Living and Stereoselective Polymerization of *Rac*-Lactide by Bimetallic Aluminum Schiff-Base Complexes

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ABSTRACT: A series of bimetallic aluminum Schiff-base complexes have been prepared and characterized. The complexes used as catalysts were applied in the lactide polymerization to test their activities and stereoselectivities. All polymerizations are living, as evidenced by the narrow polydispersities and the good fit between calculated and found number-average molecular weights of the isolated polymers. Isotactic enriched polylactide was obtained by using these complexes. Kinetic studies indicated that the polymerizations are both first-ordered with respect to lactide monomer and catalyst. © 2014 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 1344–1352

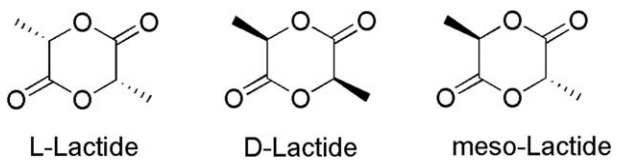
KEYWORDS: biomaterials; bimetallic; catalysts; lactide; polymerization

INTRODUCTION Poly(lactic acid) (PLA) material have attracted great interests because of their unique biodegradability and biocompatibility. They could be used in wide range of applications, such as sutures, bone fracture fixation devices, drug controlled release carriers, tissue engineering scaffolds, and green plastics.[1] PLA 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 LA monomer, the different LA stereoisomers are distinguished, namely (*S,S*)-LA (l-LA), (*R,R*)-LA (d-LA), and (*R,S*)-LA (*meso*-LA) (Scheme 1).[2] The chain chemical stereostructures of PLA are one of the most important factors that influence the physical, mechanical, and degradation properties of the polymers. Highly stereoregular poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) are crystalline polymers, with a high melting temperature and good mechanical strength.[3] Atactic PLA with a random placement of *S*- and *R*-LA units in the polymer chains are amorphous and brittle materials. Due to the crystallinity of stereoregular PLAs, these materials slowly degrade in a physiological environment, whereas atactic PLA materials degrade much faster (Scheme 2).[4]

PLAs are usually prepared by ROP of LA, generally applying metal-based catalysis. A large number of nonligated metal complexes, in particular, metal alkoxides of Al,[5] Li,[6] Ca,[7] Fe,[8] Sn,[9] and Zn,[10] have been explored for these purposes. Problems associated with the use of some of these nonligated metal alkoxides are racemization and transesterification as side reactions during the polymerization, which lead to the disturbance of the polymer microstructure, unpredictable molecular weights. It was found by Ikada that the stereocomplex polymers formed by an equivalent mixture of PLLA and PDLA have many advantages such as higher melting temperature (T_m = 230 °C).[11] Many efforts have been made to obtain crystalline PLA via direct ROP of racemic lactide (*rac*-LA; i.e., a 1:1 mixture of L-LA and D-LA) by the stereoselective catalysts.

Spassky et al.[12] discovered that Schiff-base salen complex could give a highly stereocontrolled polymerization of *rac*-LA to form isotactic and crystalline PLA with a higher T_m than optically pure PLLA. A few other excellent studies have attempted to elucidate the relationship between the aluminum Schiff-base complexes and stereoselectivity. Coates,[13] Feijen,[14] Duda,[15] and our group[16] used chiral salen- or salan-type Schiff-base catalysts via the enantiomorphic site control mechanism; Nomura[17] and we[18] used achiral salen-type Schiff-base catalysts via the chain-end control mechanism. Recently, we developed enolic complexes in the stereocontrolled polymerization of *rac*-LA to give isotactic

Additional Supporting Information may be found in the online version of this article.



SCHEME 1 Stereoisomers of lactides.

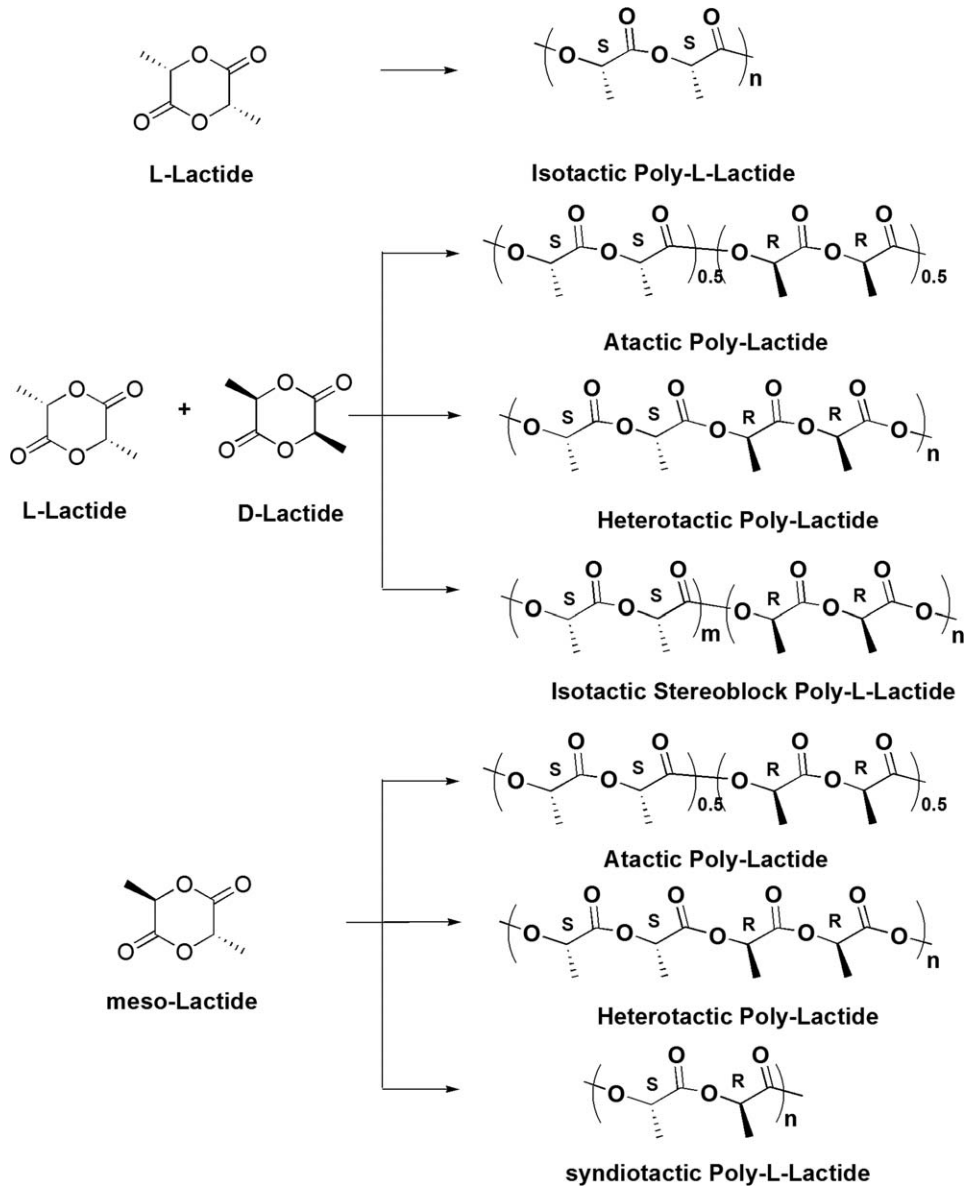
enriched polylactide.[19] So far, the monometallic salen complexes have been studied extensively as the homogeneous catalysts in the LA polymerization. To the best of our knowledge, the multimetallic salen complex has not been explored in great detail in LA polymerization, despite their great potential structure varieties of ancillary ligands.[20] The multimetallic structure may function cooperatively which could result in an increase of catalytic activity and stereoselectivity in comparison to the monometallic complexes.[21]

In this work, we reported the preliminary results of the synthesis and characterization of bimetallic salen complexes which acting as catalysts to polymerize LA in a controlled manner under mild conditions to give isotactic enriched polylactide.

EXPERIMENTAL

General

All experiments were carried out in a dry nitrogen atmosphere using standard Schlenk techniques or in a glovebox. Starting materials for the synthesis of ligands were purchased from Aldrich Inc. and used without further purification. Toluene and hexane were distilled from Na-benzophenone before use. Ethyl acetate and 2-propanol were distilled from CaH_2 under the protection of argon. *Rac*-Lactide (Purac) was purified by recrystallization from ethyl



SCHEME 2 Stereostructures of PLA.

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 were 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 standards.

Synthesis of Compounds 1, 2, and 3

1: Benzene-1,4-dicarbaldehyde (13 g), 2,2-bis-bromomethyl-propane-1,3-diol (52 g), and *p*-toluenesulfonic acid (0.3 g) in 200 mL of toluene were placed in a flask equipped with a Dean–Stark apparatus, $CaCl_2$ drying tube, and a magnetic stirrer. The solid–liquid reaction mixture was heated to reflux until 3.6 mL of H_2O evolved. The reaction mixture was then cooled to RT, filtered, and purified by ether then dried *in vacuo* at RT. The final products were white powder.

Yield: 92%. ^{1}H NMR (300.00 MHz, $CDCl_3$) δ = 7.49(s, 4H, Ar*H*), 5.40(s, 2H, ArC*H*), 4.26(d, 4H, CCH_2O), 3.96(s, 4H, CCH_2N), 3.75(d, 4H, CCH_2O), 3.31(s, 4H, CCH_2N).

2: Sodium azide (6.5 g) was added to a stirred solution of compound **1** (12.4 g) in DMSO (500 mL), the mixture was slowly heated to 110 °C and kept for 24 h and then isolated by precipitation into H_2O (600 mL), filtered, and purified by ether before dried *in vacuo* at RT. The final products were white powder.

Yield: 82%. ^{1}H NMR (300.00 MHz, $CDCl_3$). δ = 7.48(s, 4H, Ar*H*), 5.41(s, 2H, ArC*H*), 4.05(d, 4H, CCH_2O), 3.81(s, 4H, CCH_2N), 3.71(d, 4H, CCH_2O), 3.24(s, 4H, CCH_2N).

3: Under the protection of argon, $LiAlH_4$ (1.5 g) was slowly added to 200 mL THF at 0 °C. Compound **2** (4.7 g in 150 mL THF) was then added to the $LiAlH_4$ solution. The reaction vessel was kept for at 0 °C for 2 h and at RT for another 2 h. H_2O (1.5 g) was added to the mixture at 0 °C and stirred for 15 min. Then, 1.5 g NaOH solution (15% in H_2O) was added and stirred for another 15 min at 0 °C. H_2O (4.5 g) was added to the reaction vessel and kept for 30 min at 0 °C. The reaction mixture was then warm to RT, filtered, and dried *in vacuo* at RT. The final products were white powder.

Yield: 47%. ^{1}H NMR (300.00MHz, d_6-DMSO). δ = 7.38(s, 4H, Ar*H*), 5.37(s, 2H, ArC*H*), 3.94(d, 4H, CCH_2O), 3.58(d, 4H, CCH_2N), 2.84(d, 4H, CCH_2O), 2.51(d, 4H, CCH_2N).

Synthesis of Ligands

General Procedure

The ligand precursors **4, 5**, and **6** were obtained by condensation between the tetraamine compound **3** and substituented salicylaldehyde. A solution of **3** (0.1 mol L^{-1}) in ethanol (50 mL) was added dropwise to a stirred solution of substituted salicylaldehyde (0.4 mol L^{-1}) in ethanol (50 mL). The reaction mixture was refluxed for 14 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 (Supporting Information contains detailed information of ligands **4, 5**, and **6**).

Complex Synthesis

General Procedure

For complexes **4a**−**6a**, $AlEt_3$ (0.2 mmol) in toluene (5 mL) was added to the stirred 1 mL toluene (THF for 6a) solution of ligand precursors 4−6 (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.

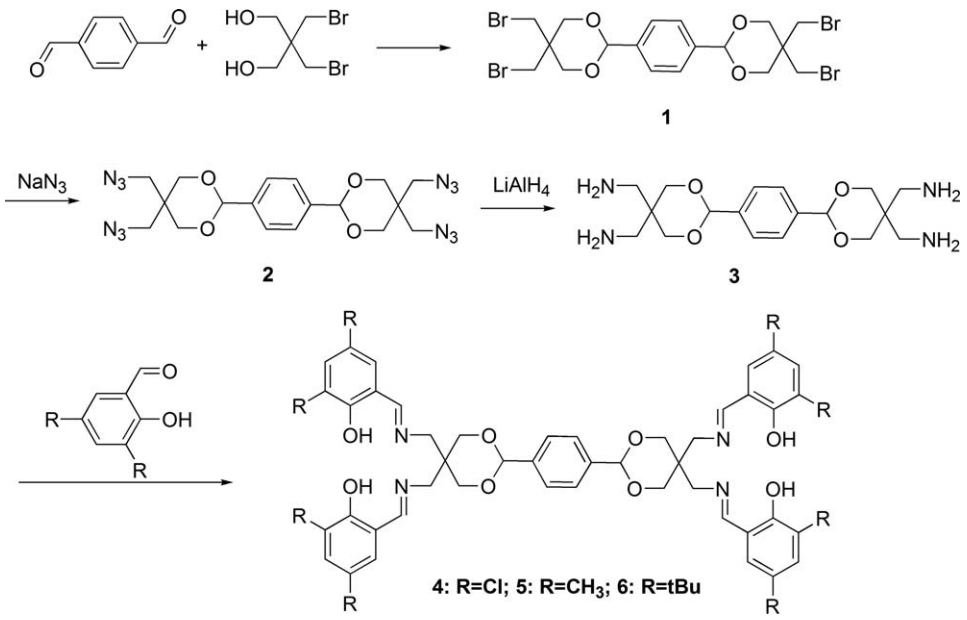
Complex **4a. 4a** was obtained as a yellow solid in 92% yield. ^{1}H NMR (400M, $CDCl_3$): δ = 8.15(s, 2H, NC*H*), 8.02(s, 2H, NC*H*), 7.55(s, 4H, Ar*H*), 7.48(s, 4H, Ar*H*), 7.09(d, 4H, Ar*H*), 5.53(s, 2H, ArC*H*), 4.15(s, 4H, CCH_2O), 4.07(d, 4H, CCH_2N), 3.88(m, 4H, CCH_2O), 3.73(d, 4H, CCH_2N), 0.89(t, 6H, $AlCH_2CH_3$), −0.03(q, 4H, $AlCH_2$). ^{13}C NMR (100 MHz, d^6-THF) δ = 171.01 (NC*H*), all benzene ring 161.02, 139.60, 134.43, 130.91, 126.48, 122.36, 120.92, 119.97, 119.11, 102.27(Ar*C*O), 72.19(C*C*H_2O), 64.50, 59.41(C*C*H_2N), 38.07(OCH_2*C*CH_2N), 8.72($AlCH_2CH_3$), 1.15($AlCH_2CH_3$). Elem. Anal.: Calcd. C 51.48, H 3.80, N 4.80; Found C 51.55, H 3.91, N 4.75.

Complex **5a. 5a** was obtained as a yellow solid in 95% yield. ^{1}H NMR (400M, $CDCl_3$): δ = 8.14(s, 2H, NC*H*), 7.98(s, 2H, NC*H*), 7.57(s, 4H, Ar*H*), 7.11(s, 4H, Ar*H*), 6.82(d, 4H, Ar*H*), 5.52(s, 2H, ArC*H*), 4.12(s, 4H, CCH_2O), 3.97(d, 4H, CCH_2N), 3.85(m, 4H, CCH_2O), 3.68(d, 4H, CCH_2N), 2.21(d, 24H, ArCH_3), 0.94(t, 6H, $AlCH_2CH_3$), −0.06(q, 4H, $AlCH_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 176.97 (NC*H*), all benzene ring 161.73, 139.77, 132.05, 129.71, 126.26, 125.93, 124.78, 117.73, 101.33 (Ar*C*O), 70.03(C*C*H_2O), 62.71, 59.25(C*C*H_2N), 39.74(OCH_2*C*CH_2N), 20.37(Ar*C*H_3), 16.07(Ar*C*H_3), 9.02 ($AlCH_2$*C*H_3), 1.05($AlCH_2$). Elem. Anal.: Calcd. C 69.44, H 6.83, N 5.59; Found C 69.48, H 6.75, N 5.67.

Complex **6a. 6a** was obtained as a white solid in 93% yield. ^{1}H NMR (400M, $CDCl_3$): δ = 8.34(s, 2H, NC*H*), 8.07(s, 2H, NC*H*), 7.56(s, 4H, Ar*H*), 7.09(s, 4H, Ar*H*), 6.97(d, 4H, Ar*H*), 5.54(s, 2H, ArC*H*), 4.10(m, 4H, CCH_2O), 3.96(s, 4H, CCH_2N), 3.80(m, 4H, CCH_2O), 3.60(s, 4H, CCH_2N), 1.41(d, 36H, ArC(CH_3)$_3$), 1.27(d, 36H, ArC(CH_3)$_3$), 1.02 (t, 6H, $AlCH_2CH_3$), −0.03(q, 4H, $AlCH_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.73(NC*H*), all benzene ring 162.51, 140.83, 139.39, 133.26, 129.74, 128.30, 126.25, 118.38; 101.22(Ar*C*O), 70.15(C*C*H_2O), 59.11, 58.39(C*C*H_2N), 39.78(OCH_2CH_2N), 35.44, 34.23(Ar*C*(CH_3)$_3$), 31.38(C(*C*H_3)$_3$), 29.44(C(*C*H_3)$_3$), 9.12($AlCH_2$)*C*H_3), 0.88($AlCH_2$). Elem. Anal.: Calcd. C 73.51, H 8.73, N 4.18; Found C 73.46, H 8.71, N 4.24.

LA Polymerization

In a glovebox, *rac*-LA (1.00 g, 6.94 mmol), 2-propanol (4.33 mg, 0.072 mmol) in 2 mL of toluene, and **4a**−**6a** (0.072 mmol) dissolved in 2 mL of toluene and another 9 mL of toluene were added successively into a flame-dried reaction vessel equipped with a magnetic stirring bar. The vessel was removed from the glovebox and placed in an oil bath



SCHEME 3 Ligands prepared for the stereoselective polymerization of lactides.

thermostated at 70 °C. At certain time intervals, an aliquot of the reaction mixture was taken out using a syringe to determine the monomer conversion by ^{1}H NMR. A few drops of acetic acid were added to quench the polymerization after it reached a certain conversion. The polymer was isolated by precipitation into cold methanol, filtering, and drying under vacuum at RT for 24 h.

RESULTS AND DISCUSSION

Ligand Synthesis

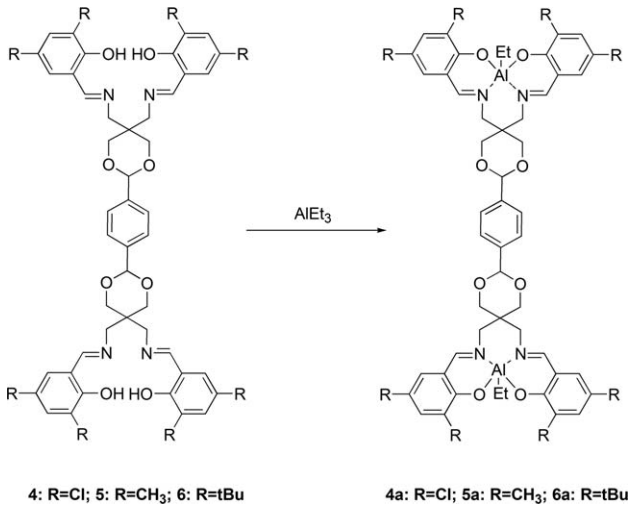
The bimetallic ligand family (Scheme 3) was synthesized from readily available starting materials by a four-step procedure. First, compound **1** was obtained by an acetalization of benzene-1,4-dicarbaldehyde, and 2,2-bis-bromomethyl-propane-1,3-diol. Subsequently, reaction of compound **1** with sodium azide afforded compound **2**. Compound **3** was obtained by the reduction of compound **2** in the presence of $LiAlH_4$. The ligand precursors **4, 5**, and **6** were obtained by condensation between the tetraamine compound **3** and substituted salicylaldehyde. Ligands **4, 5**, and **6** had the identical imine backbones but the different substituents at the salicylidene phenolate rings: —Cl for **4**, —CH_3 for **5**, and — ^{t}Bu for **6**.

Complexes Formation and Characterization

Reaction of ligands **4**−**6** with stoichiometric $AlEt_3$ formed bimetallic salen complexes **4a**−**6a**, respectively (Scheme 4). All these complexes were isolated as solid powder. The ^{1}H NMR spectrum of compound **6a** showed signals at δ –0.03 and 1.02 ppm, which were attributed to the methylene protons and methyl protons of the aluminum ethyl group, respectively. The CCH_2N protons displayed two singlets at 3.60 and 3.96 ppm; the NC*H* protons showed two singlets at 8.07 and 8.34 ppm. The intensity ratio of NC*H*, CCH_2N, and $AlCH_2$ was 1:2:1, which confirmed the structure of **6a**.

Kinetic Studies

The polymerization processes were systematically investigated by kinetic studies using bimetallic complexes **4a**−**6a**. Polymerization data were collected in Table 1. Polymerization was monitored by ^{1}H NMR spectroscopy until monomer consumption was reached. The data of conversions versus time were collected in Figure 1. The conversions increased linearly with the reaction time for complexes **4a, 5a**, and **6a** (Fig. 1, left). The linear relationship also remained at various concentrations for a certain complex (Fig. 1, right). First-order kinetics in monomer was observed [eq (1)], where k_{app} was the apparent polymerization rate constant. The first-order kinetics as shown in eq (1) implied that the concentration of active species remained unchanged, or in other



SCHEME 4 Synthetic pathway for the preparation of complexes **4a**–**6a**.

TABLE 1 Polymerization Data of *Rac*-LA Using Complexes **4a**–**6a**.[a]

	T/ (°C)	Time (h)	$[M]_0/[Cat]$	Conv (%)[b]	$M_{n(calcd)}/10^{3}$[c]	$M_{nGPC}/10^{3}$[d]	PDI[d]	P_m^e
4a	70	2	100	94	6.8	11.9	1.06	0.66
4a	70	4	160	96	11.1	19.8	1.07	0.67
4a	70	6	200	96	13.8	23.2	1.03	0.67
5a	70	10	100	98	7.1	12.4	1.08	0.76
5a	70	12	160	97	11.2	19.7	1.10	0.78
5a	70	15	200	96	13.8	23.1	1.09	0.76
6a	70	16	100	96	6.9	11.5	1.05	0.87
6a	70	18	160	95	11.0	19.7	1.07	0.88
6a	70	24	200	92	13.3	23.6	1.04	0.85
6a	90	10	200	85	12.3	20.8	1.15	0.71
6a	110	5	200	90	13.0	23.0	1.20	0.61

[a] The polymerizations were carried out in toluene solution. $[LA]_0$ = 0.5 mol/ L^{-1}.
[b] Measured by ^{1}H NMR.
[c] Calculated from the molecular weight of LA × [M/2]/[Cat] × conversion + $M_w^{isopropanol}$.
[d] Obtained from GPC analysis and calibrated against polystyrene standard. The true value of M_n could be calculated according to formula $M_n = 0.58M_{nGPC}$[5].
[e] The parameter P_m is the probability of meso meso-linkages. According to chain-end control mechanism, the expressions for the tetrad probabilities of poly(*rac*-LA) are: [mmm] = P_m^2 + (1 − P_m)P_m/2, [mmr] = [rmm] = (1 − P_m)P_m, [rmr] = (1 − P_m)^2, [mrm] = ((1 − P_m)^2 + P_m(1 − P_m))/2.

words, the growing polymer chains remained alive during the entire polymerization.

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

The number-average molecular weight (M_n) also followed a linear relationship in monomer conversion (Fig. 2 and Table 1). The molecular control and the low polydispersity indicated that the polymerization had a characteristic of controlled propagation. The theoretical M_n of **6a** close to the determined value by GPC (Table 1, entry 7–9), and, thus, reflecting the nature of living and controlled polymerization catalyzed by these complexes. It was worth noting that the calculation of the theoretical M_n was operated based on the hypothesis that bimetallic centers would involve in the propagation of polymer chains. Therefore, there would have two propagating species on **6a**, the actual concentration of monomer would be only half of the original. Fortunately, the good consistencies between M_{nGPC} and $M_{n(calcd)}$ verified this. So it was postulated that both the bimetallic centers in **6a** were active.

To determine the order in catalyst, k_{app} was plotted versus the concentration of catalyst (Fig. 3) using **6a**. The linear relationship of k_{app} versus $[Cat]_0$ revealed a first-order in catalyst. Therefore, the polymerization of *rac*-LA using **6a** followed an overall kinetic law of the following form as eq 2, where k_p was the polymerization rate constants and $k_p = k_{app}/[Cat]$.

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

We could extrapolate this equation to other complexes in the *rac*-LA polymerization. The ^{1}H NMR spectrum of oligomer prepared using **6a** at a low concentration ratio of monomer to catalyst was shown in Figure 4. The triplet of two overlapping doublets at 1.24 ppm and the quartet at 4.34 ppm, with an integral ratio close to 6:1, were assigned to the

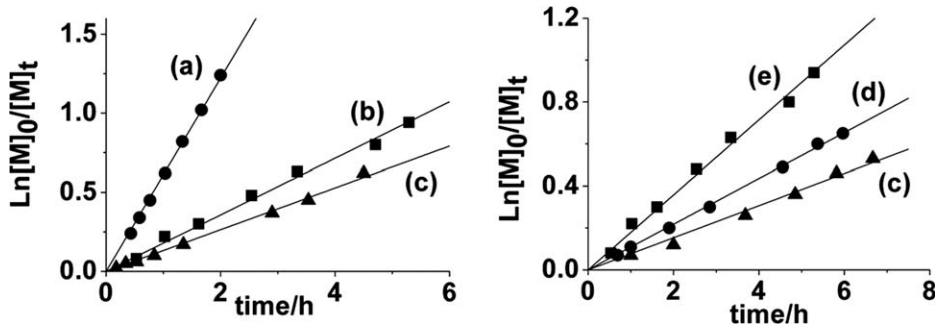


FIGURE 1 Kinetic plots of the *rac*-lactide conversion versus the reaction time: (a) **4a**, $[M]_0/[Cat]$ = 200; (b) **5a**, $[M]_0/[Cat]$ = 200; (c) **6a**, $[M]_0/[Cat]$ = 200; (d) **6a**, $[M]_0/[cat]$ = 160; (e) **6a**, $[M]_0/[Cat]$ = 100.

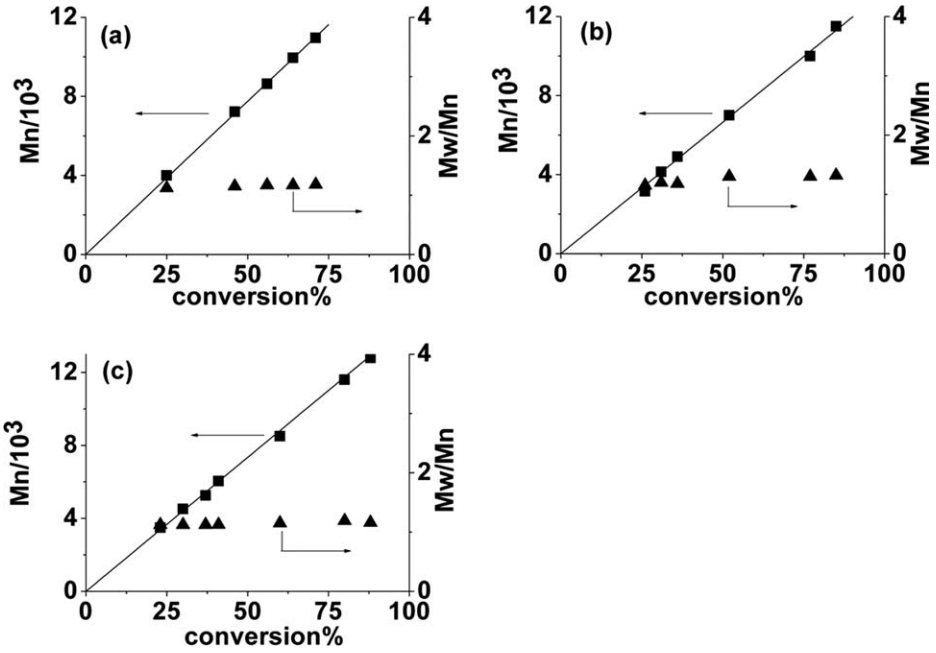


FIGURE 2 Plot of PLA M_n and polydispersity (M_w/M_n) as a function of *rac*-lactide conversion using complex **4a, 5a**, and **6a**, $[M]_0/[Cat] = 200$.

methyl protons of the isopropoxycarbonyl end group and the methine proton neighboring to the hydroxyl end group. This indicated that the polymer chains were systematically end-capped with an isopropyl ester and a hydroxyl group (Fig. 4). The M_n determined by end-group analysis is 1600, close to the theoretical value of 1700. This manifested that the ring-opening occurred through a so-called coordination–insertion mechanism (Scheme 5).[17(b),22]

The influence of temperature on the polymerization rate was also investigated (Fig. 5). The polymerization rate increased with the increasing temperature. The apparent polymerization rate constant k_{app} and polymerization rate constants k_p values were collected in Table 2. An increase in the temperature from 70 °C to 110 °C led to a 630% increase in k_p value (0.59 at 70 °C, 1.63 at 90 °C, 4.3 at 110 °C). From these three k_p values determined at different temperatures in Table 2, the activation energy of the polymerization using **6a**/2-propanol was deduced by fitting $\ln k_p$ versus $10^3/T$ according to the Arrhenius equation ($k_p = Ae^{-E_a/RT}$) (Fig. 6). The activation energy E_a was 54.3 kJ mol^{-1} by **6a**, a 23.4% reduction compared to that by tin(II) octanoate (70.9 ± 1.5 kJ mol^{-1}).[23]

Complex Structure and Stereochemistry

Determination of the stereochemical microstructures of PLA was achieved through inspection of the methine region of homonuclear decoupled ^{1}H NMR spectra of the resultant polymers.[24] The stereoselectivity decreased with the increasing temperature. For example, an increase in the temperature from 70 °C to 110 °C using **6a** led to a reduction in P_m[25] value from 0.87 to 0.61, a 30% reduction. P_m values were collected in Table 2.

The polymerization data indicated that the introduction of substituent groups on the auxiliary ligand surroundings

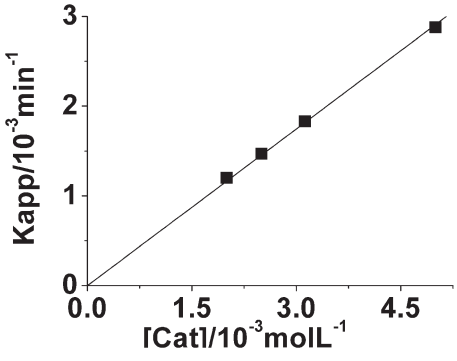


FIGURE 3 k_{app} versus the concentration of **6a** for the *rac*-LA polymerization.

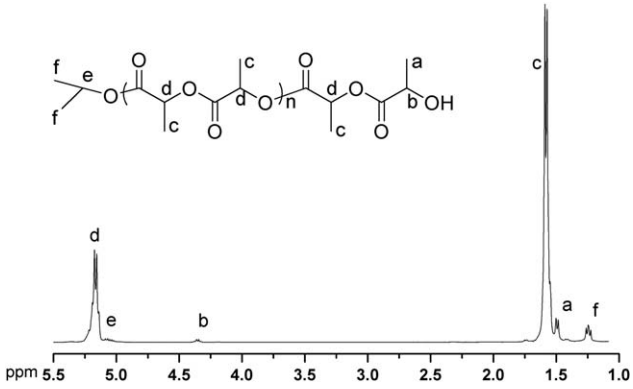
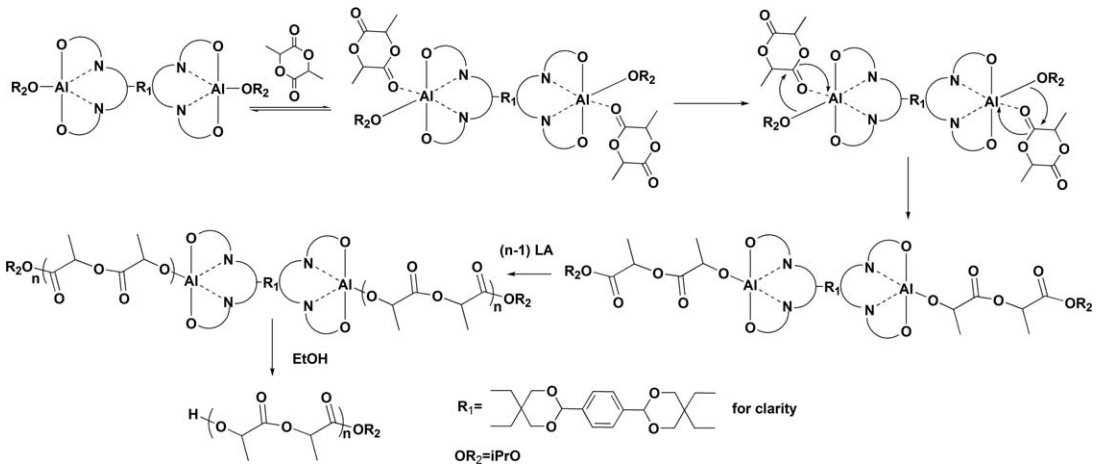


FIGURE 4 ^{1}H NMR spectrum of oligomers of *rac*-LA.



SCHEME 5 Proposed mechanism for the polymerization of lactides.

significantly affected the stereoselectivity and activity. Complexes **4a, 5a**, and **6a** had the same tetraimine backbone, different phenolate substituents, —Cl for **4a**, —CH_3 for **5a**, and — ^{t}Bu for **6a**. Consequently, they displayed different catalytic behaviors. Polymerization data revealed that **4a** had the highest activity; **4a** had its k_p value more than sevenfolds higher than that of **6a**, that is, k_p value was 4.24 L mol^{-1} min^{-1} for **4a** and 0.59 L mol^{-1} min^{-1} for **6a**. The presence of the substituent on the phenolic ring played an important role in determining the polymerization rate. The electron-withdrawing chlorine substituents on ligand increased Lewis acidity of metal centers, enhanced metal electrophilicities. This made the nucleophilic addition through the metal–alkoxide bond easier, resulting in higher polymerization rates. Similar results were found in our previous studies of monometallic enolic and salen-type Schiff-base aluminum complexes.[18(a),19(b)] In our previous systems, fluorin substituted enolic complexes and chlorine substituted salen complexes exhibited greater polymerization activities than did their non-electron-withdrawing substituted counterparts. It was also reported by Gibson[26] that chloro substituents in the phenoxide unit had higher activity than their dimethyl analogues for salan-type catalysts. The more bulky *tert*-butyl (—^{t}Bu) substituents with more steric hindrance may keep

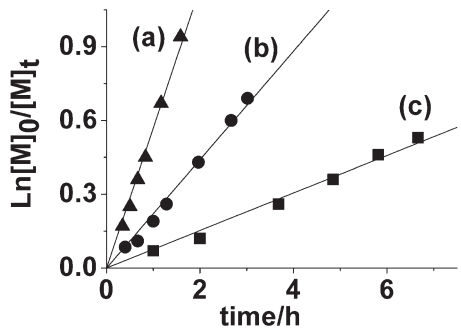


FIGURE 5 Kinetics of the rac-LA polymerization using **6a** at the reaction temperatures of (a) 110 °C; (b) 90 °C; (c) 70 °C, $[M]_0/[Cat] = 200$.

active species from being approached by LA monomer, as a result, slowing down the polymerization rate. A change of substituents from less bulky group to more bulky one led to an increase in stereoselectivity. The P_m value was 0.87 for **6a** and 0.72 for **5a**. The compound **6a** had the highest stereoselectivity. This was consistent with a previous study that the enhancement of stereoselectivity requires bulky substituents at the ortho positions for the stereoselective polymerization adopting chain-end control mechanism.[17(b),22]

Stereochemistry of *Rac*-LA

Since the ligands and complexes reported here were achiral, and there was a preference for isotactic addition during the ROPs of *rac*-LA, we considered the chain-end control mechanism.[17(b),22] In such a reaction, the ligand and the complex were achiral, the initiation reaction occured without any differentiation between the two enantiomers, and the last unit in the growing polymer chain influenced which enantiomer form of the monomers would incorporate next.

In the case of random propagation (Bernoullian statistics), the additions of different enantiomeric monomers were independent events, so the rates of addition of L- and D-monomers to the growing chain-ends were not affected by the configuration of the last repeating unit. Atatic poly(*rac*-LA)s were most probably prepared under this condition. Because there was a preference for isotactic addition during the ROPs of *rac*-LA in this research, the intensity values of the

TABLE 2 Kinetic Results of *Rac*-LA Polymerization at Different Temperatures Using **4a**–**6a**, [M]/[Cat] = 200

Entry	Cat	T/ (°C)	k_{app} (min^{-1})	k_p (L mol^{-1}min^{-1})	P_m
1	**4a**	70	0.01060	4.24	0.68
2	**5a**	70	0.00225	0.90	0.72
3	**6a**	70	0.00147	0.59	0.87
4	**6a**	90	0.00408	1.63	0.69
5	**6a**	110	0.01075	4.30	0.61

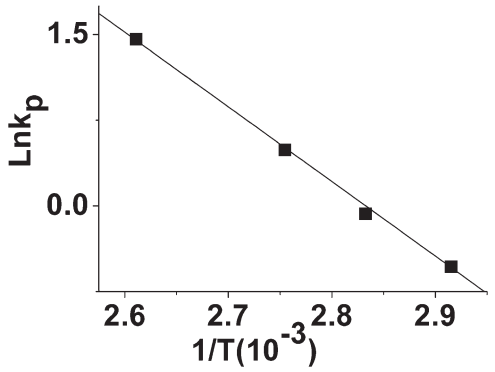


FIGURE 6 Plot of ln k_p versus $1/T$ for the polymerization of *rac*-lactide with **6a**.

individual stereosequences did not obey Bernoullian statistics, so we would prefer a Markovian process to interpret the stereosequence distribution.[27] According to first-order Markovian statistics,[28] the entropy and enthalpy difference between homo-propagation and cross-propagation were calculated as –24.04 ± 3.92 cal Kmol^{-1} and –9.50 ± 1.42 kcal Kmol^{-1}, which may explain the preference of isotactic stereosequence (please see Supporting Information for detailed calculation).

CONCLUSIONS

We reported a series of bimetallic aluminum Schiff-base complexes that acted as catalysts for the polymerization of *rac*-lactide. The complexes activities and stereoselectivities were investigated in detail. The different performance of these complexes was attributed to the different substituent groups on auxiliary ligands. Complex **4a** with electron-withdrawing chlorine substituents had the highest activity and **6a** with bulky substituents had the highest stereoselectivity. Kinetic analysis revealed that the polymerizations of *rac*-LA preceded with first-order rate dependence on both monomer and catalyst concentrations.

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