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Synthesis of biodegradable and biorenewable polylactides initiated by aluminum complexes bearing *m*-xylylenediamine derivatives *via* the ring-opening polymerization of lactides†

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A series of aluminum complexes bearing [ONNO]-type ligands were prepared using *m*-xylylenediamine and modified salicylaldehyde. These complexes were characterized by NMR spectroscopy and elemental analysis. These complexes were employed in L-lactide and *rac*-lactide polymerization. Upon activation with isopropanol, complex **3** showed the highest activity (monomer conversion 97.4%) amid these aluminum complexes for the ring-opening polymerization of L-lactide and complex **2** showed the highest stereoselectivity for the ring-opening polymerization of *rac*-lactide providing isotactic polylactide (PLA) with a P_m of 0.70. The polymerization kinetics utilizing **2** as an initiator was researched in detail. The kinetics of the polymerization data revealed that the rate of polymerization was first-order with respect to the monomer and the initiator. There was a linear relationship between the L-lactide conversion and the number-average molecular weight of PLA.

Introduction

Today, non-renewable petroleum-based materials are widely used in our daily lives because of their low cost of synthesis and processing. However, with the gradual depletion of fossil resources, the application of petroleum-based polymers has seriously polluted our environment, and more and more attention to environmental protection has led to the search for sustainable and environmentally friendly polymers that can replace non-renewable petroleum-based polymers.[1] Starting from corn or sugar beets, biodegradable, biocompatible and biorenewable polylactide (PLA) is becoming one of the most promising alternatives to petroleum-based polymers.[1a,b] PLA has been widely used in many fields such as fracture fixation devices, blood transfusion devices, sutures, controlled release drug carriers, tissue engineering stents, disposal containers, textiles and packaging.[2] Polylactide is usually synthesized by ring-opening polymerization (ROP) of lactide, which is initiated by metal complexes such as tin,[3] aluminum,[4] zinc,[5] magnesium,[6] iron,[7] titanium,[8] indium[9] and rare-earth metals.[10] Aluminum is an effective initiator for the synthesis of PLA through ROP, because it efficiently influences the microstructure of the polymer by ancillary ligands.[4,11] In the past twenty years, a lot of efforts were made on the ROP of *rac*-lactide (*rac*-LA) through a stereoselective initiator containing an ancillary ligand to obtain PLA having high stereoregularity. Many research groups have attempted to clarify the relationship between the stereoregularity of poly(*rac*-lactide) and the aluminum complex based on salen-type Schiff bases[11,12] (Fig. 1). Among them, Spassky *et al.* found an aluminum initiator supported by a salen-type Schiff base ligand prepared from *R*-(+)-1,1′-dinaphthalene-2,2′-diamine, which could highly stereo-control the polymerization of *rac*-LA. The PLA's T_m is higher than the T_m of PLLA with optical purity.[11a] Coates' team found that aluminum complexes with Schiff bases provide enriched isotactic PLA.[11b] Nomura and Ishii have focused on the effects of the backbone that connects the two Schiff bases and the substituent effects of the salicylidene moieties.[13] Feijen's group utilized a racemic and homochiral bulky Jacobsen ligand–Al complex to obtain a polymer with a T_m of around 185 °C.[14]

In recent years, we have studied a number of mononuclear and binuclear aluminum complexes based on the Schiff base ligands. These complexes proved to be highly efficient single point initiators in the ROP of L-LA and *rac*-LA. And these

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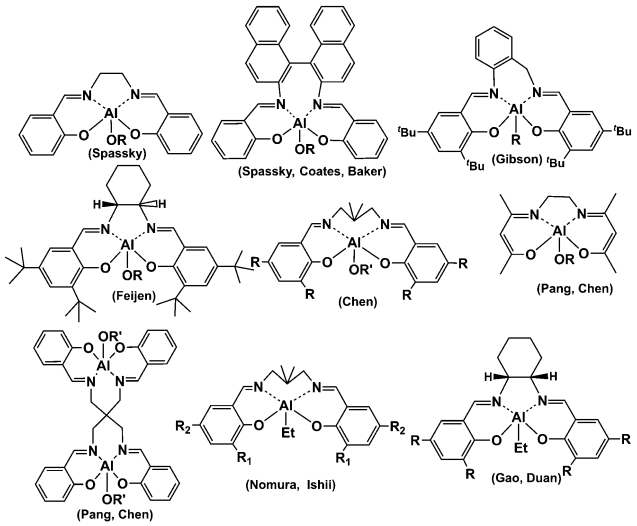
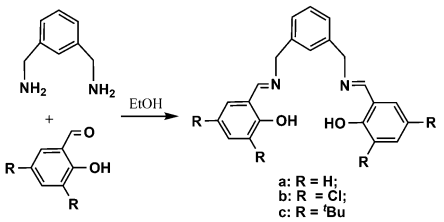


Fig. 1 Initiators for stereoselective ROP of *rac*-lactide.



Scheme 1 Preparation of pro-ligands **a**, **b** and **c**.

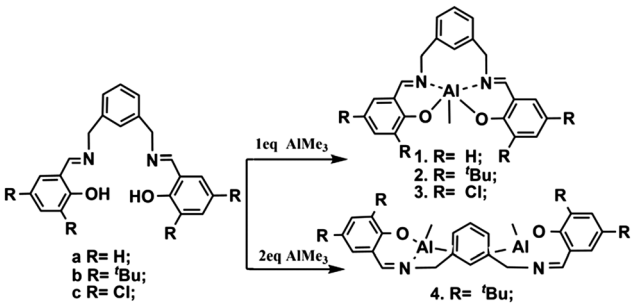
aluminum complexes can modulate the microstructure of the PLA, inducing the formation of isotactic preferences in the ROP of *rac*-LA.[12]

However, as far as we know, few have investigated salen type Schiff bases derived from *m*-xylylenediamine derivatives as bridging segments (Schemes 1 and 2) and the role of their metal complexes in the ROP of LA was studied. With the encouragement of the effective utilization of aluminum complexes containing Schiff-bases,[12] we hold that the aluminum complex bearing salen type Schiff-bases containing a bulky *m*-xylylenediamine derivative is a potential initiator to well control the ROP of L-LA and *rac*-LA. We were curious to study the catalytic properties of aluminum complexes containing *m*-xylylenediamine derivatives. In this paper, the preliminary experimental data of Salen aluminum complexes based on Schiff-base ligands containing *m*-xylylenediamine derivatives were reported, which were used as initiators to obtain polylactide by the ROP of lactides.

Results and discussion

Preparation of pro-ligands a, b and c

As shown in Scheme 1, pro-ligands **a**, **b** and **c** were prepared in good yields (73.6–87.7%) by condensation reaction of *m*-xylylenediamine and modified salicylaldehydes in absolute ethanol according to the literature.[15] All pro-ligands were



Scheme 2 Preparation of aluminum complexes **1–4**.

characterized by ^{1}H, $^{13}C\{^{1}H\}$ NMR spectroscopy and elemental analysis. The characteristic signals, singlets at δ 8.45, 8.48 and 8.36 ppm, were assigned to the protons of –N=CH– in pro-ligands **a**, **b** and **c**.

Preparation of mononuclear aluminum complexes 1, 2 and 3

As shown in Scheme 2, aluminum complexes **1–3** were prepared in high yields by reaction of commensurable trimethyl-aluminum with the corresponding pro-ligands under nitrogen and were isolated as a yellow or orange solid from toluene in 83.7–92.3% yield.

Preparation of binuclear aluminum complexes 4

As shown in Scheme 2, aluminum complex **4** was prepared by reaction of 2 eq. trimethyl-aluminum and 1 eq. pro-ligand **b** under nitrogen and a yellow solid was isolated from toluene in 89.3% yield.

All aluminum complexes were characterized by NMR spectroscopy and elemental analysis. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of mononuclear aluminum complexes **1**, **2** and **3** showed one ligand and a single aluminum atom in these aluminum complexes, and similar resonances in the region of −0.63 to −1.01 ppm for the methyl protons of the Al–CH_3 group. Meanwhile, compared with the pro-ligands' hydroxyl characteristic peaks of 13.36–14.36 in the low field, there were no corresponding signals in the mononuclear aluminum complexes, such as complex **2** (Fig. 2), which can be observed in the ^{1}H NMR spectrum. Interestingly, the ^{1}H NMR spectra of **1**, **2** and **3** revealed that the –NCH_2 groups of the ligands in these complexes were inequivalent. For example, two groups of resonances from –NCH_2 (5.37 and 4.90 ppm) were observed in the ^{1} H NMR spectrum (7 + 7′ in Fig. 2). It appeared that the geometry of **2** in solution was ''b'' rather than ''a'' (Fig. S1, ESI†), *i.e.* the aluminum atom in **2** exhibits a trigonal bipyramidal geometry and the two N donors occupied axial and equatorial positions. Similar configurations have also been seen in other aluminium complexes.[16]

Additionally, we used the representative pro-ligand **b** bulky group to react with 2 eq. trimethylaluminum to obtain the expected dinuclear complex **4**. The ^{1}H NMR spectra of complex **4** showed that the two central Al atoms were in an equivalent state, and −0.94 ppm in the high field ('8' in Fig. 2) belonged to the proton of the methyl group attached to the aluminum.

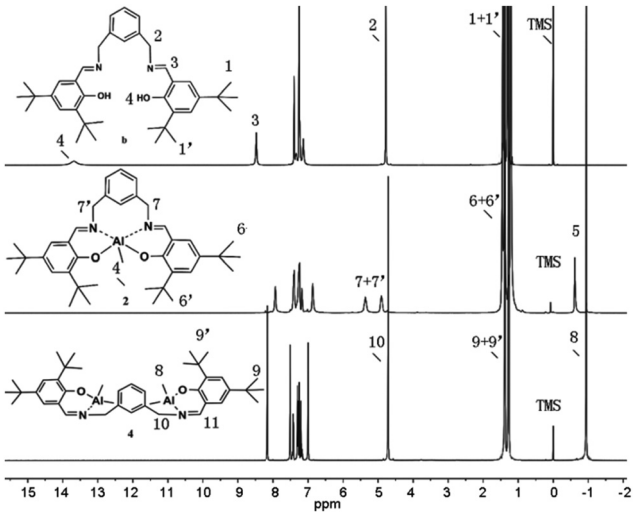


Fig. 2 Stacked figure of the representative ^{1}H NMR spectra of pro-ligand **b**, complex **2** and complex **4**.

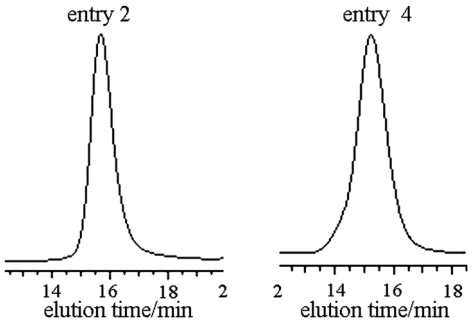


Fig. 3 Representative GPC traces (Table 1, entries 2 and 4).

Only one singlet from $-NCH_2$ (4.71 ppm) was observed in the ^{1}H NMR spectrum (7 + 7′ in Fig. 2). This chemical phenomenon also occurred in the dinuclear aluminum complex as reported by Yao and Wang.[17]

ROP of L-LA and *rac*-LA

Four aluminum complexes were evaluated as initiators for the ROP of L-LA or *rac*-LA. The polymerization was carried out in toluene or tetrahydrofuran and the representative polymerization data are shown in Table 1. These aluminum complexes showed moderate to high activity by co-catalysis of isopropanol at 70 °C (monomer conversion of 48.6–97.4%). The M_n value of PLA was calculated using ^{1}H NMR and GPC. The number average molecular weight (of GPC[18]) of all polymers is close to the theoretical molecular weight (calculated from the monomer/Al molar ratio); the $Đ$ values of PLA were relatively narrow (1.08–1.22), such as 1.08 and 1.11 (Table 1, entries 2 and 4, Fig. 3), which meant that the polymerization was well-controlled. For mononuclear complexes, as the substituent on the phenyl group increased in volume, the activity of these complexes decreased while the electron-withdrawing substituent increases the rate of polymerization. Complex **3** showed the highest activity in the mononuclear complexes under the same reactive conditions (Table 1, entries 1–4). The higher electronegativity of the substituents on the ligand may increase the Lewis acidity of the aluminium centre, thereby increasing the reaction rate. A similar situation has been reported previously.[19] In contrast to mononuclear complex **2**, binuclear aluminum complex **4** showed a higher activity, which may be due to the reduction of steric hindrance, which accelerated chain propagation during the polymerization process.

The homonuclear decoupled ^{1}H NMR spectrum of the methine part[20] of a typical poly(*rac*-LA) (Table 1, entry 13) (Fig. 4) was obtained. The P_m[21] value, 0.70, indicated that isotactic multi-block polymers were obtained. The experimental results showed that the P_m selectivities increased from 0.52 to 0.62 due to the increase of the substituent group on the phenyl ring from hydrogen atoms to *tert*-butyls (Table 1, entries 8 and 9). The reaction temperature had a significant effect on the stereoscopic regularity of the poly(*rac*-LA). When the temperature reduced from 70 to 30 °C, the P_m increased from 0.62 to 0.70 (Table 1, entries 9, 12 and 13). Binuclear aluminum

Table 1 Polymerization data of LA employing complexes **1–4**[a]

Entry	Complex	monomer	T (°C)	t (h)	$[LA]_0/[Al]_0$	Conv.[b] (%)	$M_{n(calcd)}$[c] $\times 10^{-4}$	M_{nGPC}[d] $\times 10^{-4}$	M_n[d] $\times 10^{-4}$	$Đ$[d]	k_{app} (h^{-1})	P_m[e]
1	**1**	L-LA	70	12	100	68.7	0.99	1.74	1.01	1.20	n.a.	n.a.
2	**2**	L-LA	70	12	100	53.3	0.77	1.33	0.77	1.08	n.a.	n.a.
3	**3**	L-LA	70	12	100	77.5	1.12	1.95	1.13	1.15	n.a.	n.a.
4	**4**	L-LA	70	12	100	60.3	0.87	1.50	0.87	1.11	n.a.	n.a.
5	**2**	L-LA	70	20	100	97.4	1.40	2.40	1.39	1.09	0.1703	n.a.
6	**2**	L-LA	70	12	75	92.1	0.99	1.68	0.97	1.08	0.2280	n.a.
7	**2**	L-LA	70	10	50	94.7	0.68	1.19	0.69	1.08	0.3388	n.a.
8	**1**	*rac*-LA	70	12	100	62.0	0.89	1.55	0.90	1.22	n.a.	0.52
9	**2**	*rac*-LA	70	12	100	51.7	0.74	1.29	0.75	1.10	n.a.	0.62
10	**3**	*rac*-LA	70	12	100	75.8	1.09	1.92	1.11	1.19	n.a.	0.55
11	**4**	*rac*-LA	70	12	100	57.9	0.83	1.43	0.83	1.09	n.a.	—
12	**2**	*rac*-LA	50	14	100	48.6	0.70	1.22	0.71	1.10	n.a.	0.67
13	**2**	*rac*-LA	30	20	100	51.3	0.74	1.30	0.75	1.08	n.a.	0.70

[a] The polymerization reactions were carried out in toluene solution except that some reactions were carried out in THF at 30 °C, $[LA]_0$ = 0.5 mol L^{-1}, [isopropanol]/[Al] = 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 the polystyrene standard. The true value of number-average molecular weights could be calculated according to formula $M_n = 0.58M_{nGPC}$.[18] [e] P_m is the probability of meso linkages, according to [mmm] = $P_m^2 + (1 - P_m)P_m/2$, [mmr] = [rmm] = $(1 - P_m)P_m/2$, [rmr] = $(1 - P_m)2/2$, [mrm] = $[(1 - P_m)^2 + P_m(1 - P_m)]/2$.[12c]

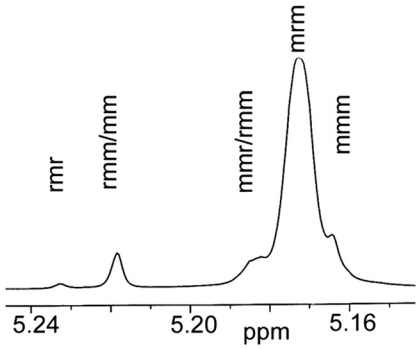


Fig. 4 Homonuclear decoupled ^{1}H NMR spectrum of the methine part of poly(*rac*-LA) by complex **2** at 25 °C, P_m = 0.70, Table 1, entry 13, 500 MHz, $CDCl_3$.

complex **4** in the ROP of *rac*-LA with isopropanol could control well the molecular weight but not the selectivity in the polymerization (Table 1, entry 11; Fig. S2, ESI†).

The kinetics of ROP of L-LA under some conditions such as monomer/initiator ratios were researched in toluene employing **2**. The molecular weight (M_n) of the polymers increased linearly accompanied by the increase of the monomer conversion and the $Đ$ values of these polymers were narrow (1.05–1.09), this illustrated the living characteristic of the catalytic systems (Fig. 6). In order to calculate the order in the initiator, k_{app} was plotted *versus* the concentration of **2** (Fig. 5 and 7). Under each condition, the first-order kinetics in a monomer was researched (Fig. 5). So the ROP of LA by **2** speculatively complied with the formula:

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

where $k_{app} = k_p[\mathrm{Al}]^x$ and k_p is the propagation speed constant. As shown in Fig. 6, k_{app} is proportional to the concentration of **2**, which means that the LA polymerization initiated by **2** is also a first-order reaction for the initiator. So the ROP of LA by **2** followed the entire kinetic equation:

$$-\mathrm{d[LA]}/\mathrm{d}t = k_p[\mathrm{Al}][\mathrm{LA}] \quad (2)$$

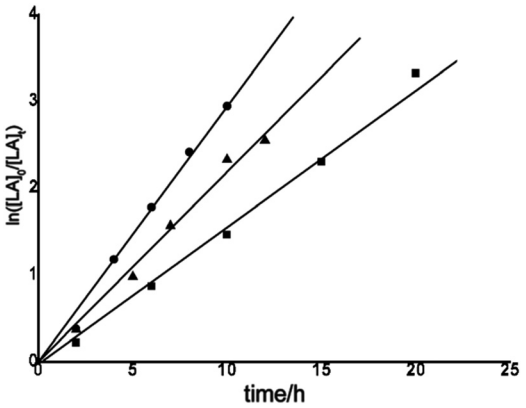


Fig. 5 Kinetics of the ROP of L-LA by **2** with isopropanol at 70 °C in toluene with $[LA]_0$ = 0.5 mol L^{-1}; $k_p = k_{app}/[Al]_0$. ■: L-LA, $[LA]_0/[Al]_0$ = 100, k_{app} = 0.1703 h^{-1}; ▲: L-LA, $[LA]_0/[Al]_0$ = 75, k_{app} = 0.2280 h^{-1}; ●: L-LA, $[LA]_0/[Al]_0$ = 50, k_{app} = 0.3388 h^{-1}.

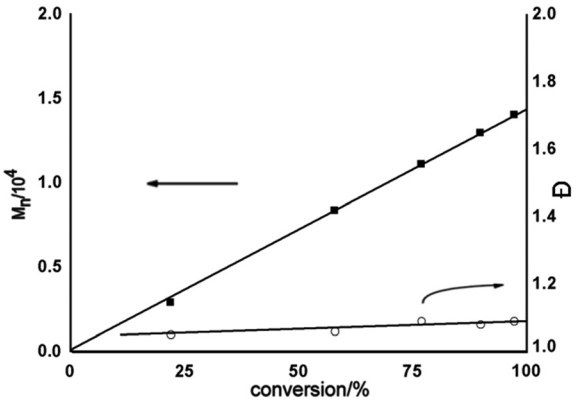


Fig. 6 The relationship between M_n or $Đ$ of the polymer and L-LA conversion employing complex **2**/isopropanol, $[LA]_0/[Al]_0$ = 100, at 70 °C in toluene.

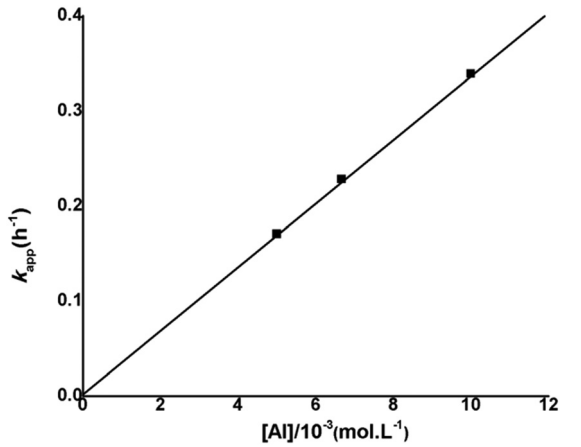


Fig. 7 k_{app} *versus* the $[Al]_0$ of **2**/the isopropanol initiator for the LA polymerization at 70 °C in toluene ($[LA]_0$ = 0.5 mol L^{-1}; $k_p = k_{app}/[Al]_0$; L-LA, $[Al]_0$ = 0.005 mol L^{-1}, k_{app} = 0.1703 h^{-1}; L-LA, $[Al]_0$ = 0.0067 mol L^{-1}, k_{app} = 0.2280 h^{-1}; L-LA, $[Al]_0$ = 0.010 mol L^{-1}, k_{app} = 0.3388 h^{-1}).

For studying the initiation mechanism, end-group analysis of the oligomers of L-LA, which were prepared by the ROP of the L-LA at a low monomer to initiator ratio ($[LA]_t:[2]_t$ = 20 : 1) (Fig. 8), was performed by means of ^{1}H NMR. It has been demonstrated that the integral ratio of the two peaks at δ 1.24 ppm which

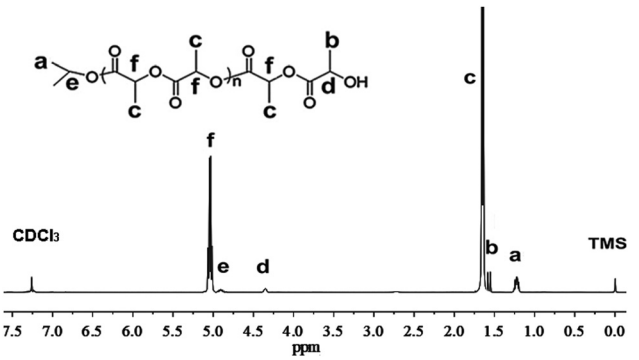


Fig. 8 ^{1}H NMR spectrum of a polymer sample obtained from the complex **2** system with $[LA]_t:[2]_t$ = 20 : 1.

was assigned to the methyl protons from the isopropoxycarbonyl end-group and at δ 4.34 ppm which was assigned to the methine proton bonded to the hydroxyl end-group was close to 6 : 1. This revealed that the aggregated chains were end-capped with an isopropyl ester and a hydroxyl group,[22] that is to say, the alkyl aluminum complex had become isopropoxy aluminum species at the start of the polymerization, so the actual initiator was the isopropoxy aluminum species. The ROP may involve a coordination insertion mechanism (Fig. S3, ESI†).[13d,23]

Experimental

General considerations

All air-sensitive operations were performed in a glovebox or a Schlenk line. ^{1}H NMR and ^{13}C{^{1}H} NMR were performed using a Bruker AV 500M apparatus at 25 °C in $CDCl_3$ for compounds and macromolecules. The $CDCl_3$ used to obtain the NMR spectra of aluminium complexes was dried over CaH_2 before being used. The monomer conversions were confirmed and the P_m values were calculated according to the literature.[1–3] Gel permeation chromatography (GPC) measurements were conducted using a Waters 515 GPC with $CHCl_3$ as the mobile phase (flow rate: 1 mL min^{-1}, at 35 °C). The molecular weight was calibrated using the PS standard. Elemental analysis was performed using a Varian EL microanalyzer. The L-LA and *rac*-LA were purchased from Aldrich and were recrystallized three times in dry EtOAc under N_2. $AlMe_3$, salicylaldehyde, *m*-xylylenediamine, 3,5-dichlorosalicylaldehyde, isopropanol, and 3,5-di-*tert*-butylsalicylaldehyde were obtained from Aldrich and applied without further purification.

Synthesis of pro-ligands

Pro-ligand a. A mixture of *m*-xylylenediamine (0.136 g, 1.00 mmol), salicylaldehyde (0.244 g, 2.00 mmol) and a catalytic quantity of formic acid in absolute ethanol (50 mL) was refluxed for 10 h. After solvent evaporation at reduced pressure, the crude product was purified by flash chromatography on silica gel with petroleum ether/acetic ether (V_1/V_2 = 12/1) and 1% NEt_3 as eluents, affording 0.258 g of a yellow solid of the product in 75.2% isolated yield. ^{1}H NMR (500 MHz, chloroform-*d*, 25 °C): δ 13.36 (bs, 2H, O*H*), 8.45 (s, 2H, N=C*H*), 7.39–7.22 (m, 8H, Ar*H*), 6.97 (d, *J* = 8.3 Hz, 2H, Ar*H*), 6.89 (t, *J* = 7.5 Hz, 2H, Ar*H*), 4.81 (s, 4H, NCH_2). ^{13}C{^{1}H} NMR (125 MHz, chloroform-*d*, 25 °C) δ 165.77 (s, 2C, N=*C*H), 161.07 (Ar*C*), 138.67 (Ar*C*), 132.41 (Ar*C*), 131.49 (Ar*C*), 129.08 (Ar*C*), 127.17 (Ar*C*), 126.82 (Ar*C*), 118.81 (Ar*C*), 118.67 (Ar*C*), 117.04 (Ar*C*), 63.16 (2C, N*C*H_2). Anal. calcd for $C_{22}H_{20}N_2O_2$ (%): C, 76.72; H, 5.85; N, 8.13. Found: C, 76.77; H, 5.82; N, 8.16. HRMS (*m*/*z*): calcd for $C_{22}H_{20}N_2O_2$: 344.15; found: 344.20 $[M + H]^+$.

Pro-ligand b. The synthesis of pro-ligand **b** was similar to that of pro-ligand **a**, using *m*-xylylenediamine (0.136 g, 1.00 mmol) and 3,5-di-*tert*-butylsalicylaldehyde (0.468 g, 2.00 mmol). The product was isolated as a yellow solid. Yield: 0.418 g, 73.6%. ^{1}H NMR (500 MHz, chloroform-*d*, 25 °C) δ 13.64 (bs, 2H, O*H*), 8.48 (s, 2H, N=C*H*), 7.31 (d, *J* = 2.4 Hz, 2H, Ar*H*), 7.21–7.14 (m, 4H, Ar*H*), 7.05 (d, *J* = 2.4 Hz, 2H, Ar*H*), 4.78 (s, 4H, NCH_2), 1.43 (s, 18H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (125 MHz, chloroform-*d*, 25 °C): δ 166.76 (s, 2C, N=*C*H), 158.02 (Ar*C*), 140.03 (Ar*C*), 138.78 (Ar*C*), 136.67 (Ar*C*), 128.92 (Ar*C*), 127.39 (Ar*C*), 127.01 (Ar*C*), 126.86 (Ar*C*), 126.01 (Ar*C*), 117.84 (Ar*C*), 63.18 (2C, N*C*H_2), 35.01 (2C, *C*(CH$_3$)$_3$), 34.11 (2C, *C*(CH$_3$)$_3$), 29.40 (6C, C(*C*H$_3$)$_3$), 29.14 (6C, C(CH_3)$_3$). Anal. calcd for $C_{38}H_{52}N_2O_2$ (%): C, 80.24; H, 9.21; N, 4.92. Found: C, 80.27; H, 9.24; N, 4.90. HRMS (*m*/*z*): calcd for $C_{38}H_{52}N_2O_2$: 568.40; found: 568.40 $[M + H]^+$.

Pro-ligand c. The synthesis of pro-ligand **c** was similar to that of pro-ligand **a**, using *m*-xylylenediamine (0.136 g, 1.00 mmol) and 3,5-di-3,5-dichlorosalicylaldehyde (0.382 g, 2.00 mmol). The product was isolated as an orange solid. Yield: 0.421 g, 87.7%. ^{1}H NMR (500 MHz, chloroform-*d*, 25 °C) δ 14.36 (bs, 2H, O*H*), 8.36 (s, 2H, N=C*H*), 7.42 (t, *J* = 2.1 Hz, 2H, Ar*H*), 7.37 (m, 1H, Ar*H*), 7.27 (m, 1H, Ar*H*), 7.25 (s, 1H, Ar*H*), 7.22 (s, 1H, Ar*H*), 7.19 (t, *J* = 2.1 Hz, 2H, Ar*H*), 4.84 (s, 4H, NCH_2). ^{13}C{^{1}H} NMR (125 MHz, chloroform-*d*, 25 °C): δ 169.85 (s, 2C, N=*C*H), 162.11 (Ar*C*), 139.20 (Ar*C*), 133.52 (Ar*C*), 132.33 (Ar*C*), 129.77 (Ar*C*), 128.02 (Ar*C*), 127.34 (Ar*C*), 119.32 (Ar*C*), 119.56 (Ar*C*), 118.32 (Ar*C*), 63.28 (2C, N*C*H_2). Anal. calcd for $C_{22}H_{16}Cl_4N_2O_2$ (%): C, 54.80; H, 3.34; N, 5.81. Found: C, 54.77; H, 3.37; N, 5.83. HRMS (*m*/*z*): calcd for $C_{22}H_{16}Cl_4N_2O_2$: 480.00; found: 480.00 $[M + H]^+$.

Synthesis of complexes

Complex 1. A mixture of **a** (0.344 g, 1.00 mmol) and $AlMe_3$ (1.00 M in toluene, 1.00 mL, 1.00 mmol) in 15 mL toluene was stirred for 10 h at 25 °C under an argon atmosphere. And it was concentrated to 2 mL to afford a yellow powder, from which the mother liquor was decanted, and the product was washed with about 0.5 mL of hexane and dried under vacuum. The product was isolated as a yellow solid. Yield: 0.497 g, 83.7%. ^{1}H NMR (500 MHz, chloroform-*d*, 25 °C): δ 8.32 (bs, 2H, N=C*H*), 7.91 (m, 2H, Ar*H*), 7.81 (s, 1H, Ar*H*), 7.37 (s, 2H, Ar*H*), 7.26 (m, 2H, Ar*H*), 7.17 (dd, *J* = 12.6, 7.2 Hz, 1H, Ar*H*), 6.93 (m, 2H, Ar*H*), 6.54 (m, 2H, Ar*H*), 5.11 (s, 2H, NCH_2), 4.83 (s, 2H, NCH_2), −1.01 (s, 3H, AlCH_3). ^{13}C{^{1}H} NMR (125 MHz, chloroform-*d*, 25 °C) δ 171.70 (1C, N=*C*H), 160.84 (1C, N=*C*H), 146.47 (Ar*C*), 142.50 (Ar*C*), 139.68 (Ar*C*), 135.94 (Ar*C*), 134.79(Ar*C*), 134.75 (Ar*C*), 129.22 (Ar*C*), 128.46 (Ar*C*), 117.39 (Ar*C*), 67.21 (1C, N*C*H_2), 55.87 (1C, N*C*H_2), −9.42 (1C, Al*C*H_3). Anal. calcd for $C_{23}H_{21}AlN_2O_2$ (%): C, 71.86; H, 5.51; N, 7.29. Found: C, 71.82; H, 5.53; N, 7.25.

Complex 2. Complex **2** as a yellow solid was obtained in a similar way to **1** by stirring pro-ligand **b** (0.568 g, 1.00 mmol) and $AlMe_3$ (1.00 mmol) for 12 h at 70 °C. Yield: 0.549 g, 90.2%. ^{1}H NMR (500 MHz, chloroform-*d*, 25 °C) δ 7.93 (bs, 2H, N=C*H*), 7.40 (d, *J* = 10.8 Hz, 2H, Ar*H*), 7.28 (m, 3H, Ar*H*), 7.16 (dd, *J* = 12.9, 7.4 Hz, 1H, Ar*H*), 6.86 (bs, 2H, Ar*H*), 5.37 (s, 2H, NCH_2), 4.90 (s, 2H, NCH_2), 1.42 (d, *J* = 34.7 Hz, 18H, C(CH_3)$_3$), 1.15 (s, 18H, C(CH_3)$_3$), −0.63 (s, 3H, AlCH_3). ^{13}C{^{1}H} NMR (125 MHz, chloroform-*d*) δ 172.04 (s, 1C, N=*C*H), 161.58 (s, 1C, N=*C*H), 140.37 (Ar*C*), 138.91 (Ar*C*), 135.93 (Ar*C*), 132.03 (Ar*C*), 129.95 (Ar*C*), 129.80 (Ar*C*), 129.41 (Ar*C*), 128.80 (Ar*C*), 118.09 (Ar*C*), 58.81 (1C, N*C*H_2), 58.67 (1C, N*C*H_2), 35.26 (2C, *C*(CH$_3$)$_3$), 34.05 (2C, *C*(CH$_3$)$_3$), 31.32 (6C, C(*C*H$_3$)$_3$), 29.25 (6C, C(*C*H$_3$)$_3$), −9.85

(s, 1C, Al*C*H$_3$). Anal. calcd for $C_{39}H_{53}AlN_2O_2$ (%): C, 76.94; H, 8.77; N, 4.60. Found: C, 76.96; H, 8.79; N, 4.63.

Complex 3. Complex **3** as an orange solid was acquired in a similar way to **1** using pro-ligand **c** (0.480 g, 1.00 mmol) and $AlMe_3$ (1.00 mmol). Yield: 0.482 g, 92.3%. ^{1}H NMR (500 MHz, chloroform-*d*, 25 °C): δ 8.40 (bs, 2H, N=C*H*), 7.90–7.80 (m, 2H, Ar*H*), 7.62 (d, J = 10.6 Hz, 2H, Ar*H*), 7.40 (m, 1H, Ar*H*), 7.29 (d, J = 10.4 Hz, 1H, Ar*H*), 6.95 (s, 2H, Ar*H*), 5.42 (s, 2H, NCH_2), 4.97 (s, 2H, NCH_2), −0.89 (s, 3H, Al*C*H$_3$). ^{13}C{^{1}H} NMR (125 MHz, chloroform-*d*, 25 °C) δ 173.01 (1C, N=*C*H), 162.35 (1C, N=*C*H), 147.20 (Ar*C*), 144.45 (Ar*C*), 140.23 (Ar*C*), 137.00 (Ar*C*), 135.66 (Ar*C*), 136.03 (Ar*C*), 130.64 (Ar*C*), 129.71(Ar*C*), 118.23 (Ar*C*), 67.87 (1C, N*C*H$_2$), 56.38 (1C, N*C*H$_2$), −9.34 (1C, Al*C*H$_3$). Anal. calcd for $C_{23}H_{17}AlCl_4N_2O_2$ (%): C, 52.90; H, 3.28; N, 5.36. Found: C, 52.93; H, 3.34; N, 5.31.

Complex 4. Complex **4** as a yellow solid was acquired in a similar way to **1** using 1 eq. pro-ligand **b** (0.568 g, 1.00 mmol) and 2 eq. $AlMe_3$ (2.00 mmol). Yield: 0.608 g, 89.3%. ^{1}H NMR (500 MHz, chloroform-*d*, 25 °C) δ 8.16 (s, 2H, N=C*H*), 7.51 (d, J = 2.6 Hz, 2H, Ar*H*), 7.43 (m, 1H, Ar*H*), 7.29 (dd, J = 7.7, 1.7 Hz, 1H, Ar*H*), 7.25 (s, 1H, Ar*H*), 7.21 (s, 1H, Ar*H*), 7.00 (d, J = 2.6 Hz, 2H, Ar*H*), 4.71 (s, 4H, NCH_2), 1.40 (s, 18H, C(CH_3)$_3$), 1.27 (s, 18H, C(CH_3)$_3$), −0.94 (s, 12H, Al(CH_3)$_2$). ^{13}C{^{1}H} NMR (125 MHz, chloroform-*d*, 25 °C): δ 168.92 (s, 2C, N=*C*H), 138.93 (Ar*C*), 138.06 (Ar*C*), 137.90 (Ar*C*), 129.59 (Ar*C*), 129.07 (Ar*C*), 128.36 (Ar*C*), 128.26 (Ar*C*), 125.33 (Ar*C*), 119.15 (Ar*C*), 60.22 (4C, N*C*H$_2$), 35.01 (2C, *C*(CH$_3$)$_3$), 33.94 (2C, *C*(CH$_3$)$_3$), 31.43 (6C, C(*C*H$_3$)$_3$), 29.61 (6C, C(*C*H$_3$)$_3$), −10.20 (4C, Al(*C*H$_3$)$_2$). Anal. calcd for $C_{37}H_{31}AlCl_2N_2O$ (%): C, 71.96; H, 5.06; N, 4.54. Found: C, 72.01; H, 5.10; N, 4.61.

Polymerization of lactide in solution. In a representative polymerization reaction, the aluminum complex (50 μmol) was loaded in a flame-dried vessel containing a magnetic bar. The ampulla was immersed in an oil bath at 70 °C. The solution was stirred for about 10 minutes, when the initiator was activated completely by the co-initiator and subsequently the required quantity of lactides in toluene (100 mL) was added. After a certain reaction time, the polymer was isolated by precipitating with cold methanol or using a refrigerated centrifuge. The solid was collected and dried under vacuum at 35 °C for 40 h.

Conclusions

In summary, we reported a number of new aluminum complexes with modified *meta*-xylylenediamine and salicylaldehyde which were used as initiators for the polymerization of L-LA and *rac*-LA. The electron withdrawing substituent increased the rate of polymerization. The microstructure analysis of the polymers catalyzed by these complexes revealed that the salen ligand had a certain ability to affect the tacticity of the polymer, and this ability varies depending on the volume of the ligand.

Conflicts of interest

There are no conflicts to declare.

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