Polymer 77 (2015) 122–128

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Non-symmetrical aluminium salen complexes: Synthesis and their reactivity with cyclic ester

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ARTICLE INFO

Article history:
Received 7 July 2015
Received in revised form
7 September 2015
Accepted 15 September 2015
Available online 16 September 2015

Keywords:
Half-salen
Ring-opening polymerization
Lactide

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.

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.

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http://dx.doi.org/10.1016/j.polymer.2015.09.036
0032-3861/

2. Experimental

2.1. 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 °C). The molecular weights were calibrated against polystyrene (PS) standards.

2.2. 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 (300 MHz, $CDCl_3$): 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 *CH*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 (100 MHz, $CDCl_3$): δ = 195.34(*C*OH), 167.06(NCH), 162.29(CH_3CN), all benzene ring: 160.96, 132.57, 131.70, 118.81, 118.65, 117.03; 95.92(*C*HCOH), 55.24, 50.37(NCH_2CH_2N), 28.91 ($HOCCH_3$), 18.97($NCCH_3$). 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 (300 MHz, $CDCl_3$): 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 *CH*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 (100 MHz, $CDCl_3$): δ = 195.32(*C*OH), 167.29(NCH), 163.00(CH_3CN), all benzene ring: 157.04, 134.70, 129.36, 127.11, 125.68, 117.60; 95.93(*C*HCOH), 60.04, 43.66(NCH_2CH_2N), 28.94($HOCCH_3$), 19.03($NCCH_3$), 20.36, 15.48(ArCH_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 (300 MHz, $CDCl_3$): 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 *CH*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 (100 MHz, $CDCl_3$):δ = 195.73(*C*OH), 165.73(NCH), 165.69(CH_3CN), all benzene ring: 162.88, 156.27, 132.55, 129.45, 123.11, 119.47; 96.28(*C*HCOH), 59.04, 43.26(NCH_2CH_2N), 28.98($HOCCH_3$), 19.06($NCCH_3$). 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 (300 MHz, $CDCl_3$): 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 *CH*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 (100 MHz, $CDCl_3$): δ = 195.34(*C*OH), 168.20(NCH), 163.16(CH_3CN), all benzene ring: 158.16, 140.54, 136.74, 127.37, 126.36, 117.83; 96.00(*C*HCOH), 60.06, 43.75(NCH_2CH_2N), 35.12, 34.24(Ar*C*(CH_3)$_3$), 31.60, 29.52(C(CH_3)$_3$), 28.96($HOCCH_3$), 19.01($NCCH_3$). 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 (300 MHz, $CDCl_3$): 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 *CH*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 (100 MHz, $CDCl_3$): δ = 195.37(*C*OH), 167.49(NCH), 165.99(CH_3CN), all benzene ring: 163.16, 139.72, 133.21, 125.07, 118.33, 117.70; 95.99(*C*HCOH), 60.17, 43.60(NCH_2CH_2N), 28.96($HOCCH_3$), 27.17(SiC(CH_3)$_3$), 18.96($NCCH_3$), 17.73(Si*C*(CH_3)$_3$), −4.68(Si(CH_3)$_2$). Elem. Anal.: Calcd. C 66.62, H 8.95, N 7.77; Found C 66.64, H 8.93, N 7.74.

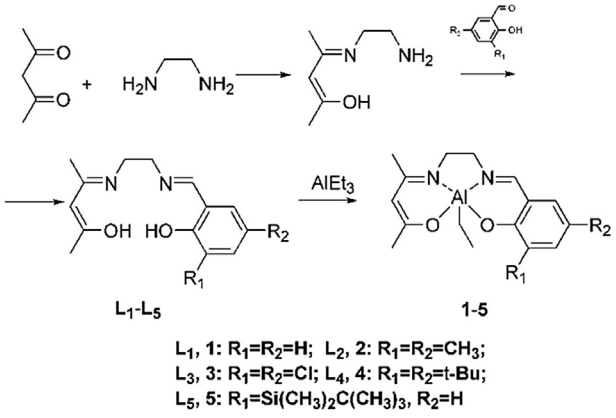
2.3. Synthesis of complexes ***1*–*5***

$AlEt_3$ (0.1 mmol) in toluene (5 mL) was added to the stirred 1 mL toluene solution of ligand L_1-L_5 (0.1 mmol) at RT. The reaction was maintained at 80 °C 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 (300 MHz, $CDCl_3$): 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 *CH*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 $AlCH_2CH_3$ 3H), −0.30(m $AlCH_2CH_3$ 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 181.48(*C*OAl), 174.63(NCH), 166.02(CH_3CN), all benzene ring: 165.60, 134.99, 132.51, 122.86, 119.17, 116.37; 99.57(*C*HCOAl), 54.07, 47.88(NCH_2CH_2N), 26.08($AlOCCH_3$), 22.92($NCCH_3$), 9.99($AlCH_2CH_3$), 0.41($AlCH_2CH_3$). 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 (300 MHz, $CDCl_3$): δ = 8.13(s NC*H* 1H), 7.11, 6.82(s Ar*H* 2H), 5.09(s *CH*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 $AlCH_2CH_3$ 3H), −0.30(m $AlCH_2CH_3$ 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 181.28(*C*OAl), 174.15(NCH), 165.44(CH_3CN), all benzene ring: 162.69, 136.73, 130.37, 129.40, 124.30, 117.78; 99.19(*C*HCOAl), 53.83, 47.71(NCH_2CH_2N), 25.83($AlOCCH_3$), 22.66($NCCH_3$), 20.23, 16.28(ArCH_3), 10.00($AlCH_2CH_3$), 0.35($AlCH_2CH_3$). 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 (300 MHz, $CDCl_3$): 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 *CH*COAl 1H), 4.07(m NCH_2CH_2N 1H), 3.70(d *J* = 7.3Hz NCH_2CH_2N 1H), 3.65(d



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