Syntheses of Biodegradable Polylactides Catalyzed by Aluminum Complexes bearing Phenanthrene Derivatives for Polymerization of Lactides

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Abstract. A methylaluminum Schiff base compound 1 bearing phenanthrene derivatives was made and used in the ROP of LA. Compound 1 was characterized by NMR and elemental analysis. Compound 1 with isopropyl alcohol exhibited good activity towards the polymerization experiment of LA. The ROP is in a coordination-insertion mechanism.

1. Introduction
Polylactic acid (PLA) is the most widely studied biodegradable material.[1] Recently, the usage of bio-degradable polymer material has been very rapid, and it has been widely used in the fields of agriculture, packaging materials, clothing fiber and biomedicine. Schiff base is mainly refers to a class of organic compounds in a characteristic of the imine or methylene amine (- RC = N -). Schiff’s base as the ligand has good coordination ability and strong flexibility with good application prospect in complex biochemistry, chemistry and other fields. Schiff base metal complexes have attracted much attention because of their novel properties. In recent years, the main research objective of Schiff base complexes is to synthesize some Schiff base complexes with high activity and physiological function.[2] However, for all we know, few research on aluminum compound supported via Schiff base originating from phenanthrene (Scheme 1) has been studied towards the ROP of LA. For the high-performance of aluminum compounds, [3-5] we believed that aluminum Schiff base complexes derived from phenanthrene derivatives maybe become potential initiators towards the ROP of LA. Here, the preparation of aluminum complexes containing phenanthrene derivatives and the preliminary results of LA polymerization as initiator were reported.

2. Experimental
2.1. Materials
Toluene was dried by sodium. CDCl₃ was distilled over calcium hydride. Lactide was recrystallized from dry ethyl acetate. AlMe₃, 9,10-phenanthrenequinone, isopropanol, 2,6-dimethylaniline had been purchased from Aldrich.
2.2. Instruments and Characterizations
All operations involved air-sensitive compounds had been performed by anaerobic and water-repellent technology. $^1$H NMR was operated on Bruker AV 500M apparatus in deuterated chloroform for compounds. The monomer conversion was tested according to the reference.[6] Gel permeation chromatography (GPC) was applied to characterize molecular weight (THF as eluent, flow rate: 1.000 mL.min$^{-1}$).

2.3. Preparation of pro-ligand a
A solution of 9,10-phenanthrenquinone (2.08 g, 0.010 mol), 2,6-dimethylaniline (2.16 g, 0.016 mol), methanol (100.0 mL) and acetic acid (16.0 mL) had been refluxed ca. 1 day. The solution was cooled down, volatiles were removed, and the residual was depurated via column chromatography to get deep green solid (yield: 2.2g, 71%).

2.4. Synthesis of complexes 1
Pro-ligand a (0.311 g, 1.0 mmol), methylaluminium toluene solution (1.00 mL, 1.0 mol/mL) and toluene (10 mL) were placed in an ampoule. The mixture reacted for 1 day at 80 °C. In glovebox, the filtrate was filtered, and the volatiles were excepted by cold trap to get white matter. The impurity was removed by leaching with hexane (2.0 mL), 0.628 g product was received, yield: 82.0%. $^1$H NMR (500 MHz, CDCl$_3$) : δ 7.95 (dd, 1H), 7.84 (d, 1H), 7.69 (dq, 1H), 7.55 (t, 1H), 7.45 (dd, 2H), 7.19 (s, 1H), 7.12 (t, 1H), 7.05 (t, 1H), 6.88 (d, 1H), 6.65 (d, 1H), 2.44 (s, 3H), 1.42 (d, 6H), -0.93 (s, 6H). Anal. Calcd for C$_{25}$H$_{26}$AlNO: C, 78.30; H, 6.83; N, 3.65. Found: C, 78.25; H, 6.78; N, 3.54.

2.5. Typical Process for LA Polymerization
Aluminum compounds (50 μmol) and isopropanol (50 μmol) were placed in an ampoule bottle containing stir bar under 70 °C. The solution was stirred for about 10 minutes, the catalyst was fully activated by isopropyl alcohol, and then the lactide required in toluene (100 mL) was added. After a certain reaction time, the polymer was precipitated with cold methanol. Collect solid, vacuum 35 °C dry 40 h.

3. Results and discussion
3.1. Complexes Synthesis and Characterization
Aluminum complex 1 was prepared by 1 eq trimethyl-aluminum and 1 eq pro-ligand a and were isolated as white solid in good yields (82.0%).

The $^1$H NMR spectrum of aluminum complex 1 showed in the parts of δ –0.93 ppm for the methyl protons of the Al-CH$_3$ group.

3.2. ROP of Lactide
The polymerization reaction was in toluene, and the polymerization data were shown in Table 1. Under the concerted catalysis of isopropyl alcohol, the aluminum complexes showed a low to high active monomer conversion (82.1-98.4%) at 70 °C. The $M_n$ of PLA was calculated by $^1$H NMR and GPC. All polymers have approximate theoretical molecular weight (calculated by monomer/cata. mole ratio). The PDI of polymers were narrow with the living polymerization characteristic.

Table 1. Polymerization data of L-LA using complex 1 $^{[a]}$

| Entry | T h | $[\text{LA}]_0/\text{[Al]}_0$ | Conv. % $^{[b]}$ | $M_n$(calcld) $\times 10^{-4}$ $^{[c]}$ | $M_n$(GPC) $\times 10^{-4}$ $^{[d]}$ | PDI $^{[d]}$ |
|-------|-----|-----------------|----------------|-----------------|-----------------|---------|
| 1     | 36  | 100             | 82.1           | 1.22            | 1.33            | 1.25    |
| 2     | 32  | 75              | 80.6           | 0.87            | 1.61            | 1.26    |
| 3     | 28  | 50              | 91.3           | 0.67            | 0.75            | 1.12    |
| 4     | 10  | 15              | 98.4           | 0.21            | 0.37            | 1.08    |

$a$The polymerization was in toluene solution at 70 °C, $[\text{LA}]_0 = 0.5$ mol. L$^{-1}$, $[\text{isopropyl alcohol}]/[\text{Al}] = 1.0$.

$^b$Measured by $^1$H NMR.

$^c$Calculated from $144.1 \times [\text{LA}]_0/[\text{Al}]_0 \times$ conv.

$^d$Obtained from GPC. The true value of number-averaged molecular weights could be determined by formula $M_n = 0.58M_{nGPC}$.

3.3. Mechanism of LA polymerization

The chain ends of the oligomers of L-LA were characterized using $^1$H NMR, which were prepared by polymerization of L-LA at low monomer/initiator ratios ($[\text{LA}]_0/[\text{1}]_0 = 15:1$) (Fig. 1). NMR spectroscopy showed an integral ratio of two peaks at 1.24 ppm (belong to the methyl proton from the isopropanoyl end group, "1") and at 4.34 ppm (affiliated to adjacent to the hydroxyl end group) The methyl proton, "5") is 6:1. This indicated that the aggregated chain is blocked by isopropyl ester. The polymerization mechanism is a coordination insertion mechanism.$^{[8, 9]}$

4. Conclusions

In conclusion, we studied an new aluminum complex bearing Schiff base which was employed as initiators for the ROP of L-LA. $^1$H NMR spectrum of oligomers uncovered that the polymerization mechanism of initiated ROP of LA was the coordination insertion mechanism.

Acknowledgments

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References

[1] Langer R., Vacanti J.P. (1993) Tissue Engineering. Science. 260: 920–926.
[2] Li D.N., Gao B. Duan Q. (2019) Syntheses of biodegradable and biorenewable polylactides initiated by aluminum complexes bearing m-xylylenediamine derivatives via the ring-opening polymerization of lactides. New J. Chem. 43: 6943 - 6950.
[3] Gao B., Li D.N., Li Y., Duan Q., Pang X., (2015) Ring-opening polymerization of lactide using chiral salen aluminum complexes as initiators: high productivity and stereoselectivity. New J. Chem., 39: 4670–4675.
[4] Gao B., Li D.N., Chen X.S. (2015) Preparation of biocompatible, biodegradable and sustainable polylactides catalyzed by aluminum complexes bearing unsymmetrical dinaphthaleneimine derivatives via ring-opening polymerization of lactides. Catal. Sci. Technol. 5: 4644–4652.
[5] Cui Y., Li D. (2016) Ring-opening polymerization of lactide using salen aluminum complexes bearing Schiff-base ligands derived from cis-1,2-cyclohexanediamine. J Coord. Chem., 69: 656-667.
[6] Gao B., Duan R.L., Pang X., Chen X.S. (2013) Stereoselective ring-opening polymerisation of rac-lactides. catalyzed by aluminum hemi-Salen complexes. Organometallics 32: 5435–5444.
[7] Florczak M., Libizowski J., Mosnacek J., Duda A., Penczek S. (2007) L, L-Lactide and ε-Caprolactone Block Copolymers by a ‘Poly(L, L-lactide) Block First’ Route. Macromol. Rapid. Commun. 28:1385–1391.
[8] Jhurry D., Bhaw-Luximon A., Spassky N., (2001) Synthesis of polylactides by new aluminium Schöll's base complexes. Macromol. Symp. 175:67–80.
[9] Li D.N., Gao B., Duan Q. (2019) Syntheses of Biodegradable and Biorenewable Polylactides Initiated by Aluminum Complexes Bearing Porphyrin Derivatives by the Ring-Opening Polymerization of Lactides, J Biomat Sci-Polym E, DOI: 10.1080/09205063.2019.1605867.