Stereoselective Ring-Opening Polymerization of D,L-Lactide, Initiated by Aluminum Isopropoxides Bearing Tridentate Nonchiral Schiff-Base Ligands

Kouki Matsubara,[1] Chihiro Terata,[1] Hiromichi Sekine,[1] Kenji Yamatani,[1] Tatsuo Harada,[1] Kiyoka Eda,[1] Misato Dan,[1] Yuji Koga,[1] Munehisa Yasuniwa[2]

[1]Department of Chemistry, Faculty of Science, Fukuoka University, Nanakuma, Jonan-Ku, Fukuoka 814-0180, Japan
[2]Department of Applied Physics, Faculty of Science, Fukuoka University, Nanakuma, Jonan-Ku, Fukuoka 814-0180, Japan
Correspondence to: K. Matsubara (E-mail: kmatsuba@fukuoka-u.ac.jp)

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ABSTRACT: Ring-opening polymerization of D,L-lactide was stereoselectively achieved using newly designed aluminum alkoxide complexes as initiators. These half-SALEN aluminum complexes bearing tridentate nonchiral Schiff-base ligands are racemates, which provide chirality in the aluminum centers, efficiently afforded a stereoblock copolymer of D,L-LA.

KEYWORDS: aluminum Schiff-base complexes; lactide; polyesters; ring-opening polymerization; stereospecific polymers

INTRODUCTION Ring-opening polymerization (ROP) of lactide (LA), a cyclic dimer of lactic acid, is easily initiated by metal carboxylates and alkoxides.[1] The applications of high-molecular-weight poly-LA, especially poly(L-LA) (PLLA) from L-LA are now widely developed as biomedical materials, such as drug delivery systems,[2] bioresorbable sutures, implants,[3] scaffolds for tissue engineering,[4] and biodegradable plastics based on biosustainable resources.[5] A series of recent studies investigating the polymerization of D,L-LA in the presence of SALEN aluminum alkoxides, where SALEN is *N,N*'-bis(salicylidene)alkyldiimine, gave highly isotactic stereoblock copolymers of PLA,[6] of which the melting points were as high as ~200 °C. This isotactic stereocontrol method using poorly applicable D,L-LA may facilitate the use of stereoblock PDLLA for similar applications to those of PLLA. In this stereoregulated polymerization initiated by several aluminum,[7–9] zinc,[10] and titanium complexes,[11] two regulating mechanisms were proposed: (i) the enantiomorphic site control (ESC) and (ii) chain end control (CEC). In the ESC process, the chiral ligand in the metal complex stereoselectively recognizes the D- or L-isomer of lactide,[7] whereas in the CEC process the chiral polymer-chain end selects one of the enantiomers, leading to the stereoregulated single-site ring-opening reaction of LA.[8] The theoretical[12] and experimental[13] data support the mechanisms of the stereoselective ROP of LA.

Most of the previously reported studies showed that the tetradentate ligands in the aluminum complexes were effective for efficient stereocontrolled ROP,[7–9] whereas bidentate ligands in the aluminum complexes, such as diphenoxides,[14] thiophenoxides,[15] phenoxyimines,[16] and hydroxy-substituted heteroscorpionate[17] were useful in the polymerization of L-LA but were unsuitable in stereoregulated ROP of D,L-LA to form isotactic PDLLA. Although several metal complexes bearing tridentate ligands have been prepared as efficient catalysts for ROP of LA, these compounds have not been employed for stereoselective ROP of D,L-LA.[18] Recently zinc complexes bearing chiral tridentate diaminophenoxy ligands were found to initiate poorly stereoselective polymerization ($P_m = 0.54$) of D,L-LA,[19] and tridentate O^N^O or O^S^O complexes of the Group III metals also polymerize D,L-LA in heterotactic selection.[20]

In the previous ESC processes, the stereochemistry at the ω-end has been regulated only by the chirality in the ligands. This is despite the fact that the coordination of a nonchiral bridging ligand can generate an asymmetric center in zirconium or titanium which gives rise to the ESC process in the single-site stereocontrolled polymerization of propylene.[21] We believed that rigid tridentate ligand having only a C_s symmetrical plane can form a stable chiral metal center. A tetrahedral chiral aluminum center may also easily isomerize to form a racemate under thermal conditions. However, if the aluminum complexes bearing such nonchiral tridentate ligands can form rigid octahedral chiral geometry with lactide coordination, the stereoselective ROP of D,L-LA could be

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controllable. Consequently, we studied the preparation of new aluminum complexes with asymmetric metal centers bearing C_s symmetric tridentate Schiff-base ligands, such as aminoalcohol- or aminophenol-derived salicylaldimine,[22] and their application to initiating the ROP of D,L-LA. These racemic complexes efficiently initiated the polymerization to form isotactic stereoblock copolymers of PDLLA, and one of the stereoblock copolymers of PDLLA was successfully generated at room temperature. Darensbourg et al. recently showed that similar stereoselective ROP of D,L-LA initiated by nonchiral half-SALEN complexes of aluminum was dependent on the structures of dimerized aluminum isomers.[23] However, chirality at the aluminum center was not focused and stereocontrol at room temperature was not realized in that report.

EXPERIMENTAL

Techniques

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a VARIAN Mercury Y plus 400 MHz spectrometer at room temperature in $CDCl_3$. Chemical shifts (δ) were recorded in ppm from the internal standard ($CHCl_3$). IR spectra were recorded in cm^{-1} on a PERKIN ELMER Spectrum One spectrometer equipped with a universal diamond ATR. Size exclusion chromatography analysis of the polymers was carried out using a JASCO HPLC system equipped with a RI-2031Plus differential refractometer and an UV-2075 Plus UV–VIS detector (254 nm) using two Shodex KF-804L+KF-804L columns at 40 °C. THF was used as eluent (1.0 mL min^{-1}). Calibration was carried out using standard samples of polystyrene. The Elem. Anal. was carried out with YANACO CHN Corder MT-5, AUTO-SAMPLER. Electrospray ionization time-of-flight mass spectrometry (ESI-TOF MS) was carried out on a JEOL JMS-T100 mass spectrometer. The sample solutions in methanol (for ligands) or isopropanol (for Al complexes) were directly infused. Thermal analysis was carried out with a differential scanning calorimeter, PERKIN ELMER Pyris 1. A PDLLA sample sealed in an aluminum sample pan was always kept under a nitrogen atmosphere during DSC measurement and the second scan was recorded. A PDLLA sample for wide-angle X-ray diffraction (WAXD) study was squeezed in a copper cylinder, and the both ends were sealed by a thin polyimide film to prevent moisture. Monochromated Cu Kα radiation ($\lambda = 1.542$ Å) was used as an incident X-ray beam at 50 kV and 80 mA. The X-ray beam passed through the sample, and a WAXD pattern was obtained with a position-sensitive proportional counter system (RIGAKU).

Materials

Toluene used for polymerization and toluene-d_8 were distilled from sodium benzophenone ketyl solution under reduced pressure just before use. Hexane used for washing the crude mixture of the Al complexes was distilled from a sodium benzophenone ketyl solution containing small amount of bis[2-(2-methoxyethoxy)ethyl]ether. Pyridine, ethyl acetate, and chloroform-*d* were distilled over calcium hydride before use. Lactides were stored under nitrogen at −35 °C and recrystallized three times from dried ethyl acetate solution and dried under reduced pressure (10^{-2} Pa) before use. Other reagents were used as purchased. Especially, aluminum isopropoxide (99.99+%) was purchased from Aldrich Chem. 2-Amino-6-methylphenol was prepared according to the literature.[24] Schiff-base ligand **(*rac*)-2** from (*rac*)-valinol was prepared according to the literature.[25]

Preparation of 2-(*tert*-Butyl)-6-[[(2-hydroxyphenyl)imino]methyl]phenol (1a)

To a solution of 2-aminophenol (545.6 mg, 0.500 mmol) and 3-(*tert*-butyl)-2-hydroxy-benzaldehyde (0.856 mL, 0.500 mmol) in methanol was added Na_2SO_4 (4.1 g) in a 50-mL round-bottom flask equipped with a reflux condenser. The suspension was stirred at 70 °C for 20 h. After filtration to remove Na_2SO_4, the solvent was concentrated and some amount of hexane was added. Then it was cooled at −30 °C, orange crystals of **1a** were separated (1.271 g, 4.72 mmol, 94% yield). ^{1}H NMR ($CDCl_3$): δ 1.47 (s, 9H, ^{t}Bu), 5.76 (br, 1H, OH), 6.93 (t, $J = 7.6$ Hz, 1H, ArH), 6.97 (t, $J = 7.6$ Hz, 1H, ArH), 7.04 (d, $J = 8.0$ Hz, 1H, ArH), 7.15 (d, $J = 7.6$ Hz, 1H, ArH), 7.22 (t, $J = 8.0$ Hz, 1H, ArH), 7.30 (d, $J = 7.6$ Hz, 1H, ArH), 7.44 (d, $J = 7.6$ Hz, 1H, ArH), 8.70 (s, 1H, N=CH), 12.87 ppm (s, 1H, OH); ^{13}C NMR ($CDCl_3$): δ 29.68 (C(CH_3)$_3$), 35.27 (C(CH_3)$_3$), 116.13 (Ph), 118.62 (Ph), 119.25 (Ph, 4°), 119.56 (Ph), 121.36 (Ph), 128.91 (Ph), 131.39 (Ph), 131.45 (Ph), 136.12 (Ph, 4°), 138.13 (Ph, 4°), 150.22 (Ph, 4°), 160.30 (Ph, 4°), 165.05 ppm (N=CH); IR (ν, cm^{-1}): 3370 (OH), 1614 (CN), 1593 (CN). MS (ESI-MS): calcd. ($C_7H_{19}NO_2$+H$^+$), 270.149; found, 270.157.

Preparation of 2-(*tert*-Butyl)-6-[[(2-hydroxy-3-methylphenyl)imino]methyl]phenol (1b)

This was prepared as **1a** from 2-amino-6-methylphenol (250.1 mg, 2.03 mmol) and 3-(*tert*-butyl)-2-hydroxy-benzaldehyde (0.348 mL, 2.03 mmol). Orange crystals, yield: 74%. ^{1}H NMR ($CDCl_3$): δ 1.46 (s, 9H, ^{t}Bu), 2.32 (s, 3H, 3-CH_3), 5.93 (br, 1H, OH), 6.86 (t, $J = 7.8$ Hz, 1H, ArH), 6.92 (t, $J = 7.8$ Hz, 1H, ArH), 6.99 (d, $J = 7.6$ Hz, 1H, ArH), 7.08 (d, $J = 7.2$ Hz, 1H, ArH), 7.29 (d, $J = 7.6$ Hz, 1H, ArH), 7.43 (d, $J = 7.6$ Hz, 1H, ArH), 8.69 (s, 1H, N=CH), 12.86 ppm (br, 1H, OH); ^{13}C NMR ($CDCl_3$): δ 15.74 (3-CH_3), 29.33 (C(CH_3)$_3$), 34.94 (C(CH_3)$_3$), 115.58 (Ph), 118.87 (Ph), 119.27 (Ph, 4°), 120.02 (Ph), 125.04 (Ph, 4°), 129.84 (Ph), 130.93 (Ph), 131.05 (Ph), 135.30 (Ph, 4°), 137.75 (Ph, 4°), 148.13 (Ph, 4°), 159.91 (Ph, 4°), 164.50 ppm (N=CH); IR (ν, cm^{-1}): 3514 (OH), 1596 (C=N); MS(ESI-MS): calcd. ($C_8H_{21}NO_2$+H$^+$), 284.165; found, 284.186.

Preparation of 1-[(2-Hydroxy-3-*tert*-butylbenzylideneamino)methyl]cyclohexanol (3)

To a solution of 1-Aminomethyl-1-cyclohexanol hydrochloride (400.0 mg, 2.50 mmol) and 3-(*tert*-butyl)-2-hydroxy-benzaldehyde (0.410 mL, 2.30 mmol) in methanol (16 mL) was added K_2CO_3 (334 mg, 2.50 mmol) in a 50-mL round-bottom flask equipped with a reflux condenser. The solution was refluxed for four days. The solvent was removed under reduced pressure and the residual solid was extracted with toluene. Removal of toluene from the solution gave a white solid, **3**, in 86% yield (572 mg, 1.98 mmol). ^{1}H NMR ($CDCl_3$): δ 1.41 (d, $J = 3.4$ Hz, 6H, CyH), 1.44 (s, 9H, *tert*-Bu), 1.50 (br, CyH), 1.53 (br, CyH), 1.63 (br, CyH), 3.56 (s, =N—CH_2—, 2H), 6.88

(t, $J = 7.8$ Hz, 1H, PhH), 7.30 (d, $J = 7.8$ Hz, 1H, PhH), 7.42 (d, $J = 7.8$ Hz, 1H, PhH), 8.46 ppm (s, 1H, N=CH); ^{13}C NMR ($CDCl_3$): δ = 21.83 (CH_2 in Cy), 25.78 (CH_2 in Cy), 29.31 (C(CH_3)$_3$), 34.82 (C(CH_3)$_3$), 35.75 (CH_2 in Cy), 70.17 (C—OH), 71.42 (CH_2-N), 117.88 (Ph), 118.62 (Ph-OH, 4°), 129.54 (Ph), 129.84 (Ph), 137.42 (Ph, 4°), 160.43 (Ph, 4°), 167.63 (N=CH); IR (ν, cm^{-1}): 3301 (OH), 1621 (C=N); MS(ESI-MS): calcd. ($C_{20}H_{24}AlNO_3$)+H^+), 290.212; found, 290.207.

Preparation of 2-(*tert*-Butyl)-6-[[(2-hydroxyphenyl)imino]methyl]phenolate Aluminum Complex (4a)

To a solution of aluminum isopropoxide (102.1 mg, 0.500 mmol) in dried toluene (2 mL) was added the ligand **1a** (134.7 mg, 0.500 mmol) in a 20 mL Schlenk tube under dried nitrogen atmosphere (equipped in a Globe box (MBraun UNI-Lab)). The solution was stirred at 80 °C for 24 h, and then, the solvent was removed *in vacuo* from the resulted suspension. The residual bright yellow solid was washed with small amount of hexane and dried, yielding **4a** (137.7 mg, 0.390 mmol, 78% yield). ^{1}H NMR ($CDCl_3$): δ 1.20 (d, $J = 7.0$ Hz, 3H, CH(CH_3)$_2$), 1.21 (d, $J = 6.2$ Hz, 3H, CH(CH_3)$_2$), 1.32 (s, 9H, C(CH_3)$_3$), 4.02 (m, 1H, CH(CH_3)$_2$), 6.09 (t, $J = 7.8$ Hz, 1H, Ph), 6.44 (t, $J = 8.3$ Hz, 1H, Ph), 6.52 (t, $J = 7.5$ Hz, 1H, Ph), 6.90 (d, $J = 7.5$ Hz, 1H, Ph), 7.13 (d, $J = 7.8$ Hz, 1H, Ph), 7.15 (d, $J = 8.3$ Hz, 1H, Ph), 7.48 (d, $J = 8.3$ Hz, 1H, Ph), 8.00 (s, 1H, N=CH). MS(ESI-MS): calcd. (($C_{18}H_{27}NO_2$)×2+H^+), 707.3216; found, 707.3221.

Preparation of 2-[[(2-Hydroxy-3-methyl-phenyl)imino]methyl]-6-*tert*-butylphenolate Aluminum Complex (4b)

This was prepared as **4a** from aluminum isopropoxide (103.3 mg, 0.5057 mmol) and the ligand **1b** (143.3 mg, 0.5057 mmol). Yellow powder, yield: 84%. ^{1}H NMR ($CDCl_3$): δ 1.08 (d, $J = 6.4$ Hz, 3H, CH(CH_3)$_2$), 1.19 (d, $J = 6.4$ Hz, 3H, CH_3), 1.31 (s, 9H, C(CH_3)$_3$), 2.12 (s, 3H, CH_3), 4.27 (sept, $J = 6.4$ Hz, 1H, CH(CH_3)$_2$), 6.70 (t, $J = 7.6$ Hz, 1H, ArH), 6.86 (t, $J = 7.6$ Hz, 1H, ArH), 7.03 (d, $J = 7.6$ Hz, 1H, ArH), 7.30 (d, $J = 7.6$ Hz, 1H, ArH), 7.34 (d, $J = 7.6$ Hz, 1H, ArH), 8.62 (s, 1H, N=CH); ^{13}C NMR ($CDCl_3$): δ 16.23 ((CH$_3$)$_2$CH), 24.76 ((CH_3)$_2$CH), 29.21 ((CH$_3$)$_3$C), 67.39 ((CH_3)$_2C$H), 111.31 (Ph), 116.39 (Ph), 117.49 (Ph), 130.22 (Ph), 160 56 ppm (N=CH). MS(ESI-MS): calcd. ($C_{21}H_{27}AlNO_3$+H^+), 368.1801; found, 368.1806.

Preparation of 2-[(1-Hydroxy-3-methylbutan-2-ylimino)methyl]-6-*tert*-butylphenolate Aluminum Complex ((*rac*)-5)

This was prepared as **4a** from aluminum isopropoxide (1.040 g, 5.090 mmol) in dried toluene (10 mL) and a ligand, (*rac*)-2-((1-hydroxy-3-methylbutan-2-ylimino)methyl)-6-*tert*-butylphenol, (1.341 g, 5.090 mmol). White powder, yield: 90%. ^{1}H NMR ($CDCl_3$): δ 0.90 (d, $J = 6.0$ Hz, 3H, CH_3), 0.93 (d, $J = 6.0$ Hz, 3H, CH_3), 0.95 (d, $J = 6.8$ Hz, 3H, CH_3), 1.07 (d, $J = 6.8$ Hz, 3H, CH_3), 1.50 (s, 9H, ^{t}Bu), 2.50 (oct, $J = 6.8$ Hz, 1H, CH in valinol), 3.01 (dd, $J = 5.2$, 10.4 Hz, 1H, O—CH_2), 3.80 (sept, $J = 6.0$ Hz, 1H, CH in alkoxide), 4.02 (dd, $J = 5.2$, 9.6 Hz, 1H, O—CH_2), 4.41 (d, $J = 9.2$ Hz, 1H, N—CH), 6.74 (t, $J = 7.8$ Hz, 1H, ArH), 7.14 (d, $J = 7.6$ Hz, 1H, ArH), 7.43 (d, $J = 7.2$ Hz, 1H, ArH), 8.21 (s, 1H, N=CH); ^{13}C NMR ($CDCl_3$): δ 20.15, 20.51, 27.86, 28.02, 29.51, 29.57, 29.71, 35.42 (4°), 61.55, 62.75, 74.35, 116.44, 119.75 (4°), 131.80, 132.28, 140.87 (4°), 164.06 (4°), 167.94. MS(ESI-MS): calcd. (($C_{19}H_{30}AlNO_3$)+($C_{16}H_{23}AlNO_2$)$^+$), 635.3580; found, 635.3585.

Preparation of 1-[(2-Hydroxy-3-*tert*-butylbenzylideneamino)methyl]cyclohexanolate Aluminum Complex (6)

This was prepared as **4a** from aluminum isopropoxide (0.468 mg, 2.30 mmol) and the ligand **3** (698 mg, 2.30 mmol). White powder, yield: 73%. ^{1}H NMR (toluene-d_8): δ 1.15-1.85 (m, 10H, CH_2 in cyclohexanol), 1.27 (d, $J = 6.2$ Hz, 3H, CH_3), 1.36 (d, $J = 6.2$ Hz, 3H, CH_3), 1.64 (s, 9H, ^{t}Bu), 2.77 (brd, $J = 9.0$ Hz, 1H, N—CH_2), 3.75 (brd, $J = 9.0$ Hz, 1H, N—CH_2), 3.80 (sept, $J = 6.2$ Hz, 1H, CH in alkoxide), 6.70 (t, $J = 7.4$ Hz, 1H, ArH), 6.92 (d, $J = 7.6$ Hz, 1H, ArH), 7.39 (d, $J = 7.2$ Hz, 1H, ArH), 7.59 (s, 1H, N=CH); ^{13}C NMR ($CDCl_3$): δ 22.37 (C(CH$_3$)$_2$), 24.35 (CH_2 in Cy), 24.41 (CH_2 in Cy), 26.55 (CH_2 in Cy), 30.07 (C(CH_3)$_3$), 35.28 (C(CH_3)$_3$), 37.23 (CH_2 in Cy), 38.12 (CH_2 in Cy), 66.87 (C(CH_3)$_2$), 69.41 (CH_2-N), 70.47 (C-OH), 116.06 (Ph), 120.66 (Ph-OH, 4°), 130.41 (Ph), 131.20 (Ph), 141.30 (Ph, 4°), 162.77 (Ph, 4°), 165.44 (N=CH). MS(ESI-MS): calcd. (($C_{21}H_{32}AlNO_3$)+($C_{18}H_{25}AlNO_2$)$^+$), 687.3893; found, 687.3886

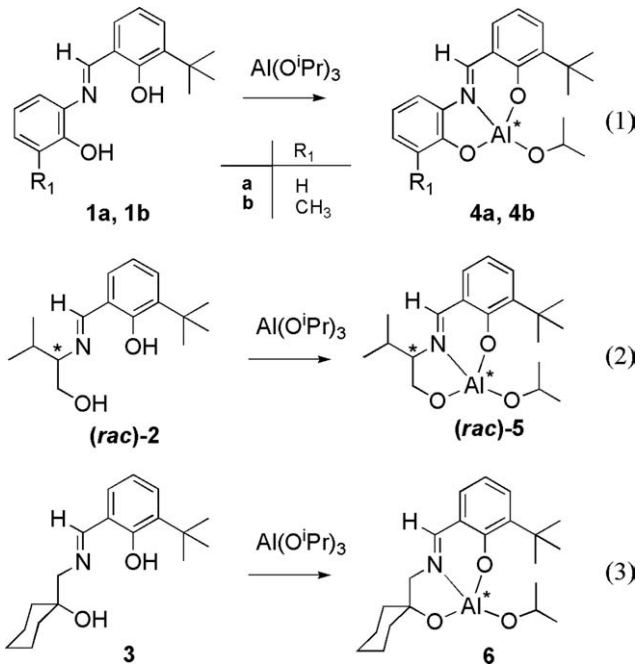
General Polymerization Procedure

The general procedure for the polymerization of lactides in pyridine is as follows. To a 20-mL screw-capped glass sample tube, lactide (216.2 mg, 1.50 mmol), aluminum complex (0.015 mmol), and pyridine (0.2 mL) were added in a glove box. The tube was sealed and stirred at desirable temperature for several hours. After dilution of the adhesive product with small amount of THF, the solution was poured into the stirring methanol (100 mL) at room temperature to form white precipitate as a PLA. To remove the aluminum residues, reprecipitation in methanol was repeated for several times.

RESULTS AND DISCUSSION

Preparation of Aluminum Alkoxides Bearing Tridentate Schiff-Base Ligands

We planned to design both chiral and achiral bridging ligands in the asymmetric aluminum complexes, because it was important to compare these complexes with and without chirality in the ligand in the stereoregulation system. These Schiff-base ligands were obtained in excellent yields by the reaction of 2-hydroxy-3-*tert*-butyl-benzaldehyde with an equivalent of either 2-aminophenol and 6-methyl-2-aminophenol, (*rac*)-valinol, or 1-(2-amino-ethyl)-cyclohexanol.[25] Besides valinol, these aminophenols and aminoalcohols do not have chirality. All the ligands reacted with aluminum isopropoxide (Al(O^{i}Pr)$_3$) efficiently upon heating at 80 °C to form complexes **4a**, **4b**, **(*rac*)-5** and **6** in high yields after washing the resulting solid with hexane [Scheme 1 (1), (2), and (3)]. These complexes were fully characterized on the basis of ^{1}H and ^{13}C NMR spectra; however, X-ray structural



SCHEME 1 Preparation of Schiff-base aluminum complexes of **4a-b, (*rac*)-5** and 6 in toluene at 80 °C for 24 h.

analysis of these compounds was not possible, because we could not obtain the crystals with enough size to analyze.

Although **4a** was barely soluble in common organic solvents at room temperature, the other complexes were characterized using ^{1}H and ^{13}C NMR, and ESI-MS spectroscopy. The compound **4a** was considered to not only form dimers but also oligomerize or polymerize via a strong Al···O network. In the ESI-MS spectra of **4a** in isopropanol, the mass signal at 707.3221 m/z was detected, assigned as a protonated dimer, $C_{40}H_{51}N_2O_6Al_2$, of which the theoretical mass is 707.3216 m/z, whereas no signals due to a monomeric form were detected (see the Supporting Information). The similar mass signals showing only its dimeric structure was observed in the spectrum of **(*rac*)-5** and **6**. The result supported the dimeric structure of **4a**, **(*rac*)-5** and **6** in solution. It is of interest that the mass signal at 368.1806 m/z was detected for only **4b** in the ESI-MS spectrum in isopropanol, showing a protonated monomeric form of **4b**, $C_{21}H_{28}AlNO_3$ (368.1801 m/z, as the theoretical mass). As a typical example, the ^{1}H NMR spectrum for **4b** (Fig. 1) showed that a set of signals due to the aryl group of **4b** appeared from δ 6.70 to 7.34, and this set of signals is similar to those for the ligand **1b** which range between δ 6.86 and 7.43. The integrated ratios between the signals due to the imine proton (δ 8.62) and the methine proton (δ 4.27) in the aluminum isopropyl group were identical, indicating that two of the three isopropoxy groups in $Al(O^{i}Pr)_3$ were removed (Scheme 2). Solvent signals could not be found in the spectra other than a negligible amount of hexane. In the absence of non-coordinating solvent, the compound could be stabilized by the formation of a dimeric structure that forms Al···O bonds, as reported previously.[18,23] However, the dimeric isomers of the *cis* and *trans* forms could not be detected.[23] The ^{1}H NMR spectrum for **(*rac*)-5** gave only one set of the signals assigned as one of the stereoisomers. It is of interest that no signals due to the other stereoisomers of **(*rac*)-5** and/or its dimer, where the chirality combination of chiral carbon derived from D,L-valinol and aluminum is different, were detected in the ^{1}H NMR spectrum at room temperature, suggesting that chirality at the D,L-valinol unit can regulate the chirality of the aluminum center and/or the structure of the dimer.

Although, in the ^{13}C NMR spectrum, the C_C or C_D in ligand **3** gave rise to two signals at δ 35.75 or 21.83, whereas for complex **6** independent four signals due to C_C, $C_{C'}$, C_D, and $C_{D'}$ appeared at δ 37.23, 38.12, 24.35, and 24.41, respectively (Fig. 2). Additionally, two ^{1}H resonances due to diasterotopic methylene protons between the imine nitrogen and a cyclohexylene group in the half-SALEN ligand of **6** appeared at δ 2.77 and 3.75; however, the corresponding protons in **3** were equivalent, observed at δ 3.56. The preliminary experiment of the various-temperature ^{1}H NMR (400 MHz) spectrum for **6** showed that these signals coalesced around 70 °C into one broad signal. The activation energy of the isomerization equilibrium was about 66 kcal mol^{-1}, and was estimated from the coalescence temperature and the difference of these signals at 22 °C. Measurement of the NMR spectra of **6** at temperatures greater than 70 °C was not possible due to limitation of the instrument, and the averaged signal of the diastereotopic protons was not observed. The result suggests that equilibrium between the stereoisomers

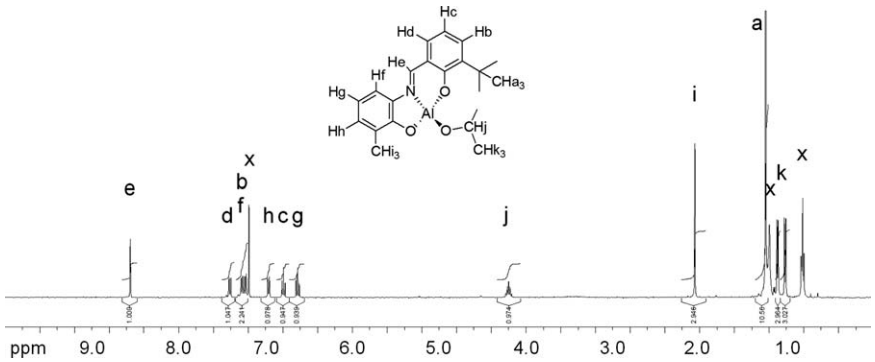
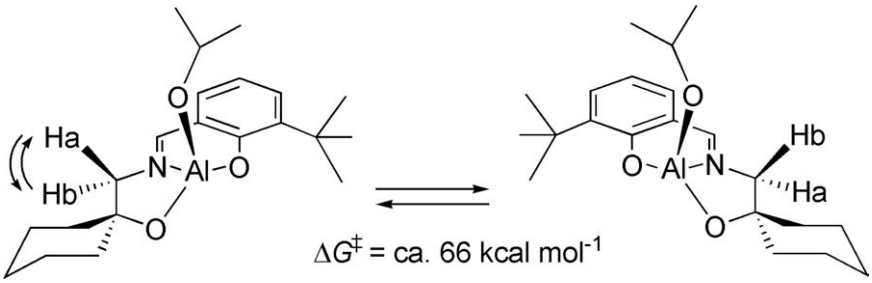


FIGURE 1 ^{1}H NMR spectra for **4b** in $CDCl_3$. Signals marked as × arise from the solvents.



SCHEME 2 The proposed isomerization process of **6** (tetrahedral) between the stereoisomers. Ha and Hb are the diastereotopic protons.

as shown in Scheme 2 may exist. Another isomerization process between dimer and monomer is likely to be possible. Observation of sharp signals due to the other protons and carbons of **6** in the NMR spectra at high temperatures supported the former isomerization process.

ROP of Lactides

Polymerization of D,L-LA was conducted using a solution method in toluene under nitrogen atmosphere in which D,L-LA and the aluminum complex were mixed at a 100:1 ratio. After polymerization, the resulting solution was dissolved in a small amount of THF and poured into methanol to form a PLA precipitate. To remove the aluminum residuals and pyridine in the polymers, dissolution in THF and precipitation from methanol were repeated several times. Table 1 shows the results of the ROP of lactides initiated by complexes **4a**, **4b,** and **(*rac*)-5** under several conditions. Interestingly, using **4b** and **(*rac*)-5** in toluene at 70 °C gave the highest yields of PLA after 96 h (Table 1, entries 2 and 6, respectively), whereas polymerization with **4a** afforded PLA in only a 21% yield (entry 1). In the previously reported systems initiated by aluminum SALEN complexes, polymerization was completed in 12−24 h.[7–9] This longer reaction time appears to be due to the use of the tridentate ligands in these aluminum complexes, which easily form dimers through interactions between aluminum and phenoxide oxygen (Scheme 3). Such dimers may have negligible activity toward the ROP of LA, because the initial coordination of the lactide C=O may be obstructed by the intermolecular Al···O interactions.[18] In particular, if **4a** forms an oligomer or polymer this compound would probably not function efficiently as an initiator. In contrast, the 6-methyl substituent may electronically and sterically weaken the Al···O interactions as indicated from the result of the ESI-MS spectrum, therefore forcing the separation of the inactive dimer into active monomers with lactide coordination in solution. The polymerization of L-LA with **(*rac*)-5** proceeded more slowly than that of D,L-LA, probably because half of the racemic complex was not active toward the L-isomer of LA (entry 7). Isotacticity, P_m, of the PLA derived from L-LA was 1.00, indicating that any epimerization process of L-LA to form *meso*-LA did not occur in the polymerization process.[23]

As an alternative method, we found that using small amount of pyridine as a solvent dramatically enhanced the activity of **4b** and **(*rac*)-5** in the ROP of LA, which was converted into PLA in 3−12 h at 70 °C (Table 1, entries 3 and 8, respectively). The reason of this faster conversion is not clear; we considered some possibilities, such as that the pyridine coordination led to the facile formation of the monomeric complex (Scheme 3) and/or regulated the aluminum geometry into five-coordinated square pyramidal or trigonal bipyramidal geometry,[26] that lactide can coordinate smoothly to form the octahedral geometry. Longer reaction times > 6 h at 70 °C with **4b** gave PDLLA quantitatively; however, the polydispersity was worse with values of ∼1.8−2.0. The

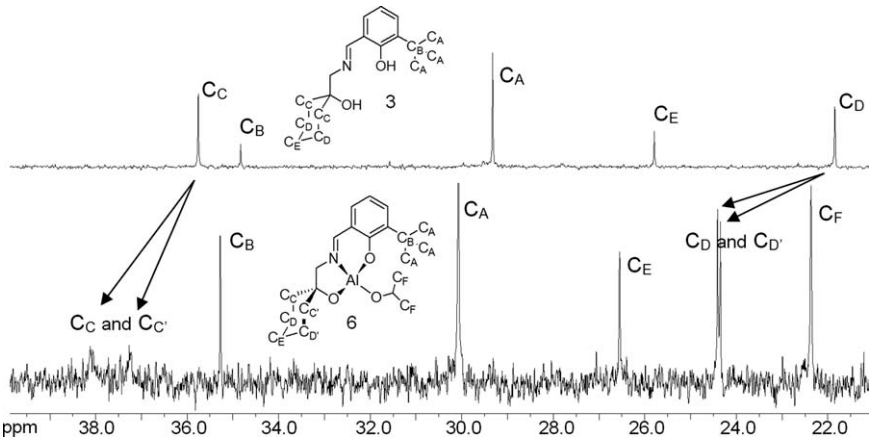


FIGURE 2 ^{13}C NMR spectra for **3** and **6** in $CDCl_3$. Because of the existence of the aluminum chirality, the signals assigned as each of the four diastereotopic carbon atoms of C_C, $C_{C'}$, C_D, or $C_{D'}$ in **6** were separated independently.

TABLE 1 Ring-Opening Polymerization of Lactide Initiated by **4a**, **4b**, **(*rac*)-5** and **6**[a]

Entry	Complex	Solvent	Monomer	Temp/ °C	Time /h	Yield/%	M_n/kg mol^{-1}[b]	Theor/kg mol^{-1}[c]	M_w/M_n[b]	P_m[d]
1	**4a**	Toluene	D,L-LA	70	96	21	9.7	3.0	1.09	0.76
2	**4b**	Toluene	D,L-LA	70	96	100	18.9	14.4	1.14	0.80
3	**4b**	Pyridine	D,L-LA	70	3	86	13.7	12.4	1.45	0.79
4	**4b**	Pyridine	D,L-LA	50	6	64	11.8	10.6	1.38	0.87
5	**4b**	Pyridine	D,L-LA	25	72	76	20.0	10.9	1.27	0.88
6	**(*rac*)-5**	Toluene	D,L-LA	70	96	80	16.4	11.5	1.14	0.86
7	**(*rac*)-5**	Toluene	L-LA	70	96	56	10.7	8.1	1.13	1.00
8	**(*rac*)-5**	Pyridine	D,L-LA	70	12	100	17.2	14.4	1.14	0.87
9	**6**	Pyridine	D,L-LA	100	24	28	3.2	4.0	1.19	0.92

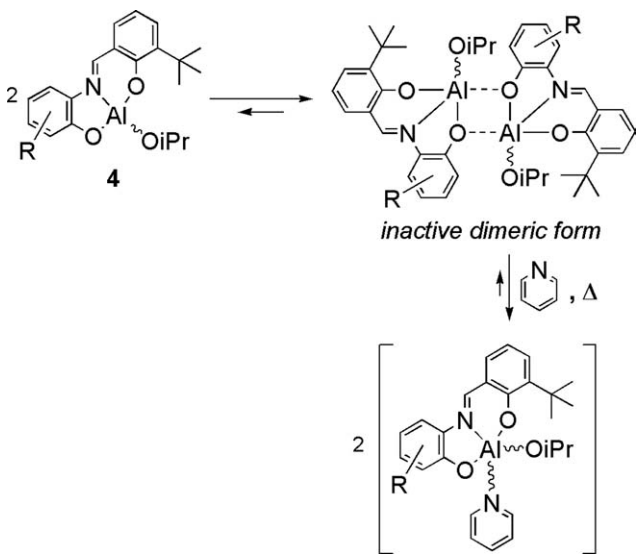
[a] Conditions: [monomer]/[Al] = 100/1, [monomer] = 1.73 mol L^{-1}.
[b] Determined by size-exclusion chromatography (SEC) in THF, calibrated with polystyrene standard (the real M_n of PLA should be reduced (0.58 times) from that of PSt).
[c] Calculated on the basis of monomer/initiator ratio and monomer conversion.
[d] P_m (meso content) of PLA was calculated from the integrated ratios of homonuclear decoupled signals at δ5.16-5.22 due to tetrads, mmm, mrm, rmm, mmr, rrm, and mrr of the methine proton.

polymerization of D,L-LA with **4b** could be conducted at room temperature for 72 h with the formation of PDLLA in high yield (entry 5). This polymer had a narrower polydispersity, 1.27, than the polymers produced by polymerization at 50 and 70 °C, 1.38 and 1.45. ROP of LA at room temperature has been shown in Lewis acidic aluminum complexes.[27] On the other hand, narrow-polydispersity PDLLA was obtained at 70 °C by the reaction with **(*rac*)-5**, in which the Lewis acidity of the aluminum center is lower than that in **4b**. The molecular weight of the PDLLA was determined to be 10−20 kg mol^{-1} by SEC. The polymerization of D,L-LA with **6** as an initiator did not proceed at 70 °C but yielded PDLLA at 100 °C in pyridine (28% after 24 h, M_n = 3.2 kg mol^{-1}, M_w/M_n = 1.19) (entry 9). The low activity of **6** may be attributed to the bulky cyclohexylene unit in the Schiff-base ligand which prevents the coordination of LA or the nucleophilic attack of the isopropoxide to the carbonyl moiety in LA.

The polydispersities of the obtained PLAs were close to 1.0, indicating a controlled/living polymerization system. First-order kinetic plots for lactide polymerization in pyridine at 70 °C [**(*rac*)-5**] or 50 °C (**4b**) and the correlation between monomer conversion and molecular weight or polydispersity from SEC are shown in Figure 3(a,b). An induction period was observed in the ROP at 50 °C initiated by **4b**, indicating existence of some activation process involving the formation of the monomeric active species or the initial reaction with LA molecules. The polymer weight increased linearly accompanied by monomer conversion of **(*rac*)-5**, thereby showing the living nature of the polymerization; however, the polymer weight decreased with **4b** when monomer conversion was high. The decrease in the polymer weight and the increase in the polydispersity with the conversion also indicated inter- and/or intramolecular transesterification of the polymer chain at the low monomer concentration due to higher Lewis acidity of the aluminum complex, **4b**, than that of **5**.

Thermal Properties and X-Ray Diffraction Study of the Stereoblock Copolymer

A DSC curve for poly(D,L-LA) (M_n = 15 kg mol^{-1}, M_w/M_n = 1.1, P_m = 0.87), which was made with **(*rac*)-5** (1 mol %) at 70 °C in pyridine, was recorded after prior heating to 250 °C at the same rate of 5 K min^{-1} and slow cooling at a rate of 2 K min^{-1} [Fig. 4 (a)]. The melting temperature was 186 °C, which was distinctly higher than that of a PLLA sample with the similar molecular weight crystallized under a normal crystallization condition,[28] also indicating the formation of the expected stereoblock copolymer from D,L-LA. Glass transition point was observed around 52 °C, which agreed well with that in the previous reports for PLLA.[29] The broad melting peak, starting from about 137 °C, indicates an inclusion of small size and/or imperfect crystals in the sample. The formation of the stereocomplex in the



SCHEME 3 Formation of the active monomeric form which could be generated in the presence of pyridine.

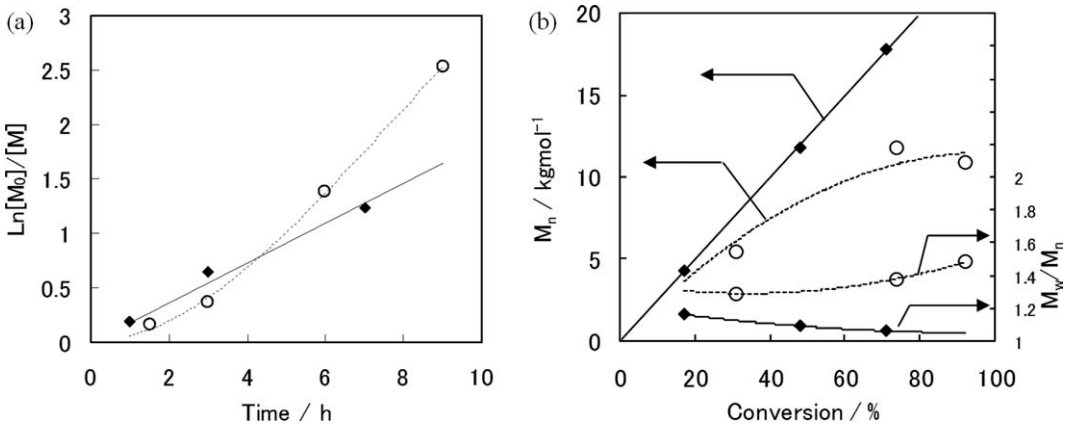


FIGURE 3 (a) Time versus $\ln[M_0]/[M]$ plots and (b) conversion versus M_n and M_w/M_n plots with $[M_0]/[I] = 100$. (◆: **(*rac*)-5**-initiated ROP of D,L-LA at 70 °C, ○: **4b**-initiated ROP at 50 °C).

PDLLA was finally confirmed by the powder X-ray analysis. As shown in Figure 4(b), three peaks, A, B, and C, at 12.11, 20.58, and 23.67° appeared in the WAXD pattern. Appearance of three intense peaks in the diffraction angle 2θ range of 9–30° has been reported for powder patterns of stereocomplex which is composed of PLLA and PDLA.[30] The diffraction pattern, peaks A and B, also agreed with the reported pattern of the stereoblock copolymer, in the 2θ range of 11–22°.[31] Broadness of the peaks suggests formation of the small size crystals in this sample. These facts strongly support the presence of the stereocomplex in the PDLLA structure.

Stereoselectivity

Investigation of the stereoselectivity in PDLLA initiated by **4a**, **4b**, **(*rac*)-5**, and **6** gave significant information. Table 1 lists the P_m values of the PLA initiated by these complexes under several conditions and Figure 6 shows the partial

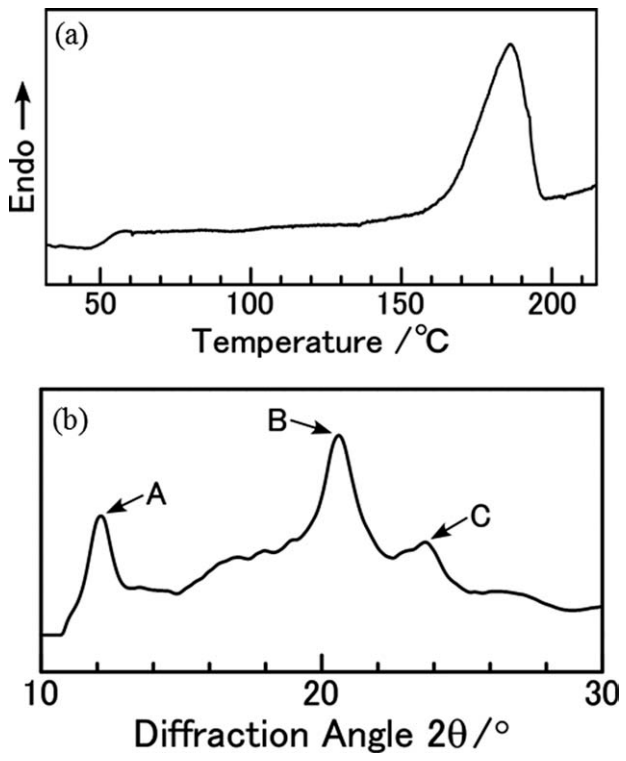


FIGURE 4 (a) DSC curve for PDLLA (M_n = 17 kg/mol, M_w/M_n = 1.1) by **(*rac*)-5**. The temperature was increased at a rate of 5 K min^{-1}. The second scan was recorded. (b) WAXD pattern of PDLLA with polyimide films. Background peaks of the polyimide did not affect the pattern.

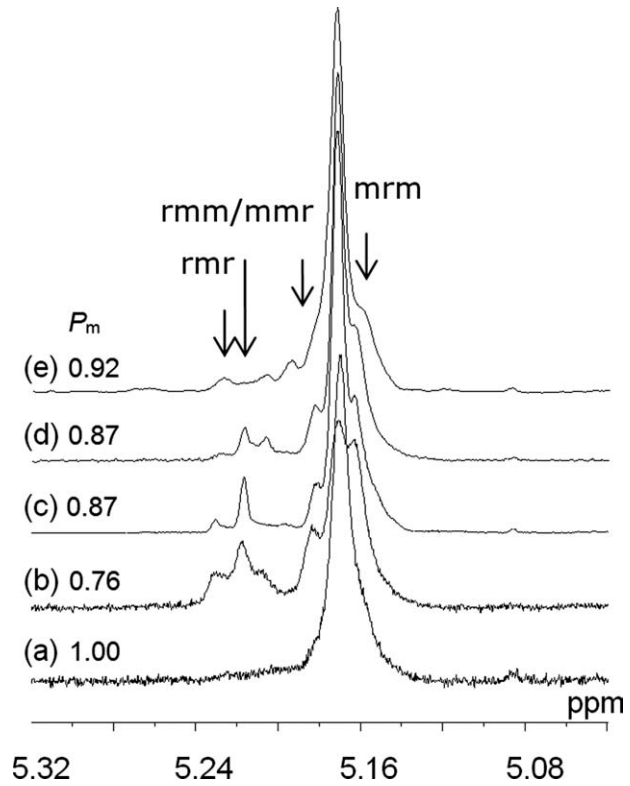


FIGURE 5 Homonuclear-decoupled ^1H NMR spectra (400 MHz, $CDCl_3$, 25 °C, methine region) of PLA generated from (a) **(*rac*)-5** with L-LA (70 °C), (b) **4a** with D,L-LA (70 °C), (c) **4b** with D,L-LA (50 °C), (d) **(*rac*)-5** with D,L-LA (70 °C), and (e) **6** with D,L-LA (100 °C). The P_m values of the polymers are shown in the spectra.

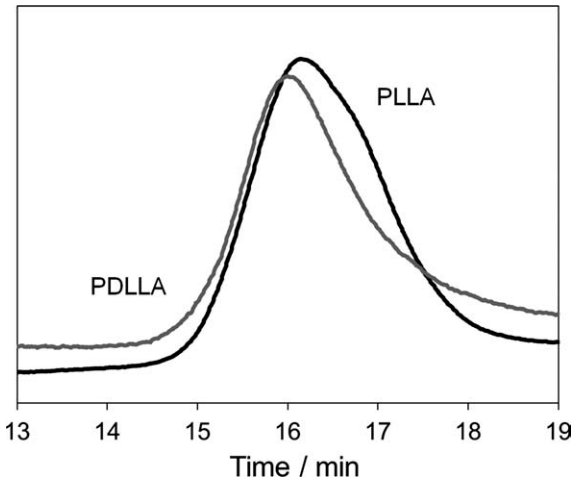


FIGURE 6 SEC chromatograms for PLLA (M_n = 6.5 kg mol^{-1}, M_w/M_n = 1.36) and PDLLA (M_n = 6.6 kg mol^{-1}, M_w/M_n = 1.47) mediated by **4b** at room temperature for 72 h (monomer/initiator ratio is 30/1). The bimodal distribution of PLLA shows that two different initiators, performing different activities toward L-LA, may exist in the reaction mixture.

homonuclear-decoupled ^{1}H NMR spectra for PLLA [Fig. 5(a)] and PDLLA made with (c) **4b** at 50 °C, (b) **4a** and (d) **(*rac*)-5** at 70 °C, and (e) **6** at 100 °C. The distributions of the signals around 5 ppm due to tetrads of the methine proton in PDLLA were similar to that of the isotactic stereoblock copolymer:[7d] integrated ratios of three signals due to the rmm, mmr, mrm tetrads were almost equal, whereas the integrated ratio due to the rmr tetrad was small. The isotacticity of PDLLA, P_m, made from **4b** decreased depending on the decrease of the polymerization temperature from 70 to 25 °C (Table 1, entries 3–5). The best performance was observed when **6** was used as the initiator; the P_m value is 0.92 (entry 9). These results suggest that the aluminum system bearing the tridentate ligand can also provide stereoregulated polymerization of D,L-LA. Pyridine rather than toluene did not affect the isotacticity of PDLLA, concluded from the similar P_m values of PDLLA polymerized in pyridine and toluene at the same temperature were similar.

The stereoregulation in PDLLA was tightly controlled with **4b** especially at low temperatures. However, the stereoselectivity was still lower than previous data acquired for SALEN aluminum complexes.[7–9] Such distortion in stereoselectivity of **4b** may be due to two factors: a rather disturbed stereoregulation system attributed to the less-bulky tridentate ligands than bulky tetradentate SALEN ligands; and thermal interconversion between chiral isomers at the aluminum center during the polymerization, which is specifically possible in the aluminum complexes bearing nonchiral tridentate ligands. Concerning about the former, the ratios of the tetrads in the homonuclear decoupled NMR spectra indicate that the intermolecular alkoxide exchange frequently occurred in these polymerizations, because the less-bulky tridentate ligands may allow to form dimer as previously reported.[32] Additionally, the high Lewis acidity of **4b**, which can polymerize LA at room temperature, may cleave the polymer chain with an alkoxide anion at the low monomer concentration to form polymers with low molecular weight [Fig. 3 (b)]. On the other hand, the chiral interconversion at the aluminum may occur in **6** rather frequently at high polymerization temperatures, as indicated in the variable-temperature NMR spectra. However, we could not determine whether such chiral interconversion in these complexes with nonchiral ligands also takes place under polymerization conditions or not. Hence, we examined ROP of (L)-LA in the presence of **4b**, **(*rac*)-5**, and **6**, (monomer/initiator ratio is 30/1) under the suitable conditions for the initiators. We found that the molecular weights of PLLA were around 4.6–7.5 kg mol^{-1}, which agreed with those calculated from monomer conversion/initiator ratios as shown in Table 2. However, the polydispersities were larger than those observed in ROP of D,L-LA, especially for PLLA initiated by **(*rac*)-5** and **6** (Table 2, entries 1 and 5). Moreover, the SEC chromatograms of PLLA initiated by **4b** at room temperature showed bimodal distribution, where a shoulder peak was observed at about 17 min in addition to the dominant signal at 16 min in contrast to the monomodal SEC distribution of PDLLA (M_n = 6.6 kg mol^{-1}, M_w/M_n = 1.47, P_m = 0.92) initiated by **4b** under the same conditions (Fig. 6). That suggests existence of two different active and less active aluminum initiators in the reaction mixture, which could be stereoisomers of the aluminum complex, one of them is a suitable isomer to polymerize L-LA and the other is not. This indicates the possibility of the ESC process proceeding in stereocontrolled ROP of D,L-LA using the aluminum complex **4b**

TABLE 2 Polymerization of L-LA initiated by **4b**, **(*rac*)-5**, and **6**[a]

Entry	Monomer	Al complex	Temp/ °C	Time/h	Yield/%	M_n/kg mol^{-1}[b]	Theor/kg mol^{-1}[c]	M_w/M_n
1	L-LA	**(*rac*)-5**	70	20	80	5.9 (3.4)	3.5	1.26
2	L-LA	**4b**	25	70	78	6.5 (3.8)	3.4	1.36
3	L-LA	**4b**	50	12	92	7.0 (4.1)	4.0	1.35
4	L-LA	**4b**	70	7	90	7.5 (4.3)	3.9	1.37
5	L-LA	**6**	110	20	65	4.6 (2.7)	2.8	1.28

[a] Conditions: [monomer]/[Al] = 30/1, [monomer] = 1.73 mol L^{-1}.
[b] Determined by size-exclusion chromatography (SEC) in THF, calibrated with polystyrene standard (the real M_n of PLA in brackets was reduced (0.58 times) from that of PSt).
[c] Calculated on the basis of monomer/initiator ratio and monomer conversion.

bearing nonchiral ligand. However, the real active structures of the aluminum complexes in the reaction mixture are still not clear. Additionally, undefined microstructures in the NMR spectra for PDLLA initiated by **5** and **6** were detected, and further studies examining the structures of the polymers is required to clarify in more detail the polymerization mechanism.

CONCLUSIONS

In summary, we have synthesized a series of aluminum alkoxides bearing nonchiral or chiral tridentate Schiff-bases, half-SALEN ligands and achieved controlled stereoselective polymerization of D,L-LA using these aluminum complexes. In particular, the P_m value of the PDLLA initiated by **6** was >0.9, whereas **4b** initiated the ROP of D,L-LA efficiently even at room temperature in a pyridine solution with high stereoselectivity. The behavior of these aluminum complexes in solution, including inversion of the chirality at the aluminum center, was investigated. The detailed identification of PDLLA showed the isotactic stereoblock copolymers generated in these processes. These results indicate the significance of chiral aluminum centers in stereocontrolled polymerization. Further studies on detailed identification of the polymers and new initiator performing higher stereoselectivity, based on the concept of a racemic metal complex with chirality at the metal center, are currently in progress.

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