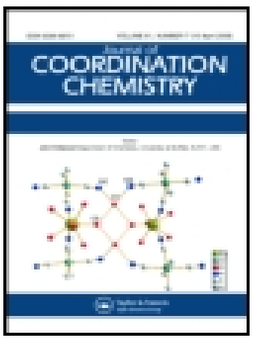

Journal of Coordination Chemistry

ISSN: 0095-8972 (Print) 1029-0389 (Online) Journal homepage: http://www.tandfonline.com/loi/gcoo20

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To cite this article: Yuan Cui, Dongni Li, Bo Gao, Yuqi Zhou, Li Chen, Baoguo Qiu, Yanhui Li, Qian Duan & Ninghai Hu (2015): Ring-opening polymerization of lactide using Salen aluminum complexes bearing Schiff-base ligands derived from cis-1,2-cyclohexanediamine, Journal of Coordination Chemistry, DOI: 10.1080/00958972.2015.1121248

To link to this article: http://dx.doi.org/10.1080/00958972.2015.1121248

Publisher: Taylor & Francis
Journal: *Journal of Coordination Chemistry*
DOI: http://dx.doi.org/10.1080/00958972.2015.1121248

Ring-opening polymerization of lactide using Salen aluminum complexes bearing Schiff-base ligands derived from *cis*-1,2-cyclohexanediamine

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Three aluminum complexes supported by Salen ligands derived from *cis*-1,2-cyclohexanediamine and salicylaldehyde derivatives were synthesized. They were characterized by ^{1}H, ^{13}C NMR spectra and elemental analysis. X-ray diffraction analysis revealed that aluminum was in distorted square pyramidal geometry in **2**. These complexes were employed as catalysts for the ring-opening polymerization of L-lactide and *rac*-lactide. Complex **2** showed the highest activity among these complexes with isopropanol for the ROP of L-lactide and **3** showed the highest stereoselectivity for the ROP of *rac*-lactide attaining partially isotactic polylactide with a P_m of 0.75. The kinetic data of the polymerization utilizing **3** as catalyst showed that the polymeric rate was first-order to the monomer and catalyst.

Keywords: Aluminum; Salen; Biodegradable; Lactide; Ring-opening polymerization

1. Introduction

People are searching for sustainable and environment-friendly polymers, which could take place of the more normally used petroleum-based polymers [1]. Biocompatible, biodegradable and sustainable polylactide (PLA), whose starting materials is from corn or sugar beets, is becoming one of the most promising polymers as a partial replacement for petroleum-based polymers [2]. PLA has been exploited for a scope of applications including disposal containers, bone fracture fixation devices, controlled release drug carriers, sutures, scaffolds, textiles, tissue engineering,

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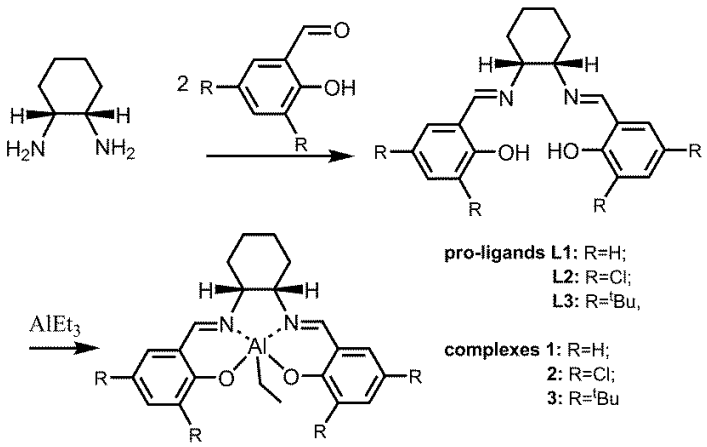
etc. [1, 2]. Presence of two chiral centers in the lactide (LA) monomer results in different LA stereoisomers, namely L-lactide (L-LA), D-lactide (D-LA) and *meso*-lactide (figure 1). The stereochemistry of the polymer chains influences PLA's physical and chemical properties [2b]. PLA is generally synthesized by the ring-opening polymerization (ROP) of lactide catalyzed by metal complexes, such as complexes of tin [3], aluminum [4], zinc [5], magnesium [6], iron [7], titanium [8], indium [9] and rare-earth metals [10]; organo-catalysts [11] and enzymes [12]. Aluminum catalysts are effective catalysts employed for ROP in the synthesis of PLA due to their high effectiveness to control the stereo-regularities of the polymer [4, 13]. Efforts have been tried to attain PLA with high stereo-regularities, derived from *rac*-lactide (*rac*-LA) and catalyzed by stereoselective catalysts based on Schiff-base ligands [4g, 13, 14]. Some groups had attempted to explain the relation among *rac*-lactide, aluminum catalysts based on Salen-type Schiff base and stereo-regularities of PLA [13, 14] (figure 2).

Spassky [13a] discovered an aluminum catalyst (see figure 2) supported by a Salen-type Schiff-base ligand, which was derived from R-(+)-1,1'-dinaphthalene-2,2'-diamine, could stereo-control polymerization of *rac*-LA. Subsequently, Coates [13b] reported that a chiral aluminum complex bearing a Salen-type Schiff base could afford enriched isotactic PLA. Feijen *et al*. [13e] reported a chiral catalyst (R,R)-cyclohexylSalenAlOiPr [(R,R)-**1**] polymerized *rac*-LA to get isotactic stereoblock PLA; the effect of the phenyl ring substituent on stereoselectivity in the ROP of the *rac*-lactide initiated by Salen aluminum complexes was not further studied.

Chen, Pang, Gao and Duan [14] reported a number of aluminum complexes based on Salen ligands. These complexes were proved to be effective catalysts for the controlled ROP of LA. Moreover, the more sterically hindered alkyl aluminum catalysts could effectively control polymer microstructures and promote the formation of an isotactic or heterotactic bias in the polymerization of *rac*-LA. Intrigued by the success of aluminum complexes based on Salen ligands in polymerization catalysis [13, 14], we are very interested in researching the catalytic behavior of aluminum complexes based on Salen type Schiff bases derived from salicylaldehyde derivatives (salicylaldehyde, 3,5-dichlorosalicylaldehyde and 3,5-di-tert-butylsalicylaldehyde from Sigma-Aldrich) and *cis*-1,2-cyclohexanediamine (see scheme 1). A ligand derived from *cis*-1,2-cyclohexanediamine has not been reported before. In this work, we report a series of

Salen aluminum complexes with Schiff-base ligands derived from *cis*-1,2-cyclohexanediamine and the applications as catalysts for the ROP of LA.



Scheme 1. The preparation of pro-ligands and complexes.

2. Experimental

2.1. *General*

All experiments used standard Schlenk or glovebox technology. THF and toluene were distilled from sodium and benzophenone immediately before use. L-lactide and *rac*-lactide from Aldrich, crystallized from dry toluene, were purified just before use by sublimation *in vacuo* (10^{-3} mbar, bath temperature: 85 °C) and distributed into glass ampoules equipped with breakseals. Elemental analyses were performed by a Varian EL microanalyzer. ^{1}H NMR and ^{13}C NMR spectra were performed on a Bruker AV 300M apparatus at 25 °C in $CDCl_3$ for compounds and polymers. The monomer conversions were confirmed by the integral at 1.65 ppm which was attributed to LA monomer and 1.59 ppm which was attributed to 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 eluent (flow rate: 1 mLmin^{-1}, at 35 °C). The molecular weight was adjusted through the PS standard. Crystallographic data were gathered on a Bruker APEX CCD diffractometer using graphite-monochromated MoK_α radiation (λ = 0.71073 Å) at 187.5 K. All non-hydrogen atoms were refined anisotropically. Hydrogens were introduced in calculated positions with the displacement factors of the host carbons. $AlEt_3$,

3,5-di-tert-butylsalicylaldehyde, *cis*-1,2-cyclohexanediamine, isopropanol, *p*-toluenesulfonic acid, 3,5-dichlorosalicylaldehyde and salicylaldehyde were from Sigma-Aldrich.

2.2. *Synthesis of pro-ligands*

General procedure: a mixture of *cis*-1,2-cyclohexanediamine (5.0 mmol), modified salicylaldehyde (10.0 mmol) and *p*-toluenesulfonic acid (0.20 mmol) in toluene (150 mL) were refluxed for 4-18 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 = 12/1) as the eluent. Then the product as yellow powder was acquired in 71.2–90.3% yields. Pro-ligand **L3** was prepared according to the reference [15].

2.2.1. Pro-ligand L1. ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.33 (bs, 2H, O*H*), 8.13 (s, 2H, N=C*H*), 7.20 (t, *J* = 6.2 Hz, 2H, Ar*H*), 7.09 (d, *J* = 6.0 Hz, 2H, Ar*H*), 6.80 (d, *J* = 6.1 Hz, 2H, Ar*H*), 6.72 (t, *J* = 6.0 Hz, 2H, Ar*H*), 3.24–3.20 (m, 2H, N-C*H*-), 1.97–1.34 (m, 8H, (CH_2)$_4$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.24 (2C, N=*C*H), 158.01, 134.55, 129.94, 126.29, 123.47, 116.38 (12C, Ar*C*), 68.96 (2C, N-*C*H-), 30.02, 27.39 ppm (4C, (*C*H_2)$_4$). Anal. Calcd for $C_{20}H_{22}N_2O_2$ (%): C, 74.51; H, 6.88; N, 8.69. Found: C, 74.49; H, 6.84; N, 8.65. MS, (EI) m/z: calcd. for $C_{20}H_{22}N_2O_2$ [M]+ 322.2. Found: 322.1.

2.2.2. Pro-ligand L2. ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.74 (bs, 2H, O*H*), 8.25 (s, 2H, N=C*H*), 7.29 (s, 2H, Ar*H*), 7.12 (s, 2H, Ar*H*), 3.41–3.15 (m, 2H, N-C*H*-), 2.06–1.24 (m, 8H, (CH_2)$_4$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.57 (2C, N=*C*H), 157.43, 137.97, 131.34, 127.68, 125.82, 118.87 (12C, Ar*C*), 69.23 (2C, N-*C*H-), 31.54 (2C, (*C*H_2)$_2$), 26.44 ppm (2C, (*C*H_2)$_2$). Anal. Calcd for $C_{20}H_{18}Cl_4N_2O_2$ (%): C, 52.20; H, 3.94; N, 6.09. Found: 52.24; H, 3.96; N, 6.11. MS, (EI) m/z: calcd. for $C_{20}H_{18}Cl_4N_2O_2$ [M]+ 458.0. Found: 458.1.

2.3. *Synthesis of Salen aluminum complexes*

General procedure: pro-ligand (2.0 mmol) dissolved in 20 mL of toluene was added to a stirred solution of $AlEt_3$ (2.0 mmol) in 10 mL of toluene. The reaction mixture was stirred at 40 °C overnight and then cooled to ambient temperature. The solvent was evaporated at reduced pressure to leave a powder. The product was purified by washing with dry hexane (1.0 mL×2).

2.3.1. Complex 1. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (s, 1H, N=C*H*), 7.97 (s, 1H, N=C*H*), 7.25 (m, 2H, Ar*H*), 7.07 (d, J = 8.9 Hz, 2H, Ar*H*), 6.88 (m, 2H, Ar*H*), 6.64 (m, 2H, Ar*H*), 3.65–3.51 (m, 1H, N-C*H*-), 2.76–2.61 (m, 1H, N-C*H*-), 2.22–1.44 (m, 8H, $(CH_2)_4$), 0.79 (t, J = 8.2 Hz, 3H, $AlCH_2CH_3$), –0.17 ppm (q, J = 8.2 Hz, 2H, $AlCH_2CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.25 (1C, N=*C*H), 164.33 (1C, N=*C*H), 156.41, 134.17, 132.23, 130.04, 128.75, 127.57, 125.00, 123.24, 122.13, 120.78, 117.54, 113.82 (12C, Ar*C*), 67.66, 62.09 (2C, N-*C*H-), 29.79, 27.10, 24.23, 23.17 (4C, $(CH_2)_4$), 9.55 (1C, $AlCH_2CH_3$), –0.47 ppm (1C, $AlCH_2CH_3$). Anal. Calcd for $C_{22}H_{25}AlN_2O_2$ (%): 70.20; H, 6.69; N, 7.44. Found: 70.23; H, 6.71; N, 7.47.

2.3.2. Complex 2. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (s, 1H, N=C*H*), 7.75 (s, 1H, N=C*H*), 7.37 (s, 1H, Ar*H*), 7.30 (s, 1H, Ar*H*), 7.13 (s, 1H, Ar*H*), 7.02 (s, 1H, Ar*H*), 3.69–3.56 (m, 1H, N-C*H*-), 2.80–2.67 (m, 1H, N-C*H*-), 2.27–1.19 (m, 8H, $(CH_2)_4$), 0.82 (t, J = 8.1 Hz, 3H, $AlCH_2CH_3$), –0.15 ppm (q, J = 8.1 Hz, 2H, $AlCH_2CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.22 (1C, N=*C*H), 166.74 (1C, N=*C*H), 158.22, 137.53, 134.28, 132.39, 129.98, 129.03, 126.94, 125.07, 124.28, 122.49, 119.00, 115.37 (12C, Ar*C*), 68.92, 64.11 (2C, N-*C*H-), 30.22, 29.07, 26.19, 24.02 (4C, $(CH_2)_4$), 9.90 (1C, $AlCH_2CH_3$), –0.18 ppm (1C, $AlCH_2CH_3$). Anal. Calcd for $C_{22}H_{21}AlCl_4N_2O_2$ (%): C, 51.39; H, 4.12; N, 5.45. Found: C, 51.36; H, 4.10; N, 5.42. Crystals of **2** suitable for an X-ray structure determination were grown from toluene solution. CCDC: 908768.

2.3.3. Complex 3. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (s, 1H, N=C*H*), 8.01 (s, 1H, N=C*H*), 7.24 (m, Ar*H*, 1H), 7.18 (m, Ar*H*, 1H), 7.10 (m, Ar*H*, 1H), 6.89, (m, Ar*H*, 1H), 3.55–2.91 (m, 2H, N-C*H*-), 1.92–1.41 (m, 8H, $(CH_2)_3$), 1.32 (s, 9H, $C(CH_3)_3$), 1.25 (s, 9H, $C(CH_3)_3$), 1.19 ppm (s, 9H, $C(CH_3)_3$), 1.08 (s, 9H, $C(CH_3)_3$), 0.72 (t, J = 8.3 Hz, 3H, $AlCH_2CH_3$), –0.29 ppm (q, J = 8.3 Hz, 2H, $AlCH_2CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.72 (1C, N=*C*H), 156.55 (1C, N=*C*H), 149.33, 140.30, 130.50, 129.12, 126.03, 125.92, 123.24, 122.41, 120.03, 118.79, 110.45, 108.76 (12C, Ar*C*), 60.17 (1C, N-*C*H-), 58.94 (1C, N-*C*H-), 35.54 (1C, $C(CH_3)_3$), 34.78 (1C, $C(CH_3)_3$), 33.73 (1C, $C(CH_3)_3$), 32.28 (1C, $C(CH_3)_3$), 28.10, 27.81, 26.10, 24.52 (4C, $(CH_2)_4$), 25.55, (3C, $C(CH_3)_3$), 24.43, (3C, $C(CH_3)_3$), 22.77, (3C, $C(CH_3)_3$), 21.05 ppm (3C, $C(CH_3)_3$), 7.89 (1C, $AlCH_2CH_3$), –2.24 ppm (1C, $AlCH_2CH_3$). Anal. Calcd for $C_{38}H_{57}AlN_2O_2$ (%): C, 75.96; H, 9.56; N, 4.66. Found: C, 75.94; H, 9.53; N, 4.62.

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2.4. *General procedure for lactide polymerization*

The substrate and solvent were prepared in sealed glass ampoules using standard Schlenk techniques. In a representative polymerization reaction, aluminum complex (0.50 mmol) and isopropanol (0.50 mmol) in toluene (80 mL) were placed in a dry ampoule with a magnetic bar. The ampoule was immersed in an oil bath at 70 °C. The solution was stirred for about 30 minutes, when the catalyst was activated completely by isopropanol and subsequently the required quantities of lactide were added. After a certain reaction time, the polymer was isolated by precipitating with cold methanol or low temperature centrifuge. The polymers were collected and dried *in vacuo* at 30 °C for 24 h.

3. Results and discussion

3.1. *Complexes preparation and characterization*

As shown in scheme 1, pro-ligands **L1**-**L3** were prepared easily in good yields (71.2 – 90.3%) by condensation between modified salicylaldehyde and *cis*-1,2-cyclohexan-diamine in toluene. Complexes **1**-**3** were synthesized by the reaction of **L1**-**L3** with $AlEt_3$ in toluene, specifically synthetic procedure shown in scheme 1. All three complexes were sensitive to air and moisture. Complexes **1**-**3** were characterized by ^1H and ^{13}C NMR in $CDCl_3$ at room temperature and elemental analysis. The ^1H and ^{13}C NMR spectra of **1**-**3** showed one Salen and one ethyl coordinated to aluminum in these complexes. For example, the resonances (δ 8.31, 7.95 and 0.82, –0.15 ppm) in the ^1H NMR spectrum of **2** were attributed to the imine protons (N=C*H*) in Salen ligand, the primary protons ($AlCH_2CH_3$) and the secondary protons ($AlCH_2CH_3$) in ethyl of **2**. ^1H NMR spectra of **1**-**3** revealed that the phenyl portions of the ligands in these complexes were inequivalent. For instance, two sets of resonances from imine protons (δ 8.31 and 7.95 ppm) were observed in the ^1H NMR spectrum, suggesting two possible isomers of **2** in solution (see figure S1), one where the Et was on the same side as the methine H atoms and one where the Et group on the opposite side. The geometry of **2** in the solid state was confirmed *via* X-ray diffraction analysis. The molecular structure is depicted in figure 3. Selected bond distances and angles are listed in table 1, the crystal data and structural refinement details for **2**·toluene are listed table S1. X-ray structural analysis revealed that **2** was mononuclear and Al was coordinated by two N, two O and one C. In five-coordinate systems, the actual geometry of

the complex can be described by a structural index parameter τ such that τ = (β–α)/60°, where β and α are the two largest angles (β>α). Thus, the geometric parameter τ is applicable to five-coordinate structures as an index of the degree of trigonality within the structural continuum between trigonal bipyramidal (τ = 1) and square pyramidal (τ = 0) [16]. In **2**·toluene (see table 1), the Al1–N1 bond length, 2.0407(16) (Å), was the longest among these bond lengths; O1–Al1–N2 and O2–Al1–N1 angles were 149.55(7) and 145.97(7)°, respectively. The τ value was 0.06, which suggested the aluminum was in distorted square pyramidal geometry.

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

All three complexes (**1**-**3**) were studied as catalysts with isopropanol for the ROP of L-LA and *rac*-LA; the results are collected in tables 2 and 3. Molecular weight of the PLA polymers was measured by GPC. ^{1}H NMR and GPC were applied to calculate the number-averaged molecular weights of PLA. These aluminum complexes with isopropanol showed low to high activities (26.4 – 97.9%) at 70 °C. The number-averaged molecular weights (M_n were calculated according to the formula $M_n = 0.58M_{n(GPC)}$ [17]) of PLA were close to theoretical ($M_{n(theory)}$ calculated from the monomer-to-catalyst molar ratio) with narrow molecular weight distributions (PDI: 1.08 – 1.27). The polymerization velocities of *rac*-LA applying **1**-**3** were slower than for L-LA polymerization velocities with **1**-**3** at the same polymerization conditions (*e.g*. table 3, entry 1 and table 2, entry 1).

The data of L-LA conversions versus polymerization time are shown in figure 4. The activities of these complexes reduced with the increase of substituent's bulk on the phenyl parts, while electron-withdrawing substituents increased polymerization rate. The results are similar to those in the literature [18]. Complex **2** displayed the highest activity (95.7% monomer conversion table 2, entry 2) at the same polymerization conditions among the three complexes (table 2, entries 1, 2 and 3). Moreover, the size of Salen ligands affected the PDI of the PLA, decreasing from 1.25 to 1.09 with increase of the bulk of the substituents on phenyl rings from H to ^{t}Bu (table 2, entries 1 and 3). The increase in bulk and its effect of decreasing the PDI has been observed previously [13].

3.3. *Kinetics studies*

The kinetics of the ROP of L-LA by **3** was investigated in toluene at 70 °C in various monomer to catalyst mole ratios, and the monomer conversion was monitored by ^{1}H NMR as a function of the polymerization time. The curves of conversions versus time are plotted in figure 4. First-order kinetics in monomer was observed according to equation (1):

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

where k_{app} was the apparent polymerization rate constant. The molecular weight of the polymers propagated linearly depending on the monomer transformation rate. The PDI of these polymers were relatively narrow (1.09 – 1.13), illustrating that the catalytic system possessed living feature (figure 5). In order to deduce the order of catalyst, k_{app} was plotted versus the concentration of **3**. As shown in figure 6, k_{app} increased linearly with the **3** concentration, manifesting that the order in catalyst was first-order. Hence, polymerization of L-LA using **3** according to the kinetic equation of equation (2):

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

where k_p was the polymerization rate constant, $k_p = k_{app}/[Al]$. A k_p value of 19.12 $Lmol^{-1}h^{-1}$ is determined for the LA polymerization catalyzed with **3** in toluene at 70 °C. This value is lower than that of LA polymerization with $Al(O^iPr)_3$ (k_p: 36.0 $Lmol^{-1}h^{-1}$) [4m] under similar conditions, which is maybe because of the rather bulky nature of the Salen ligand in **3**.

3.4. *Stereoselective polymerization studies*

The homonuclear decoupled ^{1}H NMR spectrum of the methine region [19] of the poly(*rac*-LA) was also researched (see figure 7; table 3, entries 1-6). The P_m [20] value, 0.75, demonstrated that these polymer chains were partially isotactic. The results showed that the P_m selectivities increased from 0.57 to 0.70 with increase of the bulk of the substituents (from H to ^{t}Bu) on ligands at 70 °C (see table 3, entries 1 and 3). For **3**, the P_m value increased from 0.70 to 0.75 when the reaction temperature reduced from 70 to 40 °C (table 3, entries 3 and 6). In comparison with the aluminum catalysts (*e.g.* (R,R)-**1** [13e], see figure S2, P_m: 0.92-0.93) supported by Salen ligand containing *trans*-1,2-diaminohexane backbone, these aluminum complexes with

cis-1,2-diaminohexane backbone showed lower stereoselectivities (P_m: 0.75) for the ROP of *rac*-LA.

3.5. *Mechanism of lactide polymerization*

For investigating the mechanism of initiation, end group analysis of the oligomer prepared by the ROP of the L-LA at small monomer to catalyst mole ratio ($[LA]_0 : [\mathbf{2}]_0 = 15 : 1$) was measured by ^{1}H NMR spectrum (figure 8). It showed an apparent triplet of two overlapping doublets at δ 1.24 ppm ("a" in figure 8) and a multiplet at δ 4.99 ppm ("e") with an integral ratio close to 6:1. These peaks were attributed to the methyl protons of the isopropoxycarbonyl and the methine proton, respectively. An eventual 1:1 ratio between multiplets at 4.99 ppm ("e") and 4.34 ppm ("d") confirm the other end group. This clearly revealed that the polymer was capped with one isopropyl ester group and one hydroxyl group [14b, 14c, 21], and the ROP proceeded through a so-called coordination insertion mechanism [22].

4. Conclusion

A number of Salen aluminum Schiff-base complexes were synthesized. These complexes were applied as catalysts in lactide polymerization. Kinetic data showed polymerizations were living with narrow molar mass distributions. Electron-withdrawing substituents raise the polymerization rate. Microstructural analysis of the polymers catalyzed by these complexes discovered that the Salen ligands have ability to affect the tacticity of the polymer.

Supplementary data

CCDC 908768 contains the supplementary crystallographic data for **2**; the SHELXTL-97 crystallographic software package was used for refinements [23]. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 21204082); China Postdoctoral Science Foundation (No. 2014M561268); Jilin Science & Technology

Department, Science and Technology Development Project (No. 20140204017GX); Science and Technology Bureau of Changchun City (No. 2013060); Training Programs of Innovation and Entrepreneurship for Undergraduates (No. 2015X094).

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[20] P_m is the probability of meso linkages: [mmm] = $P_m^2 + (1 - P_m)P_m/2$, [mmr] = [rmm] = $(1 - P_m)P_m/2$, [rmr] = $(1 - P_m)^2/2$, and [mrm] = $[(1 - P_m)^2 + P_m(1 - P_m)]/2$. See: B.M. Chamberlain, M. Cheng, D.R. Moore, T.M. Ovitt, E.B. Lobkovsky, G.W. Coates. *J. Am. Chem. Soc*., **123**, 3229 (2001).

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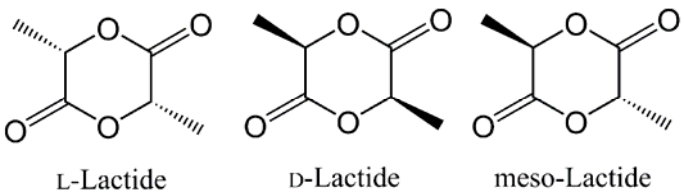

Figure 1. Stereoisomers of lactides.

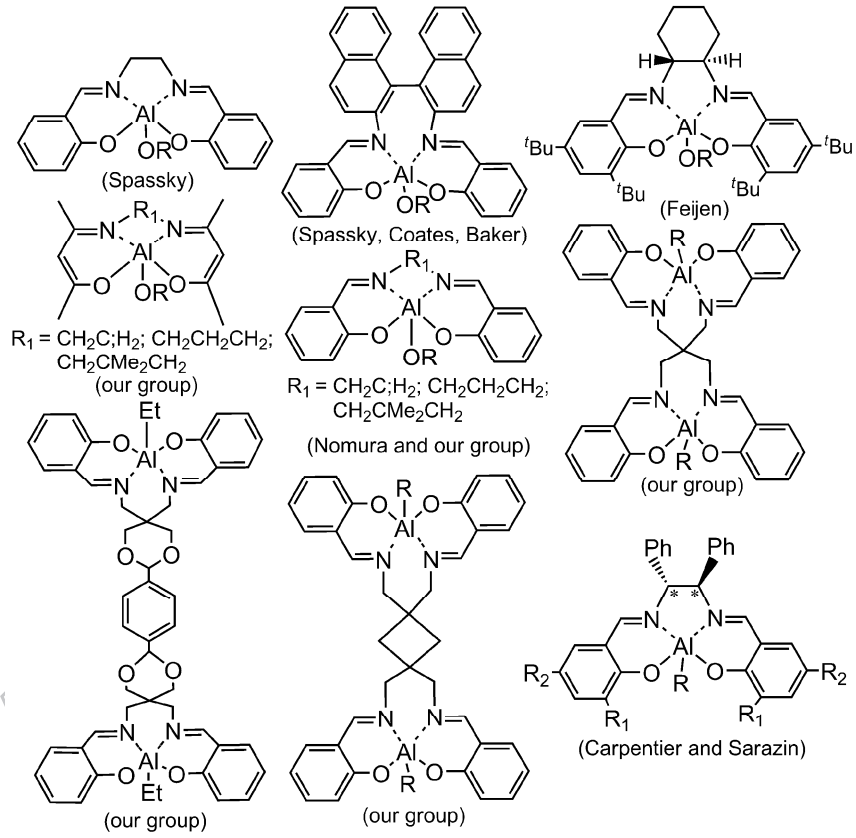

Figure 2. Salen aluminum catalysts for the ROP of lactide.

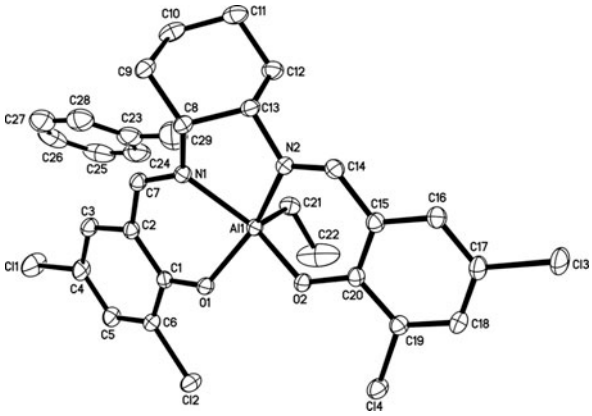

Figure 3. Perspective view of **2**·toluene with thermal ellipsoids drawn at 30% probability level. Hydrogens were omitted for clarity.

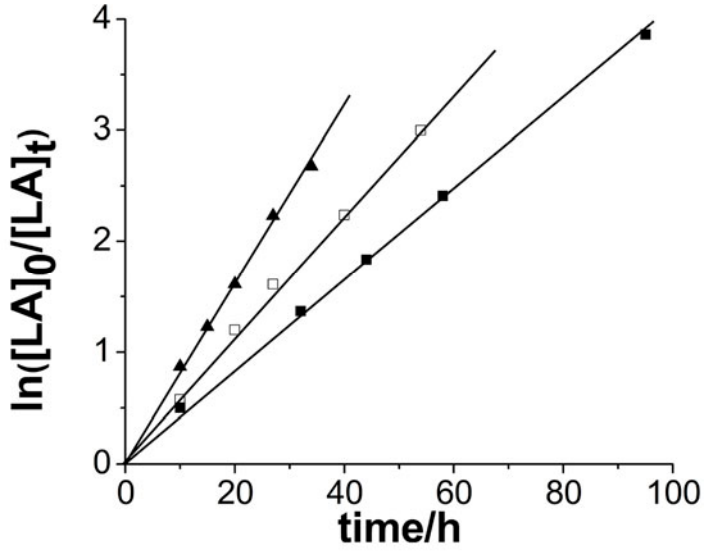

Figure 4. Kinetics of the ROP of L-LA by **3** at 70 °C in toluene (see table 2, entries 4, 5 and 6). $[LA]_0 = 0.5$ mol L^{-1}, $[isopropanol]_0/[Al]_0 = 1$; ■: $[Al]_0 = 0.005$ mol L^{-1}, $[LA]_0/[Al]_0 = 100$, $k_{app} = 4.155 \times 10^{-2}$ h^{-1}; ▲: $[Al]_0 = 0.010$ mol L^{-1}, $[LA]_0/[Al]_0 = 50$, $k_{app} = 8.298 \times 10^{-2}$ h^{-1}; □: $[Al]_0 = 0.0067$ mol L^{-1}, $[LA]_0/[Al]_0 = 75$, $k_{app} = 5.550 \times 10^{-2}$ h^{-1}, where k_{app} was the apparent polymerization rate constant.

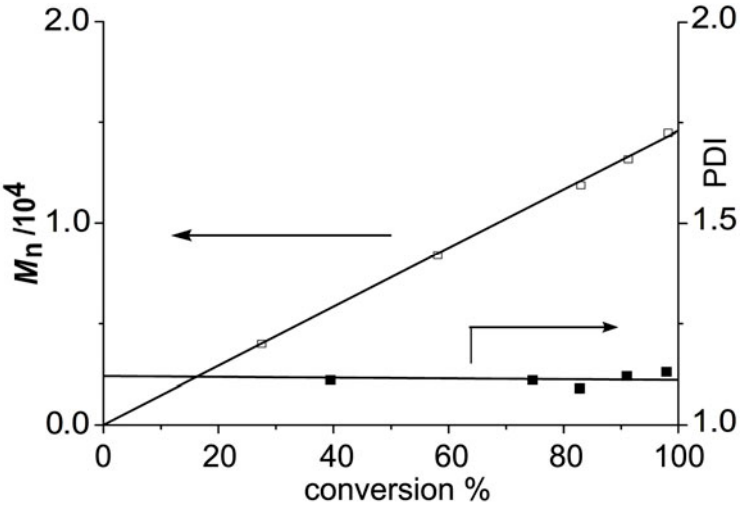

Figure 5. Plots of PLA's M_n and PDI as a function of monomer conversion using **3** with isopropanol, $[LA]_0/[\mathbf{3}]_0/[\text{isopropanol}]_0 = 100:1:1$ in toluene at 70 °C.

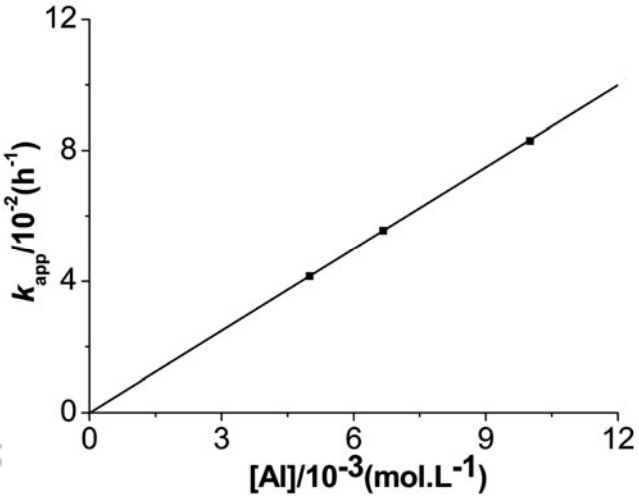

Figure 6. k_{app} versus the concentration of **3** for the L-LA polymerization in toluene at 70 °C ($[LA]_0 = 0.5$ mol L^{-1}, $k_p = 4.16$ L $mol^{-1}h^{-1}$).

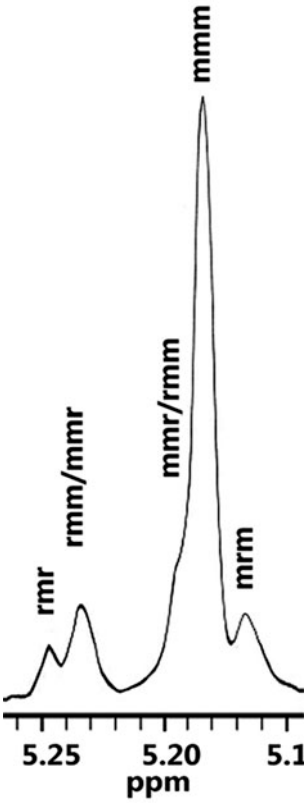

Figure 7. Homonuclear decoupled ^{1}H NMR spectrum of the methine part of poly(*rac*-LA) using **3** at 40 °C, P_m = 0.75, in $CDCl_3$ (table 3, entry 6).

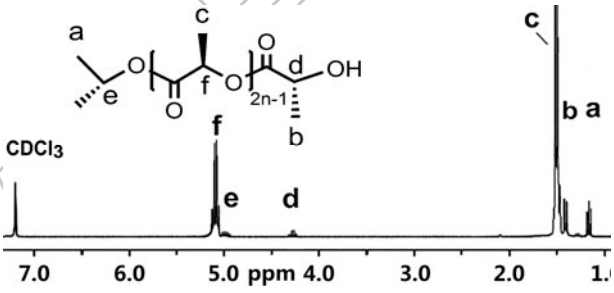

Figure 8. ^{1}H NMR spectrum of poly(L-LA) oligomer prepared by **2** with isopropanol when $[LA]_0 : [\mathbf{2}]_0 = 15 : 1$.

Table 1. Selected bond lengths (Å) and angles (deg) for **2**·toluene.

Al1–N1	2.0407(16)	Al1–N2	2.0277(16)
Al1–O1	1.8296(13)	Al1–O2	1.8162(13)
Al1–C21	1.963(2)		
O2–Al1–N2	88.15(6)	O1–Al1–O2	88.25(6)
O1–Al1–C21	104.05(8)	O2–Al1–N1	145.97(7)
O2–Al1–C21	107.82(8)	O1–Al1–N2	149.55(7)
C21–Al1–N2	105.84(8)	C21–Al1–N1	105.89(8)
O1–Al1–N1	88.02(6)	N2–Al1–N1	78.37(6)

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Table 2. Representational polymerization data of L-LA with **1**-**3**.[a]

Entry	Complex	$[LA]_0/[Al]_0$	T h	Conv. % [b]	$M_{n(theory)}$ [c]	$M_{n(GPC)}$ [d]	M_n [e]	PDI[d]
1	**1**	100	48	87.2	12600	22200	12900	1.25
2	**2**	100	48	95.7	13800	24400	14100	1.20
3	**3**	100	48	82.8	11900	20400	11800	1.09
4	**3**	100	95	97.9	14100	25000	14500	1.13
5	**3**	50	34	93.2	6700	11200	6500	1.10
6	**3**	75	54	95.1	10300	17500	10200	1.08

[a] The polymerization reactions proceeded in toluene solution at 70 °C, $[LA]_0 = 0.5$ mol L^{-1}, $[isopropanol]_0/[Al]_0 = 1$. [b] Measured by ^1H NMR. [c] Calculated from the molecular weight of LA × $[LA]_0/[Al]_0$ × conversion. [d] from GPC analysis and calibrated against polystyrene standard. [e] The actual value of number-averaged molecular weights have to be calibrated by $M_n = 0.58M_{n(GPC)}$ [17].

Table 3. Representational polymerization data of *rac*-LA with **1**-**3**.[a]

Entry	Complex	*T* h	Conv. % [b]	$M_{n(theory)}$ [c]	$M_{n(GPC)}$ [d]	$M_{n(actual)}$ [e]	PDI[d]	P_m [f]
1	**1**	48	43.6	6300	10400	6000	1.22	0.57
2	**2**	48	60.7	8700	16000	9300	1.27	0.59
3	**3**	48	26.4	3800	6800	3900	1.15	0.70
4	**3**	95	38.3	5500	9200	5300	1.18	0.67
5	**3**	192	85.9	12400	21600	12500	1.20	0.69
6[a]	**3**	148	22.6	3300	5400	3100	1.14	0.75

[a] The polymerization reactions were carried out in toluene solution at 70 °C except that a reaction, entry 6, proceeded in THF at 40 °C; $[LA]_0$ = 0.5 mol L^{-1}, $[LA]_0/[Al]_0$ = 100, $[isopropanol]_0/[Al]_0$ = 1. [b] Measured by ^1H 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 actual value of M_n has to be calibrated by $M_n = 0.58M_{n(GPC)}$ [17]. [f] Homonuclear decoupled ^1H NMR spectrum of the methine part of poly(*rac*-LA).

Graphical abstract