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Schiff base aluminum catalysts containing morpholinomethyl groups in the ring opening polymerization of *rac*-lactide

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A series of Schiff base aluminum(III) complexes bearing morpholinomethyl substituents were synthesized. Comprehensive investigations on their stereoselective and kinetic features in the ring opening polymerization of lactide were carried out. The ring opening polymerization proved to be first-order in the catalyst and the monomer. Linear relationships between the number-average molecular weight of the polylactide and the monomer conversion were consistent with a well-controlled polymerization. The propagation rate was strongly affected by morpholinomethyl substituents on the salicylaldehyde moiety.

polylactide, morpholinomethyl, ring opening polymerization

1 Introduction

Polylactide (PLA) is a biocompatible and biodegradable polyester produced from annually renewable resources, such as corn and sugar roots [1]. As petroleum resources gradually depleted, PLA, with its unique features, has become one of the most promising alternatives to petroleum-based plastics [2,3]. The physical and mechanical properties of PLA are largely determined by the stereochemistry of the polymer chain [4–8]. Metal-catalyzed ring opening polymerization (ROP) of lactide (LA) is a common method for the synthesis of PLA. In recent years, catalysts with ancillary Schiff base ligands and combined with a discrete metal center have been widely used in the ROP of lactide [9–13]. The central challenge for this class of catalysts is to combine high stereoselectivity with high polymerization rate.

Since the substituents on the ancillary organic ligands affect the stereoselectivity and the rate of the polymerization process, much research has been directed toward the development of catalyst systems [6,8,10,14–16]. Nomura *et al*. [17] and Chen *et al*. [16] reported a series of Schiff base aluminum complexes as *N*,*N*,*O*,*O*-tetradentate ligands, and showed that the electronic nature of the substituents on the salicylaldehyde moiety of the catalysts greatly affected the catalytic performance. Our work is based on the notion that, by appropriate choice of the substituents on the auxiliary ligand, it is possible to improve the catalytic properties. Carpentier synthesized a series of complexes stabilized by a chelating bis(morpholinomethyl)phenoxy ligand, complexes which proved to be very effective catalysts in the ROP of *L*-LA, with a high $[LA]_0$/[Initiator] ratio (up to 5000) [18]. Because of the lone pair electrons on the N atom, the morpholinomethyl substituent acts as a Lewis base activating group, which can control the nucleophilic activity of the catalyst [19] and therefore enhance the polymerization process. Inspired by this work, we have synthesized a series of complexes bearing a morpholinomethyl substituent on the organic ligand, and we have investigated the effect of this substituent on the ROP of *rac*-LA (Scheme 1).

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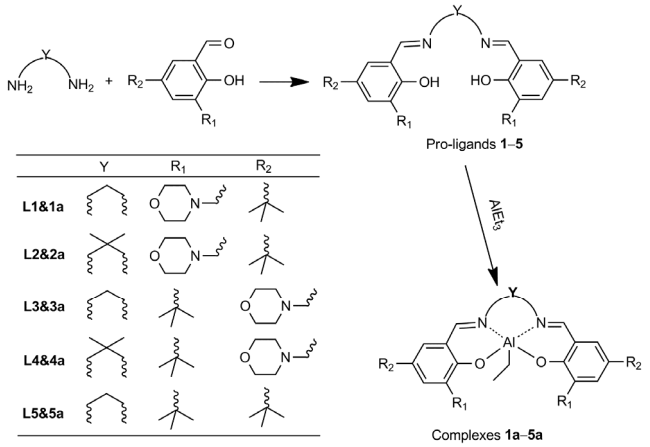


Scheme 1 Synthesis and structures of pro-ligands **1–5** and complexes **1a–5a**.

2 Experimental

All experiments were carried out under dry nitrogen atmosphere, using standard Schlenk techniques. Materials used for the preparation of pro-ligands **1–5** were purchased from Aldrich, and used without further purification. Toluene was distilled from Na-benzophenone. 2-Propanol and ethyl acetate were distilled from CaH_2 and protected by argon atmosphere. *rac*-lactide (Purac) was purified by recrystallization from ethyl acetate and dried under vacuum at room temperature before use. NMR spectra were recorded on Bruker AV 300 (Germany) and 400 MHz spectrometers in $CDCl_3$ at 25 °C. Chemical shifts are given in parts per million from tetramethylsilane. Gel permeation chromatography (GPC) measurements were conducted with a Waters 515 GPC system with $CHCl_3$ as the eluent (flow rate: 1 mL/min, at 35 °C). The molecular weights were calibrated against polystyrene (PS) standards.

2.1 Synthesis of 5-*tert*-butyl-2-hydroxy-3-(morpholinomethyl)benzaldehyde

5-*tert*-Butyl-2-hydroxybenzaldehyde was purchased from Aldrich (USA). To a suspension of paraformaldehyde (880 mg, 29.4 mmol) in glacial HOAc (11 mL), morpholine (2.32 mL, 26.6 mmol) was added. The suspension was stirred at ambient temperature for 3 h. Next, a solution of 5-*tert*-butyl-2-hydroxy-benzaldehyde (4.74 g, 26.6 mmol) in absolute ethanol (45 mL) was added, and the mixture was heated to reflux for 4 d. After cooling to ambient temperature, the mixture was brought to pH 8 with saturated K_2CO_3, extracted with $CHCl_3$, dried over Na_2SO_4, and concentrated. Chromatography on SiO_2 (30% EtOAc/hexane) afforded 5-*tert*-butyl-2-hydroxy-3-(morpholinomethyl)benzaldehyde (Compound **A**, Scheme 2) in 58% yield (4.28 g, 15.46 mmol).

2.2 Synthesis of 3-*tert*-butyl-2-hydroxy-5-(morpholinomethyl)benzaldehyde

3-*tert*-Butyl-2-hydroxybenzaldehyde was purchased from Aldrich (USA). To a suspension of paraformaldehyde (880 mg, 29.4 mmol) in glacial HOAc (11 mL), morpholine (2.32 mL, 26.6 mmol) was added. The suspension was stirred at ambient temperature for 3 h. Next, a solution of 3-*tert*-butyl-2-hydroxybenzaldehyde (4.74 g, 26.6 mmol) in absolute ethanol (45 mL) was added, and the mixture was heated to reflux for 4 d. After cooling to ambient temperature, the mixture was brought to pH 8 with saturated Na_2CO_3, extracted with $CHCl_2$, dried over Na_2SO_4, and concentrated. Chromatography on SiO_2 (10% EtOAc/hexane) afforded 3-*tert*-butyl-2-hydroxy-5-(morpholinomethyl)benzaldehyde (Compound **B**, Scheme 2) in 60% yield (4.42 g, 15.99 mmol).

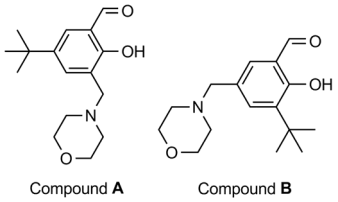
2.3 Synthesis of pro-ligands 1–5

pro-Ligands **1** and **2**: A solution of Compound **A** (0.21 mol) in absolute ethanol (20 mL) was added dropwise to a stirred solution of propane-1,3-diamine (0.1 mol) or 2,2-dimethylpropane-1,3-diamine (0.1 mol) in absolute ethanol (50 mL). The mixture was refluxed for 12 h and cooled to ambient temperature. After removal of the solvent under vacuum, a yellow powder was obtained. Petroleum ether was used for recrystallization.

pro-Ligands **3** and **4**: A solution of Compound **B** (0.21 mol) in absolute ethanol (20 mL) was added dropwise to a stirred solution of propane-1,3-diamine (0.1 mol) or 2,2-dimethylpropane-1,3-diamine (0.1 mol) in absolute ethanol (50 mL). The mixture was refluxed for 12 h and cooled to ambient temperature. After removal of the solvent under vacuum, flash chromatography on SiO_2 (5% CH_3OH/EtOAc) afforded ligand **3** in 80% yield and pro-ligand **4** in 55% yield.

pro-Ligand **5**: A solution of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (0.21 mol) in absolute ethanol (20 mL) was added dropwise to a stirred solution of propane-1,3-diamine (0.1 mol) in absolute ethanol (50 mL). The mixture was refluxed for 20 h and cooled to ambient temperature. Dichloromethane and ethanol were used for crystallization.

pro-Ligand **1**: ^{1}H NMR (300 MHz, $CDCl_3$): δ=13.53 (s, PhO*H*, 2H), 8.40 (s, NC*H*, 2H), 7.42 (s, Ph*H*, 2H), 7.18 (s, Ph*H*, 2H), 3.76 (m, CH_2CH_2O, 8H), 3.63 (s, $PhCH_2N$, 4H),



Scheme 2 Compounds used for the preparation of pro-ligands **1–5**.

3.71 (m, CCH_2N, 4H), 2.55 (m, CH_2CH_2N, 8H), 2.09 (m, CCH_2C, 2H), 1.32 (s, C(CH_3)$_3$, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=165.68 (N*C*H), 157.45, 140.64, 130.96, 126.66, 124.25, 117.83 (aromatic carbons), 56.79 (C*C*H_2N), 53.65 (CH_2*C*H_2N), 56.67 (Ph*C*H_2N), 67.05 (CH_2*C*H_2O), 31.82 (CH_2*C*CH$_2$), 33.93 (Ar*C*(CH$_3$)$_3$), 31.47 (C(*C*H$_3$)$_3$).

pro-Ligand **2**: ^{1}H NMR (300 MHz, $CDCl_3$): δ=13.60 (s, PhO*H*, 2H), 8.37 (s, NC*H*, 2H), 7.46 (s, Ph*H*, 2H), 7.19 (s, Ph*H*, 2H), 3.74 (m, CH_2CH_2O, 8H), 3.65 (s, PhCH_2N, 4H), 3.50 (s, CCH_2N, 4H), 2.55 (s, CH_2CH_2N, 8H), 1.33 (s, C(CH_3)$_3$, 18H), 1.09 (s, C(CH_3)$_2$, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=166.06 (N*C*H), 157.50, 140.67, 130.87, 126.72, 124.31, 117.79 (aromatic carbons), 68.33 (C*C*H_2N), 53.63 (CH_2*C*H_2N), 56.41 (Ph*C*H_2N), 67.08 (CH_2*C*H_2O), 36.32 (CH_3*C*CH$_2$), 33.95 (Ar*C*(CH$_3$)$_3$), 31.46 (C(*C*H$_3$)$_3$), 24.25 (*C*H$_3$C*C*H$_2$).

pro-Ligand **3**: ^{1}H NMR (300 MHz, $CDCl_3$): δ=13.94 (s, PhO*H*, 2H), 8.40 (s, NC*H*, 2H), 7.25 (s, Ph*H*, 2H), 7.09 (s, Ph*H*, 2H), 3.73 (m CH_2CH_2O, 8H), 3.44 (s, PhCH_2N, 4H), 3.72 (m, CCH_2N, 4H), 2.45 (s, CH_2CH_2N, 8H), 2.14 (m, CCH_2C, 2H), 1.32 (s, C(CH_3)$_3$, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=166.09 (N*C*H), 159.57, 137.23, 130.58, 130.08, 126.60, 118.30 (aromatic carbons), 56.82 (C*C*H_2N), 53.52 (CH_2*C*H_2N), 63.08 (Ph*C*H_2N), 67.04 (CH_2*C*H_2O), 31.82 (CH_2*C*CH$_2$), 34.80 (Ar*C*(CH$_3$)$_3$), 29.40 (C(*C*H$_3$)$_3$).

pro-Ligand **4**: ^{1}H NMR (300 MHz, $CDCl_3$): δ=13.82 (s, PhO*H*, 2H), 8.37 (s, NC*H*, 2H), 7.29 (s, Ph*H*, 2H), 7.18 (s, Ph*H*, 2H), 3.74 (m, CH_2CH_2O, 8H), 3.45 (s, PhCH_2N, 4H), 3.53 (s, CCH_2N, 4H), 2.45 (s, CH_2CH_2N, 8H), 1.32 (s, C(CH_3)$_3$, 18H), 1.08 (s, C(CH_3)$_2$, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=166.61 (N*C*H), 159.59, 137.25, 130.60, 130.05, 126.58, 118.32 (aromatic carbons), 68.31 (C*C*H_2N), 53.50 (CH_2*C*H_2N), 62.83 (Ph*C*H_2N), 67.04 (CH_2*C*H_2O), 36.30 (CH_3*C*CH$_2$), 34.81 (Ar*C*(CH$_3$)$_3$), 29.41 (C(*C*H$_3$)$_3$), 24.27 (*C*H$_3$C*C*H$_3$).

2.4 Synthesis of complexes 1a–5a

In a glovebox filled with nitrogen, pro-ligands **1–5** (0.1 mmol) were dissolved in toluene (10 mL) in a phial that was pre-dried for 2 d in a drying oven at 120 °C. Al(Et)$_3$ (0.1 mmol) dissolved in toluene was added to the phial, and the reaction was stirred for 12 h at 80 °C in an oil bath. Upon completion of the reaction, the phial was cooled to ambient temperature and toluene was removed under vacuum.

Complex **1a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.19 (s, NC*H*, 2H), 7.63 (s, Ph*H*, 2H), 7.06 (s, Ph*H*, 2H), 3.73 (m, CH_2CH_2O, 8H), 3.63 (s, PhCH_2N, 4H), 3.52 (m, CCH_2N, 4H), 2.53 (m, CH_2CH_2N, 8H), 2.30 (m, CCH_2C, 2H), 1.32 (s, C(CH_3)$_3$, 18H), 0.86 (m, Al-CH_2CH_3, 3H), –0.08 (m, Al-CH_2, 2H). ^{13}C NMR (400 MHz, $CDCl_3$): δ=168.68 (N*C*H), 161.45, 139.49, 130.06, 128.49, 128.03, 117.38 (aromatic carbons), 59.62 (C*C*H_2N), 53.30 (CH_2*C*H_2N), 55.98 (Ph*C*H_2N), 67.22 (CH_2*C*H_2O), 30.46 (CH_2*C*CH$_2$), 33.83 (Ar*C*(CH$_3$)$_3$), 31.32 (C(*C*H$_3$)$_3$), 8.88 (AlCH$_2$*C*H$_3$), 0.27 (AlCH_2CH$_3$). Elem. anal.: calcd: C 68.70, H 8.57, N 8.66%; found: C 68.65, H 8.60, N 8.70%.

Complex **2a**: ^{1}H NMR (400MHz, $CDCl_3$): δ=8.04 (s, NC*H*, 2H), 7.50 (s, Ph*H*, 2H), 7.02 (s, Ph*H*, 2H), 3.71 (m, CH_2CH_2O, 8H), 3.94 (s, PhCH_2N, 4H), 3.53 (s, CCH_2N, 4H), 2.45 (s, CH_2CH_2N, 8H), 1.29 (s, C(CH_3)$_3$, 18H), 0.94 (s, C(CH_3)$_2$, 6H), 0.86 (m, Al-CH_2CH_3, 3H), –0.11 (m, Al-CH_2, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=168.91 (N*C*H), 162.85, 137.83, 133.88, 128.16, 127.22, 117.57 (aromatic carbons), 71.33 (C*C*H_2N), 53.17 (CH_2*C*H_2N), 56.34 (Ph*C*H_2N), 67.25 (CH_2*C*H_2O), 36.13 (CH_3*C*CH$_2$), 33.95 (Ar*C*(CH$_3$)$_3$), 31.33 (C(*C*H$_3$)$_3$), 26.00 (*C*H$_3$CCH$_2$), 10.00 (AlCH$_2$*C*H$_3$), 1.54 (AlCH_2CH$_3$). Elem. anal.: calcd: C 69.41, H 8.81, N 8.30%; found: C 69.60, H 8.92, N 8.41%.

Complex **3a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.16 (s, NC*H*, 2H), 7.41 (s, Ph*H*, 2H), 7.01 (s, Ph*H*, 2H), 3.73 (m, CH_2CH_2O, 8H), 3.41 (s, PhCH_2N, 4H), 3.63 (m, CCH_2N, 4H), 2.45 (m, CH_2CH_2N, 8H), 2.25 (m, CCH_2C, 2H), 1.43 (s, C(CH_3)$_3$, 18H), 0.87 (m, Al-CH_2CH_3, 3H), –0.09 (m, Al-CH_2, 2H). ^{13}C NMR (400 MHz, $CDCl_3$): δ=163.38 (N*C*H), 161.70, 140.97, 133.00, 128.23, 128.03, 118.38 (aromatic carbons), 55.32 (C*C*H_2N), 53.54 (CH_2*C*H_2N), 62.79 (Ph*C*H_2N), 67.02 (CH_2*C*H_2O), 30.46 (CH_2*C*CH$_2$), 35.04 (Ar*C*(CH$_3$)$_3$), 29.24 (C(*C*H$_3$)$_3$), 8.90 (AlCH$_2$*C*H$_3$), 0.27 (AlCH_2CH$_3$). Elem. anal.: calcd: C 68.70, H 8.57, N 8.66%; found: C 68.60, H 8.60, N 8.65%.

Complex **4a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.04 (s, NC*H*, 2H), 7.41 (s, Ph*H*, 2H), 7.02 (s, Ph*H*, 2H), 3.73 (m, CH_2CH_2O, 8H), 3.41 (s, PhCH_2N, 4H), 3.53 (s, CCH_2N, 4H), 2.45 (s, CH_2CH_2N, 8H), 1.43 (s, C(CH_3)$_3$, 18H), 0.94 (s, C(CH_3)$_2$, 6H), 0.88 (m, Al-CH_2CH_3, 3H), –0.06 (m, Al-CH_2, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=163.40 (N*C*H), 162.34, 142.45, 132.77, 128.44, 127.22, 117.30 (aromatic carbons), 71.45 (C*C*H_2N), 53.50 (CH_2*C*H_2N), 62.30 (Ph*C*H_2N), 67.12 (CH_2*C*H_2O), 36.21 (CH_3*C*CH$_2$), 35.04 (Ar*C*(CH$_3$)$_3$), 29.26 (C(*C*H$_3$)$_3$), 25.58 (*C*H$_3$CCH$_2$), 9.88 (AlCH$_2$*C*H$_3$), 1.54 (AlCH_2CH$_3$). Elem. anal.: calcd: C 69.41, H 8.81, N 8.30%; found: C 69.60, H 8.62, N 8.42%.

Complex **5a**: The characterization of Complex **5a** has been previously reported elsewhere [17].

2.5 Polymerization of *rac*-LA

In a glovebox filled with nitrogen, *rac*-LA (7 mmol) was added to a phial that was pre-dried for 2 d in a drying oven at 120 °C. A stoichiometric amount of complexes **1a–5a** and 2-propanol as initiator (I) were added to the phial. Next, the phial was put into an oil bath at 70–150 °C. At a certain reaction time, approximately 1 mL of the reaction mixture was withdrawn with a 2 mL syringe. PLA was precipitated with cold ethanol. After centrifugation and removal of the solvent, the polymer was dried in a vacuum drying oven at 45 °C for 48 h.

3 Results and discussion

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

According to the empirical formula:

$$-d[LA]/dt=k_p[LA]^m[Cat]^n$$

the reaction order with respect to LA concentration can be determined from the monomer conversion by fixing the concentration of the catalyst and the polymerization temperature ($k_p=Ae^{-E_a/RT}$) [20]. As shown in Figure 1, first-order kinetics in the monomer is observed. The apparent polymerization constant ($k_{app}=k_p[Cat]$) can be determined from the slope of the figure [21]. To further probe the reaction order with respect to the catalyst, k_{app} was plotted vs. the catalyst concentration (Figure 2). The linear correlation between k_{app} and [Al] revealed a first-order kinetics in catalyst as well.

The number-average molecular weight (M_n) of PLA using complexes **1a–4a** showed a linear correlation with the monomer conversion, along with low polydispersities, indicating a well-controlled polymerization (Figure 3 and Table 1). The correlation between M_n and the monomer conversion using Complex **5a** as catalyst has been previously reported elsewhere [17].

In order to investigate the influence of the morpholinomethyl substituent on the polymerization rate, a series of experiments applying complexes **1a–5a** were performed. The results are plotted and summarized in Figure 4 and in Tables 1 and 2.

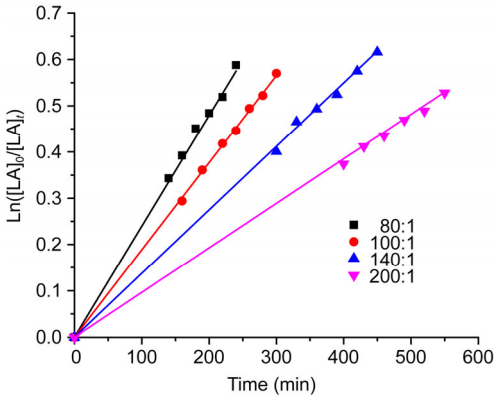


Figure 1 First-order kinetic plots for the ROP of *rac*-LA by applying **4a** and 2-propanol as catalyst and initiator, respectively, in toluene. $[LA]_0$=0.5 mol/L, T=70 °C.

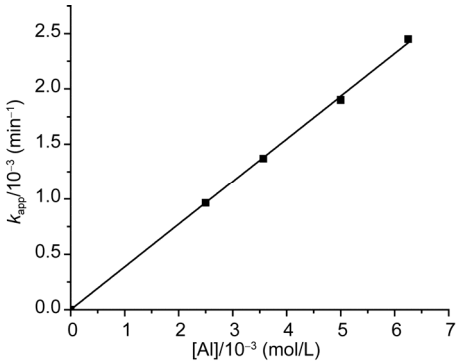


Figure 2 k_{app} vs. the concentration of **4a**, using 2-propanol initiator, for *rac*-LA polymerization.

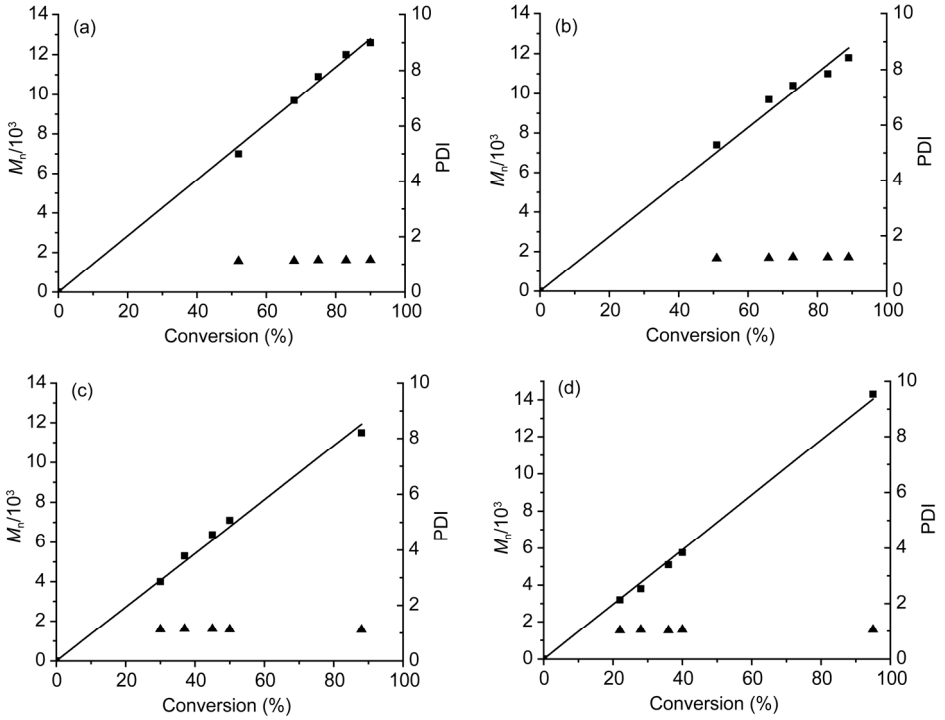


Figure 3 Plot of M_n (■) and polydispersity (▲) of PLA vs. *rac*-LA conversion, using complexes **1a–4a** and 2-propanol as catalysts and initiator, respectively, with $[M]_0/[I]$=100. (a) Complex **1a**/2-propanol; (b) Complex **2a**/2-propanol; (c) Complex **3a**/2-propanol; (d) Complex **4a**/2-propanol.

Table 1 Polymerization of *rac*-LA in toluene using complexes **1a–5a**, and 2-propanol as initiator [a)]

Entry	Complex	t (min)	$[M]_0/[I]$	Conv. [b)] (%)	$M_{n\ (calcd)}\times10^{-3}$ [c)]	$M_{n\ (NMR)}\times10^{-3}$ [d)]	$M_{n\ (GPC)}\times10^{-3}$ [e)]	PDI [e)]	P_m [f)]
1	**1a**	105	100	90	13.0	13.9	12.6	1.12	0.74
2	**2a**	120	100	89	12.8	13.5	11.8	1.19	0.76
3	**3a**	960	100	88	12.6	14.8	11.4	1.13	0.86
4	**4a**	1100	80	93	10.7	11.5	9.7	1.08	0.87
5	**4a**	1150	100	95	13.7	15.7	14.3	1.05	0.87
6	**4a**	1850	140	92	20.2	23.6	18.6	1.15	0.85
7	**4a**	2100	200	82	24.5	26.4	24.0	1.03	0.85
8	**5a**	720	100	88	12.7	13.8	10.7	1.14	0.91

a) The polymerizations were carried out in toluene; $[LA]_0$=0.5 mol/L, T=70 °C; b) determined by ^{1}H NMR; c) $M_{n\ (calcd)}$=144 g/mol×$[M]_0/[I]$×conversion +M_w (*i*PrOH); d) calculated from ^{1}H NMR; e) obtained from GPC analysis; f) P_m is the probability of the *meso*-enchainment of the polymer chain.

Table 2 Kinetic results of *rac*-LA polymerization using complexes **1a–5a**

Entry	Complex	T (°C)	$[M]_0/[cat]$	k_{app} ($\times10^{-3}$ min^{-1})	k_p (L/(mol min))
1	**1a**	70	100	20.12	4.024
2	**2a**	70	100	17.94	3.588
3	**3a**	70	100	2.27	0.454
4	**4a**	70	80	2.41	0.386
5	**4a**	70	100	1.93	0.386
6	**4a**	70	140	1.37	0.383
7	**4a**	70	200	0.96	0.384
8	**5a**	70	100	2.95	0.590

The morpholinomethyl substituent in the *ortho* position had a positive effect on the polymerization rate, as shown in Figure 4. The k_{app} and k_p of complexes **1a–5a** are summarized in Table 2. The k_p values of complexes **1a** and **2a** with morpholinomethyl substituents in the *ortho* position are 4.024 and 3.588 L/(mol min), respectively, almost ten times higher than those of complexes **3a** (0.454 L/(mol min)) and **4a** (0.386 L/(mol min)) bearing bulky *tert*-butyl groups in the ortho position. In general, single site catalysts are represented by the formula L_nMR, where M is the metal center, surrounded by the ancillary ligand L_n. The steric and electronic properties of the ligand affect the bonding between the ligand and the metal center, that is, the substituents on the ligand have a significant influence on the polymerization activity and on the stereoselectivity. As illustrated in Figure 4, the k_p values of complexes **3a** and **4a** are slightly lower than those of Complex **5a**, because these complexes differ only in the para substituent. Hence, we speculate that because of its electron-donating ability, the morpholinomethyl substituent at the para position is less efficient in improving the polymerization rate, compared with the *tert*-butyl. The morpholinomethyl moiety can increase the rate of ROP of LA when present at the *ortho* position, whereas it does not affect remarkably the reaction rate when at the para position. This finding can be presumably attributed to the synergistic effect of steric hindrance and electronic impact of the morpholinomethyl group at the *ortho* position; nevertheless, a more complicated rationale cannot be excluded.

3.2 Stereoselectivity investigation

In order to investigate the influence of the morpholinomethyl substituent on the stereoselectivity of the polymer, a series of experiments were performed at different temperatures, in the range 70–150 °C. For safety, the reaction phial was tightly sealed with a rubber stopper and copper wire. Because the catalysts studied herein were achiral, the ROP reactions of *rac*-LA were assumed to be controlled by a chain-end mechanism [13,17]. According to this mechanism, the stereogenic center of the last inserted monomer on the

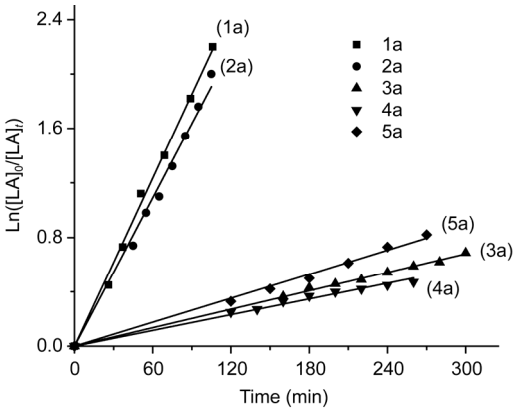


Figure 4 First-order kinetic plots for the ROP of *rac*-LA using complexes **1a–5a** and 2-propanol as catalysts and initiator, respectively, in toluene, with $[LA]_0$=0.5 mol/L, $[M]/[I]$=100:1, and T=70 °C. (1a) Complex **1a**/2-propanol; (2a) Complex **2a**/2-propanol; (3a) Complex **3a**/2-propanol; (4a) Complex **4a**/2-propanol; (5a) Complex **5a**/2-propanol.

polymer chain determines which enantiomer of *rac*-LA monomers is enchained. Thus, two outcomes were obtained: (1) isotactic PLA, formed when the stereogenic centers favor a *meso*-enchainment ($k_{R/RR}$>>$k_{R/SS}$ or $k_{S/SS}$>>$k_{S/RR}$); and (2) heterotactic PLA, formed when the stereogenic centers favor a racemic enchainment ($k_{R/SS}$>>$k_{R/RR}$ or $k_{S/RR}$>>$k_{S/SS}$) [22]. In an attempt to increase the selectivity (P_m), the four complexes were designed with two different amine bridges. The P_m of complexes having 2,2-dimethylpropane-1,3-diamine as amine bridge is 0.03–0.05 higher compared with that of complexes using propane-1,3-diamine.

The homonuclear decoupled ^{1}H NMR spectrum of the PLA's methine region using Complex **3a** is illustrated in Figure 5. The stereo microstructures of the PLA chain can be deduced from the spectrum. The stereoselectivity data of *rac*-LA using complexes **3a** and **5a** are plotted in Figure 6. An increase in temperature led to a decrease in stereoselectivity. At 70 °C, Complex **5a** had the highest stereoselectivity of 0.91, which gradually decreased to 0.67 when the temperature increased to 150 °C. The same trend was observed with Complex **3a**. However, the decrease in selectivity was less severe with Complex **3a** than with Complex **5a**. According to a previous report [19], in the addition of diethylzinc to aldehydes, an apical coordination site on the salen metal center of the catalyst could act as a Lewis acid site to activate the aldehyde, whereas the tethered base could independently activate the Et_2Zn. Thus, the morpholinomethyl group in the *ortho* position can act as a nucleophile and can stabilize the metal center. However, taking into account bond lengths and bond angles, presumably the electron-donating ability of the morpholinomethyl substituent in the para position played a role in stabilizing the metal center of the catalyst as the temperature increases.

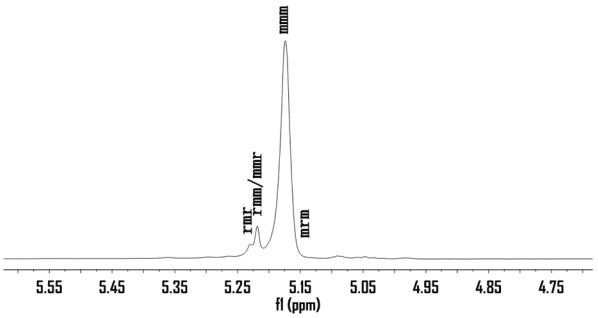


Figure 5 Homonuclear decoupled ^{1}H NMR spectrum of PLA using Complex **3a** at 70 °C.

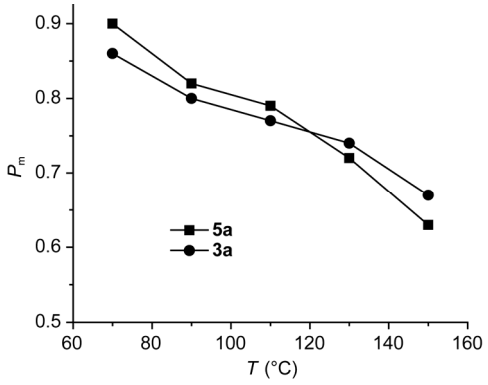


Figure 6 Stereoselectivity data of *rac*-LA using complexes **3a**/2-propanol and **5a**/2-propanol in the temperature range 70–150 °C.

4 Conclusions

A series of Schiff base aluminum(III) complexes bearing a morpholinomethyl substituent have been synthesized. The morpholinomethyl substituent in the *ortho* and *para* positions of the phenolate rings exhibit a dramatic influence on the ROP of *rac*-LA. The reaction is first-order with respect to the monomer and the catalyst. The morpholinomethyl substituent is shown to be a less efficient group than the bulky *tert*-butyl substituent in the stereoselective polymerization of *rac*-LA. Nevertheless, the morpholinomethyl substituent shows a positive effect on the rate of ROP of *rac*-LA.

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