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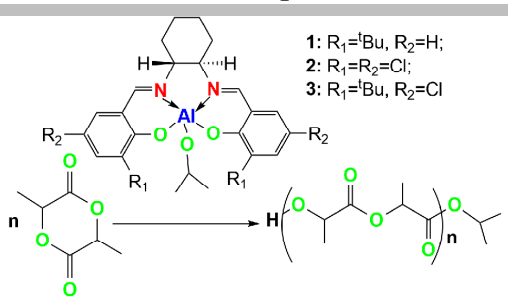
Paper

Graphical Abstract

Chiral Salen Aluminum complexes have been synthesized and investigated as initiators for L-lactide and *rac*-lactide polymerization.



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Paper

Ring-Opening Polymerization of Lactide using Chiral Salen Aluminum Complexes as Initiators: High Productivity and Stereoselectivity

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A family of aluminum complexes bearing chiral Salen ligands derived from (R,R)-1,2-diammoniumcyclohexane mono-(+)-tartrate salt and salicylaldehyde-modified were prepared. They were characterized by ^{1}H, ^{13}C NMR and elemental analysis. These complexes were used as initiators for the ring-opening polymerization (ROP) of L-lactide and *rac*-lactide. Complex **2** (R_1=R_2=Cl) showed the highest activity among these complexes for the ROP of L-lactide, and complex **3** (R_1=^{t}Bu, R_2=Cl) showed the highest stereoselectivity for the ROP of *rac*-lactide with enriched isotactic polylactide with a P_m of 0.91. The kinetics' data of the polymerization employed complex **3** as initiator indicated that the polymeric rate was both first-ordered in lactide as well as initiator.

Introduction

Today an increasing number of attentions to our environment have brouht about looking for environment friendly and sustainable polymers, which could substitude the normally used petroleum-based polymers.[1-4] Biocompatible, biodegradable and sustainable polylactide (PLA) starting from corn or sugar beet, is becoming one of the most promising polymers as a replacement for petroleum-based polymer.[5] PLA has been exploited for a wide scope of applications such as disposal containers, controlled release drug carriers, bio-absorbable bone nail, sutures, scaffolds, textiles and tissue-engineering material, etc.[3, 4] Existence of double chiral centers in the lactide (LA) leads to three species of LA stereoisomers (L-lactide (L-LA), D-lactide (D-LA) and *meso*-lactide (*meso*-LA), as shown in Fig. 1). The stereochemistry configuration of the polymer chains dominates the physical and chemical properties of PLA. Generally, PLA is prepared by the ring-opening polymerization (ROP) of lactide initiated by metal complexes, such as some alkoxides of tin, [6-8] aluminum,[9-14] zinc,[15-21] magnesium, [22-24] iron,[25, 26] titanium,[27-33] indium,[34, 35] rare-earth metals,[36-45] organo-catalysts,[46] and enzymes.[47] Aluminum catalysts were regarded as competent catalysts employed for ROP of LA because of their effectiveness in the control the stereoregular degrees of polymers.[48-56] Many efforts have been tried to get PLA with highly stereoregular degrees. This PLA is derived from *rac*-lactide (*rac*-LA) and catalyzed by stereoselective catalysts bearing Schiff base ligands. Lots of groups had tried to clarify the connection among stereochemistry of PLA, the aluminum catalysts based on Schiff base and *rac*-LA with various endeavors [48-57, 58-66] (Fig.2).

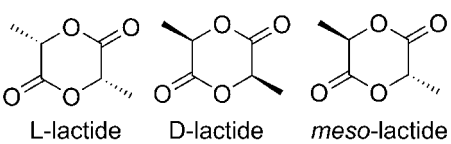
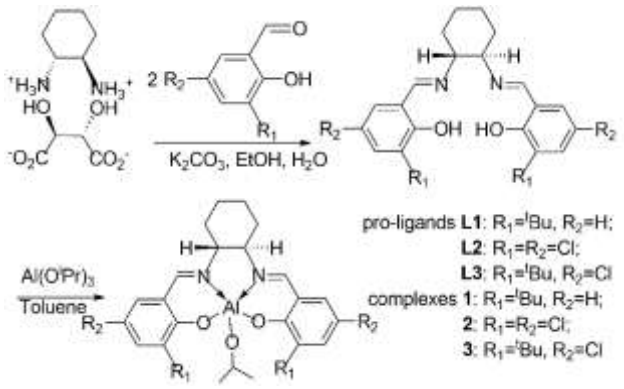


Figure 1. Stereoisomers of lactides.

One of the first catalysts employed for the stereoselective polymerization of *rac*-LA into isotactic PLA was reported by Spassky,[48] who utilized achiral Salen aluminum catalysts (Fig. 2) to prepare the multiblock copolymer $(PLLA–PDLA)_n$. Coates[49] uncovered subse-quently that a number of chiral aluminum complexes bearing Salen-type Schiff base could get the PLA of isotactic enrichment. Feijen[51, 52] applied a chiral bulky (R,R)-CyclohexylSalenAlOiPr [(R,R)-**1**] catalyst to get a polymer of isotactic enrichment. But the effect of the phenol ring substituent on stereoselectivity in the ROP of the *rac*-lactide initiated by salen aluminum complexes was not further studied in detail. Our group[57-65] have reported various of aluminum complexes based on Salen ligands. These complexes were proved to be efficient living catalysts for the stero-controlled ROP of LA. Intrigued by the success of aluminum complexes based on Salen ligands in polymerization catalysis, we are very interested in studying the catalytic behavior of aluminum complexes based on Salen type Schiff base derived from (R,R)-1,2-diaminocyclohexane and salicylaldehyde derivatives (*para* or *ortho* positional substituents on phenyl rings are selected from H, ^{t}Bu or Cl: pro-ligand **L1** R_1=^{t}Bu, R_2=H; **L2** R_1=R_2=Cl; **L3** R_1=^{t}Bu, R_2=Cl, see Scheme 1). These complexes, to our knowledge, have not been studied in the ROP of LA. In this work, we report a series of Salen aluminum complexes with Schiff base ligands and the preliminary application on initiating for the ROP of LA.



Scheme 1 The preparations of pro-ligands and aluminum complexes.

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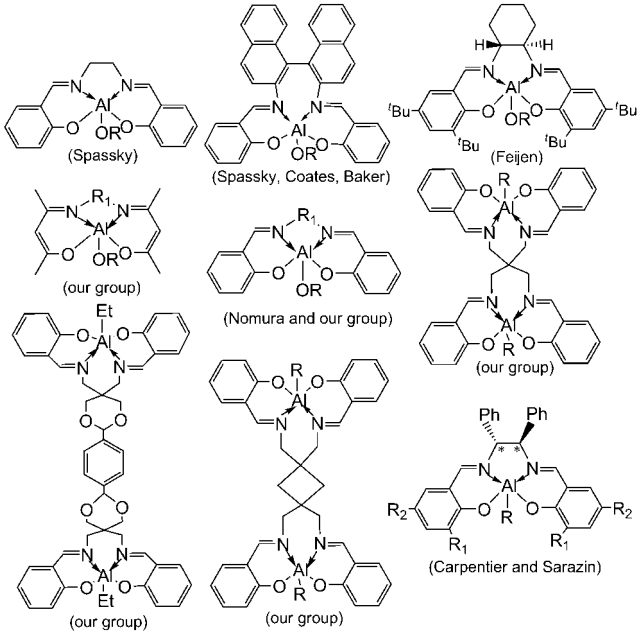

Figure 2 Salen aluminum catalysts for the ROP of LA.

Results and Discussion

Complexes synthesis and characterization

The syntheses of pro-ligands **L1**−**L3** were outlined in Scheme 1, these pro-ligands were synthesised through the condensation reaction starting from the commercial (R,R)-1,2-diammoniumcyclohexane mono-(+)-tartrate salt and salicylaldehyde-modified in high yields (86.5–91.4%) according to a described procedure.[51, 52, 67] Three singlet proton resonance signals were observed at δ 8.37, 8.57 and 8.33 ppm, which were assigned to the protons of -N=C*H*- in pro-ligands **L1**−**L3**, respectively (see ESI). This suggested that these protons of imines in ligands were equivalent. Complexes **1**−**3** were prepared by the reaction of ligands **L1**−**L3** with aluminum isopropoxide in toluene according to a described procedure (see Scheme 1).[51, 52] All three complexes were sensitive to air and moisture. Complexes **1**−**3** were characterized by ^{1}H, ^{13}C NMR in $CDCl_3$ and elemental analysis. The ^{1}H and ^{13}C NMR spectra of complexes **1**−**3** showed one Salen ligand and one isopropoxy were coordinated to aluminum atom. For example, ^{1}H NMR spectrum of **3** showed the resonances at δ 0.87, 0.83 and 3.65 ppm were assigned to the methyl protons and methine proton of the isopropoxy, respectively. Interestingly, the ^{1}H NMR spectra of complexes **1–3** revealed that both the protons of cyclohexyl as well as phenyl moieties are resolved into two different chemical environments in these ligands. For instance, two sets of resonances from imine protons (δ 8.32, 8.07 ppm) and the α-protons of the cyclohexane moiety (δ ca. 3.94, 3.13 ppm) were observed in the ^{1}H NMR spectrum of complex **3** (see ESI). This spectroscopic inequivalence showed that these complexes maybe adopted distorted square pyramidal or distorted trigonal bipyramidal geometries in solution. Similar observations were also previously reported by the references.[51, 52]

Ring-opening polymerization of L-LA and *rac*-LA

ROP of L-LA and *rac*-LA used complexes **1–3** as initiators had been systematically examined in toluene or THF as shown in Table 1 and Table 2. Experimental results revealed that these complexes were efficient initiators for ROP of LA. Molecular weight of the PLA polymers was measured by GPC. ^{1}H NMR and GPC were applied to calculate the monomer conversion and the number-averaged molecular weights of the PLA. These aluminum complexes showed moderate to high productivities (79–96%) at 70 °C. The number-averaged molecular weights (M_n were calculated according to formula $M_n = 0.58M_{n(GPC)}$[68]) of PLA were close to theoretical ones ($M_{n(calcd)}$ calculated from the monomer-to-catalyst molar ratio) with narrow molecular weight distributions (PDI: 1.08–1.26). The data of L-LA conversions versus polymerization time were shown in Figure 3. It is noteworthy that the activities of these complexes reduced with the raise of substituent's bulk on the phenyl parts, while electron-withdrawing substituents increased polymerization rate. Complex **2** displayed the highest activity (93.7% monomer conversion Table 1, Entry 2) at the same polymerization conditions among these complexes (Table 1, Entries 1, 2 and 3). Similar situations also appeared in the previous reports.[69-71] Moreover, the Salen ligands had certain ability to affect the PDI of the PLA, and this ability depended on volume of ligands. For instance, the PDI decreased from 1.26 to 1.08 with the raise of the bulk of the *para* positional substituents on phenyl rings from Cl to ^{t}Bu (see Table 1, Entries 2, 3).

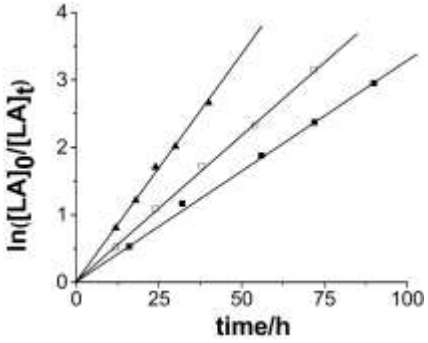

Figure 3. Kinetics of the ROP of L-LA by **3** at 70 °C in toluene. see Table 1, Entries 4, 5 and 6. $[LA]_0$ = 0.5 mol L^{-1}; ■: $[Al]_0$ = 0.005 mol L^{-1}, $[LA]_0/[Al]_0$ = 100, k_{app} = 9.122 × 10^{-6} s^{-1}; □: $[Al]_0$ = 0.0067 mol L^{-1}, $[LA]_0/[Al]_0$ = 75, k_{app} = 12.15 × 10^{-6} s^{-1}; ▲: $[Al]_0$ = 0.010 mol L^{-1}, $[LA]_0/[Al]_0$ = 50, k_{app} = 18.47 × 10^{-6} s^{-1}; where k_{app} was the apparent polymerization rate constant, the slop of curve.

Table 1 Representative polymerization data of L-LA with complexes **1–3**.[a]

Entry	Com-plex	*T* h	$[LA]_0/[Al]_0$	Conv. % [b]	$M_{n(calcd)}$ ×10^{-4}[c]	$M_{n(GPC)}$ ×10^{-4}[d]	M_n ×10^{-4}[e]	PDI[d]	k_{app}[f] ×10^{-6} s^{-1}
1	**1**	56	100	79	1.13	1.90	1.10	1.11	N.A.
2	**2**	56	100	94	1.35	2.26	1.31	1.26	N.A.
3	**3**	56	100	85	1.22	2.12	1.23	1.08	N.A.
4	**3**	90	100	95	1.37	2.34	1.36	1.10	9.122
5	**3**	72	75	96	0.72	1.21	0.70	1.13	12.15
6	**3**	40	50	93	0.67	1.12	0.65	1.11	18.47

[a] The polymerization reactions carried out in toluene solution at 70 °C; $[LA]_0$ = 0.5 mol L^{-1}. [b] Measured by ^{1}H NMR. [c] Calculated from the molecular weight of LA × $[LA]_0/[Al]_0$ × conversion + $M_w^{isopropoxy}$. [d] Obtained from GPC analysis and calibrated against polystyrene standard. [e] The calibration value of M_n could be calculated according to formula $M_n = 0.58M_{n(GPC)}$.[68] [f] Apparent rate constant in the ROP of L-LA.

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Table 2 Representative polymerization data of *rac*-LA with complexes **1**–**3**.[a]

Entry	Complex	*T* h	Conv. % [b]	$M_{n(calcd)}$ ×10^{-4}[c]	$M_{n(GPC)}$ ×10^{-4}[d]	M_n ×10^{-4} [e]	PDI[d]	P_m [f]
1	**1**	56	48	0.70	1.19	0.69	1.15	0.85
2	**2**	56	63	0.90	1.62	0.94	1.22	0.57
3	**3**	56	55	0.79	1.31	0.76	1.16	0.88
4	**3**	90	64	0.92	1.62	0.94	1.17	0.87
5	**3**	240	92	1.32	2.20	1.28	1.14	0.88
6	**3**	180	26	0.37	0.60	0.35	1.10	0.91

[a] The polymerization reactions proceeded in toluene at 70 °C except that a reaction, Entry 6, carried out in THF at 25 °C; $[LA]_0$ = 0.5 mol L^{-1}, $[LA]_0/[Al]_0$ = 100. [b] Measured by ^{1}H NMR. [c] Calculated from the molecular weight of LA × $[LA]_0/[Al]_0$ × conversion. [d] Obtained from GPC analysis and calibrated against polystyrene standard. [e] The calibration value of M_n have to be calibrated by M_n= 0.58$M_{n(GPC)}$.[68] [f] Homonuclear decoupled ^{1}H NMR spectra of the methine part of poly(*rac*-LA).

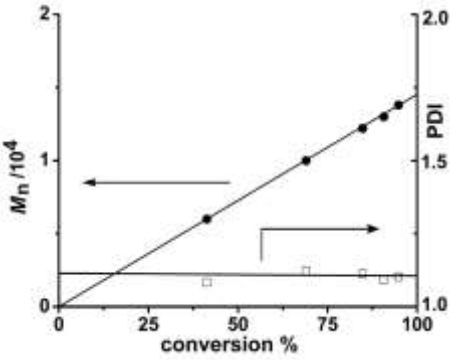

Figure 4. Plots of PLA' s M_n and PDI in the light of L-LA conversion employing complex **3**, $[LA]_0/[Al]_0$ = 100, in toluene at 70 °C.

Kinetic Studies

Kinetic studies of L-lactide polymerization with representative **3** as initiator was conducted in various monomer/initiator ratios ($[LA]_0$ = 0.5 mol L^{-1}, $[LA]_0/[Al]_0$ ranged from 50 to 100) in toluene at 70 °C, and the monomer conversion was monitored by ^{1}H NMR as a function of the polymerization time. The data of conversions versus time were plotted in Fig. 3. First-order kinetics in monomer was observed equality (1)

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

(where k_{app} was the apparent polymerization rate constant, the slop of curve). The molecular weight of the polymers propagated linearly depending on the raise of the monomer transformation rate as well as the PDI of these polymers were relatively narrow (1.08–1.12, see Fig. 4), this manifested the living feature of the catalytic system. In order to deduce the order of initiator, k_{app} was plotted versus the concentration of **3**. As shown in Fig. 5, k_{app} increased linearly with the **3** concentration, manifesting that the order in initiator was first-order. Hence, the polymerization of L-LA using **3** followed the kinetics equation (2)

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

(where k_p was the polymerization rate constant, $k_p = k_{app}/[Al]$).

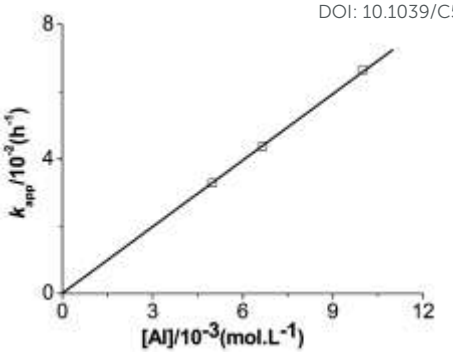

Figure 5. k_{app} versus the concentration of **3** for the L-LA polymerization in toluene at 70 °C ($[LA]_0$ = 0.5 mol L^{-1}, k_p = 1.831 ×10^{-3} L mol^{-1}s^{-1}).

Figure 6. Homonuclear decoupled ^{1}H NMR spectrum of the methine part of poly(*rac*-LA) using **3** at 25 °C, P_m = 0.91, in $CDCl_3$ (Table 2, Entry 6).

Stereoselective polymerization

Furthermore, the poly(*rac*-LA) (Table 2, Entry 6) with the homonuclear decoupled ^{1}H NMR spectrum of the methane fragment[72] (Fig. 6) was also researched. The P_m value, 0.91, manifested that the poly(*rac*-LA) obtained was predominantly isotatic.[73] The experimental results showed that the P_m selectivities increased obviously from 0.57 to 0.88 with the raise of the bulk of the substitutes on ligands in these complexes at 70 °C in toluene (see Table 2, Entries 2 and 3). For complex **3**, the P_m value increased lightly from 0.88 to 0.91 with the temperature from 70 to 25 °C (Table 2, Entries 3, 5).

Mechanism of lactide polymerization

In order to research the mechanism of polymerization initiated by Salen aluminum complex, end group analysis of the oligomer, which was prepared by the ROP of the L-LA at small monomer to initiator ratio ($[LA]_0/[\mathbf{3}]_0$ = 12/1) was measured by ^{1}H NMR (Fig. S1). Two groups of peaks appearing as a triplet at 1.24 ppm and the quartet at 4.34 ppm, with an integral ratio of 6/1, were ascribed to the methyl protons of the isopropoxycarbonyl end group and the methane proton neighboring the hydroxyl end group. This clearly revealed that the polymer was capped with one isopropyl ester

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group and one hydroxyl group,[58, 59, 74, 75] so the polymerization possibly selected a coordination insertion mechanism.[76-79]

Conclusions

In conclusion, a number of novel Salen aluminum complexes were synthesized and characterized. All these complexes were viable initiators for lactide polymerization with high monomer conversion. Kinetics studies revealed polymerizations were living with the narrow molar mass distributions. Within the series of Salen ligands, the electron withdrawing ligand promoted polymerization rate. Microstructural analysis of polylactide initiated by these complexes indicated that the chiral Salen ligands had competent ability to control the stereoregular degrees of the polymer, and this sort of ability varied with the volume of substituents on phenyl rings in ancillary ligands.

Experimental

General considerations

All experiments were performed under a dry nitrogen atmosphere using standard Schlenk techniques or an inert-gas glovebox. ^{1}H NMR and ^{13}C NMR spectra were performed on Bruker AV 300M apparatus at 25 °C in $CDCl_3$ for compounds and polymers. Elemental analysis was perfomed by a Varian EL microanalyzer. The monomer conversions were confirmed by the integral signals at 1.65 ppm standed for LA monomer and 1.59 ppm standed for PLA in $CDCl_3$. P_m values were computed from different tetrad intensities measured by homonuclear decoupled ^{1}H NMR spectrum. Gel permeation chromatography (GPC) measurements were 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. Toluene and THF used for polymerization were distilled from sodium benzophenone ketyl solution just before use. Pentane, ethyl acetate and chloroform-d were distilled over calcium hydride. Lactides were stored under nitrogen at -20 °C and recrystallized from dry ethyl acetate and dried under reduced pressure. (R,R)-1,2-diammoniumcyclohexane mono-(+)-tartrate salt was purchased from Aldrich and stored under dry nitrogen at -20 °C. Other reagents such as aluminum isopropoxide, 3-tert-butylsalicylaldehyde, 3-tert-butyl-5-chlorosalicylaldehyde and 3,5-dichlorosalicylaldehyde were purchased from J&K company.

General procedure for the synthesis of Salen aluminum complexes

The pro-ligand (2.85 mmol), aluminum isopropoxide (0.583 g, 2.85 mmol), and toluene (20 mL) were added into a flamed-dried Schlenk tube equipped with a magnetic stirring bar. The mixture was stirred for 3 days at 80 °C and then slowly cooled to ambient temperature, the solution was transferred to a glovebox and the solvent was removed under reduced pressure. The residual solid was then washed with cold pentane (1.0 mL×2), filtered, and dried under reduced pressure. Yield: 87.8–92.6%. Complex **3** was prepared according to the reference.[80]

Complex 1: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (s, 1H, N=C*H*), 8.03 (s, 1H, N=C*H*), 7.24 (d, J = 7.9 Hz, 1H, Ph*H*), 7.17 (d, J = 7.9 Hz, 1H, Ph*H*), 7.08 (d, J = 7.4 Hz, 1H, Ph*H*), 7.01 (d, J = 7.4 Hz, 1H, Ph*H*), 6.90–6.72 (m, 2H, Ph*H*), 3.88–3.80 (m, 1H, N-C*H*-), 3.72 (sept, J = 6.0 Hz, 1H, OC*H*(CH_3)$_2$), 3.11–3.06 (m, 1H, N-C*H*-), 2.35–2.00 (m, 4H, (CH_2)$_4$), 1.47 (s, 9H, C(CH_3)$_3$), 1.44 (s, 9H, C(CH_3)$_3$), 1.40–1.34 (m, 4H, (CH_2)$_2$), 0.86 (d, J = 6.0 Hz, 3H, OCH(CH_3)$_2$), 0.82 ppm (d, J = 6.0 Hz, 3H, OCH(CH_3)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.34 (1C, N=*C*H), 163.04 (1C, N=*C*H), 154.89 (1C, Ph*C*), 152.24 (1C, Ph*C*), 138.54 (1C, Ph*C*), 138.06 (1C, Ph*C*), 128.99 (1C, Ph*C*), 127.80 (1C, Ph*C*), 127.00 (1C, Ph*C*), 126.25 (1C, Ph*C*), 120.13 (1C, Ph*C*), 119.83 (1C, Ph*C*), 118.00 (1C, Ph*C*), 116.42 (1C, Ph*C*), 63.06 (1C, N-*C*H-), 62.24 (1C, O*C*H(CH_3)$_2$), 61.81 (1C, N-*C*H-), 35.02, 34.43 (2C, *C*(CH_3)$_3$), 29.87 (1C, *C*H$_2$), 28.03 (1C, *C*H$_2$), 27.55 (3C, C(*C*H$_3$)$_3$), 27.02 (3C, C(*C*H$_3$)$_3$), 26.17 (1C, *C*H$_2$), 26.03 (1C, *C*H$_2$), 24.39 (1C, OCH(*C*H$_3$)$_2$), 23.36 ppm (1C, OCH(*C*H$_3$)$_2$). Anal. Calcd for $C_{31}H_{43}AlN_2O_3$ (%): C, 71.79; H, 8.36; N, 5.40. Found: C, 71.76; H, 8.34; N, 5.43.

Complex 2: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (s, 1H, N=C*H*), 8.09 (s, 1H, N=C*H*), 7.56 (s, 1H, Ph*H*), 7.53 (s, 1H, Ph*H*), 7.20 (s, 1H, Ph*H*), 7.16 (s, 1H, Ph*H*), 4.07–3.90 (m, 1H, N-C*H*-), 3.73 (sept, J = 6.0 Hz, 1H, OC*H*(CH_3)$_2$), 3.26–3.11 (m, 1H, N-C*H*-), 2.68–1.42 (m, 8H, (CH_2)$_4$), 0.94 (d, J = 6.0 Hz, 3H, OCH(CH_3)$_2$), 0.89 ppm (d, J = 6.0 Hz, 3H, OCH(CH_3)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.67 (1C, N=*C*H), 166.80 (1C, N=*C*H), 157.97 (1C, Ph*C*), 155.23 (1C, Ph*C*), 139.58 (1C, Ph*C*), 136.44 (1C, Ph*C*), 132.04 (1C, Ph*C*), 129.77 (1C, Ph*C*), 128.53 (1C, Ph*C*), 127.84 (1C, Ph*C*), 126.23 (1C, Ph*C*), 123.35 (1C, Ph*C*), 121.90 (1C, Ph*C*), 116.93 (1C, Ph*C*), 67.64 (1C, O*C*H(CH_3)$_2$), 65.17 (1C, N-*C*H-), 64.02 (1C, N-*C*H-), 30.38 (1C, *C*H$_2$), 29.03 (1C, *C*H$_2$), 27.95 (1C, *C*H$_2$), 26.40 (1C, *C*H$_2$), 26.07 (1C, OCH(*C*H$_3$)$_2$), 25.89 ppm (1C, OCH(*C*H$_3$)$_2$). Anal. Calcd for $C_{23}H_{23}AlCl_4N_2O_3$ (%): C, 50.76; H, 4.26; N, 5.15. Found: C, 50.79; H, 4.28; N, 5.19.

General procedure for lactide polymerization

The substrate and solvent were prepared in sealed glass ampoules using the standard Schlenk techniques. In a representative polymerization reaction, aluminum complex (0.50 mmol) and required quantities of lactides in toluene (100 mL) were placed in a dry ampoule with a magnetic bar at 70 °C. To the vigorously stirred solution, a required quantities of lactides were added, resulted in $[LA]_0$ = 0.50 mol L^{-1} and $[LA]_0$: $[Al]_0$ = 100 : 1. At selected reaction time intervals, ca. 0.60 mL aliquots were removed and the conversion was determined by ^{1}H NMR. At high conversion, the reaction was terminated by adding glacial acetic acid, the polymer was precipitated by cold methanol or refrigerated centrifuge. The polymers were collected and dried in vacuo at 40 °C for 24 h.

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Notes and references

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† Electronic Supplementary Information (ESI) available: The ^{1}HNMR spectrum of poly(L-LA) oligomer in Figs S1. See DOI: 10.1039/b000000x/

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