RSC Advances

PAPER

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Cite this: *RSC Adv.*, 2014, **4**, 22561

Bimetallic Schiff-base aluminum complexes based on pentaerythrityl tetramine and their stereoselective polymerization of racemic lactide†

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Received 10th March 2014
Accepted 31st March 2014

DOI: 10.1039/c4ra02092h

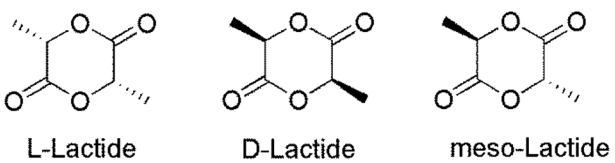
www.rsc.org/advances

A series of Schiff base aluminum(III) complexes with bimetallic active centers are synthesized. Their catalytic properties in the solution polymerization of racemic lactide (*rac*-LA) are examined. The modifications in the auxiliary ligand exhibited a dramatic influence on the catalytic performance. Among these complexes, **3a** has the highest stereoselectivity ($P_m = 0.91$) owing to the bulky *tert*-butyl groups on the salicylaldehyde. Kinetic studies indicate that the polymerizations are both first-ordered with respect to the monomer and catalyst. Other factors that influence the polymerization such as the polymerization time and the temperature, as well as the monomer concentration, are discussed in detail.

Introduction

In recent years many researchers have been focused on biodegradable polymers as petrochemical-based resources are gradually depleted. Poly(lactic acid) (PLA) from bio-based resources is particularly attractive as a biodegradable and biocompatible polymer because the ester linkage is easy to hydrolyse to CO_2 and water.[1–3]

Poly(lactic acid)s are generally synthesized by the ring-opening polymerization (ROP) of lactide (LA), the cyclic dimer of lactic acid. Due to the presence of two chiral centers in the lactide monomer the different lactide stereoisomers are distinguished, namely L-lactide (L-LA), D-lactide (D-LA) and *meso*-lactide (Scheme 1). The stereochemistry of the monomeric units in the polymer chains plays an important role in the mechanical, physical and degradation properties of PLA materials.[4,5] The synthesis of stereoregular PLA materials starting from a racemic mixture of L-LA and D-LA, referred to as *rac*-LA, can be traced back to 1996 by the pioneering studies of Spassky and coworkers.[6] They show that an enantiomerically pure Schiff base aluminum alkoxide catalyst-initiator preferably polymerized L-LA over D-LA from *rac*-LA, leading to an isotactic type PLA material with a gradient of L- and D-LA units in the polymer chains. A few other studies have attempted to elucidate the relationship between the monometallic aluminum salen Schiff base complexes and the stereoselectivity.[7–13] Among them, Coates,[14] Feijen[15] and Duda[16] used chiral salen-type Schiff base catalysts *via* the enantiomorphic site control mechanism; Nomura[17] used achiral salen-type Schiff base catalysts *via* the chain-end control mechanism.



Scheme 1 Stereoisomers of lactides.

Although monometallic salen Schiff base complexes have been studied extensively as LA polymerization catalysts, little research about Schiff base complexes with bimetallic active centers has been reported for *rac*-LA polymerization.[18–20] It is postulated that these complexes with bimetallic active centers might combine a high stereoselectivity and a high activity because of the synergetic effect of the two salicylidene moieties. Inspired by the successful preparation and application of symmetrical and unsymmetrical bimetallic salen complexes,[21] we are very interested in studies on the catalysis of bimetallic aluminum salen complexes. The research described in this paper is focused on the design and application of these complexes with bimetallic active centers for the controlled and stereoselective ROP of lactides.

Experimental section

General

All experiments were carried out under argon using Schlenk techniques. Starting materials for the synthesis of ligand **1–3**

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† Electronic supplementary information (ESI) available: Crystal structure of ligand 2 and calculation of the entropy and enthalpy difference. See DOI: 10.1039/c4ra02092h

were purchased from Aldrich Inc. and used without further purification. Toluene was distilled from Na-benzophenone. Ethyl acetate and 2-propanol were distilled from CaH_2 under the protection of argon. *rac*-Lactide (Purac) was purified by recrystallization from ethyl acetate and dried under vacuum at room temperature (RT) before use. NMR spectra were recorded on Bruker AV 300 M and Bruker AV 400 M in $CDCl_3$ at 25 °C. Chemical shifts are given in parts per million from tetramethylsilane. Gel permeation chromatography (GPC) measurements were conducted with a Waters 515 GPC with $CHCl_3$ as the eluent (flow rate: 1 mL min^{-1}, at 35 °C). The molecular weights were calibrated against polystyrene (PS) standards.

Synthesis of ligands (general procedure)

A solution of pentaerythrityl tetramine (1 mmol) in ethanol (50 mL) was added dropwise to a stirred solution of substituted salicylaldehyde (4 mmol) in ethanol (50 mL). The reaction mixture was refluxed for 12 h before cooling to RT. After removal of the solvent under vacuum, a crystalline solid was produced and purified by recrystallization in ethanol–$CHCl_3$ mixture.

1. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 13.20(s, ArO*H* 4H), 8.40(s, NC*H* 4H), 7.33(m, Ar*H* 4H), 7.23(m, Ar*H* 4H), 6.97(m, Ar*H* 4H), 6.89(m, Ar*H* 4H), 3.75(s, CCH_2N 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.92(N*C*H), all benzene ring 160.80, 132.39, 131.33, 118.60, 118.21, 116.55; 60.93(N*C*H_2), 43.53((CH$_2$)$_4$*C*). Elem. anal.: calcd C 72.24, H 5.88, N 10.21%; found C 72.28, H 5.84, N 10.19%.

2. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 13.21(s, ArO*H* 4H), 8.34(s, NC*H* 4H), 7.05(s, Ar*H* 4H), 6.88(s, Ar*H* 4H), 3.78(s, CCH_2N 8H), 2.29(s, ArCH_3 24H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.03(N*C*H), 156.58, 134.58, 128.91, 126.98, 125.18, 117.19 all benzene ring; 61.08(N*C*H_2), 43.29((CH$_2$)$_4$*C*), 20.09(Ar*C*H_3), 15.02(Ar*C*H_3). Elem. anal.: calcd C 74.52, H 7.32, N 8.48%; found C 74.50, H 7.38, N 8.51%.

3. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 13.71(s, ArO*H* 4H), 8.55(s, NC*H* 4H), 7.46(s, Ar*H* 4H), 7.18(s, Ar*H* 4H), 3.84(s, CCH_2N 8H), 1.53(s, ArC(CH_3)$_3$ 36H), 1.35(s, ArC(CH_3)$_3$ 36H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.87(N*C*H), all benzene ring 157.70, 139.96, 136.34, 126.93, 125.86, 117.32; 61.16(N*C*H_2), 43.79((CH$_2$)$_4$*C*), 34.74, 33.78(Ar*C*(CH$_3$)$_3$), 31.11(C(*C*H$_3$)$_3$), 29.11(C(*C*H$_3$)$_3$). Elem. anal.: calcd C 78.27, H 9.70, N 5.62%; found C 78.30, H 9.68, N 5.67%.

Synthesis of complexes

$AlEt_3$ (0.2 mmol) in toluene (5 mL) was added to the stirred 1 mL toluene solution of ligands **1–3** (0.1 mmol) at RT. The reaction was maintained at 80 °C for 12 h, and the reaction mixture was then slowly cooled to RT. The toluene was removed under vacuum.

1a. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.05(m, NC*H* 4H), 7.36(m, Ar*H* 4H), 7.01(m, Ar*H* 4H), 6.80(m, Ar*H* 4H), 6.54(m, Ar*H* 4H), 3.75(m, CCH_2N 8H), 0.62(m, AlCH$_2$CH_3 6H), −0.12(m, AlCH_2 4H). ^{13}C NMR (100 MHz, d^8-THF) δ = 173.13(N*C*H), all benzene ring: 168.38, 136.92, 134.60, 123.35, 120.69, 117.07; 64.70(N*C*H_2), 44.14((CH$_2$)$_4$*C*), 10.21(AlCH$_2$*C*H$_3$), 2.19(Al*C*H$_2$CH$_3$). Elem. anal.: calcd C 67.67, H 5.83, N 8.53%; found C 67.71, H 5.85, N 8.55%.

2a. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.01(m, NC*H* 4H), 6.95(m, Ar*H* 4H), 6.72(m, Ar*H* 4H), 3.71(m, CCH_2N 8H), 2.14(s, ArCH_3 24H), 0.86(m, AlCH$_2$CH_3 6H), −0.09(m, AlCH_2 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.53(N*C*H), all benzene ring: 163.54, 137.65, 130.48, 128.89, 124.58, 117.09; 63.60(N*C*H_2), 41.95((CH$_2$)$_4$*C*), 20.12(Ar*C*H_3), 15.73(Ar*C*H_3), 9.64(AlCH$_2$*C*H$_3$), 1.11(Al*C*H$_2$CH$_3$). Elem. anal.: calcd C 70.29, H 7.08, N 7.29%; found C 70.26, H 7.10, N 7.25%.

3a. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.19(m, NC*H* 4H), 7.43(m, Ar*H* 4H), 6.91(m, Ar*H* 4H), 3.80(m, CCH_2N 8H), 1.50(m, ArC(CH_3)$_3$ 36H), 1.32(m, ArC(CH_3)$_3$ 36H), 0.70(m, AlCH$_2$CH_3 6H), −0.19(m, AlCH_2 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.79(N*C*H), all benzene ring: 168.11, 157.96, 140.58, 136.57, 130.65, 127.00, 126.12, 117.81; 62.17(N*C*H_2), 45.11((CH$_2$)$_4$*C*), 35.09, 33.84(Ar*C*(CH$_3$)$_3$), 31.34(C(*C*H$_3$)$_3$), 29.35(C(*C*H$_3$)$_3$), 8.64(AlCH$_2$*C*H$_3$), 1.34(Al*C*H$_2$CH$_3$). Elem. anal.: calcd C 74.96, H 9.30, N 5.07%; found C 75.01, H 9.27, N 5.09%.

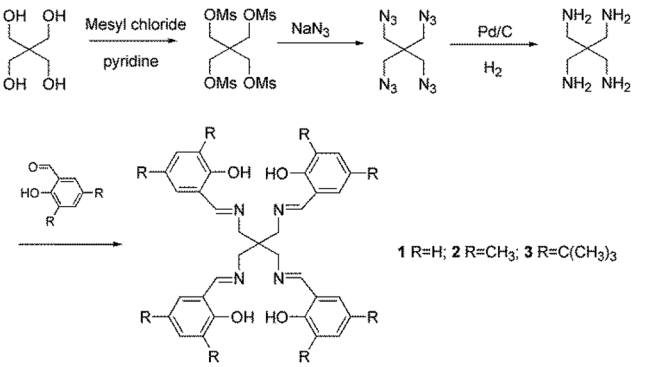
Polymerization of *rac*-LA

In a typical polymerization experiment, complexes **1a–3a** (10 μmol), the required amount of *rac*-LA in toluene were loaded in a flame-dried vessel containing a magnetic bar. The vessel was placed in a thermostated oil bath. Conversion of the monomer was determined on the basis of ^{1}H NMR spectroscopic studies. After a certain reaction time, the polymer was isolated by precipitation with cold methanol. The precipitate was collected and dried under *vacuum* at RT for 36 h.

Results and discussion

Ligand synthesis

Pentaerythrityl tetramine was synthesized by a three-step procedure as shown in Scheme 2. The versatile ligand family was synthesized from pentaerythrityl tetramine with substituted salicylaldehyde. Ligands **1–3** had identical aliphatic backbones but the different salicylaldehyde substituents: H for **1**, CH_3 for **2** and C(CH$_3$)$_3$ for **3**. The ^{1}H NMR spectra of ligand **2** shows signals at δ 8.34 and 3.78 which were attributed to the N=C*H* protons and NCH_2 protons of the pentaerythrityl tetramine, respectively. The intensity ratio of the signals at 8.34 and 3.78 ppm was 1 : 2, which confirmed the structure of ligand **2**.



Scheme 2 Synthetic pathway for the preparation of ligands.

Further evidence came from the single crystal of ligand **2** (see ESI, Fig. S1†).

Complex formation

Bimetallic Schiff base aluminum complexes **1a–3a** were obtained *via* the reaction of ligands **1–3** with stoichiometric $AlEt_3$ in toluene, respectively (Scheme 3). All these complexes were isolated as pale yellow powder. The ^{1}H NMR spectrum of compound **2a** shows signals at δ 0.86 and −0.09 ppm, which are attributed to the methyl protons and methylene protons of the aluminum ethyl group, respectively. Comparing with ligand **2** which the signals of N=C*H* protons and NCH_2 protons were at 8.34 and 3.78, the corresponding signals of complex **2a** moved to higher fields at 8.01 and 3.71, respectively. The intensity ratio of the signals at 8.01, 3.71, 0.86 and −0.09 ppm was 2 : 4 : 3 : 2, which confirmed the structure of **2a**.

Ring-opening polymerization of *rac*-LA in solution

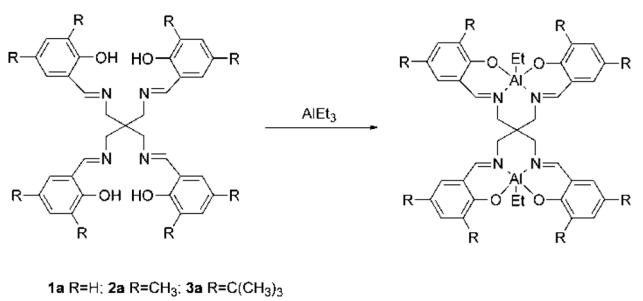
Bimetallic complexes **1a–3a** were investigated in the *rac*-LA polymerization. All polymerizations were carried out in toluene, and the levels of conversion were monitored by ^{1}H NMR determination of samples withdrawn from the reaction mixtures at a certain time interval. In the presence of propan-2-ol as an initiator, **1a–3a** catalyzed PLAs with similar number average molecular weights as calculated, as well as narrow molecular weight distributions, indicating well-controlled polymerization. Representative polymerization results are summarized in Table 1. The data of conversions *vs.* time were collected (Fig. 1).

First-order kinetics in monomer was observed in each case [eqn (1)], where k_{app} was the apparent polymerization rate constant.

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

The number-average molecular weight (M_n) also followed a linear relationship in monomer conversion (Fig. 2). To determine the order in catalyst, k_{app} was plotted *vs.* the concentration of **3a** (Fig. 3). k_{app} increased linearly with **3a** concentration, manifesting that there was only one initiating species for all the bimetallic complexes during the polymerization process. This indicated that the order in **3a** was first-order too. Therefore, the polymerization of *rac*-LA using **3a** followed an overall kinetic equation of the form shown in eqn (2), where k_p was the polymerization rate constant and $k_p = k_{app}/[\mathrm{cat}]$.

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



Scheme 3 Synthetic pathway for the preparation of complexes **1a–3a**.

Table 2 shows k_{app} and k_p values using **1a–3a** at different temperature. The first-order kinetics in monomer was further confirmed as **3a** had almost the same k_p values at various monomer concentrations (Table 2, entry 7, 8 and 9).

^{1}H NMR spectrum of PLA oligomers at a low monomer-to-initiator ratio showed a triplet of two overlapping doublets at 1.24 ppm and a quartet at 4.34 ppm with an integral ratio close to 6 : 1 (Fig. 4). These peaks were assigned to the methyl protons of the isopropoxycarbonyl end group and the methine proton neighboring the hydroxyl end group, respectively. This clearly indicates that the oligomer was systematically capped with one isopropyl ester group and one hydroxyl group. This confirmed that the aluminum isopropoxides were the actual active species in LA polymerizations when applying aluminum ethyls/2-propanol as catalyst/initiator systems.

As for a certain complex, the polymerization rate was largely determined by the reaction temperature (Fig. 5). An increase in the temperature from 70 °C to 110 °C led to a 256% increase in k_p value (for **3a**, from 0.70 to 2.49 in Table 2). The activation energy of the polymerization was calculated by fitting k_p values determined at different temperatures to the Arrhenius equation ($k_p = Ae^{-E_a/RT}$) as shown in Table 2. An activation energy E_a of 34.83 kJ mol^{-1} was deduced by plotting ln k_p *versus* $1/T$ (Fig. 6). This value was much lower compared to that by tin(II) octanoate (70.9 ± 1.5 kJ mol^{-1}).[24]

Complex structure and stereoselective polymerization

The substituents on the ligand phenolate rings also affect the polymerization rate significantly. Polymerization data revealed that **2a** had the highest activity: k_p value was 1.3 L mol^{-1} min^{-1} for **1a**, 5.2 L mol^{-1} min^{-1} for **2a** and 0.7 L mol^{-1} min^{-1} for **3a**. Complexes **1a–3a** had the same pentaerythrityl tetramine backbone, but the different substituted salicylaldehydes: H for **1a**, –CH_3 for **2a** and –^{t}Bu for **3a**. The more bulky substituents with more steric hindrance would keep active species from being approached by lactide monomer, as a result, slowing down the polymerization rate. Introducing methyl groups resulted in a remarkable increase in k_p value. It is worth noting that in our recent study of monometallic salan or bis(pyrrolidene) Schiff base complexes, the introduction of methyl groups resulted in a remarkable decrease in k_p.[25,26] It was postulated that the substituents took a complicated way to affect the complexes behavior.

The stereochemical microstructures of the resultant PLAs were determined from the methine region of the homonuclear decoupled ^{1}H NMR spectra (Fig. 7). The P_m value was 0.65 for **1a**, 0.73 for **2a** and 0.91 for **3a**. **3a** had the highest stereoselectivity among the three complexes (Table 1, entry 1, 4 and 8). A change of substituents from less bulky group (H) to more bulky one (^{t}Bu) led to a 40% increase in stereoselectivity.

Table 1 Polymerization data of *rac*-LA with complexes **1a–3a**[a]

Entry	Complex	Temp. (°C)	*t* (min)	$[M]_0/[cat]$	Conv.[b] (%)	$M_{n(calcd)}$[c] $\times 10^{-3}$	$M_{n(NMR)}$[d] $\times 10^{-3}$	$M_{n(GPC)}$[e] $\times 10^{-3}$	PDI[e]	P_m[f]
1	**1a**	70	300	100	88	6.3	6.8	5.9	1.14	0.65
2	**1a**	70	410	150	82	8.9	9.5	9.3	1.18	0.65
3	**1a**	70	512	200	91	13.1	14.0	12.4	1.15	0.65
4	**2a**	70	90	100	90	6.5	6.6	5.7	1.20	0.73
5	**2a**	70	147	150	89	9.6	11.1	9.2	1.16	0.72
6	**2a**	70	185	200	94	13.5	15.7	12.0	1.14	0.73
7	**3a**	70	674	100	92	6.5	7.8	6.2	1.15	0.90
8	**3a**	70	648	150	89	9.6	11.4	8.2	1.16	0.91
9	**3a**	70	751	200	86	12.4	14.2	10.8	1.14	0.91
10	**3a**	90	287	100	88	6.3	8.1	7.2	1.29	0.78
11	**3a**	110	194	100	90	6.5	8.4	7.6	1.35	0.68

[a] All polymerizations were carried out in toluene solution, $[LA]_0 = 0.5$ mol L^{-1}. [b] Measured by ^1H NMR. [c] Calculated from the molecular weight of LA $\times$ $[M/2]_0/[cat]$ $\times$ conversion + M_w(iPrOH). [d] Obtained from ^1H NMR analysis. [e] Obtained from GPC analysis and calibrated against polystyrene standard. The true value of M_n could be calculated according to formula $M_n = 0.58M_{nGPC}$.[22] [f] P_m.[23]

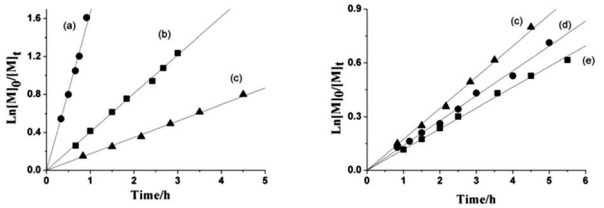


Fig. 1 Kinetic plots of the *rac*-lactide conversion *vs.* the reaction time. (a) Complex **2a**, $[M]_0/[cat] = 100$; (b) complex **1a**, $[M]_0/[cat] = 100$; (c) complex **3a**, $[M]_0/[cat] = 100$; (d) complex **3a**, $[M]_0/[cat] = 150$; (e) complex **3a**, $[M]_0/[cat] = 200$.

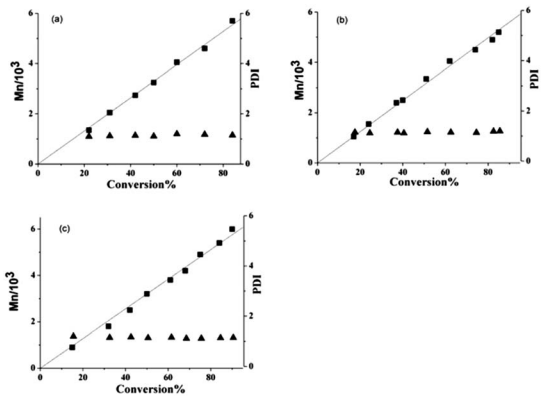


Fig. 2 Plot of PLA Mn (■) and polydispersity (▲) as a function of *rac*-lactide conversion using (a) complex **1a**, $[M]_0/[cat] = 100$; (b) complex **2a**, $[M]_0/[cat] = 100$; (c) complex **3a**, $[M]_0/[cat] = 100$.

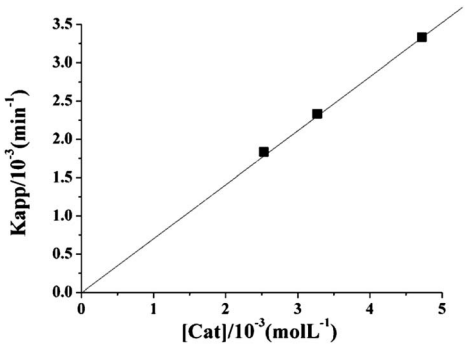


Fig. 3 k_{app} *vs.* the concentration of **3a** for the *rac*-LA polymerization.

Table 2 Kinetic results of *rac*-LA polymerization at different temperatures

Entry	Complex	Temp. (°C)	$[M]_0/[cat]$	k_{app} ($min^{-1} \times 10^{-3}$)	k_p (L mol^{-1} min^{-1})
1	**1a**	70	100	6.65	1.33
2	**1a**	70	150	4.33	1.30
3	**1a**	70	200	3.38	1.35
4	**2a**	70	100	26.20	5.24
5	**2a**	70	150	17.33	5.20
6	**2a**	70	200	12.93	5.17
7	**3a**	70	100	3.65	0.73
8	**3a**	70	150	2.33	0.70
9	**3a**	70	200	1.78	0.71
10	**3a**	90	100	8.05	1.61
11	**3a**	110	100	12.45	2.49

It was consistent with previous results in the monometallic Schiff base systems[17,27] that the enhancement of stereoselectivity requires bulky substituents at the *ortho* positions for the stereoselective polymerization adopting chain end control mechanism.

The stereoselectivity decreased with increasing temperature. For example, an increase in the temperature from 70 °C to 90 °C and 110 °C using **3a** led to a reduction in P_m value of 14% and 25%, respectively (from 0.91 to 0.78 and 0.68). P_m values are collected in Table 1.

In an effort to understand the preference of isotactic stereosequence, further investigations were applied. It was anticipated that the stereoselectivity in the polymerization of *rac*-LA took place *via* a chain-end control mechanism, since the ligands

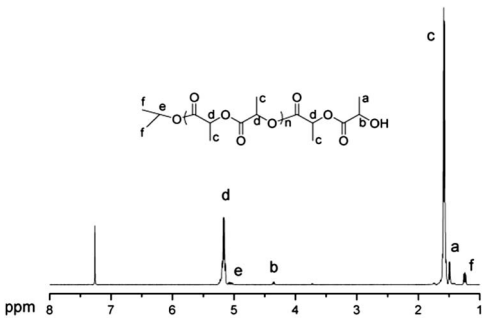


Fig. 4 ^{1}H NMR spectrum of oligomers of *rac*-LA.

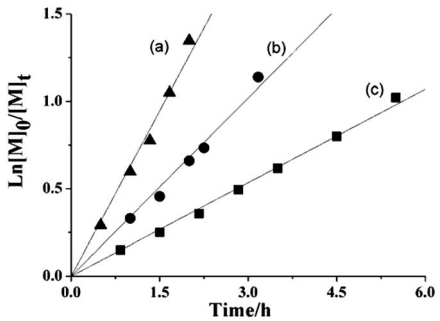


Fig. 5 Kinetics of the *rac*-LA polymerization using **3a** at the reaction temperatures of (a) 110 °C; (b) 90 °C; (c) 70 °C, $[M]_0/[cat] = 100$.

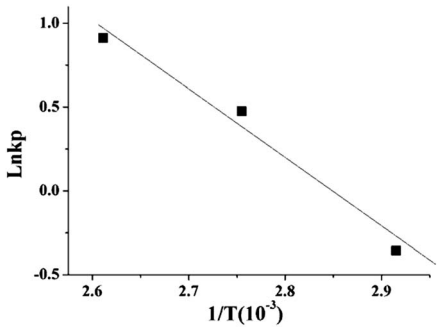


Fig. 6 Plot of ln K_p *vs.* $1/T$ for the polymerization of *rac*-lactide with **3a**.

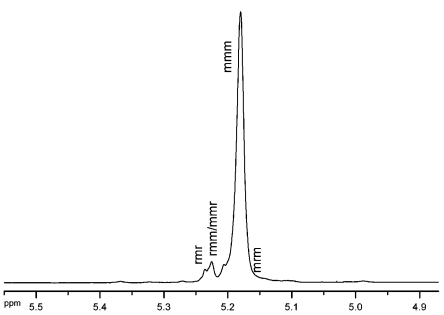


Fig. 7 Homonuclear decoupled ^{1}H NMR spectra by using **3a**.

were achiral in this research. As for the so-called chain-end control mechanism, the initiation reaction occurred without any differentiation between the lactide enantiomers, and the last unit in the growing polymer chain influenced which enantiomer form of the monomers would incorporate into the molecular chain in the next step. If the stereogenic center in the last unit favors a *meso*-enchainment, the isotactic PLA was obtained; if the stereogenic center in the last unit favors a *racemic*-enchainment, the syndiotactic PLA would be obtained.

As there is a preference for isotactic addition during the ROPs of *rac*-LA in research, the intensity values of the individual stereosequences do not obey Bernoullian statistics, so a Markovian statistics and absolute reaction rate theory would be preferred to interpret the stereosequence distribution.[28–30] According to first-order Markovian statistics,[31,32] the entropy and enthalpy difference between homo-propagation and cross-propagation were calculated as -23.23 cal K^{-1} mol^{-1} and -9.42 kcal K^{-1} mol^{-1}, respectively, which explained the preference of isotactic stereosequence (for detailed calculation please see ESI†).

Conclusion

A series of new bimetallic Schiff base aluminum complexes were designed and prepared from pentaerythrityl tetramine with different substituted salicylaldehydes. The catalytic behavior of the complexes in *rac*-lactide polymerization was examined. The polymerization data manifested that their performance varied remarkably due to the modifications in the auxiliary ligand. The P_m value was 0.65 for **1a**, 0.73 for **2a** and 0.91 for **3a**. **3a** had the highest stereoselectivity owing to the bulky *tert*-butyl groups on the salicylaldehyde. Polymerization data revealed that **2a** had the highest activity: k_p value was 1.3 L mol^{-1} min^{-1} for **1a**, 5.2 L mol^{-1} min^{-1} for **2a** and 0.7 L mol^{-1} min^{-1} for **3a**. Activation energy, E_a, of 34.83 kJ mol^{-1} was deduced by using **3a**, which was much lower compared to that of tin(II) octanoate (70.9 ± 1.5 kJ mol^{-1}). The different performance of these complexes was attributed to the different substituent groups on auxiliary ligands. As the complexes in this paper had no chirality, it was presumed that the polymerization followed a so-called chain-end control mechanism. Research toward the origin of the activity and stereoselectivity of bimetallic Schiff base aluminum complexes is currently in progress.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (nos 21204082, 51173183, 51103058, 51203155 and 51321062) and the Ministry of Science and Technology of China (no. 2011AA02A202).

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