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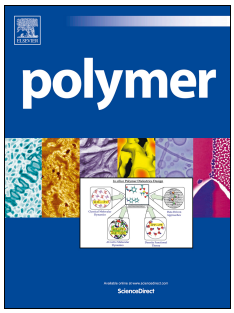

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Graphical Abstract

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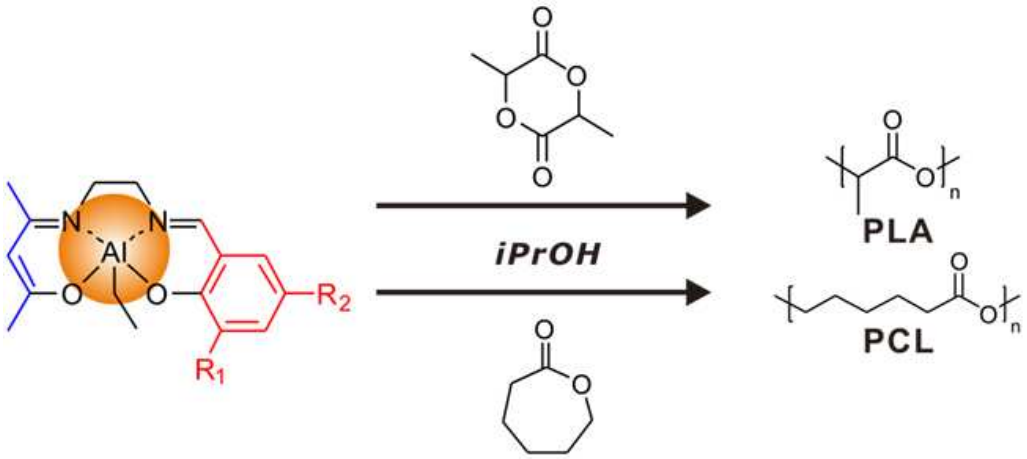

Non-Symmetrical Aluminium Salen Complexes: Synthesis and Their Reactivity with Cyclic Ester

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Abstract: Non-symmetrical aluminium salen complexes that contained different substituents were designed and synthesized. All the ligands and their complexes were characterized by ^{1}H, ^{13}C NMR and elemental analysis. These complexes can be used as catalysts to produce polylactide and poly-ε-caprolactone. All polymerizations were living and molar mass distributions were narrow. The $M_{n(obsd)}$ of the isolated polymers were in good agreement with $M_{n(calcd)}$. The polymerization rate of electrophilic substituted complex was higher than the non-electrophilic substituted analogies. The bulky substituents with more steric hindrance of the complexes had relatively lower activity. Kinetic studies showed that the polymerizations were both first-ordered with respect to lactide and ε-caprolactone monomers.

Keywords: half-Salen, ring-opening polymerization, lactide

1. Introduction

Fossil-based polymers are extensively used in our life. Millions of tons of fossil-based polymers are produced and disposed of every year.[1] As fossil resources are being depleted gradually, and the growing amount of waste created by these polymers have generated serious pollution of our ecosystem, recent research efforts have been focused on the development of biodegradable alternatives.[2-4] Due to the biocompatible and biodegradable properties, poly(lactic acid) (PLA), whose starting materials are from corn or sugar beets, becomes a leading candidate in this respect.[5-10] PLA can degrade via hydrolytic cleavage of the ester bonds of the polymer backbone. The ring-opening polymerization (ROP) of lactide (LA) is the general way to produce PLA.[11-13] Because of the presence of two chiral centers in the lactide monomer, different lactide stereoisomers are distinguished, namely, (S,S)-LA (L-LA), (R,R)-LA (D-LA), and (R,S)-LA (*meso*-LA). The stereochemistry of the monomeric units in the polymer chains plays an important role in mechanical, physical, and degradation properties of PLA materials.[14-16] The polymerization process is typically catalyzed or initiated by Lewis acidic metal alkoxide complexes of tin,[17-18] zinc,[19] or the rare-earth metals.[20-21] Aluminum catalysts were effective initiators in the preparation of PLA for their high Lewis acidity and low toxicity.[12, 22-25]

Symmetric salen Schiff base aluminum catalysts have achieved considerable progress in the synthesis of PLA polymers.[11, 26-29] As far as we know, researches on non-symmetrical salen Schiff base complex were still not fully exploited.[30] Recently, our research group reported two types of aluminum complexes: one derived from enolic ligands and another from symmetric salen Schiff base ligands.[31-33] Enolic ligands could be obtained from the reaction of β-diketone and diamine. Ideal Schiff base ligands and their aluminum complexes can be obtained through keto-enol tautomerism. These complexes proved to be highly effective single-site living initiators for the controlled ROP of lactones. Intrigued by the success of

these two types of aluminum complexes, it was believed that the combination of these two types of aluminum complexes would produce a new family of non-symmetrical complexes. These complexes are regarded as promising catalysts for the ROP of lactones. Herein we report a number of aluminum non-symmetrical salen complexes and the preliminary application on their use as catalysts for the ROP of lactides and ε-caprolactone.

2. Experimental

General

All experiments were carried out in a dry nitrogen atmosphere in a glovebox. Starting materials for the synthesis of ligands, rac-LA and ε-caprolactone were purchased from Aldrich Inc. Ethyl acetate and 2-propanol were distilled from CaH_2 under the protection of argon. rac-Lactide was purified by recrystallization from ethyl acetate and dried under vacuum at room temperature before use. NMR spectra were recorded on Bruker AV 400 M. Chemical shifts were given in parts per million from tetramethylsilane. Gel permeation chromatography (GPC) measurements were conducted with a Waters 515 GPC with $CHCl_3$ as the eluent (flow rate: 1 mL min^{-1} at 35 ^oC). The molecular weights were calibrated against polystyrene (PS) standards.

Synthesis of ligands L_1-L_5

Ligand family was prepared as shown in Scheme 1. A solution of 2,4-pentanedione (15 mmol) in dichloromethane (15 mL) was added to a solution of 1,2-diaminoethane (30 mmol) in dichloromethane (15 mL) slowly, and the solution was refluxed for 1 h. The excess 1,2-diaminoethane was removed under vacuum at 60 °C.[34] A solution of the residue in dichloromethane (20 mL) was added dropwise to a solution of

corresponding substituted salicylaldehyde (15 mmol) in ethanol (15 mL). The corresponding ligands were obtained after purification by flash column chromatography.

L_1: ^{1}H NMR (300MHz, $CDCl_3$): δ = 13.01(s ArO*H* 1H), 10.93(s CO*H* 1H), 8.36(s NC*H* 1H), 7.32(m Ar*H* 1H), 7.25(d *J*=5.0Hz Ar*H* 1H), 6.97(t *J*=7.3Hz Ar*H* 1H), 6.89(t *J*=7.5Hz Ar*H* 1H), 4.96(s C*H*COH 1H), 3.77(t *J*=5.8Hz NCH_2CH_2N 2H), 3.61(dd *J*=12.1,6.0Hz NCH_2CH_2N 2H), 1.99, 1.91(s NCCH_3, HOCCH_3 6H). ^{13}C NMR (100MHz, $CDCl_3$): δ = 195.34(*C*OH), 167.06(N*C*H), 162.29(CH_3*C*N), all benzene ring: 160.96, 132.57, 131.70, 118.81, 118.65, 117.03; 95.92(*C*HCOH), 55.24, 50.37(N*C*H_2*C*H_2N), 28.91 (HOC*C*H_3), 18.97(NC*C*H_3). Elem. Anal.: Calcd. C 68.27, H 7.37, N 11.37; Found C 68.26, H 7.37, N 11.35.

L_2: ^{1}H NMR (300MHz, $CDCl_3$): δ = 13.00(s ArO*H* 1H), 10.89(s CO*H* 1H), 8.29(s NC*H* 1H), 7.01, 6.89(s Ar*H* 2H), 4.94(s C*H*COH 1H), 3.73(t *J*=6.0Hz NCH_2CH_2N 2H), 3.58(dd *J*=12.2,6.1Hz NCH_2CH_2N 2H), 2.25(d *J*=5.3Hz ArCH_3 6H), 1.98, 1.90(s NCCH_3, HOCCH_3 6H). ^{13}C NMR (100MHz, $CDCl_3$): δ = 195.32(*C*OH), 167.29(N*C*H), 163.00(CH_3*C*N), all benzene ring: 157.04, 134.70, 129.36, 127.11, 125.68, 117.60; 95.93(*C*HCOH), 60.04, 43.66(N*C*H_2*C*H_2N), 28.94(HOC*C*H_3), 19.03(NC*C*H_3), 20.36, 15.48(Ar*C*H_3). Elem. Anal.: Calcd. C 70.04, H 8.08, N 10.21; Found C 70.06, H 8.10, N 10.22.

L_3: ^{1}H NMR (300MHz, $CDCl_3$): δ = 13.95(s ArO*H* 1H), 10.86(s CO*H* 1H), 8.27(s NC*H* 1H), 7.40(d *J*=2.4Hz Ar*H* 1H), 7.15(dd *J*=5.9,2.2Hz Ar*H* 1H), 4.95(s C*H*COH 1H), 3.78(t *J*=5.6Hz NCH_2CH_2N 2H), 3.62(dd *J*=11.7,5.8Hz NCH_2CH_2N 2H), 2.06, 2.01(s NCCH_3, HOCCH_3 6H). ^{13}C NMR (100MHz, $CDCl_3$):δ = 195.73(*C*OH), 165.73(N*C*H), 165.69(CH_3*C*N), all benzene ring: 162.88, 156.27, 132.55, 129.45, 123.11, 119.47; 96.28(*C*HCOH), 59.04, 43.26(N*C*H_2*C*H_2N), 28.98(HOC*C*H_3), 19.06(NC*C*H_3). Elem. Anal.: Calcd. C 53.35, H 5.12, N 8.89; Found C 53.32, H 5.09, N 8.90.

L_4: ^{1}H NMR (300MHz, $CDCl_3$): δ = 13.45(s ArO*H* 1H), 10.90(s CO*H* 1H), 8.35(s NC*H* 1H), 7.39(t *J*=5.6Hz Ar*H* 1H), 7.08(d *J*=2.4 Hz Ar*H* 1H), 4.95(s C*H*COH 1H),3.77(t *J*=6.1Hz NCH_2CH_2N 2H), 3.61(q *J*=6.1Hz NCH_2CH_2N 2H), 1.99, 1.92(s NCCH_3, HOCCH_3 6H), 1.43, 1.30(s C(CH_3)$_3$ 18H). ^{13}C NMR (100MHz, $CDCl_3$): δ = 195.34(*C*OH), 168.20(N*C*H), 163.16(CH_3*C*N), all benzene ring: 158.16, 140.54, 136.74, 127.37, 126.36, 117.83; 96.00(*C*HCOH), 60.06, 43.75(NCH_2*C*H_2N), 35.12, 34.24(Ar*C*(CH_3)$_3$), 31.60, 29.52(C(*C*H_3)$_3$), 28.96(HOC*C*H_3), 19.01(NC*C*H_3). Elem. Anal.: Calcd. C 73.70, H 9.56, N 7.81; Found C 73.72, H 9.54, N 7.79.

L_5: ^{1}H NMR (300MHz, $CDCl_3$): δ = 13.23(s ArO*H* 1H), 10.89(s CO*H* 1H), 8.32(s NC*H* 1H), 7.43(dd *J*=7.2,1.7Hz Ar*H* 1H), 7.23(d *J*=1.6Hz Ar*H* 1H), 6.87(t *J*=7.4Hz Ar*H* 1H), 4.93(s C*H*COH 1H), 3.75(t *J*=5.9Hz NCH_2CH_2N 2H), 3.62(dd *J*=12.3,6.1Hz NCH_2CH_2N 2H), 1.98, 1.89(s NCCH_3, HOCCH_3 6H), 0.91(s SiC(CH_3)$_3$ 9H), 0.33(s Si(CH_3)$_2$ 6H). ^{13}C NMR (100MHz, $CDCl_3$): δ = 195.37(*C*OH), 167.49(N*C*H), 165.99(CH_3*C*N), all benzene ring: 163.16, 139.72, 133.21, 125.07, 118.33, 117.70; 95.99(*C*HCOH), 60.17, 43.60(NCH_2*C*H_2N), 28.96(HOC*C*H_3), 27.17(SiC(*C*H_3)$_3$), 18.96(NC*C*H_3), 17.73(Si*C*(CH_3)$_3$), -4.68(Si(*C*H_3)$_2$). Elem. Anal.: Calcd. C 66.62, H 8.95, N 7.77; Found C 66.64, H 8.93, N 7.74.

Synthesis of complexes 1-5

$AlEt_3$ (0.1 mmol) in toluene (5 mL) was added to the stirred 1mL toluene solution of ligand L_1-L_5 (0.1 mmol) at RT. The reaction was maintained at 80 ºC for 16 h, and the reaction mixture was then slowly cooled to RT. The toluene was removed under vacuum (Scheme 1).

Complex 1: ^{1}H NMR (300MHz, $CDCl_3$): δ = 8.21(s NC*H* 1H), 7.35(m Ar*H* 1H), 7.20(d *J*=7.7Hz Ar*H* 1H), 7.08(d *J*=8.5Hz Ar*H* 1H), 6.72(t *J*=7.2Hz Ar*H* 1H), 5.10(s C*H*COAl 1H), 4.07(dd *J*=18.0,11.6Hz NCH_2CH_2N 1H), 3.66(dd *J*=13.1,6.2Hz, NCH_2CH_2N 1H), 3.56(dd *J*=12.0,5.7Hz NCH_2CH_2N 1H), 3.34(m

NCH_2CH_2N 1H), 2.08, 2.02(s NCCH_3, AlOCCH_3 6H), 0.86(t *J*=8.0Hz AlCH$_2$CH_3 3H), -0.30(m AlCH_2CH$_3$ 2H). ^{13}C NMR (100MHz, CDCl$_3$): δ = 181.48(*C*OAl), 174.63(N*C*H), 166.02(CH$_3$*C*N), all benzene ring: 165.60, 134.99, 132.51, 122.86, 119.17, 116.37; 99.57(*C*HCOAl), 54.07, 47.88(N*C*H$_2$*C*H$_2$N), 26.08(AlOC*C*H$_3$), 22.92(NC*C*H$_3$), 9.99(AlCH$_2$*C*H$_3$), 0.41(Al*C*H$_2$CH$_3$). Elem. Anal.: Calcd. C 63.99, H 7.05, N 9.33; Found C 64.03, H 7.04, N 9.35.

Complex 2: ^{1}H NMR (300MHz, CDCl$_3$): δ = 8.13(s NC*H* 1H), 7.11, 6.82(s Ar*H* 2H), 5.09(s C*H*COAl 1H), 4.06(m NCH_2CH_2N 4H), 3.63(dd *J*=14.0,5.7Hz NCH_2CH_2N 4H), 3.53(ddd *J* =12.2,6.0,1.8 Hz NCH_2CH_2N 4H), 3.31(m NCH_2CH_2N 4H), 2.30, 2.24(s ArCH_3 6H), 2.05, 2.01(s NCCH_3, AlOCCH_3 6H), 0.86(t *J*=8.1Hz AlCH$_2$CH_3 3H), -0.30(m AlCH_2CH$_3$ 2H). ^{13}C NMR (100MHz, CDCl$_3$): δ = 181.28(*C*OAl), 174.15(N*C*H), 165.44(CH$_3$*C*N), all benzene ring: 162.69, 136.73, 130.37, 129.40, 124.30, 117.78; 99.19(*C*HCOAl), 53.83, 47.71(N*C*H$_2$*C*H$_2$N), 25.83(AlOC*C*H$_3$), 22.66(NC*C*H$_3$), 20.23, 16.28(Ar*C*H$_3$), 10.00(AlCH$_2$*C*H$_3$), 0.35(Al*C*H$_2$CH$_3$). Elem. Anal.: Calcd. C 65.84, H 7.67, N 8.53; Found C 65.81, H 7.71, N 8.50.

Complex 3: ^{1}H NMR (300MHz, CDCl$_3$): δ = 8.16(s NC*H* 1H), 7.46(m Ar*H* 1H), 7.20(dd *J*=17.6,4.8Hz Ar*H* 1H), 5.11(s C*H*COAl 1H), 4.07(m NCH_2CH_2N 1H), 3.70(d *J*=7.3Hz NCH_2CH_2N 1H), 3.65(d *J*=7.9Hz NCH_2CH_2N 1H), 3.40(m NCH_2CH_2N 1H), 1.98, 1.89(s NCCH_3, AlOCCH_3 6H), 0.80(m AlCH$_2$CH_3 3H), -0.34(m AlCH_2CH$_3$ 2H). ^{13}C NMR (100MHz, CDCl$_3$): δ = 182.00(*C*OAl), 175.99(N*C*H), 171.63(CH$_3$*C*N), all benzene ring: 164.05, 136.66, 134.00, 131.92, 129.66, 119.82; 99.59(*C*HCOAl), 54.13, 47.39(N*C*H$_2$*C*H$_2$N), 25.90(AlOC*C*H$_3$), 22.83(NC*C*H$_3$), 9.78(AlCH$_2$*C*H$_3$), 0.54(Al*C*H$_2$CH$_3$). Elem. Anal.: Calcd. C 52.05, H 5.19, N 7.59; Found C 52.07, H 5.21, N 7.58.

Complex 4: ^{1}H NMR (300MHz, CDCl$_3$): δ = 8.18(s NC*H* 1H), 7.47(d *J*=2.5Hz Ar*H* 1H), 7.00(d *J*=2.5Hz Ar*H* 1H), 5.06(s C*H*COAl 1H), 4.10(m NCH_2CH_2N 1H), 3.65(dd *J*=13.2,6.8Hz NCH_2CH_2N 1H), 3.50(dd

J=12.1,6.4Hz NCH_2CH_2N 1H), 3.34(m NCH_2CH_2N 1H), 2.00, 1.99(s NCCH_3, AlOCCH_3 6H), 1.49, 1.32(s C(CH_3)$_3$ 9H), 0.88(t *J*=8.1Hz AlCH$_2$CH_3 3H), -0.29(q *J*=7.8Hz AlCH_2CH$_3$ 2H). ^{13}C NMR (100MHz, $CDCl_3$): δ = 181.54(*C*OAl), 174.11(N*C*H), 166.01(CH$_3$*C*N), all benzene ring: 163.31, 140.98, 137.32, 129.74, 126.37, 118.15; 98.77(*C*HCOAl), 57.31, 47.82(N*C*H$_2$*C*H$_2$N), 35.40, 34.09(Ar*C*(CH$_3$)$_3$), 31.59, 29.41(C(*C*H$_3$)$_3$), 25.78(AlOC*C*H$_3$), 22.62(NC*C*H$_3$), 10.21(AlCH$_2$*C*H$_3$), 0.51(Al*C*H$_2$CH$_3$). Elem. Anal.: Calcd. C 69.87, H 9.04, N 6.79; Found C 69.85, H 9.05, N 6.82.

Complex 5: ^{1}H NMR (300MHz, $CDCl_3$): δ = 8.15(s NC*H* 1H), 7.49(d *J*=7.0Hz Ar*H* 1H), 7.17(m Ar*H* 1H), 6.71(t *J*=7.3Hz Ar*H* 1H), 5.05(s C*H*COAl 1H), 4.08(dd *J*=18.3,11.6Hz NCH_2CH_2N 1H), 3.60(dd *J*=13.2,6.7Hz, NCH_2CH_2N 1H), 3.49(dd *J*=11.9,6.3Hz NCH_2CH_2N 1H), 3.33(m NCH_2CH_2N 1H), 2.00(s NCCH_3, AlOCCH_3 6H), 0.96(s SiC(CH_3)$_3$ 9H), 0.83(t *J*=8.0Hz AlCH$_2$CH_3 3H), 0.36(s Si(CH_3)$_2$ 6H), -0.35(q *J*=7.6Hz AlCH_2CH$_3$ 2H). ^{13}C NMR (100MHz, $CDCl_3$): δ = 181.75(*C*OAl), 174.36(N*C*H), 171.12(CH$_3$*C*N), all benzene ring: 165.36, 142.59, 133.91, 130.38, 118.23, 115.81; 98.76(*C*HCOAl), 53.79, 47.78(N*C*H$_2$*C*H$_2$N), 27.62(SiC(*C*H$_3$)$_3$), 25.58(AlOC*C*H$_3$), 22.79(NC*C*H$_3$), 17.91(Si*C*(CH$_3$)$_3$), 10.21(AlCH$_2$*C*H$_3$), 0.21(Al*C*H$_2$CH$_3$), -4.61(Si(*C*H$_3$)$_2$). Elem. Anal.: Calcd. C 63.73, H 8.51, N 6.76; Found C 63.77, H 8.48, N 6.74.

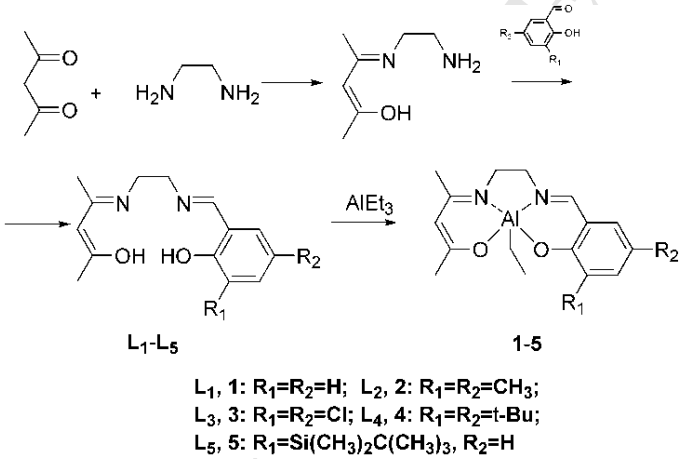
Polymerization procedure

In a typical polymerization experiment, complexes 1–5 (10 mmol), the required amount of LA or CL in toluene were loaded in a flame-dried vessel containing a magnetic bar. The vessel was placed in a thermostated oil bath. Conversion of the monomer was determined on the basis of ^{1}H NMR spectroscopic studies. After a certain reaction time, the polymer was isolated by precipitation with cold methanol. The precipitate was collected and dried under vacuum at RT for 36 h.

3. Result and discussion

Synthesis of ligands and aluminum complexes

The synthetic pathway of non-symmetrical ligands and aluminum complexes family was described in Scheme 1. All ligands and complexes were characterized by ^{1}H, ^{13}C NMR spectroscopy and elemental analysis. The ligand precursors $\mathbf{L_1}$-$\mathbf{L_5}$ were obtained by the condensation reaction between acetylacetone, 1,2-diaminoethane and the corresponding substituted salicylaldehyde.[34] The analytical results were in accord with their respective formulas. For example, ^{1}H NMR spectrum of $\mathbf{L_1}$ showed signals at about δ 8.36 and 4.96 ppm, which were attributed to the N=C*H* proton from salicylaldehyde part and C*H*COH proton from acetylacetone part, respectively. The intensity ratio of the signals at 8.36 and 4.96 ppm was 1:1. This was consistent with the structure of ligand $\mathbf{L_1}$. Complexes **1**-**5** were obtained via the reaction of ligands $\mathbf{L_1}$-$\mathbf{L_5}$ with $AlEt_3$ under nitrogen atmosphere . The ^{1}H NMR spectra of complex **1** showed signals at about δ 0.86 and –0.30 ppm, which were attributed to the methyl protons and methylene protons of the aluminum ethyl group, respectively. The N=C*H* proton displayed signal at 8.21 ppm. The intensity ratio of the three signals at 0.86, –0.30 and 8.21 ppm was 3:2:1, which confirmed the structure of complex **1**.



Scheme 1 Synthetic pathway for the preparation of ligands and complexes.

Ring-opening polymerization of L-LA and rac-LA

Complexes **1**-**5** were investigated as catalysts for the ROP of L-LA and *rac*-LA in the presence of 2-propanol.

The representational polymerization data were listed in Table 1 and Table 2. Molecular weight of the PLA was determined by ^{1}H NMR spectroscopy and gel permeation chromatography (GPC).

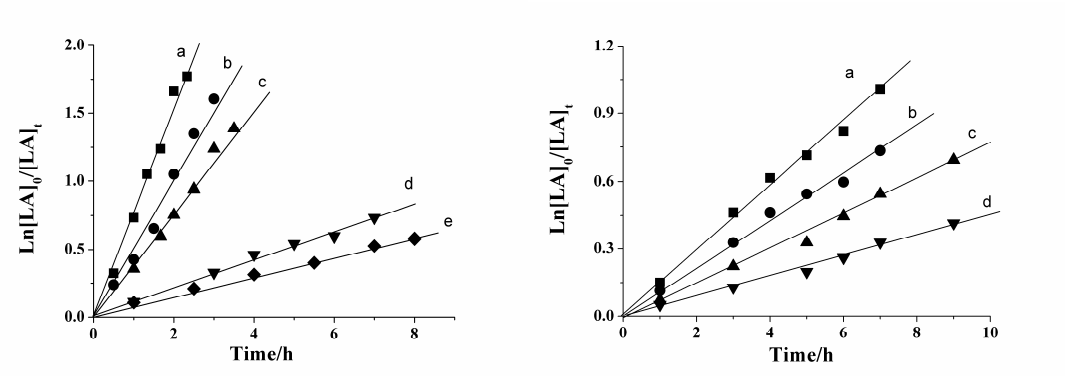


Fig. 1 Kinetic plots of the L-LA conversion vs. the reaction time. Left: $[M]_0/[cat]=60$, (a) complex **3**; (b) complex **1**; (c) complex **2**; (d) complex **4**; (e) complex **5**. Right: (a) $[M]_0/[cat]=40$; (b) [M]0/[cat]=60; (c) [M]0/[cat]=80; (d) $[M]_0/[cat]=120$ by using complex **4**.

Kinetic studies of L-LA polymerization

Polymerization of L-LA was investigated in detail. Polymerization data indicated that the number-averaged molecular weights $M_{n(GPC)}$ of PLA were close to theoretical ones ($M_{n(calcd)}$ calculated from the monomer-to-catalyst molar ratio). The polydispersity index (PDI) of PLAs ranged from 1.1 to 1.2. Plots of L-LA monomer conversions versus reaction time with complexes **1**-**5** were showed in Figure 1. For all the five complexes, L-LA monomer conversions increased linearly with reaction time (Figure 1, left). Obviously the activity of **1**-**5** was remarkably influenced by the substituent groups on the salicylaldehyde. Complex **3** (with chloride substituent) showed the highest conversion under the same reaction condition. The activities of these complexes reduced accompanied with the raise of substituent's bulk on the phenyl parts, k_p values were 1.26 $Lmol^{-1}min^{-1}$ for **1**, 0.86 $Lmol^{-1}min^{-1}$ for **2**, 0.20 $Lmol^{-1}min^{-1}$ for **4** and 0.12 $Lmol^{-1}min^{-1}$ for **5** (Table 1, entry 1,

2, 7 and 12). k_p value for complex **1** (R_1=H) was more than 10 times higher than that of complex **5** (R_1=$Si(CH_3)_2C(CH_3)_3$, TBDMS). While electron-withdrawing substituents increased polymerization rate as k_p value was 1.68 $Lmol^{-1}min^{-1}$ for **3** (Table 1, entry 3). Similar situations also appeared in our previous reports as for the symmetric salen Schiff base aluminum catalysts system.[26,28] The more bulky substituents with more steric hindrance may keep active species from being approached by lactide monomer, as a result, slowing down the polymerization rate. While Lewis acidity as well as electrophilicities of metal centers was enhanced by the electron-withdrawing substituents of chlorine, so LA monomer was easy to nucleophilic addition, as a result, increase the polymerization rate.[13] At certain reaction time, took complex **4** as example, the reaction with lower monomer/catalyst ratio showed higher monomer conversion (Figure 1, right). This was consistent with our previous reports of enolic and/or symmetric salen Schiff base complexes.[26,28,32] First-order kinetics in monomer was observed [equation (1)], and k_{app} was the apparent polymerization rate constant.

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

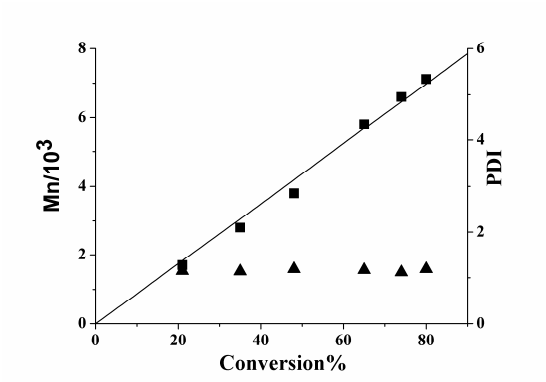


Fig. 2 Plot of PLA Mn (■) and polydispersity (▲) as a function of L-LA conversion using complex **1**, $[M]_0/[cat]=60$.

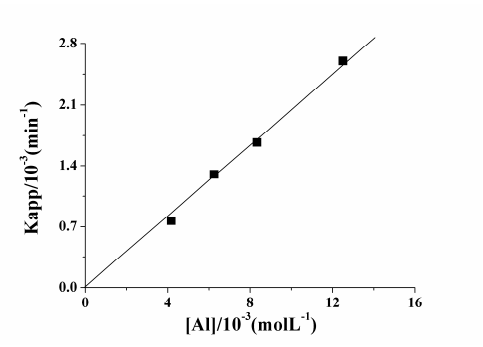


Fig. 3 k_{app} vs. the concentration of complex **4** for the L-LA polymerization.

Linear relationship between number-average molecular weight (M_n) and monomer conversion was observed (Figure 2). k_{app} was plotted versus the concentration of **4** to determine the order in catalyst (Figure 3). From this plot, k_{app} increased linearly with complex **4** concentrations, manifesting that the order in **4** was first-order too. Therefore, the polymerization of L-LA using **4** followed an overall kinetic equation of the form as equation (2), k_p was the polymerization rate constants, $k_p = k_{app}/[\mathbf{4}]$.

$$-d[LA]/dt = k_p[LA][\mathbf{4}] \qquad \text{equation (2)}$$

Table 1 Polymerization data of L-LA with complexes **1-5**.[a]

Entry	Complex	Temp (°C)	*t* (h)	$[M]_0/[Cat]$	Conv[b] (%)	$M_{n(calcd)}$[c]$\times10^{-3}$	$M_{n\,(NMR)}$[d] $\times10^{-3}$	M_n[e]$\times10^{-3}$	PDI[e]
1	**1**	90	6	60	95	8.3	8.1	8.5	1.18
2	**2**	90	7	60	90	7.8	7.5	8.0	1.14
3	**3**	90	4	60	94	8.2	7.9	8.7	1.17
4	**4**	70	24	40	82	4.8	4.5	4.3	1.11
5	**4**	80	16	40	85	5.0	4.7	5.2	1.14
6	**4**	90	17	40	91	5.3	5.6	5.8	1.19
7	**4**	90	20	60	87	7.6	8.0	7.8	1.17
8	**4**	90	30	80	90	10.4	10.9	10.6	1.15
9	**4**	90	42	120	85	14.8	15.1	14.1	1.19
10	**4**	100	8	40	90	5.2	5.7	5.4	1.21
11	**4**	110	6	40	93	5.4	5.8	6.2	1.24
12	**5**	90	25	60	86	7.5	7.4	7.9	1.10

[a] All polymerizations were carried out in toluene solution, $[LA]_0 = 0.5$ mol L^{-1}. [b] Measured by ^{1}HNMR. [c] Calculated from the molecular weight of LA × $[M]_0/[Cat]$ × conversion + Mw(iPrOH). [d] Obtained from ^{1}H NMR analysis. [e] The values of M_n were calculated according to formula $M_n = 0.58Mn_{GPC}$[35].

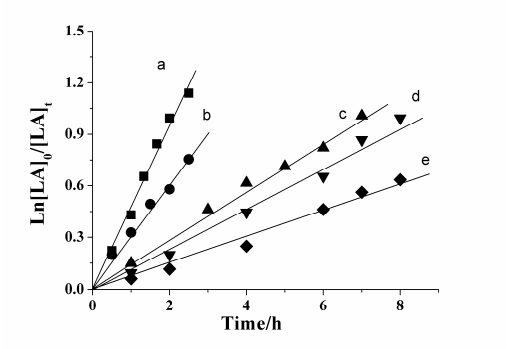


Fig. 4 Kinetics of the L-LA polymerization using complex **4** at the reaction temperatures of (a) 110 °C; (b) 100°C; (c) 90°C; (d) 80 °C; (e) 70 °C, $[M]_0/[Cat]=40$.

Investigation of the influence of temperature on the polymerization of LA monomer was proceeded (Figure 4). Decrease the temperature from 90°C to 80°C would result in a decrease in k_p value from 0.22 $Lmol^{-1}min^{-1}$ to 0.16 $Lmol^{-1}min^{-1}$, further decrease to 70°C led to a reduction in k_p to 0.11 $Lmol^{-1}min^{-1}$, a 50% reduction. At the same time, an increase in the temperature to 110°C led to a 191% increase in k_p value (from 0.22 $Lmol^{-1}min^{-1}$ to 0.64 $Lmol^{-1}min^{-1}$) using complex **4**.

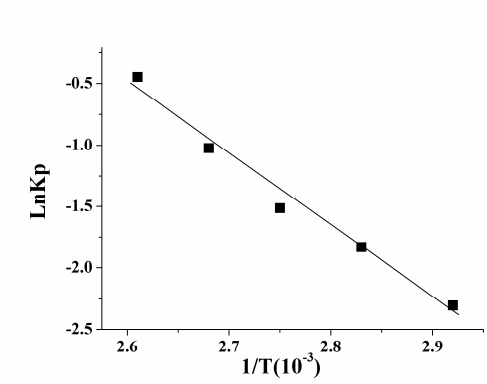


Fig. 5 Plot of Lnk_p vs 1/T for the polymerization of L-LA with complex **4**.

The activation energy of the polymerization was calculated by fitting k_p values determined at different temperatures to the Arrhenius equation ($k_p=Ae^{-Ea/RT}$), an activation energy Ea of 48.5 $kJmol^{-1}$ was deduced by plotting lnk_p versus 1/T (Figure 5).

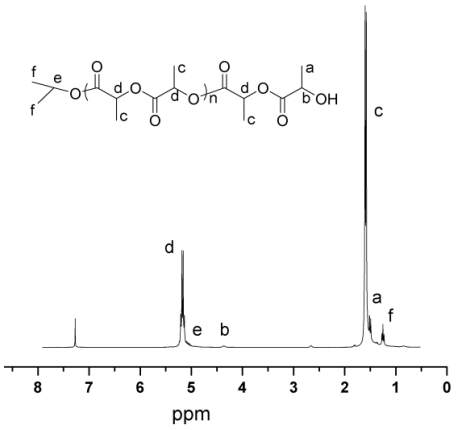


Fig. 6 ^{1}H NMR spectrum of oligomer of L-LA.

In order to explore the mechanism of initiation, ^{1}H NMR spectrum of PLA oligomers was investigated. A triplet of two overlapping doublets at 1.24 ppm and a quartet at 4.34 ppm with an integral ratio close to 6:1 (Figure 6) were assigned to the methyl protons of the isopropoxycarbonyl and the methine proton neighboring the hydroxyl end groups, respectively. This clearly indicated that the polymer was capped with one isopropyl ester group and one hydroxyl group.[11,33,35] The actual initiator was the aluminium alkoxide propagating species. The ROP selected a coordination insertion mechanism (Scheme 2).[24,36-37]

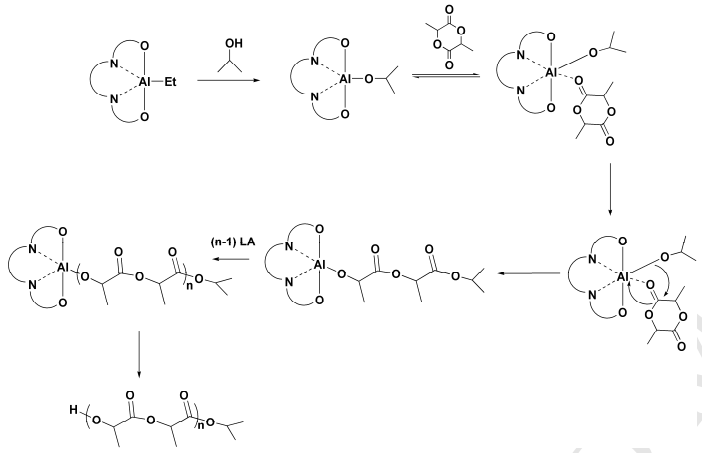
Stereoselective polymerization of *rac*-LA

To test the stereo-controllability of complexes **1**-**5**, the ring opening polymerizations of *rac*-LA by **1**-**5** were also studied. The stereochemical microstructures of the poly(*rac*-LA) were determined from the methine fragment of the homonuclear decoupled ^{1}H NMR spectra by **1-5** (Figure 7). Similar activity trends were found as in L-LA polymerization (Figure 8).

Table 2 Polymerization data of *rac*-LA with complexes **1-5**.[a]

Entry	Complex	*t* (h)	$[M]_0/[Cat]$	Conv[b] (%)	$M_{n(calcd)}$[c]×10^{-3}	$M_{n\ (NMR)}$[d] ×10^{-3}	M_n[e]×10^{-3}	PDI[e]	P_m
1	**1**	4.5	60	90	7.8	7.6	8.1	1.16	047
2	**2**	8	60	96	8.4	8.7	8.2	1.15	0.50
3	**3**	4	60	95	8.3	8.8	8.4	1.19	0.43
4	**4**	18	40	92	5.4	6.0	5.8	1.19	0.64
5	**4**	20	60	85	7.4	8.0	7.7	1.20	0.65
6	**4**[f]	36	40	93	5.4	5.7	5.9	1.12	0.68
7	**4**	24	80	83	9.6	10.7	9.9	1.15	0.63
8	**4**	36	120	80	13.9	14.2	14.4	1.17	0.64
9	**5**	24	60	83	7.2	7.0	7.5	1.12	0.67

[a] All polymerizations were carried out in toluene solution at 90 °C, $[LA]_0 = 0.5$ mol L^{-1}. [b] Measured by ^{1}HNMR. [c] Calculated from the molecular weight of LA × $[M]_0/[Cat]$ × conversion + Mw(iPrOH). [d] Obtained from ^{1}H NMR analysis. [e] The values of M_n were calculated according to formula $M_n = 0.58Mn_{GPC}$[35]. [f] Reaction temperature 70 °C.



Scheme 2 Proposed mechanism for the polymerization of LA.

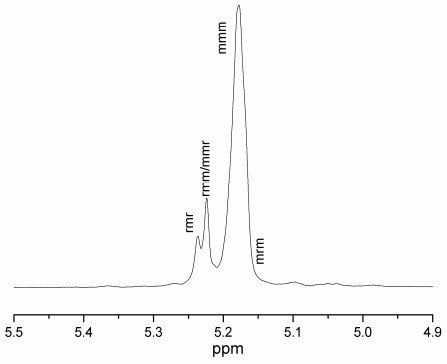


Fig. 7 Homonuclear decoupled ^{1}H NMR spectrum of the methane part of poly(*rac*-LA) using complex **5.**

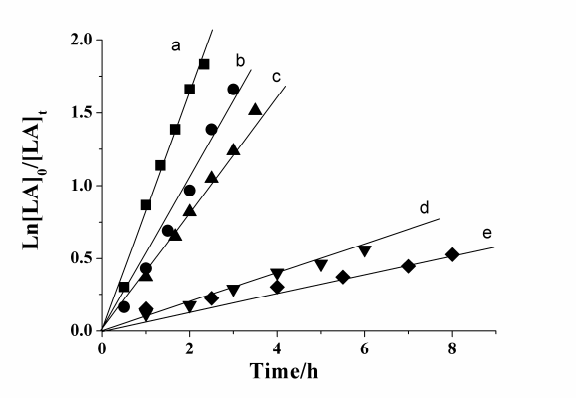


Fig. 8 Kinetic plots of the *rac*-LA conversion vs. the reaction time, $[M]_0/[cat]=60$. (a) complex **3**; (b) complex **1**; (c) complex **2**; (d) complex **4**; (e) complex **5**.

Parameter P_m was used to describe the controllability.[37] The substituent groups on the salicylaldehyde showed remarkable influence. Complexes with small steric hindrance showed no stereoselectivity (complexes **1** and **2** had Pm values of 0.47 and 0.50). Complex **5** had the highest stereoselectivity among the five complexes (Table 2, entry 1, 2, 3, 5 and 9). The enhancement of stereoselectivity was attributed to the bulky substituents of the salicylaldehydes of ligand.[24] Lowered the temperature from 90 °C to 70 °C, the P_m value raised, i.e., from 0.65 to 0.68 for complex **4** (Table 2, entry 5, 6).

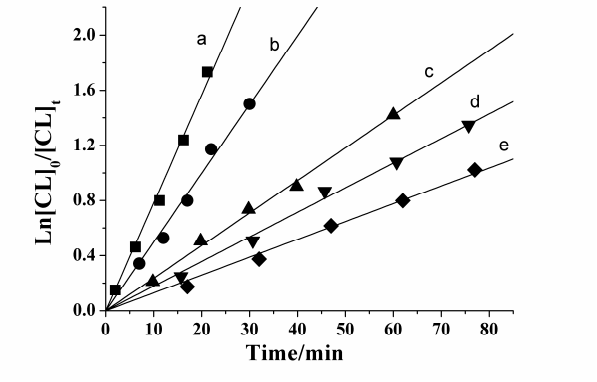


Fig. 9 Kinetic plots of the ε-CL conversion vs. the reaction time $[M]_0/[cat]=100$. (a) complex **3**; (b) complex **1**;

(c) complex **2**; (d) complex **4**; (e) complex **5**.

Table 3 Polymerization data of ε-CL with complexes **1**-**5**.[a]

Entry	Complex	t (min)	$[M]_0/[Cat]$	Conv[b] (%)	$M_{n(calcd)}$[c]$\times10^{-3}$	$M_{n\,(NMR)}$[d] $\times10^{-3}$	M_n[e]$\times10^{-3}$	PDI[e]	k_p/Lmol^{-1}min^{-1}
1	**1**	55	100	93	10.7	10.9	11.0	1.41	10.40
2	**2**	100	100	90	10.0	9.7	10.2	1.42	4.81
3	**3**	40	100	95	10.9	11.3	11.4	1.54	16.01
4	**4**	55	50	80	4.6	5.1	4.9	1.48	3.42
5	**4**	150	100	90	10.3	9.8	10.6	1.50	3.38
6	**4**	170	150	91	15.6	16.7	16.2	1.51	3.34
7	**4**	200	200	80	18.3	19.4	19.3	1.57	3.39
8	**5**	155	100	85	9.8	10.8	10.5	1.40	1.44

[a] All polymerizations were carried out in toluene solution at 60 °C, $[CL]_0 = 0.5$ mol L^{-1}. [b] Measured by ^{1}HNMR. [c] Calculated from the molecular weight of CL × $[M]_0/[Cat]$ × conversion + Mw(iPrOH). [d] Obtained from ^{1}H NMR analysis. [e] The values of M_n were calculated according to formula $M_n = 0.56Mn_{GPC}$[39].

Recently, our research lab has successfully developed some enolic Schiff base aluminum complexes; they were used as catalysts to prepare isotactic enriched PLA from rac-LA.[32] In comparison, complexes **1**-**5** in this work had effectively one half of the enolic complexes structurally, and this would offer the opportunity for the comparison of the two types of complexes, as we only need to compare another half part from salen Schiff base. Comparing with our previous result of enolic Schiff base complex 1a (see reference 32, with symmetrical enolic ligand surrounding), complexes**1** and **2** had lower P_m. This may indicate that the steric hindrance of the corresponding half Schiff base with H or CH_3 substituent group was small. This was also consistent with the activity data shown in Table 2 that a less bulky structure due to smaller substitutent led to complex having higher catalytic activity. Considering the large steric hindrance, it was not surprise that complex **5** with TBDMS substituent group showed higher P_m and lower k_p comparing with 1a in reference 32. It is worth noting that complex **4** and 1a had similar P_m and k_p, this might suggest their similar ligand surroundings. The reason for these phenomena is still not very clear and is under investigation.

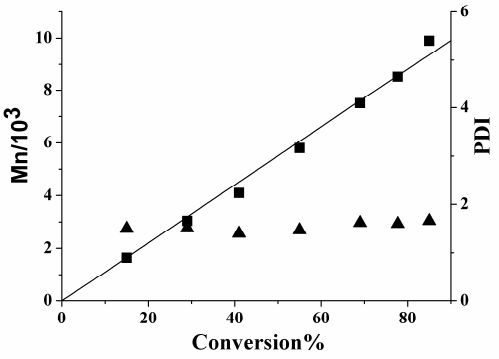


Fig. 10 Plot of PCL Mn (■) and polydispersity (▲) as a function of ε-CL conversion using complex **1**, $[M]_0/[cat]=100$.

Ring-opening polymerization of ε-CL

Complexes **1**-**5** can also efficiently control the ring-opening polymerization of ε-caprolactone. Polymerization was systematically examined and the data were collected in Table 3. Kinetic studies were explored to further understand the nature of ε-CL polymerization process. As for the ε-CL monomer, first-order kinetics was proofed by the good linear relationship of the $\ln([\varepsilon\text{-CL}]_0/[\varepsilon\text{-CL}])$ *vs.* reaction time (Figure 9).

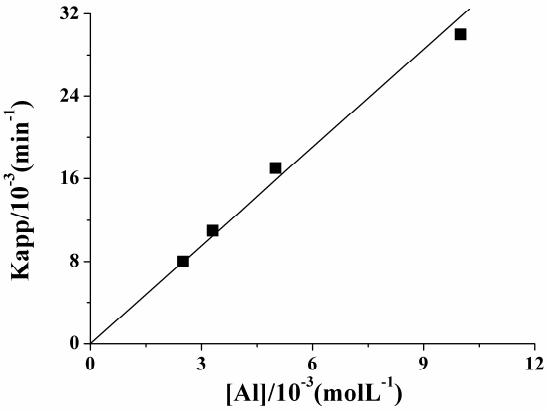


Fig. 11 k_{app} vs. the concentration of complex **4** for the ε-CL polymerization.

Similar conclusions were found as in L-LA and rac-LA polymerization: the activity of complex decreased with the increase of substituents' bulk on salicylaldehyde (Table 3, entry 1, 2, 3, 5 and 8). Complex **1** (with less bulky group, H) had its k_p value more than 3 times greater than complex **4** (with bulky group, ^{t}Bu), i.e., 10.40 $Lmol^{-1}min^{-1}$ vs. 3.41 $Lmol^{-1}min^{-1}$; and even more than 7 times greater than complex **5** (with more bulky group, TBDMS), i.e., 10.40 $Lmol^{-1}min^{-1}$ vs. 1.44 $Lmol^{-1}min^{-1}$. Electron-withdrawing substituents on salicylaldehyde as complex **3** increased polymerization rate remarkable (k_p value 16.0 $Lmol^{-1}min^{-1}$). This principle was also consistent with previous reports about symmetric salen Schiff base aluminum catalysts.[24] The number-average molecular weight (M_n) increased linearly along with the ε-CL monomer conversion (Figure 10). Complexes **1**-**5** showed lower control efficiency in the polymerization of ε-CL as slightly wide polydispersity of PCL than that of PLAs. This may suggest that ε-CL was less sterically demanding monomer when comparing with LA monomer. [40] To determine the order in catalyst, k_{app} was plotted against $[catalyst]_0$ (Figure 11). In this plot, k_{app} increased linearly with the catalyst concentration, indicating a first order in catalyst.

4. Conclusion

In conclusion, a series of non-symmetrical aluminium salen complexes **1**-**5** with half enolic and half salen Schiff base structure were prepared. These complexes were active on the polymerization of cycle ester. Kinetic study disclosed that **1**-**5** showed differentiation upon LA and ε-CL polymerization due to the different substituents on salicylaldehyde part. Larger substituents with more steric hindrance had relatively lower activity. The electron-withdrawing substituents enhanced the Lewis acidity, therefore increased the polymerization rate of LA and ε-CL. Complexes **4** and **5** even showed moderate selectivity to rac-lactide to give isotactic enriched polylactide. All the polymerizations of LA and ε-CL proceeded with first-order rate dependence on both

monomer and catalyst concentrations.

Acknowledgement

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38. P_m is the probability of meso linkages, according to $[mmm]=P_m^2+(1-P_m)P_m/2$, $[mmr]=[rmm]=(1-P_m)P_m/2$, $[rmr]=(1-P_m)^2/2$, $[mrm]=[(1-P_m)^2+P_m(1-P_m)]/2$.

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Highlights

- A number of Non-Symmetrical Aluminium Salen complexes were synthesized.
- These complexes were active in lactide and caprolactone polymerization.
- First-ordered kinetics with respect to lactide and caprolactone were observed.