Stereoselective Polymerization of *rac*-Lactide Using a Monoethylaluminum Schiff Base Complex

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A monoethylaluminum Schiff base complex (**2**) with formula LAlEt (L = *N*,*N*'-(2,2-dimethylpropylene)-bis(3,5-di-*tert*-butylsalicylideneimine) was synthesized and employed for the stereoselective ring-opening polymerization of *rac*-lactide (*rac*-LA). The complex **2** was characterized by nuclear magnetic resonance, crystal structure, and elemental analysis. It contains a five-coordinate aluminum atom with distorted trigonal bipyramidal geometry in the solid state. In the presence of 2-propanol, **2** showed high stereoselectivity for the polymerization of *rac*-LA. The polymerization yielded crystalline poly(*rac*-LA) with a high melting temperature (193−201 °C). NMR, differential scanning calorimetry, and wide-angle X-ray diffraction indicated that the poly(*rac*-LA) was highly isotactic, and a stereocomplex was formed between poly-L- and poly-D-lactide block sequences. By the analysis of electrospray-ionization mass spectrometry and ^{1}H NMR, the polymer was demonstrated to be endcapped in both terminals with an isopropyl ester and a hydroxy group, respectively. The polymerization was of first order in *rac*-LA concentration. The relationship between the *rac*-LA conversion and molecular weights of the polymer was linear so that the polymerization could be well controlled.

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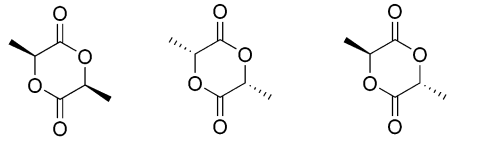
Introduction

Poly(lactic acid)s (PLAs) are biocompatible and biodegradable materials. They have many environmental, biomedical, and pharmaceutical applications and have received much attention especially for the last two decades.[1−21] PLAs are usually synthesized by ring-opening polymerization (ROP) of lactide catalyzed by various metal alkoxide species.[7−9] Because lactides have three different stereoisomers (Chart 1), their polymers may have different chain configurations and the physical and mechanical properties of PLAs, as well as their rate of degradation, are intimately dependent on the chain stereochemistry. For instance, isotactic poly(L-lactide) (PLLA) is a semicrystalline polymer with a melting transition near 180 °C,[17] while atactic poly(*rac*-LA) (*rac*-LA is a 1:1 mixture of L-lactide and D-lactide) and poly(*meso*-lactide) are amorphous polymers. However, interestingly, the equivalent mixture of L-PLA and D-PLA forms a crystalline stereocomplex with a high melting temperature at 230 °C,[18−20] so that the stereocomplex of PLA will have a higher working temperature than its amorphous analogues because the mechanical properties of crystalline polymers are stable up to the melting point of the polymer. And recently, some different physical properties have been found in the systems containing PLA stereocomplexes. For example, Domb and Slivniak found that stereocomplexes of enantiomeric lactic acid and sebacic acid ester anhydride triblock copolymers formed spontaneously uniform porous spherical particles in melt or solution.[14] Kimura et al. discovered that the stereocomplex of PLLA-terminated poly(ethylene glycol) (PEG) and poly(D-lactide)-terminated PEG formed a thermoresponsive hydrogel. It shows an interesting sol−gel transition that was induced by the stereocomplexation around 37 °C.[22] Although stereocomplexes of PLAs have many different properties, the requirement for an enantiopure monomer places restrictions on the polymer synthesis. Fortunately, some single-site catalysts can directly produce a stereocomplex by stereoselective ROP of *rac*-LA. Stereoselectivity, accordingly, is very important for the polymerization of lactides.

Chart 1. Stereoisomers of Lactides



Conventional catalysts usually polymerize *rac*-LA to produce atactic PLAs with random placements of −*RR*− and −*SS*− stereosequences.[8] Recently, it is reported that a few catalysts polymerized *rac*-LA to stereoregular PLAs. For example, [LiO^{t}Bu][23] and [LZnOSiMe$_3$] [L = tris(indazolyl)-borate][24] have shown some stereoselectivity in the ROP of *rac*-LA. And [(bdi)ZnO^{i}Pr] (bdi = β-diiminate)[25,26] was discovered to polymerize *rac*-LA to mostly heterotactic (−*RRSSRRSS*−) PLA, but these catalysts have not polymerized *rac*-LA to stereocomplexes.

It is a challenging work to obtain crystalline poly(*rac*-LA). But several aluminum Schiff base catalysts have been successfully exploited for the stereoselective ROP of *rac*-

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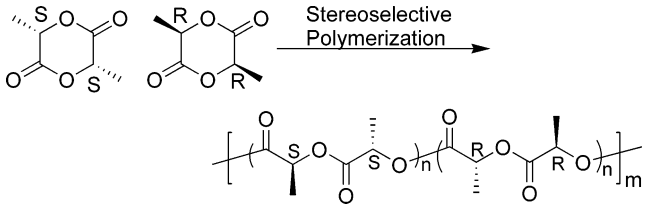
Scheme 1. Synthesis of Stereoblock Copolylactide by Stereoselective Polymerization of *rac*-LA



LA since Spassky et al.[27] discovered that (*R*)-SalBinap)-AlOMe could polymerize *rac*-LA to crystalline PLAs with higher T_m (187 °C) than an optically pure PLA. For instance, Baker et al.[28] and Ovitt and Coates[29,30] reported the polymerization of *rac*-LA with *rac*-(SalBinap)AlO^{i}Pr yielded highly crystalline, predominantly isotactic polymer (T_m = 179−191 °C). Feijen et al.[31,32] succeeded in the synthesis of crystalline PLAs (T_m = 183.5 °C) with long isotactic sequences in toluene or solvent-free polymerization of *rac*-LA by using cyclohexylsalen aluminum alkoxides. Spassky et al.[33] and Nomura et al.[34] presented that a series of aluminum-achiral ligand complexes polymerized *rac*-LA to form a PLA stereocomplex (T_m = 170−192 °C). These high T_m's of poly(rac-LA)s indicated the formation of a stereocomplex. Ovitt and Coates[29] discovered that the crystalline poly(*rac*-LA) was a kind of stereoblock copolymer (Scheme 1). Despite these achievements, however, these aluminum Schiff base catalysts have not been fully characterized because of the lack of crystal structure data. And the search for the catalysts with high stereoselectivity seems to be far from over. From this viewpoint, in this work a monoethylaluminum Schiff base complex (Scheme 2, compound **2**) was synthesized and used to carry out the ROP of *rac*-LA resulting in high stereoselectivity and an excellent molecular-weight control property. The structure of the catalyst and the mechanism of the stereoselective polymerization of *rac*-LA were discussed in detail.

Experimental Section

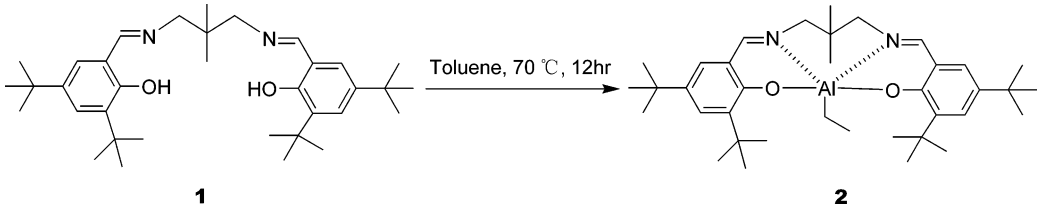
General Details. $AlEt_3$ (Aldrich) was used as received. Toluene was distilled from Na−benzophenone. 2-Propanol and ethyl acetate were distilled from CaH_2. *rac*-LA (from Purac) was purified by recrystallization from ethyl acetate and dried under a vacuum at room temperature before use. NMR spectra were recorded on a Bruker AV 300M, Bruker AV 400M, or Bruker AV 600M 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 410 GPC with tetrahydrofuran (THF) as the eluent (flow rate: 1 mL/min, at 35 °C). The molecular weights were calibrated against polystyrene (PS) standards. the Crystallographic data were collected on a Rigaku Rapid diffractometer (Mo Kα 0.710 73 Å), and calculations were performed using the SHELXL-97 crystallographic software package. Differential scanning calorimetry (DSC) analyses were determined at a heating rate of 10 °C/min on a Perkin Elmer Pyris 1. The values originated from the second heating scan. A wide-angle X-ray diffraction (WAXD) measurement was carried out from 5 to 30° using a D/Max 2500V PC system. Electrospray-ionization mass spectrometry (ESI-MS) was recorded on a Finnigan LCQ mass spectrometer operated in positive-ion mode.

Synthesis of *N,N'*-(2,2-Dimethyl-1,3-propylene)bis(3,5-di-*tert*-butylsalicylideneimine) (1). To a stirred ethanol solution (400 mL) of 3,5-di-*tert*-butylsalicylaldehyde (20.6 g, 88.0 mmol) was added 2,2-dimethyl-1,3-propanediamine (4.09 g, 40.0 mmol) in ethanol (50 mL). The reaction was refluxed for 14 h before being cooled to room temperature. Removal of the solvent under a vacuum gave a yellow crystalline solid that was yielded and purified by recrystallization in ethanol (yield: 19.9 g, 93%). ^{1}H NMR (400M, $CDCl_3$): δ = 13.81 (broad, 2H), 8.36 (s, 2H), 7.39 (s, 2H), 7.11 (s, 2H), 3.48 (s, 2H), 1.46 (s, 18H), 1.31 (s, 18H), 1.10 (s, 6H). Elem anal. Calcd: C, 78.60; H, 10.18; N, 5.24. Found: C, 79.22; H, 10.32; N, 5.14.

Synthesis of [2,2-Dimethyl-1,3-propylenebis(3,5-di-*tert*-butylsalicylideneiminato)] Ethyl Aluminum(III) (2). To a stirred toluene solution (4 mL) of compound **1** (4.0 mmol, 2.14 g) was added $AlEt_3$ (4.0 mmol, 0.46 g) in toluene (4 mL). The reaction was allowed to stir at 70 °C for 12 h. The mixture solution was slowly cooled to room temperature to yield pale yellow and green crystals. A crystal of approximately 0.68 × 0.51 × 0.38 mm^3 was selected for X-ray diffraction data collection. ^{1}H NMR (600M, $CDCl_3$) spectrum of compound **2**: δ = 8.11 (s, 2H), 7.47 (s, 2H), 7.00 (s, 2H), 3.43 (d, 2H, J = 12 Hz), 3.28 (d, 2H, J = 12 Hz), 1.49 (s, 18H), 1.30 (s, 18H), 1.15 (s, 3H), 1.03 (s, 3H), 0.74 (t, 3H), −0.31 (q, 2H). Elem anal. Calcd: C, 75.47; H, 9.76; N, 4.76. Found: C, 76.09; H, 9.42; N, 4.95. Crystal data of compound **2**: $C_{37}H_{57}AlN_2O_2$; M_r = 588.83; T = 293(2) K; monoclinic, space group $P2_1/n$; a = 10.135(2), b = 17.391(4), c = 20.788(4) Å, β = 98.25(3)°, V = 3626.1(13) Å^3; Z = 4; ρ_{calcd} = 1.079 Mg m^{-3}; F000 = 1288; final R indices [$I > 2\sigma(I)$] R1 0.0524, wR2 0.1144.

Polymerization. Under the protection of argon, the *rac*-LA (44.1 mmol, 6.36 g), 2-propanol (0.362 mmol, in 4.6 mL of toluene), catalyst **2** (0.362 mmol, in 5.5 mL of toluene), and toluene (72 mL) were added to a dried reaction vessel equipped with a magnetic stirrer bar. The vessel was placed in an oil bath at 70 °C. The conversion of the monomer was monitored by ^{1}H NMR. The polymer was

Scheme 2. Synthesis of Compound **2**



1 **2**

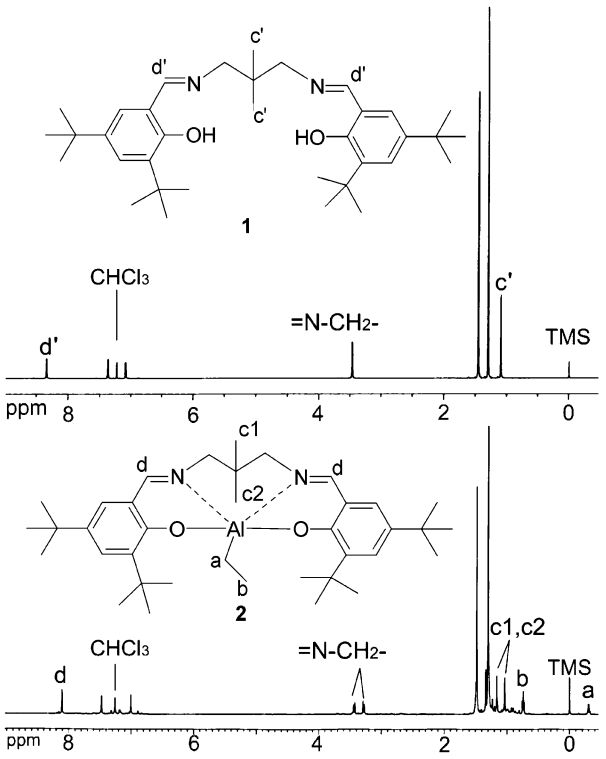


Figure 1. ^{1}H NMR spectra of compound **1** (400M, $CDCl_3$) and **2** (600M, $CDCl_3$).

isolated by precipitation into cold methanol and by filtration and was dried under vacuum at room temperature for 24 h.

Results and Discussion

Synthesis of Catalyst. Compound **1** was easily prepared by the 2:1 condensation of 2,2-dimethyl-1,3-propanediamine and 3,5-di-*tert*-butylsalicylaldehyde in refluxing absolute ethanol. Elemental analysis and ^{1}H NMR revealed that *N*,*N*'-(2,2-dimethyl-1,3-propylene)bis(3,5-di-*tert*-butylsalicylideneimine) was formed in high yield. Compound **2** was prepared by the reaction of the ligand (**1**) and $AlEt_3$.[35] The ^{1}H NMR spectrum (Figure 1) of compound **2** (see for comparison that of compound **1**) showed signals at δ −0.31 and +0.74 ppm with an integral ratio of 2:3, which are attributed to the methylene protons and methyl protons of the Et group on Al, respectively. The $-C(CH_3)_2-$ protons display two single peaks at 1.15 and 1.03 ppm, the $=N-CH_2-$ protons show resonances at 3.43 and 3.28 ppm, and the $-N=CH-$ protons show a signal at 8.11 ppm. The integral ratio of the signals at 1.15, 1.03, and 0.74 ppm is 1:1:1. And the equal intensities of the signals at 3.43, 3.28, 8.11, and −0.31 ppm confirmed the formation of the [2,2-dimethyl-1,3-propylenebis(3,5-di-*tert*-butylsalicylideneiminato)] ethyl aluminum(III). The geometry of five-coordinate aluminum Schiff base complexes is either square pyramidal or trigonal bipyramidal.[36] For complex **2**, it contains a central Al atom in a distorted trigonal bipyramidal geometry in the solid state. This geometry was confirmed by X-ray diffraction (Figure 2). The N(1)−Al−O(2) angle is 167.41(8)°, while the N(2)−Al−O(1) angle is 121.90(8). The remaining angles range from 82.90(7)° for N(1)−Al−N(2) to 121.00(10) for O(1)−Al−C(36). The amount of the distortion can be

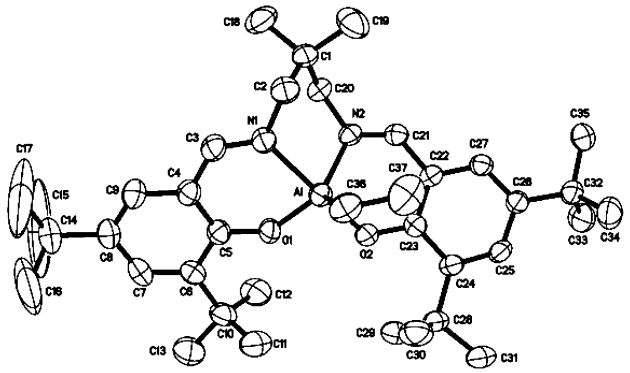


Figure 2. Crystal structure of compound **2**.

Table 1. Polymerization of *rac*-LA in the Presence of **2** and Isopropanol[a]

entry	time, min	conv.,[b] %	$M_{n,GPC}$[c] × 10^{-3}	M_n[d] × 10^{-3}	PDI[c]	P_m[e]	T_m,[f] °C
1	49	17.0	5.2	3.0	1.09	0.87	196
2	115	32.0	8.1	4.7	1.21	0.88	201
3	237	53.2	14.8	8.6	1.18	0.90	198
4	332	64.3	17.8	10.3	1.18	0.90	197
5	404	72.0	19.3	11.2	1.21	0.89	195
6	495	77.8	21.2	12.3	1.19	0.90	194
7	598	83.6	23.2	13.5	1.15	0.89	193
8	1035	91.2	25.7	14.9	1.05	0.90	193

[a] $[LA]_0$ = 0.5 M, $[LA]_0$:$[Al]_0$:[2-propanol]$_0$ = 122:1:1; solvent, toluene; temperature, 70 °C. [b] Measured by ^{1}H NMR. [c] Determined by GPC in THF, relative to PS standard. [d] Calculated from the valaue of M_n determinated by GPC according to formula $M_n = 0.58M_{n,GPC}$.[39] [e] The parameter P_m is the probability of meso linkages. According to CEM, the expressions for the terad probabilities of poly(*rac*-LA) are[25] [mmm] = $P_m^2 + (1 - P_m)P_m/2$, [mmr] = [rmm] = $(1 - P_m)P_m$, [rmr] = $(1 - P_m)^2$, and [mrm] = $[(1 - P_m)^2 + P_m(1 - P_m)]/2$. [f] Determined by DSC (heating rate: 10 °C/min, second scan).

measured by τ.[36] The τ value ranges from 0 (perfectly square pyramidal) to 1 (perfectly trigonal bipyramidal). For compound **2**, the τ value is 0.76, which indicates more trigonal bipyramidal geometry in the solid state. It is similar to Salpen(^{t}Bu)AlCl.[36] Because of the distorted trigonal bipyramidal geometry of the central Al atom, the mirror image of **2** cannot duplicate itself. It indicates that compound **2** is chiral in the solid state. But in solution, the structure of compound **2** is different. If the chirality of **2** in the solid state is maintained in solution, two different peaks for $-N=CH-$ protons and four different signals for $=N-CH_2-$ protons should appear in the ^{1}H NMR spectrum owing to the distorted trigonal bipyramidal geometry of complex **2**. In reality, only one peak appears for $-N=CH-$ protons and two signals appear for $=N-CH_2-$ protons, respectively. These facts indicate that an exchange between the two conformational stereoisomers of **2** is fast on the NMR scale. The fast exchange results in fast racemization of **2** in solution.

Polymerization. The polymerization (Table 1) of *rac*-LA with **2** in the presence of 2-propanol afforded crystalline PLAs. The PLAs showed melting points significantly higher than that of enantiopure isotactic PLA ($T_m \approx 180$ °C); furthermore, the poly(*rac*-LA)s even showed a melting point as high as 201 °C (Figure 3), the highest value in all reported stereoblock copolylactides synthesized from *rac*-LA. This fact is strong proof that a stereocomplex between poly-L- and poly-D-lactide sequences was formed. In the diffraction

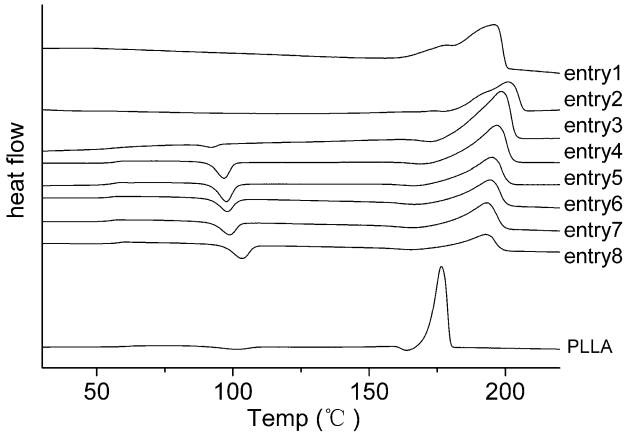


Figure 3. DSC traces (heating rate: 10 °C/min, second scan) of PLLA and poly(*rac*-LA)s in Table 1.

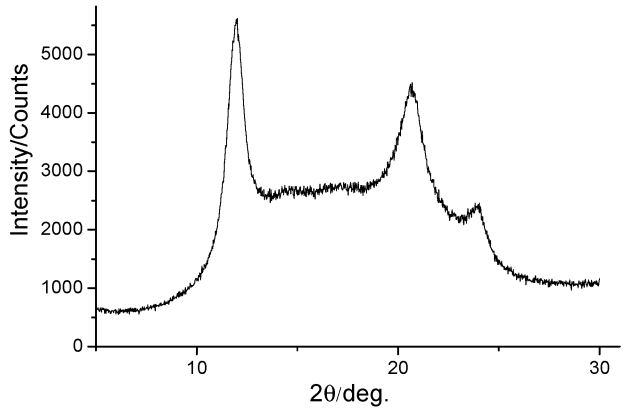


Figure 4. WAXD spectrum of the experimental powder pattern of poly(*rac*-LA) (Table 1, entry 3).

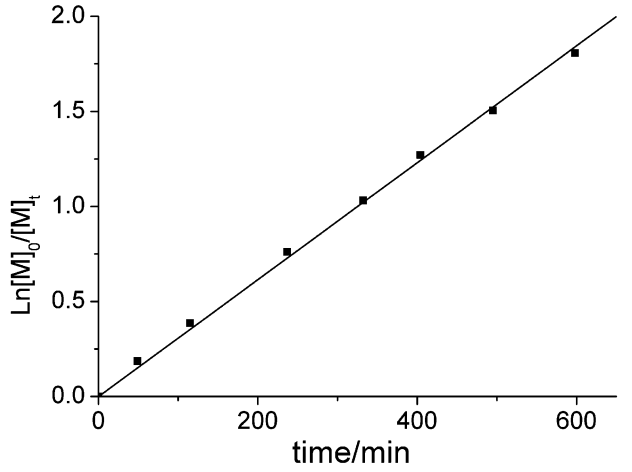


Figure 5. Kinetics of the ROP of *rac*-LA in toluene at 70 °C; $[M]_0$ = 0.5 mol/L, $[M]_0$:$[Al]_0$:[2-propanol] = 122:1:1 ($k_{app} = 3.08 \times 10^{-3}$ min^{-1}).

pattern (Figure 4) of poly(*rac*-LA), three peaks were observed at 2θ values of 12, 21, and 24°, which also matched that of the stereocomplex.[18,37,38] The kinetics of the *rac*-LA polymerization in toluene was investigated at 70 °C, and the monomer conversion was monitored by ^{1}H NMR as a function of the polymerization time. The polymerization was of first order in *rac*-LA concentration (Figure 5). This first-order kinetics implied that the concentration of the active species remained unchanged during polymerization or the growing polymer chains remained alive. Baran et al. have

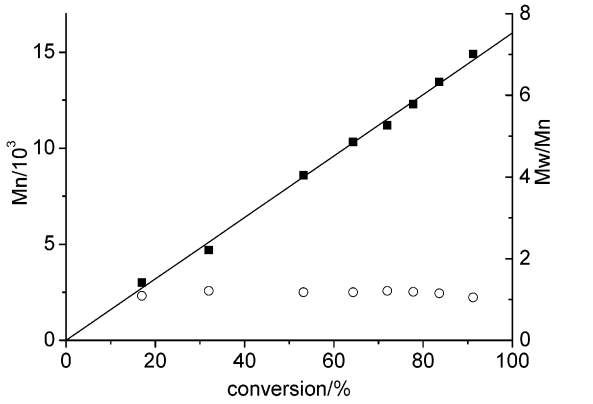


Figure 6. Molecular weight (squares) and polydispersity index (M_w/M_n, circles) of poly(*rac*-LA) versus conversion of monomer with [*rac*-LA]$_0$:[Al]$_0$:[2-propanol]$_0$ = 122:1:1 at 70 °C in toluene, [*rac*-LA]$_0$ = 0.5 mol/L.

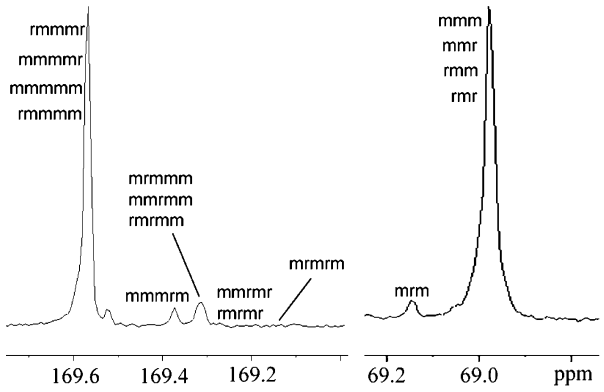


Figure 7. ^{13}C NMR spectrum of stereoblock poly(*rac*-LA) (Table 1, entry 8, 75 MHz, $CDCl_3$)

shown that, for polylactide in THF, the ratio of real M_n and M_n based on PS calibration equals 0.58.[39] Therefore, the values of M_n could be calculated according to this correction factor. Figure 6 depicted the molecular weight and polydispersity index of the poly(*rac*-LA) as a function of the monomer conversion. The average molecular weights increase linearly with conversion. The low polydispersity index implied that transesterification was very slight during the polymerization. These phenomena indicate that the polymerization of *rac*-LA is well controlled in the presence of complex **2** and 2-propanol.

^{13}C NMR (Figure 7) and homonuclear decoupled ^{1}H NMR (Figure 8) spectra manifested that the poly(*rac*-LA)s obtained were predominantly isotatic.[29,31−32] The homonuclear decoupled ^{1}H NMR spectrum of the methine region of poly(*rac*-LA) can show tetrad stereosequence sensitivity probabilities.[40] The degree of stereoselectivity of compound **2**, which may be defined by the parameter P_m (P_m is the probability of meso linkages), can be determined from the relative tetrad intensities.[34] For this initiator system, $P_m \approx$ 0.90 (Table 1).

The ^{1}H NMR spectrum of oligomers of polycolactide (prepared with a concentration ratio of [*rac*-LA]:[**2**]:[2-propanol] = 7:1:1 after quenching with a little acetic acid in 24 h) is shown in Figure 9. The two doublets appearing as a triplet at 1.24 ppm and the quartet at 4.34 ppm, with an integral ratio close to 6:1, were assignable to the methyl protons of the isopropoxycarbonyl end group and the methine

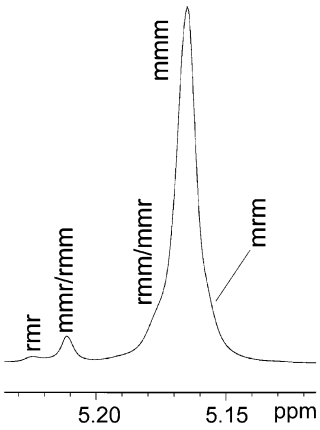


Figure 8. Homonuclear decoupled ^{1}H spectrum of the methine region of poly(*rac*-LA) (Table 1, entry 8, 600 MHz, $CDCl_3$).

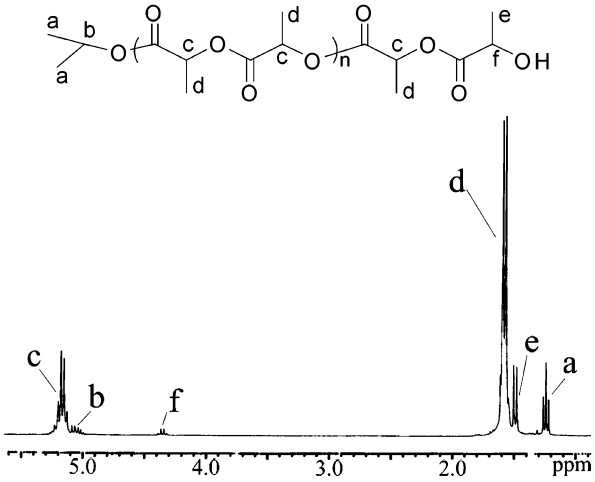


Figure 9. ^{1}H NMR spectrum of oligomer of poly(*rac*-LA) (300 MHz, $CDCl_3$).

proton neighboring the hydroxyl end group.[41] Analysis of the oligomers by ESI-MS exhibited oligomers of the formula $H(OCHMeCO)_{2n}O^iPr^{\bullet}Na^+$ ($n = 4-13$) as well as the cation corresponding to the catalyst (ligand Al^+). Small peaks in the spectrum with masses intermediate to those of the primary species were due to transesterification caused by excessive reaction time (Figure 10). These features confirmed that the polymer chains were end-capped with an isopropyl ester and a hydroxy group, respectively. And it indicated that the Al−Et bond itself was not active for the ROP of lactide. First, it reacted with 2-propanol to produce an Al−isopropoxy bond, and then, the latter initiated the ROP of lactide.

For the stereoselective ROP of *rac*-LA, achiral aluminum Schiff base catalysts operated a chain-end control mechanism (CEM),[33,34] whereas chiral aluminum Schiff base catalysts induced a process with a site control mechanism.[27−32] As described previously, because of the fast racemization in solution, it is likely that complex **2** follows a CEM.

Conclusions. A monoethylaluminum Schiff base complex (**2**) with a doubtless spatial structure suitable for the stereocontrollable ROP of *rac*-LA was reported in this paper. The crystal structure of the complex **2** contained a five-coordinate aluminum atom with distorted trigonal bipyramidal geometry. The complex **2** in the presence of 2-propanol carried out the ROP of *rac*-LA with high stereoselectivity

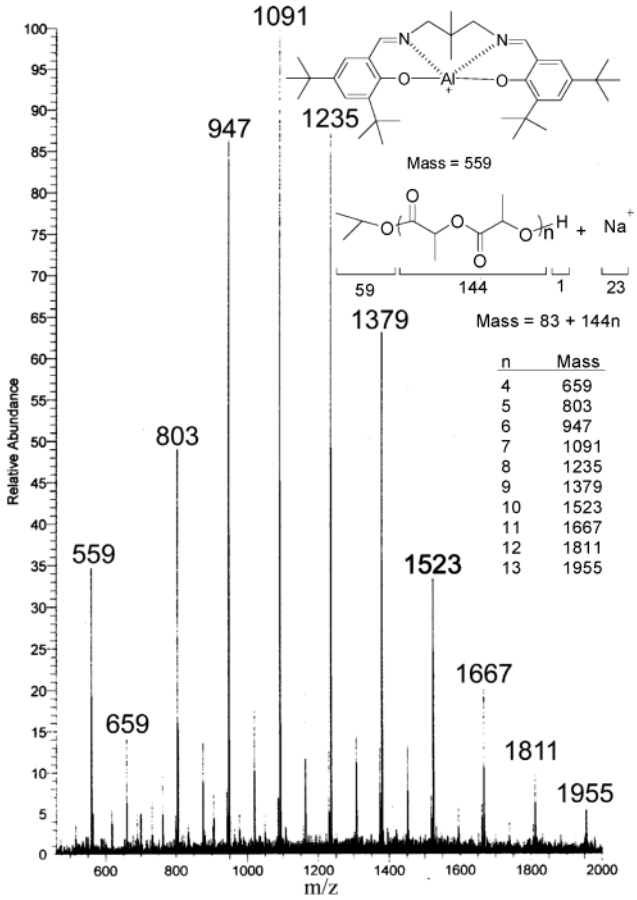


Figure 10. ESI-MS of oligomer of poly(*rac*-LA).

and excellent molecular-weight control. The correlative PLAs exhibit comparable or higher isotacticity than the known poly(*rac*-LA)s prepared by other stereoselective catalysts. The polymerization is supposed to follow a CEM. And further studies will be focused on the stereoselective mechanism and the synthesis of novel catalysts with a center metal fixed in a cage to form a chiral structure.

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Supporting Information Available. The data of the crystal structure of compound **2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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