Controlled and Stereospecific Polymerization of *rac*-Lactide with A Single-Site Ethyl Aluminum and Alcohol Initiating System

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ABSTRACT: A single-site ethyl aluminum complex, [2,2-diethyl-1,3-propylenebis(3,5-di-*tert*-butyl-salicylideneiminato)] ethyl aluminum (**2**), with a geminal diethyl substitutent on the diamino bridge was synthesized by the reaction of $AlEt_3$ with 1 equiv of *N,N′*-(2,2-diethyl-1,3-propylene)bis(3,5-di-*tert*-butylsalicylideneimine). X-ray diffraction showed that complex **2** contained a five-coordinate aluminum atom with a distorted trigonal bipyramidal geometry in the solid state. ^{1}H-NMR and ^{13}C-NMR spectra indicated that the two conformational enantiomers of **2** tautomerized quickly on the NMR timescale in solution. In the presence of isopropyl alcohol, the ring-opening polymerization (ROP) of *rac*-lactide with complex **2** produced a crystalline stereoblock polylactide (PLA). The stereoblocks contained an average of 12 units ($\bar{L}$ = 12) of enantiomerically pure lactic acid. There was a linear relationship between the monomer conversion and number-average molecular weights of the polymer. An induction period was observed for the polymerization. The induction period increased with decreasing concentration of catalyst **2** and isopropyl alcohol. In the presence of poly(ethylene glycol) (PEG), a PLA/PEG/PLA stereocomplex was prepared directly by the ROP of *rac*-lactide with complex **2,** which was confirmed by NMR, gel permeation chromatography, wide-angle X-ray diffraction, and differential scanning calorimetry. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 102–108, 2005

Key words: ring-opening polymerization; block copolymers; stereospecific polymers

INTRODUCTION

The ring-opening polymerization (ROP) of lactide (LA) is the major pathway for the synthesis of polylactide (PLA); PLA has been used increasingly environmental, biomedical, and pharmaceutical applications.[1–5] The physical and mechanical properties of PLA are intimately linked to the chain stereochemistry.[6–9] The stereoselective ROP of LA is a convenient way to control the microstructure of PLAs; therefore, it has been paid more and more attention.[10–12] Specifically, because crystalline poly(*rac*-lactide) [poly(*rac*-LA); *rac*-lactide (*rac*-LA) is a 1:1 mixture of L-lactide (LLA) and D-lactide (DLA)] has a higher working temperature than homochiral poly(L-lactide) (PLLA) or poly(D-lactide) (PDLA), the synthesis of crystalline poly(*rac*-LA) stereocomplex by stereospecific ROP has become a focus of researchers.[13–24]

Stereocomplexes of PLLA/poly(ethylene glycol) (PEG)/PDLA and PLLA/PEG/PDLA can form novel bioresorbable and thermoresponsive hydrogels that have potential applications as injectable drug-delivery systems.[25–28] The hydrogels are induced by stereocomplexation occurring between PLLA and PDLA blocks and can show sol–gel transitions around 37°C. However, the synthesis of PLLA/PEG/PDLA and PLLA/PEG/PDLA requires enantiopure LLA and DLA, which results in restrictions on the preparation of the PLA/PEG/PLA stereocomplex. However, because the stereospecific catalysts can polymerize *rac*-LA to the PLA stereocomplex directly,[13–24] it should be feasible to prepare the PLA/PEG/PLA stereocomplex by the stereospecific ROP of *rac*-LA of PEG in this study.

In this article, we report on an aluminum Schiff base ethyl catalyst, [2,2-diethyl-1,3-propylenebis(3,5-di-*tert*-butyl-salicylideneiminato)] ethyl aluminum (**2**), with a geminal diethyl substitutent on the diamino bridge. Catalyst **2** showed good controllability and stereoselectivity for the ROP of *rac*-LA and produced a novel structure for the PLA/PEG/PLA stereocomplex. This was the first time that the PLA/PEG/PLA stereocom-

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plex was synthesized by the direct polymerization of *rac*-LA.

EXPERIMENTAL

General

2,2-Diethyl-propane-1,3-diamine was prepared according to reported methods.[29] $AlEt_3$ and PEG (Aldrich, Milwaukee, WI) were used as received. The number-average molecular weight (M_n) of PEG was 4600 Da, and its molecular weight distribution (MWD) was 1.06. Toluene was distilled from Na benzophenone. Ethyl acetate was distilled from CaH_2. *rac*-LA (Purac) was purified by recrystallization from ethyl acetate and dried *in vacuo* at room temperature before use. NMR spectra were recorded on a Bruker AV 300-, 400-, or 600-MHz instrument in $CDCl_3$ or dimethyl sulfoxide (DMSO)-d_6 at room temperature. Chemical shifts were given in parts per million from tetramethylsilane (for $CDCl_3$) or the impurity in solvent (for DMSO-d_6). Gel permeation chromatography (GPC) measurements were carried out with a Waters instrument (515 HPLC pump) equipped with a Wyatt interferometric refractometer. GPC columns were eluted with $CHCl_3$ at 25°C at 1 mL/min. The molecular weights were calibrated against polystyrene standards. Differential scanning calorimetry (DSC) analyses were conducted on a PerkinElmer Pyris 1. Wide-angle X-ray diffraction (WAXD) measurements were carried out from 5 to 35° with a D/Max 2500 V PC system.

Synthesis of *N,N′*-(2,2-diethyl-1,3-propylene)bis(3,5-di-*tert*-butylsalicylideneimine) (1)

To a stirred solution of 3,5-di-*tert*-butylsalicylaldehyde (4.83 g, 20.6 mmol) in 60 mL of ethanol, 2,2-diethyl-propane-1,3-diamine (1.30 g, 10.0 mmol) in ethanol (20 mL) was added dropwise. The reaction mixture was refluxed for 18 h before being cooled to room temperature. After removal of the solvent *in vacuo*, a yellow crystalline solid was obtained and purified by recrystallization in ethanol (yield = 5.07 g, 90%):

Anal.: Calcd for $C_{37}H_{58}N_2O_2$: C, 78.95%; H, 10.39%; N, 4.98%; Found: C, 79.31%; H, 10.57%; N, 4.80%. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 13.75 (broad, 2H, O***H***), 8.38 (s, 2H, ***H***C═N), 7.38 (s, 2H, Ph***H***), 7.09 (s, 2H, Ph***H***), 3.48 (s, 4H, NC***H***$_2$), 1.48 (q, 4H, C***H***$_2$CH$_3$), 1.46 [s, 18H, C(C***H***$_3$)$_3$], 1.30 [s, 18H, C(C***H***$_3$)$_3$], 0.94 ppm (t, 6H, CH$_2$C***H***$_3$).

Synthesis of 2

Under the protection of argon, Schiff base ligand **1** (3.0 mmol, 1.69 g), $AlEt_3$ (3.0 mmol, 0.34 g), heptane (6 mL), and toluene (3 mL) were added to a dried reaction vessel equipped with a magnetic stirring bar. The reaction was conducted at 100°C for 24 h. Pale yellow and green crystals of **2** (yield = 2.16 mmol, 1.33 g, 72%) were formed after the solution was slowly cooled to room temperature. A crystal of approximately 0.22 × 0.18 × 0.08 mm^3 was selected for X-ray diffraction data collection:

Anal.: Calcd: C, 75.93%; H, 9.97%; N, 4.54%. Found: C, 75.35%; H, 9.79%; N, 4.37%. ^{1}H-NMR (400 MHz, $CDCl_3$, δ) spectrum of compound **2**: 8.08 (s, 2H, ***H***C═N), 7.47 (s, 2H, Ph***H***), 6.98 (s, 2H, Ph***H***), 3.42 (d, 2H, NC***H***$_2$, J = 12 Hz), 3.28 (d, 2H, NC***H***$_2$, J = 12 Hz), 1.55 [q, 2H, C(C***H***$_2$CH$_3$)$_2$], 1.49 [s, 18H, C(C***H***$_3$)$_3$], 1.40 [q, 2H, C(C***H***$_2$CH$_3$)$_2$], 1.30 [s, 18H, C(C***H***$_3$)$_3$], 0.95 [t, 3H, C(CH$_2$C***H***$_3$)$_2$], 0.90 [t, 3H, C(CH$_2$C***H***$_3$)$_2$], 0.72 (t, 3H, AlCH$_2$C***H***$_3$), −0.32 ppm [q, 2H, AlC***H***$_2$CH$_3$]. ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 170.2 (H***C***—N); 163.5, 140.7, 137.3, 130.2, 126.9, 118.3 (***C*** aromatic ring); 64.6 (N***C***H$_2$); 41.4 [***C***(CH$_2$CH$_3$)$_2$], 35.5 [***C***(CH$_3$)$_3$]; 34.0 [***C***(CH$_3$)$_3$]; 31.4 [C(***C***H$_3$)$_3$]; 29.6 [C(***C***H$_3$)$_3$]; 26.3 [C(***C***H$_2$CH$_3$)$_2$]; 26.2 [C(***C***H$_2$CH$_3$)$_2$]; 10.5 (AlCH$_2$***C***H$_3$); 7.7 [C(CH$_2$***C***H$_3$)$_2$]; 7.6 [C(CH$_2$***C***H$_3$)$_2$]; 2.9 ppm (broad, Al***C***H$_2$CH$_3$).

X-ray crystallography

Crystallographic data of complex **2** were collected on a Bruker APEX CCD diffractometer with Mo Kα radiation (λ 0.71073 Å) with a φ scan followed by a ω scan to fill the sphere. All calculations were performed with the SHELXTL crystallographic software package:

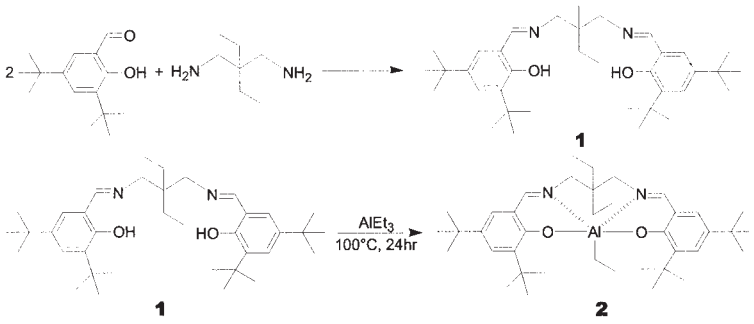
Crystal data for **2**: $C_{39}H_{61}AlN_2O_2 \cdot 0.25(C_7H_8)$, M = 639.91, temperature = 293(2) K, monoclinic, space group $P2_1/n$; a = 10.680(3), b = 20.574(6), c = 19.680(6) Å; β = 105.745(15)°; V = 4162(2) Å^3, Z = 4, μ(Mo Kα;) = 0.081 mm^{-1}; ρ_{calcd} = 1.021 Mg/m^3, F000 = 1402, 21232 reflections collected, 7255 independent reflections (R_{int} = 0.0717), final R indices [$I > 2\sigma$ (I)]: R1 0.0685, wR2 0.1449.

Stereospecific polymerization of *rac*-LA

In a typical experiment, *rac*-LA (17.4 mmol, 2.51 g), isopropyl alcohol (0.295 mmol in 4.8 mL of toluene), catalyst **2** (0.295 mmol in 6.5 mL of toluene), and toluene (21 mL) were added to a dried reaction vessel equipped with a magnetic stirring bar under the protection of argon. 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 isolated by precipitation into cold methanol and by filtration and was dried *in vacuo* at room temperature for 24 h.

Synthesis of the PLA/PEG/PLA stereocomplex

Under the protection of argon, *rac*-LA (5.27 mmol, 0.76 g), PEG (1.26 g), catalyst **2** (0.55 mmol, 0.34 g), and



Scheme 1 Preparation of ethyl aluminum Schiff-base complex **2.**

toluene (10 mL) were added to a dried reaction vessel equipped with a magnetic stirring bar. The solution was stirred for 24 h at 70°C. The polymer was isolated by precipitation into diethyl ether and by filtration and was dried *in vacuo* at room temperature for 24 h (yield = 1.86 g, 92%). M_n of the copolymer was 7.3 $\times$ 10^3 Da, which was determined by the integration of ^{1}H-NMR resonances belonging to C**H**$_3$ protons of PLA block and C**H**$_2$ protons of PEG block. The MWD [weight-average molecular weight (M_w)/M_n, determined by GPC] was 1.07.

RESULTS AND DISCUSSION

Synthesis and characterization of catalyst 2

2,2-Diethyl-propane-1,3-diamine was prepared from 2,2-diethyl-propane-1,3-diol according to reported methods.[29] **1** was easily synthesized in high yield by the condensation of 2,2-diethyl-propane-1,3-diamine and 3,5-di-*tert*-butyl-salicylaldehyde. The reaction of Schiff base ligand **1** with equivalent $AlEt_3$ resulted in the formation of complex **2** in toluene and heptane at 100°C for 24 h as pale yellow and green crystals (Scheme 1). The ^{1}H-NMR spectra of **1** and **2** were shown in Figure 1. For Schiff base **1**, the —C(CH_2CH_3)$_2$ group showed a quartet at δ = 1.48 and a triplet at δ = 0.94 ppm; the —N═CH— and —NCH_2— protons displayed singlets at δ = 8.38 and 3.48 ppm, respectively. For catalyst **2**, however, the —C(CH_2CH_3)$_2$ group afforded two quartets (1.55 and 1.40 ppm) and two triplets (0.95 and 0.90 ppm), the —N═CH— proton appeared as one singlet that shifted to a higher field (8.08 ppm), and the ═NCH_2— protons displayed two doublets at δ = 3.42 and 3.28 ppm. In addition, the —$AlCH_2CH_3$ protons showed signals at 0.72 ppm (triplet) and −0.32 ppm (quartet) with an integral ratio of 3:2. The equal intensities of the signals at δ 1.55, 8.08, 3.42, and −0.32 ppm confirmed the formation of **2**.

The solid-state structure of **2** determined by X-ray analysis is shown in Figure 2. Complex **2** contained a five-coordinated central Al atom. The τ value of **2** was 0.75, which clearly indicated that the central Al

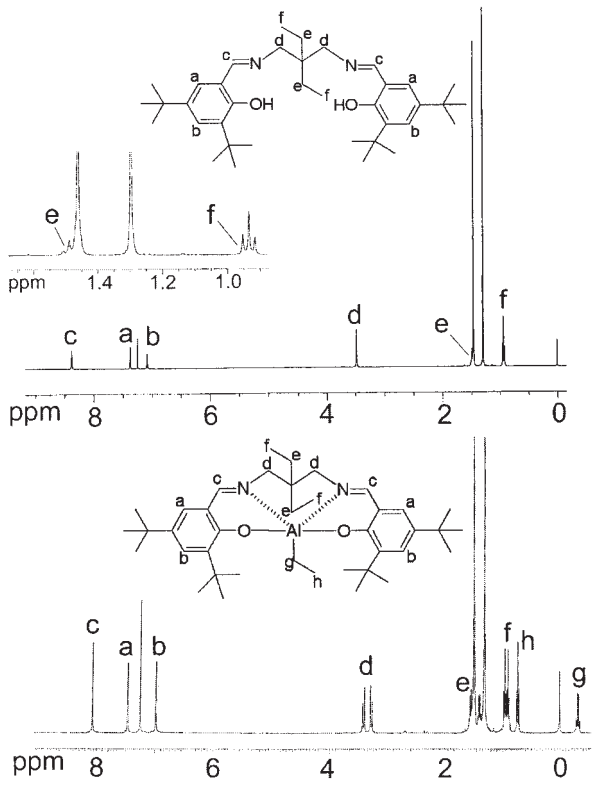


Figure 1 ^{1}H-NMR spectra of **1** and **2** (400 MHz, $CDCl_3$).

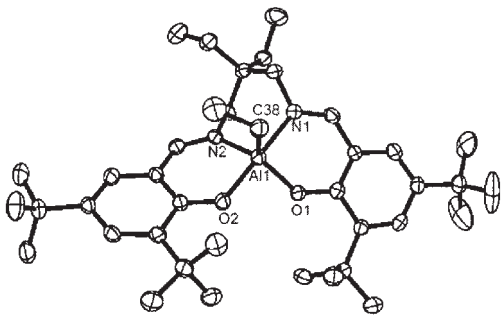


Figure 2 Crystal structure of complex **2**. Selected bond lengths: Al1—O1 1.776(2), Al1—C38 1.969(3), Al1—N1 2.059(3), Al1—O2 1.833(2), and Al1—N2 2.013(3) Å. Selected bond angles: O1—Al1—C38 121.14(13), O1—Al1—N2 122.80(11), C38—Al1—N2 115.72(13), and O2—Al1—N1 167.86(11)°.

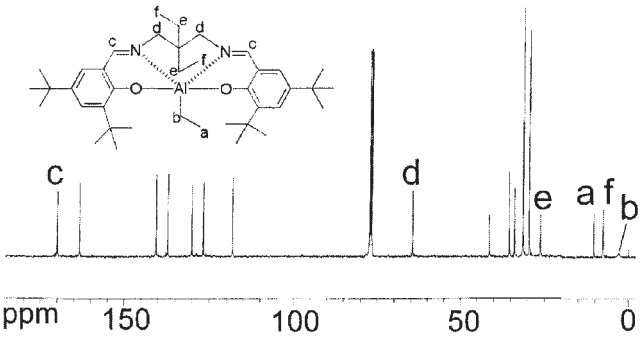


Figure 3 ^{13}C-NMR spectrum of complex **2** (100 MHz, $CDCl_3$).

adopted a distorted trigonal bipyramidal geometry in the solid state.[30] As expected, the axial N1 and O2 atoms formed somewhat longer bonds to the Al atom [2.059(3) and 1.833(2) Å, respectively] than the equatorial N2 and O1 atoms [2.013(3) and 1.776(2) Å, respectively]. Compared with the geminal dimethyl substituted analogue,[18] the bond distances of Al—C [1.969(3) Å], Al—N, and Al—O did not differ significantly, the angles of N1—Al—O2 [167.86(11)°] and N2—Al—O1 [122.80(11)°] were slightly wider; however, the angle of N2—Al—C38 [115.72(13)°] was somewhat narrower.

Because of the distorted trigonal bipyramidal geometry in the solid state, complex **2** possessed two conformational enantiomers. However, the two conformational enantiomers were not stable in solution, which was supported by the NMR analysis of complex **2**. In the ^{1}H-NMR spectrum of **2**, there were only two peaks (1.49 and 1.30 ppm) for the four —$C(CH_3)_3$ groups, one peak (8.08 ppm) for the two —N═CH— groups, two peaks (7.48 and 7.02 ppm) for the four Ar—H protons, and two peaks (3.42 and 3.28 ppm) for the four ═NCH_2— protons. In the ^{13}C-NMR spectrum

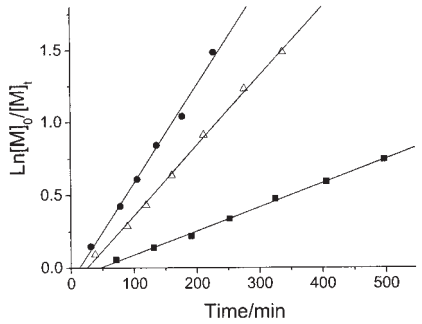


Figure 4 Kinetics of the ROP of *rac*-LA in toluene at 70°C ([M_0] = 0.5 mol/L);. (■) induction period = 45 min, k_{app} = 1.65 × 10^{-3} min^{-1}, and $[M]_0/[Al]_0$/[Isopropyl alcohol] = 120:1:1; (△) induction period = 25 min, k_{app} = 4.81 × 10^{-3} min^{-1}, and $[M]_0/[Al]_0$/[Isopropyl alcohol] = 59:1:1; and (●) induction period = 13 min, k_{app} = 6.72 × 10^{-3} min^{-1}, and $[M]_0/[Al]_0$/[Isopropyl alcohol] = 40:1:1.

Figure 5 ^{1}H-NMR spectrum of poly(*rac*-LA) (Table I, entry 3; $CDCl_3$, 300 MHz; TMS = tetramethylsilane).

(Fig. 3) of **2**, the four —$C(CH_3)_3$ groups showed only two peaks at 31.4 and 29.6 ppm for the methyl carbons, the two aromatic rings exhibited only six peaks, and the —N═CH— and ═NCH_2— groups displayed the signals at δ = 64.6 and 170.2 ppm, respectively. Because the ^{1}H-NMR and ^{13}C-NMR spectra exhibited equivalent chemical shifts for two —N═CH groups, two ═NCH_2— groups, and two aromatic rings of complex **2**, it was deduced that the two conformational enantiomers of complex **2** tautomerized fast on the NMR timescale in solution.[18]

Stereospecific polymerization of *rac*-LA

The kinetics of the ROP was examined in toluene at 70°C (Fig. 4). The monomer conversion was monitored as a function of polymerization time by the ^{1}H-NMR spectrum. In each case, an induction period was observed, followed by a linear relationship. The induction period increased with decreasing concentration of catalyst **2** and isopropyl alcohol. The existence of an induction period implied that catalyst **2** had not initiated the ROP of *rac*-LA directly; it first reacted with isopropyl alcohol to form aluminum alkoxide (an actual active species), and then, the latter initiated the ROP of LA. These phenomena were in agreement with the end-group analysis of poly(*rac*-LA). As shown in Figure 5, the two weak signals at δ = 1.24 (two doublets appearing as a triplet) and 4.34 ppm (a quartet),

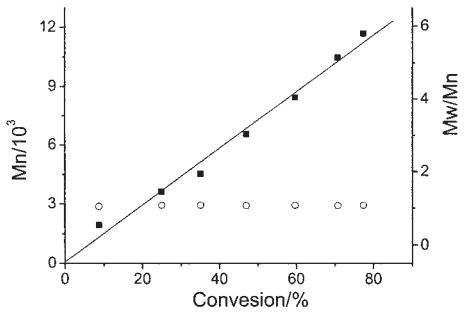


Figure 6 Poly(*rac*-LA) (■) M_n and (○) MWD (M_w/M_n) versus conversion with [*rac*-LA]/[Al]/[Isopropyl alcohol] = 59:1:1 at 70°C in toluene ([*rac*-LA] = 0.5 mol/L).

TABLE I
ROP of *rac*-LA in the Presence of Catalyst 2 and Isopropanol

Entry	Time (min)	Conversion (%)[a]	$M_n \times 10^{-3}$	PDI[b]	P_m	Tm, (°C)[c]
1	38	8.76	1.9	1.05	—	—
2	89	25.05	3.6	1.08	81.6	183
3	119	35.12	4.5	1.08	81.8	189
4	160	47.02	6.5	1.07	82.1	188
5	211	59.75	8.4	1.08	82.0	187
6	276	70.8	10.5	1.07	81.9	185
7	337	77.39	11.7	1.08	82.7	182

P_m = probability of meso linkages.[13–22] $[LA]_0 = 0.5M$; $[LA]_0$:$[A1]_0$:$[Isopropanol]_0$ = 59:1:1; solvent-toluene; temperature = 70°C.
[a] Measured by ^{1}H-NMR.
[b] Determined by GPC in $CHCl_3$ relative to a polystyrene standard.
[c] Determined by DSC (heating rate = 10°C/min, second scan).

with an integral ratio close to 6:1, were assignable to the methyl protons of the isopropoxycarbonyl end group and the methine proton neighboring to the hydroxyl end group, respectively.[31] Figure 6 depicts the dependence of the M_n and MWD of poly(*rac*-LA) on the monomer conversion. The linear relation between M_n and *rac*-LA conversion and the low MWD (1.05–1.08) revealed the slight transesterification during polymerization. These phenomena indicated that the polymerization of *rac*-LA by catalyst **2** and isopropyl alcohol was controllable.

rac-LA was polymerized by catalyst **2** to form a crystalline polymer [melting temperature (T_m) 182–189°C] in the presence of isopropyl alcohol (Table I). This T_m higher than that of homochiral PLAs implied the formation of a PLA stereocomplex.[13] The tacticity of the poly(*rac*-LA) with catalyst **2** and isopropyl alcohol was determined by the inspection of the homonuclear decoupled ^{1}H-NMR spectrum of the methine region (Fig. 7). The mmm tetrad was the predominant peak, which indicated that the poly(*rac*-LA) was dominantly isotatic.[13–24] In Figure 7, in addition to the major mmm signal, there were three small rmm, mmr, and mrm tetrads with approximately equal intensity and an almost negligible rmr resonance. This indicated that a stereoblock-type PLA (Scheme 2) was formed.[16,22] The degree of stereoselectivity of this initiating system, defined by the parameter P_m, was 0.84 according to the chain-end control polymerization mechanism,[13–24] which indicated that the stereoblocks contained an average of 12 units ($\bar{L} = 12$) of enantiomerically pure lactic acid $\{\bar{L} = 2[1 + P_m/(1 - P_m)]\}$.

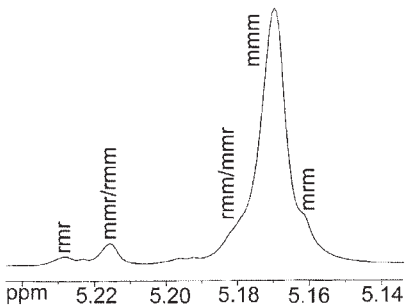
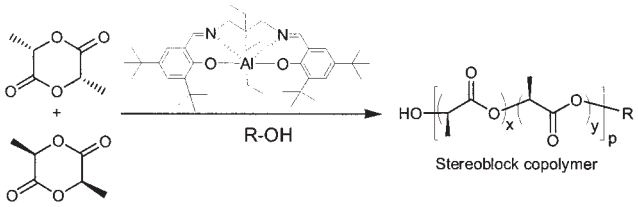


Figure 7 Homonuclear decoupled ^{1}H-NMR spectrum of the methine region of poly(*rac*-LA) (Table I, entry 7; 600 MHz, $CDCl_3$).

Synthesis of the PLA/PEG/PLA stereocomplex

rac-LA could be polymerized by catalyst **2** to form a PLA stereocomplex in the presence of equivalent isopropyl alcohol, and the poly(*rac*-LAs) were endcapped by isopropoxycarbonyl and hydroxy groups so that a PLA/PEG/PLA stereocomplex could be synthesized by the direct ROP of *rac*-LA with a catalyst **2** and PEG initiating system. Because the resolution of the NMR spectra of PLA/PEG/PLA can be considerably improved with DMSO-d_6 as solvent instead of $CDCl_3$,[32] the ^{1}H-NMR spectrum (Fig. 8) of the PLA/PEG/PLA copolymer was recorded in DMSO-d_6. The singlet at δ = 3.51 ppm was assignable to methylene protons (*k*, —CH_2CH_2O—) of the main chain of the PEG blocks. The signals in the range δ = 5.21–5.11 ppm [*d*, *e*, and *g*, —O—C*H*(CH_3) —] and in the range δ = 1.49–1.42 ppm [*c*, *f*, and *h*, —O—CH(C*H*$_3$)—] belonged to PLA blocks, including both PEG connecting and main chain units. The HOC*H*(CH_3)— (*a*) protons of the hydroxylated lactyl end units appeared in



Scheme 2 Stereospecific polymerization of *rac*-LA.

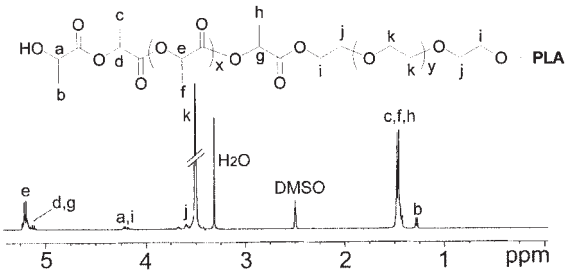


Figure 8 ^{1}H-NMR spectrum of the PLA/PEG/PLA triblock copolymer (DMSO-d_6, 400 MHz).

the δ = 4.25–4.13 ppm range, together with the methylene protons of PLA connecting units (*i*, PLA—COO—CH_2—). The methyl protons (*b*) of the lactyl end units showed a doublet at δ = 1.28 ppm and were well separated from the other methyl groups. The integral ratio of signals at δ = 3.51 and 4.25–4.13 ppm was close to 68:1, which indicated that all of the —OH groups of PEG initiated the ROP of *rac*-LA from the calculation of the component of the copolymer chain. The equal intensities of the signals at δ = 4.25–4.13 and 1.28 ppm suggested that the all of the PLA blocks were connected with PEG blocks. The integral ratio of signals at δ = 1.49–1.42 and 1.28 ppm was 55:3, which implied that the polymerization degree of poly(*rac*-LA) block was about 9. The GPC curve (Fig. 9) of the copolymer exhibited a single peak, the MWD of the copolymer was very narrow (M_w/M_n = 1.07), and the retention time of the copolymer was shorter than that of PEG. These phenomena confirmed the formation of the PLA/PEG/PLA triblock copolymer. In the X-ray diffraction pattern (Fig. 10) of the copolymer (see for comparison the PLA stereocomplex and the PEG homopolymer), the peaks at 2θ values of 19 and 23° corresponded to the PEG block,[33] and the peaks at 2θ values of 12 and 21° were assigned to the PLA stereocomplex block (the peak at 24° was missing, possibly due to low resolution).[34,35] The DSC curve (Fig. 11, second run) of the PLA/PEG/PLA copolymer showed an exothermal peak at 17°C (crystallization

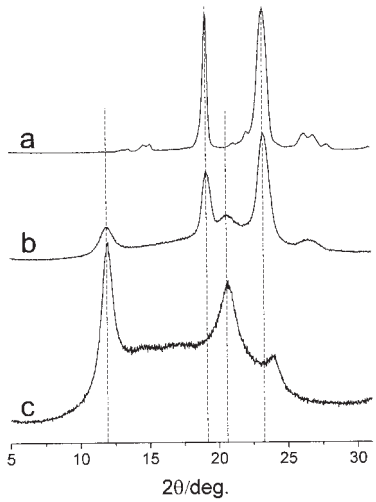


Figure 10 WAXD curves of (a) PEG, (b) the PLA/PEG/PLA triblock copolymer, and (c) the PLA stereocomplex.

peak of the PEG block), two endothermal peaks at 49°C (T_m of the PEG block) and 140°C (T_m of the PLA stereocomplex block), which was consistent with the WAXD spectrum. These features implied that a PLA/PEG/PLA stereocomplex was obtained by the direct ROP of *rac*-LA with the catalyst **2** and PEG initiating system.

CONCLUSIONS

An ethyl aluminum Schiff base complex catalyst (**2**) with a geminal diethyl substitution in the diamino bridge is reported in this article. Catalyst **2** contained a five-coordinate aluminum atom with a distorted trigonal bipyramidal geometry in the solid state. In solution, its two conformational enantiomers tautomerized quickly on the NMR timescale. The catalyst showed good stereoselectivity and controllability for the ROP of *rac*-LA in the presence of isopropyl alcohol. The polymerization yielded a semicrystalline stereoblock PLA with a high T_m. A new structural PLA/PEG/PLA stereocomplex was obtained by the catalyst **2** and

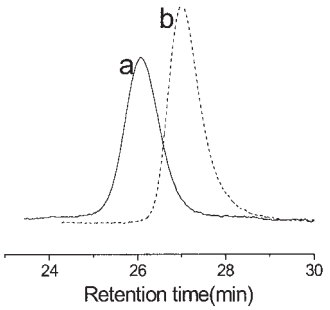


Figure 9 Gel permeation chromatograms of (a) the PLA/PEG/PLA triblock copolymer and (b) PEG (M_n = 4600 Da).

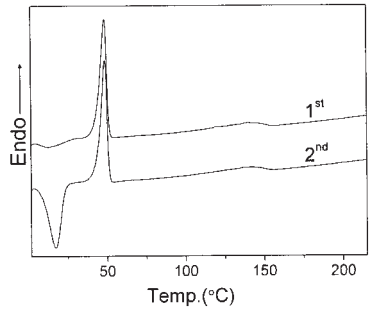


Figure 11 DSC traces of the PLA/PEG/PLA triblock copolymer (heating rate = 20°C/min).

PEG initiating system. This was the first time that a PLA/PEG/PLA stereocomplex was synthesized by the direct polymerization of *rac*-LA.

References

1. Lunt, J. Polym Degrad Stab 1998, 59, 145.
2. Yuan, M. L.; Xiong, C. D.; Liand, X. H.; Deng, X. M. J Appl Polym Sci 1999, 73, 2857.
3. Chabot, F.; Vert, M.; Chapelle, S.; Granger, P. Polymer 1983, 24, 53.
4. Chiellini, E.; Solaro, R. Adv Mater 1996, 8, 305.
5. Kricheldorf, H. R.; Berl, M.; Scharnagl, N. Macromolecules 1988, 21, 286.
6. Zhang, X. C.; Goosen, M. F. A.; Wyss, U. P.; Pichora, D. J Macromol Sci Rev Macromol Chem Phys 1993, 33, 81.
7. Ikada, Y.; Jamshidi, K.; Tsuji, H.; Hyon, S. H. Macromolecules 1987, 20, 904.
8. Tsuji, H.; Horii, F.; Hyon, S. H.; Ikada, Y. Macromolecules 1991, 24, 5651.
9. Brizzolara, D.; Cantow, H. J.; Diederichs, K.; Keller, E.; Domb, A. J. Macromolecules 1996, 29, 191.
10. Chamberlain, B. M.; Cheng, M.; Moore, D. R.; Ovitt, T. M.; Lobkovsky, E. B.; Coates, G. W. J Am Chem Soc 2001, 123, 3229.
11. Cai, C. X.; Amgoune, A.; Lehmann, C. W.; Carpentier, J. F. Chem Commun 2004, 330.
12. Hormnirun, P.; Marshall, E. L.; Gibson, V. C.; White, A. J. P.; Williams, D. J. J Am Chem Soc 2004, 126, 2688.
13. Spassky, N.; Wisniewski, M.; Pluta, C.; LeBorgne, A. Macromol Chem Phys 1996, 197, 2627.
14. Radano, C. P.; Baker, G. L.; Smith, M. R. J Am Chem Soc 2000, 122, 1552.
15. Ovitt, T. M.; Coates, G. W. J Am Chem Soc 2002, 124, 1316.
16. Ovitt, T. M.; Coates, G. W. J Polym Sci Part A: Polym Chem 2000, 38, 4686.
17. Majerska, K.; Duda, A. J Am Chem Soc 2004, 126, 1026.
18. Tang, Z.; Chen, X.; Pang, X.; Yang, Y.; Zhang, X.; Jing, X. Biomacromolecules 2004, 5, 965.
19. Tang, Z.; Chen, X.; Yang, Y.; Pang, X.; Sun, J.; Zhang, X.; Jing, X. J Polym Sci Part A: Polym Chem 2004, 42, 5974.
20. Zhong, Z.; Dijkstra, P. J.; Feijen, J. Angew Chem Int Ed Engl 2002, 41, 4510.
21. Wisniewski, M.; LeBorgne, A.; Spassky, N. Macromol Chem Phys 1997, 198, 1227.
22. Zhong, Z.; Dijkstra, P. J.; Feijen, J. J Am Chem Soc 2003, 125, 11291.
23. Nomura, N.; Ishii. R.; Akakura. M.; Aoi, K. J Am Chem Soc 2002, 124, 5938.
24. Ishii, R.; Nomura, N.; Kondo, T. Polym J 2004, 36, 261.
25. Fujiwara, T.; Mukose, T.; Yamaoka, T.; Yamane, H.; Sakurai, S.; Kimura, Y. Macromol Biosci 2001, 1, 204.
26. Li, S. M.; Vert, M. Macromolecules 2003, 36, 8008.
27. Stevels, W. M.; Ankone, M. J. K.; Dijkstra, P. J.; Feijen, J. Macromol Chem Phys 1995, 196, 3687.
28. Lim, D. W.; Park, T. G. J Appl Polym Sci 2000, 75, 1615.
29. Newman, M. S.; Busch, D. H.; Cheney, G. E.; Gustafsow, C. R. Inorg Chem 1972, 11, 2890.
30. Munoz-Hernandez, M. A.; Keizer, T. S.; Wei, P. R.; Parkin, S.; Atwood, D. A. Inorg Chem 2001, 40, 6782.
31. Zhong, Z.; Dijkstra, P. J.; Birg, C.; Westerhausen, M.; Feijen, J. Macromolecules 2001, 34, 3863.
32. Rashkov, I.; Manolova, N.; Li, S. M.; Espartero, J. L.; Vert, M. Macromolecules 1996, 29, 50.
33. Li, S. M.; Rashkov, I.; Espartero, J. L.; Manolova, N.; Vert, M. Macromolecules 1996, 29, 57.
34. Watanabe, J.; Eriguchi, T.; Ishihara, K. Biomacromolecules 2002, 3, 1109.
35. Brizzolara, D.; Cantow, H. J.; Diederichs, K.; Keller, E.; Domb, A. J. Macromolecules 1996, 29, 191.