallics 28 (2009) 1469-1475; (f) M. Bouyahyi, T. Roisnel, J.-F.o. Carpentier, Organometallics 29 (2009) 491-500; (g) D.J. Darensbourg, O. Karroonnirun, S.J. Wilson, Inorg. Chem. 50 (2011) 6775-6787; (h) A. Otero, A.n. Lara-Sánchez, J. Fernández-Baeza, C. Alonso-Moreno, J.A. Castro-Osma, I. Márquez-Segovia, L.F. Sánchez-Barba, A.M. Rodríguez, J.C. Garcia-Martinez, Organometallics 30 (2011) 1507-1522; (i) C. Bakewell, R.H. Platel, S.K. Cary, S.M. Hubbard, J.M. Roaf, A.C. Levine, A.J.P. White, N.J. Long, M. Haaf, C.K. Williams, Organometallics 31 (2012) 4729-4736; (j) H.-L. Chen, S. Dutta, P.-Y. Huang, C.-C. Lin, Organometallics 31 (2012) 2016-2025; (k) M. Lamberti, I. D'Auria, M. Mazzeo, S. Milione, V. Bertolasi, D. Pappalardo, Organometallics 31 (2012) 5551-5560; (1) Y. Wang, H. Ma, Chem. Commun. 48 (2012) 6729-6731; (m) J. Haetge, I. Djerdj, T. Brezesinski, Chem. Commun. 48 (2012) 6726-6728; (n) S. Pracha, S. Praban, A. Niewpung, G. Kotpisan, P. Kongsaeree, S. Saithong, T. Khamnaen, P. Phiriyawirut, S. Charoenchaidet, K. Phomphrai, Dalton Trans. 42 (2013) 15191-15198; (o) C.-Y. Li, D.-C. Liu, B.-T. Ko, Dalton Trans. 42 (2013) 11488-11496; (p) A. Meduri, T. Fuoco, M. Lamberti, C. Pellecchia, D. Pappalardo, Macromolecules 47 (2014) 534-543; (q) A. Pilone, K. Press, I. Goldberg, M. Kol, M. Mazzeo, M. Lamberti, J. Am. Chem. Soc. 136 (2014) 2940-2943; (r) B. Gao, D. Li, Y. Li, Q. Duan, R. Duan, X. Pang, New J. Chem. 39 (2015) 4670-4675; (s) S. Liu, J. Zhang, W. Zuo, W. Zhang, W.-H. Sun, H. Ye, Z. Li, Polymers 9 (2017) 83.

[7] (a) Y. Kim, J.G. Verkade, Organometallics 21 (2002) 2395-2399; (b) Y. Kim, G.K. Jnaneshwara, J.G. Verkade, Inorg. Chem. 42 (2003) 1437-1447; (c) A.J. Chmura, M.G. Davidson, C.J. Frankis, M.D. Jones, M.D. Lunn, Chem. Commun. (2008) 1293-1295; (d) P. McKeown, J. Brown-Humes, M.G. Davidson, M.F. Mahon, T.J. Woodman, M.D. Jones, Dalton Trans. 46 (2017) 5048-5057; (e) B. Gao, X. Li, R. Duan, X. Pang, New J. Chem. 39 (2015) 2404-2408.

[8] (a) B.M. Chamberlain, B.A. Jazdzewski, M. Pink, M.A. Hillmyer, W.B. Tolman, Macromolecules 33 (2000) 3970-3977; (b) Z. Zhang, X. Xu, W. Li, Y. Yao, Y. Zhang, Q. Shen, Y. Luo, Inorg. Chem. 48 (2009) 5715-5724; (c) H. Ma, T.P. Spaniol, J. Okuda, Inorg. Chem. 47 (2008) 3328-3339; (d) W. Li, Z. Zhang, Y. Yao, Y. Zhang, Q. Shen, Organometallics 31 (2012) 3499-3511; (e) C. Bakewell, T.-P.-A. Cao, N. Long, X.F. Le Goff, A. Auffrant, C.K. Williams, J. Am. Chem. Soc. 134 (2012) 20577-20580; (f) T.-Q. Xu, G.-W. Yang, C. Liu, X.-B. Lu, Macromolecules 50 (2017) 515-522.

[9] (a) P. Kurcok, J. Penczek, J. Franek, Z. Jedlinski, Macromolecules 25 (1992) 2285-2289; (b)
J. Wu, T. Yu, C. Chen, C. Lin, Coord. Chem. Rev. 250 (2006) 602-626; (c) Y.-L. Peng, Y. Huang,

H.-J. Chuang, C.-Y. Kuo, C.-C. Lin, Polymer 51 (2010) 4329-4335; (d) B. Calvo, M.G. Davidson, D. García-Vivó, Inorg. Chem. 50 (2011) 3589-3595; (e) W.-Y. Lu, M.-W. Hsiao, S.C.N. Hsu, W.-T. Peng, Y.-J. Chang, Y.-C. Tsou, T.-Y. Wu, Y.-C. Lai, Y. Chen, H.-Y. Chen, Dalton Trans. 41 (2012) 3659-3667; (f) H.-Y. Chen, L. Mialon, K.A. Abboud, S.A. Miller, Organometallics 31 (2012) 5252-5261; (g) S.-C. Rosca, D.-A. Rosca, V. Dorcet, C.M. Kozak, F.M. Kerton, J.-F. Carpentier, Y. Sarazin, Dalton Trans. 42 (2013) 9361-9375; (h) F.M. García-Valle, R. Estivill, C. Gallegos, T. Cuenca, M.E.G. Mosquera, V. Tabernero, J. Cano, Organometallics 34 (2015) 477-487; (i) Q. Zhang, W. Zhang, S. Wang, G.A. Solan, T. Liang, N.M. Rajendran, W.-H. Sun, Inorg. Chem. Front. 3 (2016) 1178-1189; (j) N.M. Rajendran, Y. Xi, W. Zhang, Y. Sun, W.-H. Sun, Eur. J. Inorg. Chem. 2017 (2017) 2653-2660; (k) B.-B. Wu, L.-L. Tian, Z.-X. Wang, RSC Advances 7 (2017) 24055-24063; (l) B.-B. Wu, Z.-X. Wang, RSC Adv. 7 (2017) 11657-11664; (m) C. Yao, Y. Yang, S. Xu, H. Ma, Dalton Trans. 46 (2017) 6087-6097. [10] (a) P.L. Arnold, J.-C. Buffet, R.P. Blaudeck, S. Sujecki, A.J. Blake, C. Wilson, Angew. Chem. Int. Ed. 47 (2008) 6033-6036; (b) P.L. Arnold, J.-C. Buffet, R. Blaudeck, S. Sujecki, C. Wilson, Chem.- Eur. J. 15 (2009) 8241-8250.

[11] J. Zhang, C. Jian, Y. Gao, L. Wang, N. Tang, J. Wu, Inorg. Chem. 51 (2012) 13380-13389.
[12] (a) J. Zhang, J. Xiong, Y. Sun, N. Tang, J. Wu, Macromolecules 47 (2014) 7789-7796; (b) Z. Dai, Y. Sun, J. Xiong, X. Pan, N. Tang, J. Wu, Catal. Sci. Technol. 6 (2016) 515-520; (c) J. Xiong, J. Zhang, Y. Sun, Z. Dai, X. Pan, J. Wu, Inorg. Chem. 54 (2015) 1737-1743; (d) Z. Dai, Y. Sun, J. Xiong, X. Pan, J. Wu, ACS Macro Lett. 4 (2015) 556-560; (e) Y. Sun, J. Xiong, Z. Dai, X. Pan, N. Tang, J. Wu, Inorg. Chem. 55 (2016) 136-143; (f) Y. Li, H. Zhao, X. Mao, X. Pan, J. Wu, Dalton Trans. 45 (2016) 9636-9645; (g) Y. Cui, C. Chen, Y. Sun, J. Wu, X. Pan, Inorg. Chem. Front. 4 (2017) 261-269; (h) C. Chen, Y. Cui, X. Mao, X. Pan, J. Wu, Macromolecules 50 (2017) 83-96; (g) B. B. Wu, L. L. Tian, Z. X. Wang, *Rsc Advances* 7 (2017), 24055-24063; (h) B. B. Wu, Z. X. Wang, *RSC Adv.* 7 (2017), 11657-11664; (i) C. Yao, Y. Yang, S. Xu, H. Ma, *Dalton Trans.* 46 (2017), 6087-6097.

[13] H. Tsuji, Macromol. Biosci. 5 (2005) 569-597.

[14] G.L. Miessler, D.A. Tarr, Upper Saddle River, NJ (2004) 345.

[15] M. Save, M. Schappacher, A. Soum, Macromol. Chem. Phys. 203 (2002) 889-899.

[16] G.M. Sheldrick, SHELXL-97 Program; University of Göttingen:Göttingen, Germany, 1996.

[17] M.-L. Hsueh, B.-H. Huang, J. Wu, C.-C. Lin, Macromolecules 38 (2005) 9482-9487.

[18] The PLA stereochemistry was assessed by comparison of the tetrad resonances observed in the homonuclear decoupled ¹HNMR spectra with the values predicted by Bernoullian statistics. The resolution of the integrals for the peaks corresponding to the *rmr*, *rmm*, *mmr*, *mmm*, and *mrm* tetrads was improved using peak deconvolution methods. The Pm values were determined for all five tetrads, and their average was used as the P_m for the complex. (a) J. Coudane, C. Ustariz-Peyret, G. Schwach, M. Vert, J. Polym. Sci. Pol. Chem. 35 (1997) 1651-1658; (b) M.H. Chisholm, S.S. Iyer, D.G. McCollum, M. Pagel, U. Werner-Zwanziger, Macromolecules 32 (1999) 963-973; (c) J.E. Kasperczyk, Macromolecules 28 (1995) 3937-3939; (d) K.A.M. Thakur, R.T. Kean, E.S. Hall, J.J. Kolstad, T.A. Lindgren, M.A. Doscotch, J.I. Siepmann, E.J. Munson, Macromolecules 30 (1997) 2422-2428.

[19] P.J.P. de Oliveira, C.L. Barros, F.E. Jorge, A. Canal Neto, M. Campos, J. Mol. Struct. (Theochem) 948 (2010) 43-46.

[20] (a) J.E. Kasperczyk, Macromolecules 28 (1995) 3937-3939; (b) N. Spassky, M. Wisniewski,

C. Pluta, A. Le Borgne, Macromol. Chem. Phys. 197 (1996) 2627-2637.

-3 MANUSCR [21] X. Pan, A. Liu, X. Yang, J. Wu, N. Tang, Inorg. Chem. Commun. 13 (2010) 376-379.



A series of alkali metal complexes with 2, 2'-ethylidenebis(4,6-di-tert-butylphenol) (EDBP-H₂) as a ligand have been synthesized. The relative order of activities for this series of complexes is Li > Na > K > Rb. The relative order of stereoselectivities for this series of complexes is $\text{Rb} \approx \text{K} > \text{Na} >> \text{Li}$. The first example of Rb complex in the ROP of *rac*-lactide in this paper was also described, showing a medium activity, a nice polymerization control, and a certain isoselectivity.

CCF