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Synthesis, characterization of sodium and potassium complexes and the application in ring-opening polymerization of L-lactide

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ABSTRACT

A novel sterically bulky phenol (2,4-di-tert-butyl-6-(1-(3,5-di-tert-butyl-2-(2-(2-methoxyethoxy)ethoxy) phenyl)ethyl)phenol)(HL) and corresponding dimeric sodium and potassium complexes $[ML]_2$ (1: M = Na, 2: M = K) have been prepared and structurally characterized. Experimental results showed that complexes **1** and **2** can efficiently initiate the ring-opening polymerization of lactide in a controlled fashion, yielding polymers with expected molecular weight and low polydispersity indexes.

Polylactide (PLA) is one of the most important biodegradable materials for its wide applications in biomedical and pharmaceutical fields [1], and over the past three decades much attention has been devoted to the development of new catalytic/initiating systems for the preparation of polylactide (PLA). Among several catalytic systems reported previously, the ring-opening polymerization (ROP) of lactide is the most effective method for the synthesis of PLA [2]. Many metal complexes have been used to initiate/catalyze ring-opening polymerization of lactides due to the advantages of well controlled molecular weight and low polydispersity index (PDI) [3]. As a result, a variety of metal complexes coordinated with sterically bulky ligands such as β-diketiminate, salen, diol, etc., have been developed and used as catalytic/initiating systems for the ROP of lactides [4]. Although these complexes are excellent catalysts for the ROP of lactides with high yields, their utilization to some extent is limited by difficulties in removal of the catalyst from the resultant polymers as well as the toxicity of metal cation [5]. To address this issue, many attempts have been made to discover the nontoxic metal complexes (e.g., sodium [6], potassium [7], magnesium [8], calcium [9], iron [10]) and highly active metal-free [11] catalysts for the ROP of lactides. Due to the fact that sodium and potassium cations are nontoxic, essential for life and also readily available, sodium and potassium cations are preferentially selected as one component of metal complex catalyst during our investigation on the development of novel effective catalysts for ROP of lactides. $EDBPH_2$ is an interesting ligand because it has been approved as an indirect food additive (as an antioxidant in polymer packaging) by the U.S. Food and Drug Administration [12], and some of its metal complexes are excellent catalysts with good controlled features for ROP of cyclic ester [13]. Based on these views, we have designed and synthesized a novel sterically bulky monovalent phenol ligand derived from $EDBPH_2$ and its related nontoxic sodium and potassium catalysts. The catalytic activities of sodium and potassium complexes towards ROP of lactides have been investigated, and the positive experimental results have proved that two designed catalysts, especially with sodium cation, are effective in the current ROP of lactides.

According to the previous studies, a novel sterically bulky phenol and the corresponding metal complexes were prepared in an almost quantitative yield (Scheme 1) [1] [14]. Single crystals of 1 and 2 suitable

[1] (a) Data for ligand 3: (0.481 g, 89% Yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27 (1H, d, J = 2.4Hz, ArH); 7.23 (1H, d, J = 2.4Hz, ArH); 7.13 (1H, d, J = 2.4Hz, ArH); 7.09 (1H, d, J = 2.4Hz, ArH); 4.68 (1H, q, J = 7.2Hz, CH); 4.14–4.02 (2H, m, CH_2); 4.02–3.89 (2H, m, CH_2); 3.82–3.78 (2H, m, CH_2); 3.68–3.63 (2H, m, CH_2); 3.36 (3H, s, CH_3); 1.71 (3H, d, J = 6.9Hz, CH_3); 1.38 (9H, s, $C(CH_3)_3$); 1.36 (9H, s, $C(CH_3)_3$); 1.29 (9H, s, $C(CH_3)_3$); 1.24 (9H, s, $C(CH_3)_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.13; 150.68; 146.58; 141.63; 140.95; 138.00; 135.24; 131.24; 123.34; 122.29; 121.28; 120.19; 74.95; 72.01; 71.09; 70.32; 59.03; 35.39; 35.06; 34.58; 34.35; 31.74; 31.40; 29.73; 20.83. LC–MS: m/z 558.2 $[M + NH_4]^+$. Anal. Calcd for $C_{35}H_{56}O_4$: C, 77.73; H, 10.44. Found: C, 77.69; H, 10.42. (b) Data for sodium complex 1: (0.596 g, 91% Yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46(2H, br, ArH);7.23 (2H, br, ArH); 7.18 (2H, br, ArH); 6.99 (2H, s, ArH); 4.68 (2H, br, CH); 3.96 (4H, br, CH_2); 3.86 (4H, br, CH_2); 3.68 (4H, br, CH_2); 3.55 (4H, br, CH_2); 3.37 (6H, s, CH_3);2.81 (6H, s, CH_3); 1.44 (18H, s, $C(CH_3)_3$); 1.40 (18H, s, $C(CH_3)_3$); 1.36 (18H, s, $C(CH_3)_3$); 1.26 (18H, s, $C(CH_3)_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.13; 151.68; 148.48; 143.63; 141.85; 138.70; 135.44; 132.04; 123.64; 122.89; 121.48; 120.39; 76.88; 72.13; 71.14; 59.06; 35.56; 35.87; 35.00; 34.63; 34.03; 31.90; 31.86; 21.75; 14.43 Anal. calcd for $C_{70}H_{110}Na_2O_8$: C, 74.69; H, 9.85. Found: C, 74.60; H, 9.83. (c) Data for complex 2: Yield 87%. ^{1}H NMR (300 MHz, $CDCl_3$): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51(2H, br, ArH);7.33 (2H, br, ArH); 7.24 (2H, br, ArH); 6.98(2H, s, ArH); 4.73 (2H, br, CH); 4.12 (4H, br, CH_2); 3.95 (4H, br, CH_2); 3.67 (4H, br, CH_2); 3.61 (4H, br, CH_2); 3.42 (6H, s, CH_3);2.83 (6H, s, CH_3); 1.53 (18H, s, $C(CH_3)_3$); 1.46 (18H, s, $C(CH_3)_3$); 1.40 (18H, s, $C(CH_3)_3$); 1.28 (18H, s, $C(CH_3)_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.13; 152.18; 149.08; 143.73; 141.65; 138.77; 135.64; 132.14; 123.84; 122.79; 121.86; 120.99; 76.96; 72.23; 71.44; 59.86; 36.06; 35.88; 35.67; 34.93; 34.53; 31.96; 32.06; 21.95; 14.83 Anal. calcd for $C_{70}H_{110}K_2O_8$: C, 72.62; H, 9.58. Found: C, 72.60; H, 9.51.

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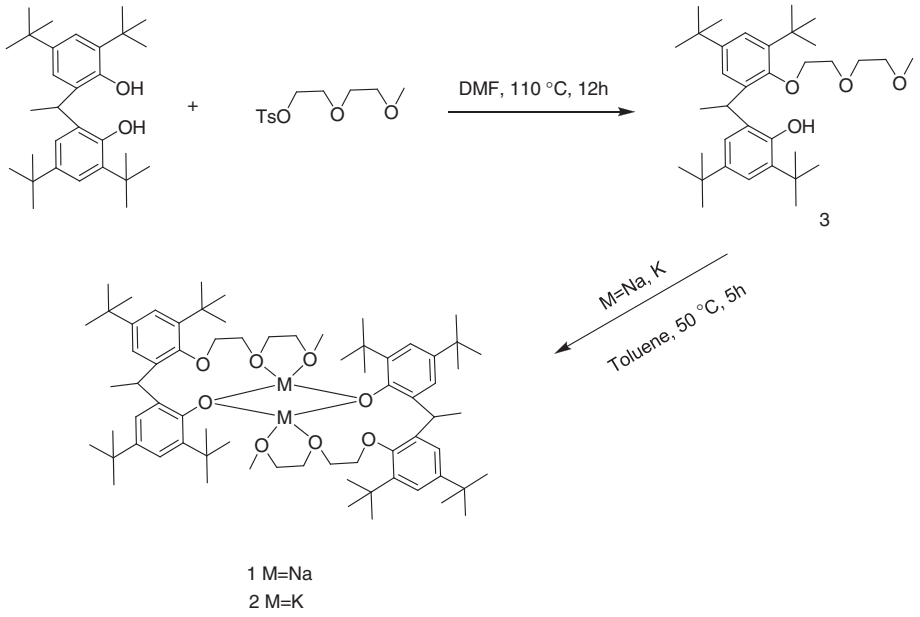

Scheme 1. Preparation of ligand and corresponding metal complexes.

for X-ray structural determination were obtained from toluene [2]. The ORTEP drawing of the molecular structures of 1 and 2 are given in Figs. 1 and 2, respectively. The molecular structures of these compounds show that the two complexes have dimeric character, bridging with the oxygen atoms of the phenol group with similar structures. The geometry around of the sodium atoms in 1 is distorted tetrahedron, sodium interacted with two bridging phenolate oxygen atoms, and two oxygen atoms of 2-(2-methoxy-ethoxy)-ethyl group. Two sodium atoms in this complex are equivalent with Na–O bond distance of Na(1)–O(3) 2.494(2) Å, Na(1)–O(4) 2.409(3) Å, Na(1)–O(1) 2.183(2) Å, Na(1)–O(1A) 2.302(2) Å. The molecular structure of 2 is all similar to that of 1 with K–O bond distance of K(1)–O(3) 2.692(3) Å, K(1)–O(4) 2.686(4) Å, K(1)–O(1) 2.481(3) Å, K(1)–O(1A) 2.625(3) Å.

Complexes 1 and 2 (0.02 mmol) as catalyst are systematically tested for the ring-opening polymerization of lactides in THF (10 mL) at 60 °C, as shown in Table 1. Experimental results indicate that both complex 1 and 2 are efficient in the ROP of L-lactides, and the polymerization is completed within 36 h at 60 °C. The reaction conversion could reach 93.4% with complex 1 as the catalyst at a monomer-to-catalyst ratio of 100:1 (Table 1, entry 1). It is interesting that EDBP-Na reported by Lin [6] catalyzes the ROP of L-lactide with methanol as initiator, while complex 1 can catalyzes the reaction directly without methanol. Actually complex 1 cannot activate methanol to initiate the ROP of lactide, because methanol cannot easily replace long ether group to coordinate to Na^+ and be activated to initiate the ROP reaction. For the different ROP mechanism, the activity of complex 1 is lower comparing to EDBP-Na. A good polymerization control is demonstrated by the linear relationship between *M*n and $[LA]_0/[complex]_0$ and the polymers with low PDI, ranging from 1.28 to 1.36 (Fig. 3). The ^1H NMR of PLLA with $[LA]_0/[Complex]_0$ ratio of 100 show a characteristic methine peak (Fig. 4) at 4.36 ppm and broad carboxyl terminal group peak at 3.74 ppm in $CDCl_3$, indicating that the two terminal groups of the polymer are the hydroxyl and carboxyl terminal group respectively. LC–MS mass spectrum was employed to investigate the components of the end group of the polymer at the same ratio. The spectrum shows that oligomers HO$(COCHMeO)_nH\cdot M^+$ (M = K, Na) were obtained in the protic reagent (Fig. 5). Furthermore, epimerization of the chiral centers in PLLA does not occur, which confirmed by the study of homonuclear decoupled ^1H NMR in the methine region [15].

Additionally, an acceptable polymerization control also is demonstrated by the study on the linear relationship between *M*n and $[LA]_0/[complex]_0$ with complex 2 as the catalyst at every monomer-to-catalyst (Fig. 6) (Table 1, entry 6–9). The PDI of the

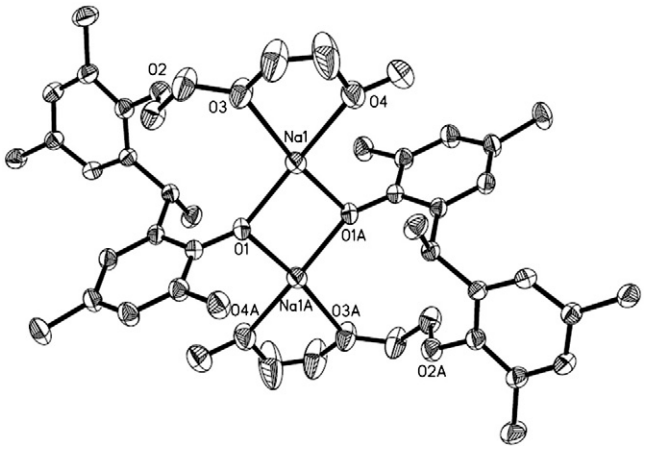

Fig. 1. X-ray structure of complex 1 as 30% ellipsoids (methyl carbons of the *tert*-butyl groups are omitted for clarity, hydrogen atoms omitted). Selected bond lengths (Å): Na(1)–O(3) 2.494(2), Na(1)–O(4) 2.409(3), Na(1)–O(1) 2.183(2), Na(1)–O(1A) 2.302(2).

[2] (a) Crystal data for sodium complex: $C_{42}H_{63}NaO_4$, M = 654.91, monoclinic, space group $P2(1)/c$, a = 16.6089(4) Å, b = 14.6139(4) Å, c = 17.1502(4) Å , α = 90.00, β = 91.7240(10), γ = 90.00, V = 4160.83(18) Å^3, T = 296(2) K, Z = 4, Dc = 1.044 g/cm^3, F_{000} = 1428, $2\theta_{max}$ = 26.50, 24367 reflections collected, 8593 unique (R_{int} = 0.0808), no. of observed reflections 3732 ($I>2\sigma(I)$); R_1 = 0.0684, wR_2 = 0.1808. (b) Crystal data for potassium complex: $C_{42}H_{63}KO_4$, M = 671.02, monoclinic, space group $P2(1)/c$, a = 16.6160(4) Å, b = 15.0181(4) Å, c = 17.1759(5) Å , α = 90.00, β = 90.3110(10), γ = 90.00, V = 4286.0(2) Å^3, T = 296(2) K, Z = 4, Dc = 1.038 g/cm^3, F_{000} = 1460, $2\theta_{max}$ = 20.40, 13877 reflections collected, 4211 unique (R_{int} = 0.0302), no. of observed reflections 3097 ($I>2\sigma(I)$); R_1 = 0.0559, wR_2 = 0.1507.

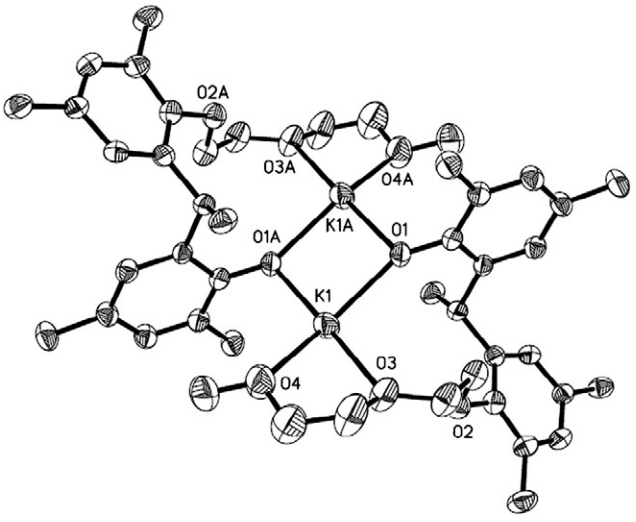

Fig. 2. X-ray structure of complex 2 as 30% ellipsoids (methyl carbons of the *tert*-butyl groups are omitted for clarity, hydrogen atoms omitted). Selected bond lengths (Å): K(1)–O(3) 2.692(3), K(1)–O(4) 2.686(4), K(1)–O(1) 2.481(3), K(1)–O(1A) 2.625(3).

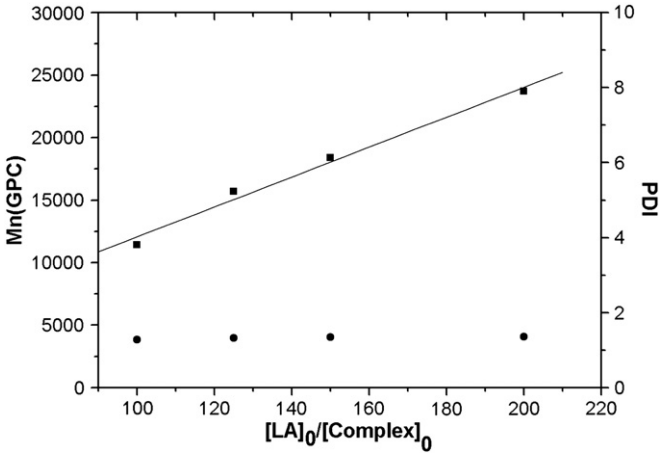

Fig. 3. Polymerization of L-LA catalyzed by 1 in THF at 60 °C. The relationship between Mn (■) ((PDI (●)) of the polymer and the initial mole ratio $[LA]_0/[complex]_0$ is shown.

polylactides obtained are narrow, ranging from 1.24 to 1.41. Experimental results show sodium complex 1 is more active than potassium complex 2, because Na^+ is the more strong Lewis acid of than K^+ and the lactide is easier to coordinate to Na^+ to be activated. Although the two catalysts have similarity dimeric structures to EDBP-/K reported by Pan et al., catalyst 1 and 2 are more active which may attribute to the more bulky long ether group surrounding the Na^+ and K^+ [6,7].

Complexes 1 and 2 were also examined in the polymerization of *rac*-lactides, as shown in Table 1 (entry 5, 10). The homonuclear decoupled ^1H NMR spectrum at the methine region of the PLA derived from 1 and 2 are isotactic predominance with $Pm = 0.64$ for 1 and $Pm = 0.59$ for 2, respectively [16]. The low selectivity may be owing to the insufficient bulk of the ligand, and the modification of this type of ligand is actively ongoing in our laboratory.

In conclusion, two nontoxic sodium and potassium bulky phenolate complexes have been synthesized and characterized, and the two complexes can efficiently catalyze ring-opening polymerization of lactides in good controlled manner with slight isotactic selectivity. Compared with catalyst 2, it was interestingly found that sodium complex 1 can catalyze ROP of L-lactides in THF at 60 °C giving a narrower molecular weight distribution and higher conversion. At the present stage, the ROP of *rac*-lactide by designed complexes proceeded with the low selectivity, and a full understanding of the factors influencing the molecular design of single-site catalyst precursors for stereoselective ROP of lactides remains to be further explored in detail.

Acknowledgments

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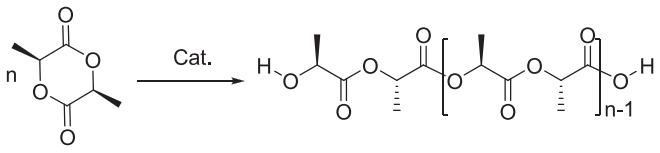
Table 1
Ring-opening polymerization of lactide using complex **1** and **2**[a].



Entry	Complex	$[LA]_0/[Complex]_0$	Time (h)	*M*n (obsd)[b]	*M*n (calcd)[c]	PDI	Conversion (%)
1	**1**	100:**1**	36	19,600 (11,400)	13,600	1.28	93.4
2	**1**	125:**1**	36	27,000 (15,700)	16,100	1.32	88.7
3	**1**	150:**1**	36	31,700 (18,400)	19,600	1.35	90.1
4	**1**	200:**1**	36	40,800 (23,700)	26,700	1.36	92.2
5	**1**	100:**1**[d]	36	26,800 (15,500)	13,200	1.35	90.8
6	**2**	100:**1**	36	18,300 (10,600)	12,100	1.24	83.3
7	**2**	125:**1**	36	25,100 (14,600)	15,600	1.38	86.2
8	**2**	150:**1**	36	23,300 (13,500)	16,100	1.40	74.1
9	**2**	200:**1**	36	30,400 (17,600)	20,300	1.41	70.2
10	**2**	100:**1**[d]	36	26,500 (15,400)	13,100	1.32	90.3

a. Conditions: 0.02 mmol of complex, 10 mL of THF at 60 °C.
b. Obtained from GPC analysis, and calibrated by polystyrene standard. The true value of *M*n could be calculated according to formula $Mn_{obsd} = 0.58Mn_{GPC}$.
c. Calculated from the molecular weight of L-lactide times $[LA]_0/[Complex]_0$ times conversion yield plus the molecular weight of H_2O: $Mn_{calcd} = (M/I) \times conv \times 144 + 18$.
d. At 60 °C, 10 mL of THF and rac-lactide were used.

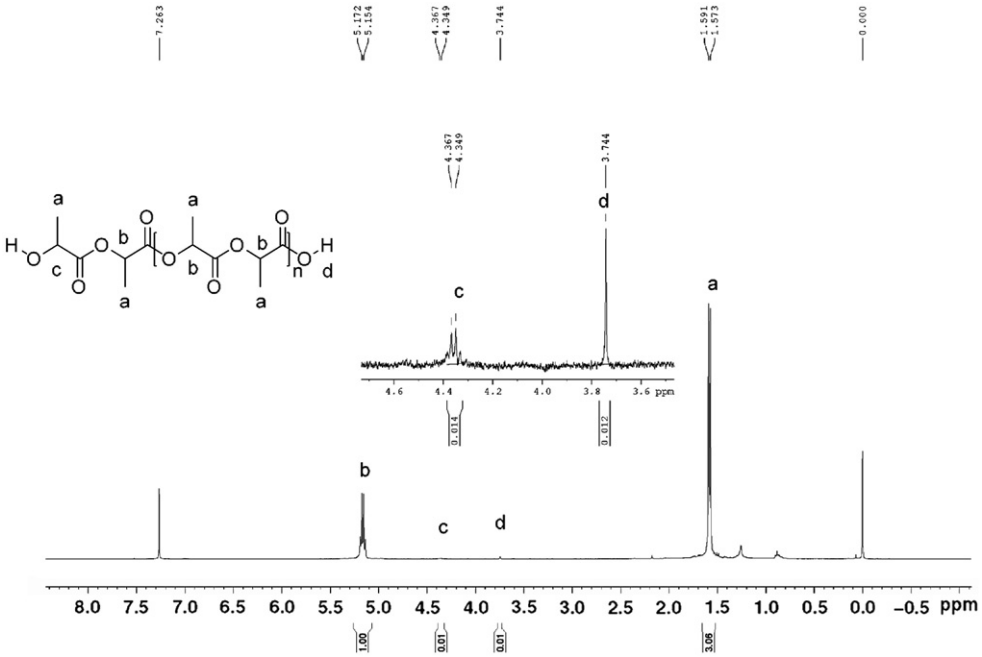


Fig. 4. ^{1}H NMR PLA-100 (from Table 1, entry 1) in $CDCl_3$.

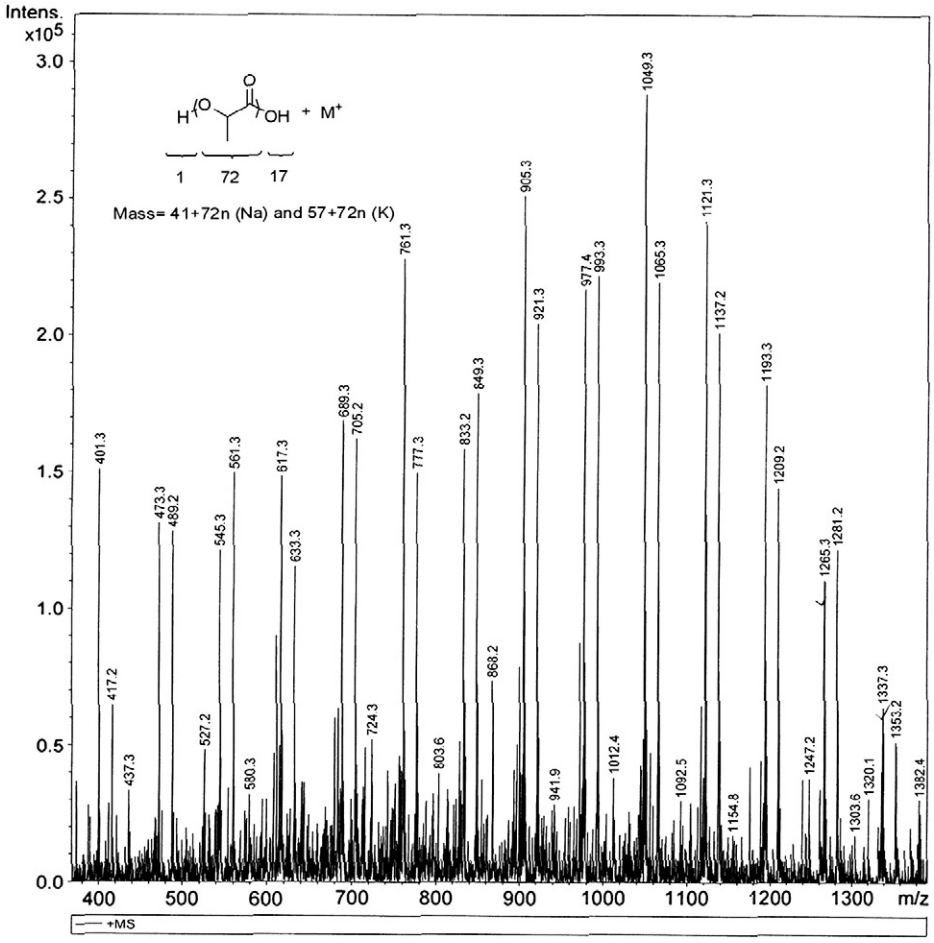


Fig. 5. LC–MS mass spectrum of PLA-100 (from Table 1, entry 1).

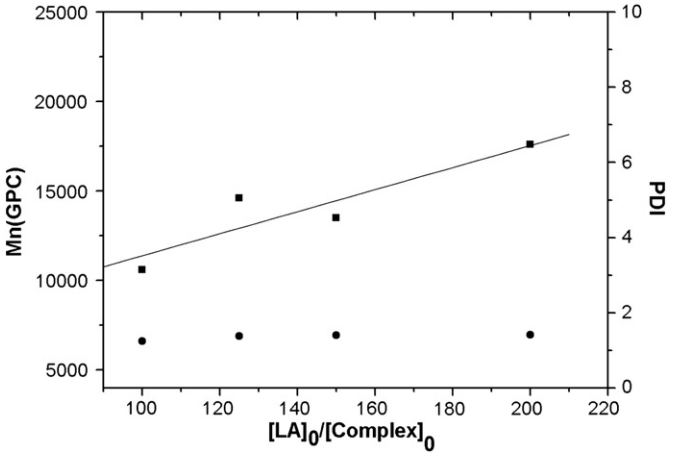


Fig. 6. Polymerization of L-LA catalyzed by 2 in THF at 60 °C. The relationship between Mn(■) ((PDI (●)) of the polymer and the initial mole ratio $[LA]_0/[complex]_0$ is shown.

Appendix A. Supplementary material

CCDC 775419 and 775420 contain the supplementary crystallographic data for thispaper. These data can be obtained free of charge from the Cambridge Crystallographic DataCentre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary material to this article can be found online at doi:10.1016/j.inoche.2010.09.021.

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