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PAPER

Hemi-salen Aluminum Catalysts bearing N, N, O-Tridentate Type Binaphthyl-Schiff-base Ligands for the Living Ring-Opening Polymerisation of Lactide

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Abstract

Four hemi-salen aluminum complexes based on tridentate N, N, O-type binaphthyl-Schiff-base derivatives (**1**: R = ^{i}Pr; R_1 = H; **2**: R = ^{i}Pr; R_1 = Cl; **3**: R = 2-adamantyl; R_1 = H; **4**: R = 2-adamantyl; R_1 = ^{t}Bu) were prepared. These complexes were characterized by ^{1}H, ^{13}C NMR spectroscopy and elemental analysis, these four complexes were employed for ring-opening polymerisation of L-lactide and *rac*-lactide. Complex **2**, which was based on pro-ligand **L2** with smaller steric hindrance and electron-withdrawing substituents, displayed the highest activity for ROP of L-lactide among these complexes, and complex **4**, which was supported by pro-ligand **L4** with the biggest steric hindrance, showed the highest stereoselectivity for the ROP of *rac*-lactide with partially isotactic polylactide with a P_m of 0.65. Kinetic studies revealed the ROP of L-lactide initiated by complex **3** had first-order dependency on [LA] as well as [Al].

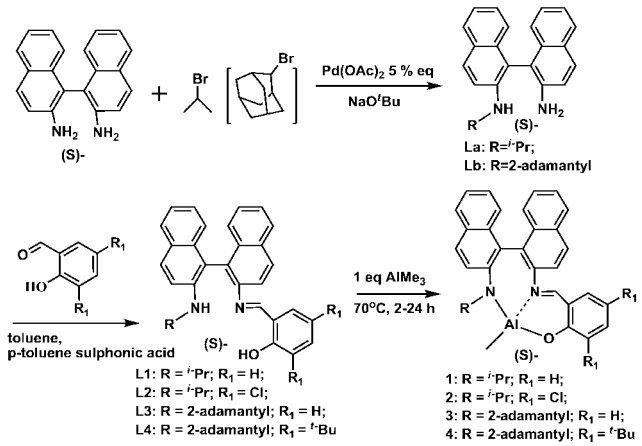
Introduction

In recent decades, biodegradable aliphatic polyesters had developed for a extensive scope of applications including surgical suture, bone fracture fixation device, controlled release drug carrier, tissue engineering stent and environmentally-friendly packaging.[1, 2] Particularly, polylactide (PLA) derived from a renewable resource such as corn and sorghum, is marketed as one of the most promising biodegradable polyesters .[2] Normally, PLA is synthesised by the ring-opening polymerisation (ROP) of lactide by initiators containing some coordination complexes of tin,[3] aluminum,[4] zinc,[5] magnesium,[6] iron,[7] titanium,[8] indium,[9] rare-earth metals;[10] organo-initiators[11] and enzymes.[12] Aluminum catalysts were effective initiators in the preparation of PLA for their high Lewis acidity and low toxicity.[4] Many efforts in the selection of proper ancillary ligands had been devoted to improve the performances of aluminum complexes in polymerisations.[13] These ligands played significant role in preventing the transesterification and formation of macrocycles. Researchers had carried out some successful studies on acquiring PLAs containing low PDI and high stereoselectivity by the salen based aluminum complexes [13, 14] (Fig. S1). Spassky[13a] reported an aluminium initiator supported by salen-type Schiff base ligand, which was derived from R-(+)-1,1'-dinaphthalene-2,2'-diamine, it could stereo-control polymerisation of lactide (LA). The PLA's T_m was higher than optically pure PLLA's. Coates[13b] uncovered that a chiral aluminum complex bearing a salen-type Schiff base could afford enriched isotactic PLA. Penczek, Florczak and Duda[13h, 13j] reported that selectivity of $Al(OiPr)_3$ catalyst could be accomplished through coordination with $SB(OH)_2$ ((S)-(+)-2,20-[1,10-binaphtyl-2,20-diylbis(nitryl-methilidyne)]diphenol),allowing synthesis of the block structure PCL-PLA-PCL. They claimed that there were controlled synthesis of diblock PLA-b-PCL and triblock PCL-b-PLA-b-PCL copolymers with the 'poly(L-lactide) block first' route.

Recently, our group[14] had explored many aluminum complexes based on salen Schiff base ligands. These complexes were proved to be efficient initiators in the ROP of lactide. Whereas, to our knowledge, little research on tridentate N, N, O-type binaphthyl-Schiff-base (hemi-salen) ligand (see Scheme 1, one side moiety is alkyl bonded to binaphthyl, the other is salicylaldehyde alkyl bonded to binaphthyl in hemi-salen ligand) with their metal complexes have been studied in the ROP of LA. In consideration of outstanding performances of the aluminum complexes based on Schiff-base,[14] we firmly believed the aluminium complexes based on tridentate N, N, O-type binaphthyl-Schiff-base ligands would be potential catalysts for the ROP of LA. In addition, we speculate that this type of aluminum complex bearing hemi-salen ligand (*e.g.* the alkyl is isopropyl) with smaller steric hindrance may achieve higher activity in comparison with corresponding salen aluminium catalysts (*e.g.* complex (R)-4 in the reference 13 (b)) for the ROP of LA. In this paper, therefore, we have prepared a series of aluminium complexes bearing hemi-salen ligands and studied the catalytic behaviour of this type of aluminum complexes as initiators for the ROP of LA in detail.

Result and discussion

As shown in Scheme 1, heating (*S*)-(–)-1,1'-dinaphthalene-2,2'-diamine with equivalent bromoalkane in toluene solution afforded the formation of compounds **La** and **Lb** in moderate yields (65.7 – 75.3%) according to the literatures.[15a, 15b] Pro-ligands $\mathbf{L_1}$ – $\mathbf{L_4}$ were prepared in good yields (68.7 – 87.4%) by combination of the correspondent compounds and modificatory salicylaldehydes together with a catalytic quantity of *p*-toluenesulfonic acid in toluene under refluxing. [15c] Aluminum complexes **1** – **4** were preparared *via* integrating identical quantity of trimethyl-aluminum and correspondent pro-ligands in shielding gas and were isolated as yellow or orange solid in high yields (74.2 – 93.0%).



Scheme 1. Synthetic route for pro-ligands and complexes.

Synthesis of pro-ligands and aluminum complexes

All aluminum complexes were characterized by ^{1}H, ^{13}C NMR spectroscopy and elemental analysis. The ^{1}H and ^{13}C NMR spectra of **1** – **4** showed similar patterns in the parts of δ –0.85 to –0.97 ppm for the methyl protons of the Al-C*H*$_3$ group in the ^{1}H NMR spectra and δ –8.45 to –9.93 ppm in the ^{13}C NMR spectra. It meant one methyl group neighboring Al atom and only one chemical setting for each ligand. Furthermore, ^{1}H NMR spectra of **1** – **4** exhibited sharp signals, implying there was no fluctuation in these Al atoms' coordination environment. The case in point was, as shown in Fig. S2, only one set of methyl group protons ("**a**" in Fig. S2) of **4** was observed, and the peak was a sharp singlet at δ –0.97 ppm, meanwhile two broad singlets ("**d**" and "**e**" at δ 3.83 and 12.78 ppm, respectively) for N*H* and O*H* disappeared comparing with **L4**. This strongly indicated the coordination of oxygen and nitrogen atoms. The ^{1}H-^{1}H and ^{13}C-^{1}H COSY spectra of complex **4** (Fig. S3 and Fig. S4) offered conclusive assignment of the proton and ^{13}C NMR signals. Two singlets (δ 1.09, 1.25 ppm) were assigned to the H-b and H-b' protons in the *tert*-butyl group of the salicylaldehyde section which were coupled with H-a protons from the methyl group on AlC*H*$_3$ (Fig. S3). The assignment of the CH carbon nuclei was based on the cross-peaks in the ^{13}C-^{1}H HMQC spectrum. The CH carbon nuclei in downfield was assigned to -N=*CH*- ("**c**" as shown in Fig. S4), the CH carbon nuclei in upfield was assigned to the methyl group from Al-*CH*$_3$ ("**a**" as shown in Fig. S4).

Lactide polymerisation

All the four aluminum complexes were studied as catalysts for the ROP of LA. The representational polymerisation data were listed in Table 1, Table 2 and Table 3. These aluminum complexes displayed low to high activities (26.4 – 97.3% L-LA conversion; 20.9 – 96.4% *rac*-LA conversion) using the co-catalysis of isopropanol at 70 °C. GPC were applied to calculate the number-averaged molecular weights of the PLA. The number-averaged molecular weights ($M_{n(actual)}$ which were calculated according to formula $M_{n(actual)} = 0.58M_{n(GPC)}$[16]) of PLA were close to theoretical ones ($M_{n(calcd)}$ which were calculated from the monomer-to-catalyst molar ratio). It is noteworthy that the activities of these complexes reduced synchronizing with the raise of substituent's bulk on the phenyl parts, while electron-withdrawing substituents increased polymerisation rate. Complex **2** showed the highest activity (97.3% monomer conversion Table 1, Entry 2) at the same polymerisation parameters amid the four complexes (Table 1, Entries 1 – 4). Similar situations also appeared in the previous reports.[17] In comparison with salen aluminium catalysts (*e.g.* complex (R)-4 in the reference 13 (b) with 90% monomer conversion at 30 h), complexes **1** and **2** with small steric hindrance showed higher catalytic activities (with 93.6 and 97.3% monomer conversion at 28 h, respectively). Moreover, the tridentate N, N, O-tridentate ligands had certain ability to influence the PDI of the polymer, and this ability varied depending on bulk of ligands. For instance, the PDI decreased from 1.23 to 1.12 in company with the raise of the bulk of the substitutes on alkyl's parts from isopropyl to 2-adamantyl (see Table 1, Entries 1, 4); and reduced slightly from 1.12 to 1.09 with the enlargement of the volume of the substitutes on phenyl rings from H to ^{t}-Bu (see Table 1, Entries 4, 6 and Fig. S5 in ESI). To investigate the influence of high monomer/catalyst molar ratio (the proportion [LA]/[cat.] > 100/1) on the ROP of L-lactide, polymerisation reactions with different monomer/catalyst molar ratios (125 : 1, 200 : 1 and 400 : 1) were proceeded (Table 1, Entries 9 − 11). As shown in Table 1, the molecular weight M_n of the PLA increased with the increase in the monomer/catalyst molar ratio, accompanied with relatively wide PDI and lower monomer conversion.

Table 1 Representational polymerisation data of L-LA with complexes **1** − **4** .[a]

Entry	Complex	$[LA]_0/[cat.]_0$	T h	Conv. % [b]	$M_{n(calcd)}$ $\times10^{-4}$[c]	$M_{n(GPC)}$ $\times10^{-4}$[d]	$M_{n(actual)}$ $\times10^{-4}$[e]	PDI[d]
1	**1**	100	28	93.6	1.35	2.37	1.37	1.23
2	**2**	100	28	97.3	1.40	2.42	1.40	1.17
3	**3**	100	28	81.1	1.17	1.98	1.15	1.11
4	**3**	100	36	96.7	1.39	2.44	1.42	1.12
5	**4**	100	28	26.4	0.38	0.64	0.37	1.10
6	**4**	100	36	36.3	0.52	0.89	0.52	1.09
7	**3**	50	14	93.1	0.67	1.14	0.66	1.11
8	**3**	75	24	95.3	1.03	1.79	1.04	1.13
9	**3**	125	36	80.2	1.44	2.45	1.42	1.15
10	**1**	200	55	87.9	2.53	4.29	2.49	1.32
11	**1**	400	69	82.0	4.72	7.98	4.63	1.36

[a] The polymerisation reactions carried out in toluene solution at 70 °C, $[LA]_0$ = 0.5 mol L^{-1}, [isopropanol]/[cat.] = 1.0. [b] Measured by ^{1}H NMR. [c] Calculated from the molecular weight of LA × $[LA]_0/[Al]_0$ × conversion + $M_w^{isopropanol}$. [d] Obtained from GPC analysis and calibrated against polystyrene standard. [e] The actual value of number-averaged molecular weights could be calculated according to formula $M_{n(actual)} = 0.58M_{n(GPC)}$.[16]

Table 2 Apparent polymerisation rate constants of L-LA employed complex **3** as a catalyst in different $[LA]_0/[cat.]_0$ ratios.[a]

Entry	$[LA]_0/[Al]_0$	T (h)	$[cat.]_0$ (10^{-3} mol L^{-1})	k_{app} (10^{-2} h^{-1}) [b]
7	50	14	10.00	19.13
8	75	24	6.67	12.75
4	100	36	5.00	9.56
9	125	36	4.00	7.54

[a] The polymerisation reactions carried out in toluene solution at 70 °C, $[LA]_0$ = 0.5 mol L^{-1}, [isopropanol]/[Al] = 1.0. [b] k_{app} deduced from the slope of curve in Fig. 1.

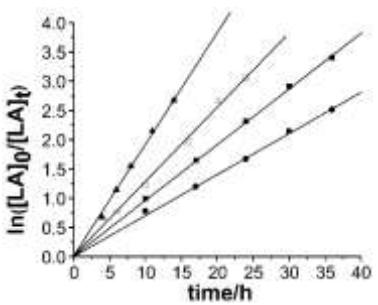


Figure 1. Kinetics of the ROP of L-LA by **3** with isopropanol at 70 °C in toluene. $[LA]_0$ = 0.5 mol L^{-1}; ■: $[LA]_0/[cat.]_0$ = 100; ▲: $[LA]_0/[cat.]_0$ = 50; □: $[LA]_0/[cat.]_0$ = 75; ●: $[LA]_0/[cat.]_0$ = 125.

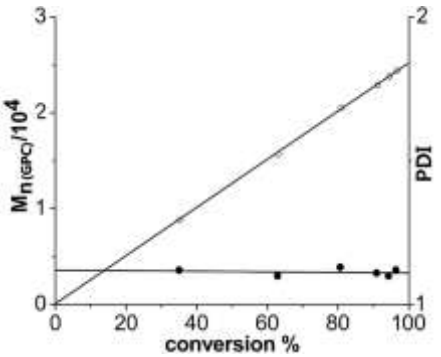


Figure 2. Plots of PLA' s $M_{n(GPC)}$ and PDI in the light of L-LA conversion employing complex **3**/isopropanol, $[LA]_0/[Al]_0$ = 100, in toluene at 70 °C.

Table 3 Representational polymerisation data of *rac*-LA with complexes **1** − **4**.[a]

Entry	Complex	*T* h	Conv. % [b]	$M_{n(calcd)}$ $\times10^{-4}$[c]	$M_{n(GPC)}$ $\times10^{-4}$[d]	$M_{n(actual)}$ $\times10^{-4}$ [e]	PDI[d]	P_m [f]
1	**1**	28	92.7	1.33	2.28	1.32	1.26	0.50
2	**2**	28	96.4	1.39	2.35	1.36	1.19	0.52
3	**3**	28	81.5	1.17	1.97	1.14	1.16	0.56
4	**4**	28	27.0	0.39	0.61	0.35	1.13	0.58
5[a]	**4**	72	20.9	0.30	0.51	0.30	1.11	0.65

[a] The polymerisation reactions carried out in toluene solution at 70 °C except that a reaction, Entry 5, processed in THF at 30 °C; $[LA]_0$ = 0.5 mol L^{-1}, [isopropanol]/$[cat.]_0/[LA]_0$= 1:1:100. [b] Measured by ^{1}H NMR. [c] Calculated from the molecular weight of LA × $[LA]_0/[Al]_0$ × conversion + $M_w^{isopropanol}$. [d] Obtained from GPC analysis and calibrated against polystyrene standard. [e] The actual value of number-averaged molecular weights could be calculated according to formula $M_{n(actual)} = 0.58M_{n(GPC)}$.[16] [f] Homonuclear decoupled ^{1}H NMR spectrum of the methine part of poly(*rac*-LA).

Kinetics of lactide polymerisation

In consideration of the various PDIs (Table 1, Entries 1, 2, 3) of poly(L-LA) by using complexes **1** – **3** as catalysts for the ROP of the L-LA, the kinetics of the ROP of L-LA by representative complex **3** with isopropanol was investigated in toluene at 70 °C in different monomer/initiator ratios (see Table 1 and Table 2, Entries 4, 7, 8 and 9), and the monomer conversions were monitored by ^{1}H NMR at the different polymerisation time. The kinetics of the ROP of L-LA was deduced according to the reference 13b. The data of conversions versus time were plotted in Fig. 1, where x-axis is reaction time, y-axis is $\ln([LA]_0/[LA]_t)$. The apparent polymerisation rate constants of LA in different $[LA]_0/[Al]_0$ ratios were depicted in Table 2. First-order kinetics in monomer was observed (1),

$$-d[LA]/dt = k_{app}[LA] \quad (1)$$

(where k_{app} is the apparent polymerisation rate constant of L-LA). The molecular weight of the polymers propagated linearly depending on the raise of the monomer transformation rate. The PDI of these polymers were relatively narrow (1.10 – 1.12). This showed a living feature in the catalytic system (Fig. 2). In order to deduce the order of initiator, k_{app} was plotted versus the concentration of **3**. As shown in Fig. 3, k_{app} increased linearly with the **3** concentration, manifested that the order in catalyst was first-order. Hence, the polymerisation of L-LA with **3** obeyed the following kinetic law (2),

$$-d[LA]/dt = k_p[LA][cat.] \quad (2)$$

(where k_p was the polymerisation rate constant, $k_p = k_{app}/[cat.]$). A k_p value of 19.12 L $mol^{-1}h^{-1}$ is determined for **3** initiated LA polymerization in toluene at 70 °C.

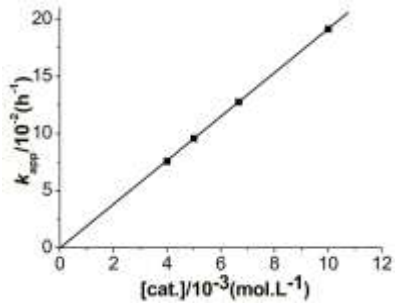


Figure 3. k_{app} versus the concentration of **3**/isopropanol initiator for the L-LA polymerisation in toluene at 70 °C ($[LA]_0$ = 0.5 mol L^{-1}, k_p = 19.12 L $mol^{-1}h^{-1}$).

Stereoselective polymerisation

Furthermore, the poly(*rac*-LA) (Table 3, Entry 1 − 5) with the homonuclear decoupled ^{1}H NMR spectrum of the methine fragment[18] was also studied. The P_m[19] value, 0.65, demonstrated that these polymer chains (employed complexes **4** as catalyst at 30 °C) were partially isotactic (see Fig. 4). The P_m value, 0.50, showed that these polymer chains (employed complexes **1** with small steric hindrance as catalyst at 70 °C) were atactic, and the P_m values increased from 0.50 to 0.58 with the raise of the bulk of the substitutes on ligands at 70 °C (see Table 3, Entries 1 − 4). For complex **4**, lowered the temperature from 70 to 30 °C, the P_m value raised from 0.58 to 0.65 (Table 3, Entries 4, 5). In comparison with the aluminium catalysts (*e.g.* complex (R)-**4** in the reference 13 (b)) supported by salen ligands, complexes **1** and **2** with small steric hindrance showed lower stereoselectivities for the ROP of rac-LA.

Figure 4. Homonuclear decoupled ^{1}H NMR spectrum of the methine part of poly(*rac*-LA) using **4** at 30 °C, P_m = 0.65, in $CDCl_3$ (Table 3, Entry 5).

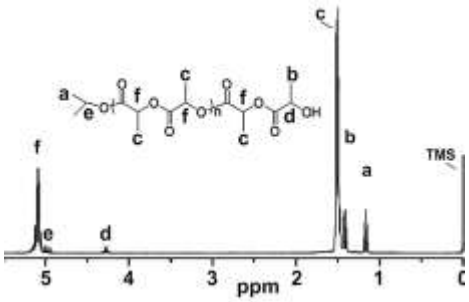


Figure 5. ^{1}H NMR spectrum of poly(L-LA) oligomer synthesised by the complex **3** system with $[LA]_0 : [\mathbf{3}]_0 = 20 : 1$.

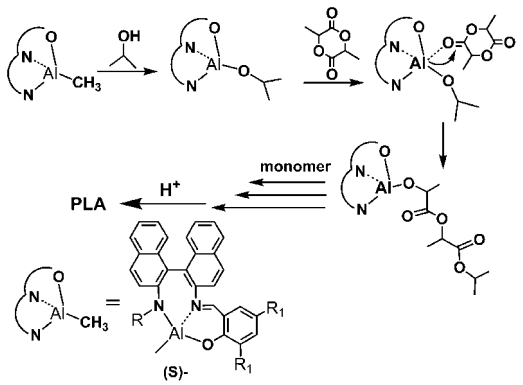


Figure 6. Proposed mechanism for the ROP of lactide initiated by aluminum complexes and isopropanol.

Mechanism of lactide polymerisation

So as to exploring the mechanism of initiation, end-group analysis of the oligo(lactide), which was synthesised by the ROP of the L-LA at low monomer to initiator ratio ($[LA]_0 : [\mathbf{3}]_0 = 20 : 1$) was measured by ^{1}H NMR (Fig. 5). It revealed that the integral ratio of the two peaks at δ 1.24 ppm (the methyl protons on the isopropoxycarbonyl end-group) and δ 4.34 ppm (the methine proton connected to the hydroxyl end-group) was close to 6 : 1. This implied that the aggregating chains were end-capped by an isopropyl ester and a hydroxyl group, [14b, 14c, 20] *i.e.* the alkyl aluminum complex had converted to isopropoxy aluminum species at the start of the polymerisation, so the actual initiator was the aluminium alkoxide propagating species (Fig. 6). The ROP selected a coordination insertion mechanism.[21]

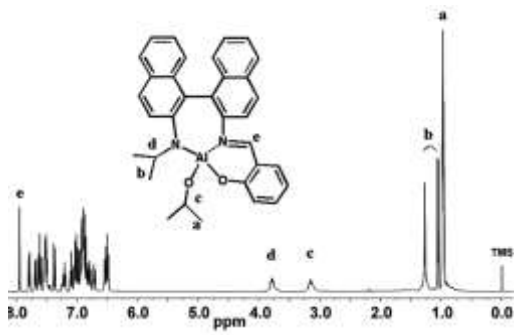


Figure 7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the product obtained by reacting of **1** and isopropanol (mole ratio: 1/1).

In order to further understand the polymerization reaction of lactide initiated by the catalytic system, the product obtained by reacting of complex **1** with isopropanol (mole ratio: 1/1) was characterized by ^{1}H NMR at room temperature. As shown in Fig. 7, the ^{1}H NMR spectrum showed the disappearance of the resonances for protons from Al-CH_3 in the upfield region. The appearance of the resonances for protons from $(CH_3)_2$C<u>H</u>OAl signals in *δ 0.98* and <u>3.21</u> ppm demonstrated the formation of an isopropoxy aluminum species.

Experimental

General

All operations refer to air and water-sensitive were employed by Schlenk line or glovebox techniques. Tetrahydrofuran and toluene were distilled from sodium and benzophenone immediately before use. L-lactide and *rac*-lactide from Aldrich crystallized from dry toluene was purified just before use by sublimation in vacuo (10^{-3} mbar, bath temperature: 85 °C) and distributed into the glass ampoules equipped with breakseals. Elemental analysis were accomplished by a Varian EL microanalyzer, ^{1}H NMR, ^{1}H-^{1}H COSY, ^{13}C NMR and ^{1}H-^{13}C HMQC spectra were performed on Bruker AV 300M or 400M apparatus at 25 ℃ in $CDCl_3$ for compounds and polymers. The monomer conversions were confirmed by according to the references.[14b, 14c] Gel permeation chromatography (GPC) was conducted with a Waters 515 GPC with $CHCl_3$ as the eluant (flow rate: 1 mLmin^{-1}, at 35 °C). The molecular weight was adjusted through PS standard. 2-bromoadamantane, (*S*)-1,1'-dinaphthalene-2,2'-diamine, palladousacetate, 2-bromopropane, $AlMe_3$, isopropanol, BINAP, 3,5-di-tert-butylsalicylaldehyde, salicylaldehyde, methanol, 3,5-dichlorosalicylaldehyde and *p*-toluenesulfonic acid were obtained from Aldrich.

Synthesis of compounds La and Lb

General process: upon stirring a solution of $Pd(OAc)_2$ (0.36 g, 1.0 mmol) and BINAP (1.25 g, 1.0 mmol) in toluene in a Schlenk flask under argon, the bromoalkane (20.0 mmol), (*S*)-(–)-1,1'-dinaphthalene-2,2'-diamine (5.68 g, 20.0 mmol) and sodium *tert*-butyl alcohol (2.88 g, 30.0 mmol) were added. The mixture was stirred at 25 ℃ for 15 min. The Schlenk flask was heated to ca. 65 °C. After 4 – 9 h the mixture was cooled to 25 °C, poured into diethyl ether (180 mL), and separated with separating funnel. The solution was dried and distilled dry. The product as colourless solid were attained by flash chromatography on silica gel with petroleum ether/acetic ether (V_1/V_2 = 15/1) as the eluent, in 65.7 – 75.3% yields.

La: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 9.0 Hz, 1H, Ar*H*), 7.81 – 7.74 (m, 3H, Ar*H*), 7.25 (d, *J* = 9.0 Hz, 1H, Ar*H*), 7.22 – 7.00 (m, 5H, Ar*H*), 6.96 (d, *J* = 8.1 Hz, 1H, Ar*H*), 3.85 – 3.68 (m, 1H, C*H*$(CH_3)_2$), 3.54 (bs, 3H, *NH*, *NH*$_2$), 1.02 (d, *J* = 6.2 Hz, 3H, CH(C*H*$_3$)$_2$), 0.95 (d, *J* = 6.2 Hz, 3H, CH(C*H*$_3$)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ143.97, 142.84, 133.89, 133.66, 129.41, 128.40, 127.97, 127.61, 126.63, 126.59, 124.05, 123.75, 122.26, 121.91, 121.86,118.18, 115.28, 115.23, 112.79, 112.30, 44.74, 23.30. Anal. Calcd for $C_{23}H_{22}N_2$ (%): C, 84.63; H, 6.79; N, 8.58. Found: C, 84.60; H, 6.75; N, 8.54. HRMS (*m/z*): Calcd for $C_{23}H_{22}N_2$: 326.18. Found: 326.10.

Lb: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 – 7.73 (m, 4 H, Ar*H*), 7.24 – 7.12 (m, 6 H, Ar*H*), 7.09 – 7.00 (m, 2 H, Ar*H*), 4.02 –

3.41 (bs, 3H, *NH*, NH_2), 3.60(s, 1 H), 1.95 – 1.90 (m, 1 H), 1.82 – 1.74 (m, 5 H), 1.61 – 1.57 (m, 2 H), 1.49 – 1.44 (m, 1 H), 1.35 – 1.31 (m, 2 H), 1.29 – 1.25 (m, 1 H), 1.19 – 1.16 (m, 1 H), 1.14 – 1.10 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.34, 142.90, 133.96, 133.85, 129.42, 129.32, 128.40, 128.02, 127.97, 127.30, 126.60, 126.58, 124.23, 123.66, 122.31, 121.55, 118.09, 114.70, 112.20, 112.45, 56.65, 37.54, 37.41, 37.35, 32.08, 31.88, 31.25, 31.08, 27.31, 27.00. Anal. Calcd for $C_{30}H_{30}N_2$ (%): C, 86.08; H, 7.22; N, 6.69. Found: C, 86.12; H, 7.27; N, 6.73. HRMS (*m*/*z*): Calcd for $C_{30}H_{30}N_2$: 418.57. Found: 418.61.

Synthesis of pro-ligands

General process: a mixture of **La** or **Lb** (2.0 mmol), (substituted) salicylaldehyde (2.0 mmol) and *p*-toluenesulfonic acid (0.08 mmol) in toluene (60 mL) was reflowed for 4 – 12 h. After solvent evaporation at reduced pressure, the crude product was purified by flash chromatography on silica gel using petroleum ether/acetic ether (V_1/V_2 = 15/1) as the eluent. Then the products were attained in 68.7 – 87.4% yields.

Pro-ligand L1: yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.14 (bs, 1H, O*H*), 8.61 (s, 1H, N=C*H*), 8.04 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.94 (d, *J* = 8.1 Hz, 1H, Ar*H*), 7.87 (t, *J* = 8.3 Hz, 2H, Ar*H*), 7.81 – 7.73 (m, 1H, Ar*H*), 7.62 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.48 – 7.43 (m, 1H, Ar*H*), 7.35 (d, *J* = 8.2 Hz, 1H, Ar*H*), 7.32 – 7.01 (m, 5H, Ar*H*), 6.97 (d, *J* = 7.9 Hz, 1H, Ar*H*), 6.80 – 6.74 (m, 2H, Ar*H*), 3.82 – 3.74 (m, 1H, C*H*(CH_3)$_2$), 3.56 (bs, 1H, N*H*), 1.26 (s, 3H, CH(CH_3)$_2$), 1.04 (d, *J* = 6.3 Hz, 3H, CH(CH_3)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.02 (1C, N=*C*H), (144.68, 143.75, 143.11, 142.60, 133.93, 132.78, 131.98, 129.81, 129.44, 128.01, 127.10, 126.31, 126.07, 124.06, 123.68, 123.58, 122.26, 121.90, 121.60, 118.50, 118.14, 117.84, 117.20, 115.27, 114.86, 113.94, (26C, Ar*C*)), 44.73 (1C, *C*H(CH_3)$_2$), 23.69 (2C, CH(*C*H_3)$_2$). Anal. Calcd for $C_{30}H_{26}N_2O$ (%): C, 83.69; H, 6.09; N, 6.51. Found: C, 83.72; H, 6.11; N, 6.55. HRMS (*m*/*z*): calcd for $C_{30}H_{26}N_2O$: 430.54. Found: 430.52.

Pro-ligand L2: red powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.02 (bs, 1H, O*H*), 8.79 (s, 1H, N=C*H*), 8.08 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.98 (d, *J* = 8.2 Hz, 1H, Ar*H*), 7.90 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.83 (t, *J* = 8.3 Hz, 1H, Ar*H*), 7.64 (s, 1H, Ar*H*), 7.54 (s, 1H, Ar*H*), 7.39 – 7.07 (m, 5H, Ar*H*), 7.03 (d, *J* = 8.2 Hz, 1H, Ar*H*), 6.85 – 6.78 (m, 2H, Ar*H*), 3.81 – 3.75 (m, 1H, C*H*(CH_3)$_2$), 3.60 (bs, 1H, N*H*), 1.28 (s, 3H, CH(CH_3)$_2$), 1.07 (d, *J* = 6.0 Hz, 3H, CH(CH_3)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.40 (1C, N=*C*H), (145.94, 144.53, 143.99, 143.31, 134.87, 133.40, 132.63, 130.29, 129.93, 129.22, 128.03, 126.96, 126.63, 125.01, 124.22, 123.89, 123.07, 122.73, 122.42, 119.33, 118.97, 118.20, 117.91, 116.00, 115.34, 114.87, (26C, Ar*C*)), 45.12 (1C, *C*H(CH_3)$_2$), 24.03 (2C, CH(*C*H_3)$_2$). Anal. Calcd for $C_{30}H_{24}Cl_2N_2O$ (%): C, 72.15; H, 4.84; N, 5.61. Found: C, 72.20; H, 4.90; N, 5.67. HRMS (*m*/*z*): calcd for $C_{30}H_{24}Cl_2N_2O$: 498.13. Found: 498.20.

Pro-ligand L3: yellow powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.81 (bs, 1H, O*H*), 8.63 (s, 1H, N=C*H*), 8.08 (d, *J* = 8.4 Hz, 1H, Ar*H*), 7.99 (d, *J* = 8.1 Hz, 1H, Ar*H*), 7.87 (t, *J* = 8.3 Hz, 2H, Ar*H*), 7.77 – 7.69 (m, 2H, Ar*H*), 7.64 (d, *J* = 8.2 Hz, 1H, Ar*H*), 7.54 – 7.49 (m, 1H, Ar*H*), 7.37 – 7.26 (m, 5H, Ar*H*), 7.01 (d, *J* = 8.6 Hz, 1H, Ar*H*), 6.83 – 6.78 (m, 2H, Ar*H*), 3.71 (bs, 1H, N*H*,), 3.66 – 3.78 (m, 1 H), 2.01 – 1.93 (m, 1H), 1.89 – 1.82 (m, 1H), 1.78 – 1.74 (m, 5H), 1.59 – 1.54 (m, 2H), 1.51 – 1.45 (m, 2H), 1.36 – 1.34 (m, 1H), 1.32 – 1.29 (m, 1H), 1.21 – 1.17 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.52 (1C, N=*C*H), 159.78, 145.29, 143.34, 139.99, 137.01, 133.02, 133.62, 132.93, 129.95, 129.59, 128.56, 128.20, 127.96, 127.60, 127.31, 127.07, 126.90, 126.55, 126.34, 125.96, 123.71, 122.81, 118.33, 117.89, 117.30, 114.40, 113.82, 56.73, 37.52, 37.24, 34.87, 34.06, 32.78, 31.99, 31.58, 31.78, 29.86, 29.34, 27.50, 27.08. Anal. Calcd for $C_{37}H_{34}N_2O$: C, 85.02; H, 6.56; N, 5.36. Found: C, 85.07; H, 6.61; N, 5.40. HRMS (*m*/*z*): calcd for $C_{37}H_{34}N_2O$: 522.27. Found: 522.41.

Pro-ligand L4: yellow powder.^{1}H NMR (300 MHz, $CDCl_3$): δ 12.78 (s, 1H, O*H*), 8.64 (s, 1H, N=C*H*), 8.07 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.96 (d, *J* = 8.1 Hz, 1H, Ar*H*), 7.83 (d, *J* = 9.0 Hz, 1H, Ar*H*), 7.74 – 7.66 (m, 2H, Ar*H*), 7.50 – 7.45 (m, 2H, Ar*H*), 7.36 – 7.23 (m, 3H, Ar*H*), 7.14 – 7.05 (m, 2H, Ar*H*), 7.00 (s, 1H, Ar*H*), 6.83 (d, *J* = 7.7 Hz, 1H), 3.83 (bs, 1H, N*H*), 3.74 – 3.67 (m, 1 H), 1.99 – 1.90 (m, 1H), 1.87 – 1.80 (m, 1H), 1.76 – 1.72 (m, 5H), 1.58 – 1.52 (m, 3H), 1.49 – 1.43 (m, 2H), 1.34 – 1.32 (m, 1H), 1.30 – 1.27 (m, 1H), 1.24 (d, *J* = 1.8 Hz, 18H, C(CH_3)$_3$), 1.19 – 1.15 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.45 (1C, N=*C*H), 158.32, 144.53, 142.55, 139.59, 136.69, 134.23, 133.66, 132.64, 129.64, 129.16, 128.18, 128.04, 127.89, 127.47, 127.18, 126.98, 126.64, 126.28, 126.10, 125.84, 123.50, 121.08, 118.04, 117.76, 117.19, 114.26, 113.43, 56.66, 37.48, 37.20, 34.83, 33.96, 32.21, 31.75, 31.34, 31.22, 29.65, 29.07, 27.24, 26.96. Anal. Calcd for $C_{45}H_{50}N_2O$: C, 85.13; H, 7.94; N, 4.41. Found: C, 85.19; H, 8.00; N, 4.45. HRMS (*m*/*z*): calcd for $C_{45}H_{50}N_2O$: 634.89. Found: 634.92.

Synthesis of Complexes

General process: A mixture of pro-ligand **Ln** (**n=1, 2, 3** or **4**, 1.00 mmol) and $AlMe_3$ (1.00 M in toluene, 1.00 mmol) in 12 mL toluene was stirred for 2 – 24 h at 70 °C under an argon atmosphere. And concentrated to ca. 1.5 mL to give a yellow or red powder, and the product was washed with about 0.5 mL of hexane and dried in vacuum. The products were attained in 74.2–93.0% yields.

Complex 1: yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.32 (s, 1H, N=C*H*),8.02 (d, *J* = 8.2 Hz, 1H, Ar*H*), 7.89 (d, *J* = 8.4 Hz, 1H, Ar*H*), 7.73 (t, *J* = 8.2 Hz, 2H, Ar*H*), 7.67 – 7.59 (m, 1H, Ar*H*), 7.54 (d, *J* = 8.1 Hz, 1H, Ar*H*), 7.40 – 7.35 (m, 1H, Ar*H*), 7.30 – 6.97 (m, 6H, Ar*H*), 6.84 – 6.61 (m, 3H, Ar*H*), 3.79 – 3.72 (m, 1H, C*H*(CH_3)$_2$), 1.23 (s, 3H, CH(CH_3)$_2$), 1.01 (s, 3H, CH(CH_3)$_2$), – 0.89 (s, 3H, AlCH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.05 (1C, N=*C*H), (144.12, 143.54, 143.03, 142.49, 133.81, 132.70, 131.74, 129.62, 129.30, 127.85, 127.01, 126.13, 125.82, 123.99, 123.41, 123.27, 122.13, 121.85, 121.43, 118.34, 118.01, 117.63, 117.07, 115.15, 114.69, 113.77, 26C, Ar*C*), 44.67 (1C, *C*H(CH_3)$_2$), 23.51 (2C, CH(*C*H_3)$_2$), -9.03 (1C, Al*C*H_3). Anal. Calcd for $C_{31}H_{27}AlN_2O$ (%): C, 79.13; H, 5.78; Al, 5.73; N, 5.95. Found: C, 79.10; H, 5.72; N, 5.91.

Complex 2: red powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H, N=C*H*), 8.06 (d, *J* = 8.4 Hz, 1H, Ar*H*), 7.94 (d, *J* = 8.3 Hz, 1H, Ar*H*), 7.88 (d, *J* = 8.5 Hz, 1H, Ar*H*), 7.82 (t, *J* = 8.3 Hz, 1H, Ar*H*), 7.60 (s, 1H, Ar*H*), 7.51– 7.03 (m, 6H, Ar*H*), 7.00 (d, *J* = 8.4 Hz, 1H, Ar*H*), 6.86 – 6.74 (m, 2H, Ar*H*), 3.82 – 3.76 (m, 1H, C*H*(CH_3)$_2$), 1.27 (s, 3H, CH(CH_3)$_2$), 1.05 (s, 3H, CH(CH_3)$_2$), –0.85 (s, 3H, AlCH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.11 (1C,

N=*C*H), (144.77, 144.43, 143.72, 143.20, 134.63, 133.27, 132.50, 130.05, 129.72, 129.01, 127.95, 126.84, 126.48, 124.83, 124.04, 123.59, 122.90, 122.50, 122.31, 119.14, 118.67, 118.01, 117.69, 115.78, 115.11, 114.55, (26C, Ar*C*)), 43.57 (1C, *C*H(CH_3)$_2$), 23.08 (2C, CH(*C*H_3)$_2$), -8.45 (1C, Al*C*H_3). Anal. Calcd for $C_{31}H_{25}AlCl_2N_2O$ (%): C, 69.02; H, 4.67; N, 5.19. Found: C, 69.06; H, 4.69; N, 5.22.

Complex 3: yellow powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.29 (s, 1H, N=C*H*), 8.04 (d, *J* = 8.4 Hz, 1H, Ar*H*), 7.95 (d, *J* = 8.1 Hz, 1H, Ar*H*), 7.71 – 7.63 (m, 3H, Ar*H*), 7.55 (t, *J* = 7.9 Hz, 2H, Ar*H*), 7.49 (t, *J* = 8.2 Hz, 1H, Ar*H*), 7.42 – 7.38 (m, 1H, Ar*H*), 7.34 – 7.22 (m, 4H, Ar*H*), 6.96 (d, *J* = 8.2 Hz, 1H, Ar*H*), 6.80 – 6.73 (m, 2H, Ar*H*), 3.70 – 3.58 (m, 1 H), 2.20 (bs, 1H), 1.86 – 1.79 (m, 1H), 1.74 – 1.70 (m, 5H), 1.55 – 1.50 (m, 2H), 1.47 – 1.42 (m, 2H), 1.33 – 1.30 (m, 1H), 1.29 – 1.25 (m, 1H), 1.19 – 1.14 (m, 1H), –0.93 (s, 3H, Al*C*H_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.17 (1C, N=*C*H), 157.44, 142.10, 140.93, 139.21, 136.67, 132.55, 132.02, 132.27, 129.79, 129.24, 128.10, 127.77, 127.25, 127.00, 126.62, 126.11, 125.88, 125.79, 125.33, 125.02, 123.22, 122.34, 118.01, 117.54, 117.00, 114.09, 113.24, 56.45, 37.23, 37.09, 34.50, 33.86, 32.13, 31.40, 31.12, 30.98, 29.48, 29.27, 27.31, 26.79, -9.84 (1C, Al*C*H_3). Anal. Calcd for $C_{38}H_{35}AlN_2O$: C, 81.11; H, 6.27; N, 4.98. Found: C, 81.06; H, 6.23; N, 4.96.

Complex 4: yellow powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.26 (s, 1H, N=C*H*), 8.02 (d, *J* = 6.6 Hz, 1H, Ar*H*), 7.90 (d, *J* = 6.1 Hz, 1H, Ar*H*), 7.75 (d, *J* = 6.6 Hz, 1H, Ar*H*), 7.66 (d, *J* = 6.6 Hz, 1H, Ar*H*), 7.60 (d, *J* = 5.9 Hz, 1H, Ar*H*), 7.48 – 7.38 (m, 1H, Ar*H*), 7.30 – 7.26 (m, 1H, Ar*H*), 7.23 (s, 1H, Ar*H*), 7.09 – 6.98 (m, 4H, Ar*H*), 6.83 (d, *J* = 8.3 Hz, 1H), 6.19 (d, *J* = 2.2 Hz, 1H), 3.57 – 3.49 (m, 1 H), 2.30 – 2.26 (m, 1H), 1.96 – 1.91 (m, 1H), 1.81 – 1.70 (m, 5H), 1.58 – 153 (m, 2H), 1.43 – 1.33 (m, 2H), 1.25 (s, 9H, C(CH_3)$_3$), 1.17 – 1.12 (m, 2H), 1.09 (s, 9H, C(CH_3)$_3$), 1.02 – 0.94 (m, 1H), – 0.97 (s, 3H, Al*C*H_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.76(1C, N=*C*H), 161.91, 144.74, 144.34, 139.87, 138.26, 134.00, 133.51, 132.76, 132.25, 130.22, 129.66, 128.84, 128.30, 128.20, 127.96, 127.40, 127.11, 126.91, 126.54, 125.84, 123.96, 122.83, 121.89, 118.38, 113.52, 111.48, 56.75, 37.46, 37.39, 37.14, 35.02, 33.72, 32.72, 31.95, 31.61, 31.07, 29.16, 27.17, 26.87, -9.93 (1C, Al*C*H_3). Anal. Calcd for $C_{46}H_{51}AlN_2O$ (%): C, 81.86; H, 7.62; N, 4.15. Found: C, 81.82; H, 8.00; N, 3.97.

General procedure for lactide polymerisation

In a representational polymerisation reaction: polymerising mixtures were prepared in sealed glass ampoules using the standard Schlenk techniques. Under dry argon atmosphere, aluminum complex **3** (0.56 g, 1.0 mmol), a solution of 1.0 mmol isopropanol in 1.0 mL of toluene and a certain amount of toluene were loaded in a flame-dried ampoule containing a magnetic bar. The ampoule was immersed in an oil bath at 70 °C. The solution was stirred for about 10 minutes, when the catalyst was activated completely by isopropanol, the lactide (14.4g, 100 mmol) was added, resulted in $[LA]_0$ = 0.50 mol L^{-1} and $[LA]_0$:$[isopropanol]_0$:$[\mathbf{3}]_0$ = 100:1:1. Ca. 0.80 mL aliquots were removed and the conversion was determined by ^{1}H NMR every two hours. At high conversion (96.7%), the reaction was terminated by adding glacial acetic acid followed by removal of the solvent *in vacuo*. The remaining residues were dissolved in chloroform and polymers were precipitated in cold methanol. The polymers were dried *in vacuo* at 35 °C for 40 hours.

Conclusions

In conclusion, we reported four new aluminum complexes supported by tridentate ligands prepared from modificatory bromoalkane, modificatory salicylaldehyde and binaphthyl diamine. They were employed as catalysts for the ROP of LA. The reaction results revealed that electron-withdrawing substituents on ligand raised the polymerisation rate. Microstructural analyses of the polymers catalyzed by these complexes revealed that the tridentate N, N, O-tridentate ligands had certain ability to affect the PDI and the steric regularity of the polymers. In comparison with the aluminium catalyst supported by salen ligand, complexes **1** and **2** with small steric hindrance showed higher catalytic activities and lower stereoselectivities for the ROP of LA.

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† Electronic Supplementary Information (ESI) available: Figure S1–S5 are available free of charge by the internet at http://pubs.rsc.org. See DOI: 10.1039/c000000x/

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