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PAPER

# Stereoselective Ring-Opening Polymerization of *rac*-Lactides Catalyzed by Titanium Complexes Containing N, N-Bidentate Phenanthrene Derivatives

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## Abstract

Three titanium complexes with N, N-bidentate phenanthrene derivatives (**1**: R = <sup>i</sup>Pr, **2**: R = C<sub>6</sub>H<sub>5</sub>, **3**: R = 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) were synthesized. These complexes were characterized by <sup>1</sup>H/<sup>13</sup>C NMR spectroscopy and elemental analyses and employed for ring-open polymerization (ROP) of L-lactide and *rac*-lactide. Complex **1** displayed the highest activity among these complexes for ROP of L-lactide, and complex **3** showed the highest stereoselectivity for the ROP of *rac*-lactide attaining partially heterotactic poly(lactide) (PLA) with a *P<sub>T</sub>* of 0.63. The polymerization kinetic employing **3** as catalyst was researched. Kinetics studies revealed that the polymerization rate was first-order as to monomer.

Keywords: titanium; stereoselective; ring-opening polymerization.

## Introduction

Nowadays, polylactide (PLA) deriving from lactic acid acts as a renewable resource such as corn and sugarbeet.<sup>1,2</sup> It is recognized as one of the most promisingly environmentally-friendly polyester exhibiting biological degradation.<sup>2,3,4</sup> Presence of two chiral centers in the lactide (LA) monomer results in the different lactide stereoisomers, namely L-lactide (L-LA), D-lactide (D-LA) and *meso*-lactide (Fig. 1). The stereochemistry of the polymer chains influence PLA's physical and chemical properties.<sup>1a</sup> In general, PLA is synthesized by the ring-opening polymerization (ROP) of lactide that initiated by metal complexes, such as some Sn,<sup>5,6</sup> Al,<sup>7-9,22,23</sup> Zn,<sup>10-12</sup> Mg,<sup>13-15</sup> Ti,<sup>16,17</sup> In,<sup>18</sup> rare-earth metals complexes.<sup>19-21</sup> Among them, some titanium complexes were proved to be efficient in the ROP of lactide. It have been reported that the activities of titanium complexes in lactide polymerization were obviously influenced by the identity of the metal and the ligand.<sup>16,17</sup> In the past twenty years, many efforts had been made for the selection of proper ancillary ligands for enhancing the performance of initiators in polymerizations. A number of research workers had tried to expound the relation among *rac*-lactide (*rac*-LA), metal complexes and tacticity of polymers (see Fig. 2).<sup>22,23</sup> In recent years, our lab have studied many aluminum and zinc metal complexes based on nitrogen-based ligands.<sup>23</sup> These complexes were proved to be well efficient initiators in the ROP of lactide.

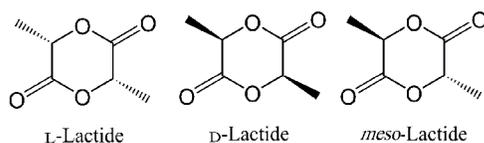


Figure 1. Stereoisomers of lactides.

Recently, we are curious about the catalytic behaviour of titanium complexes with containing N, N-bidentate phenanthrene derivative. As far as we know, little study on titanium complexes

bearing this type of ligands have been investigated for the stereoselective ROP of *rac*-LA (Figure 3).

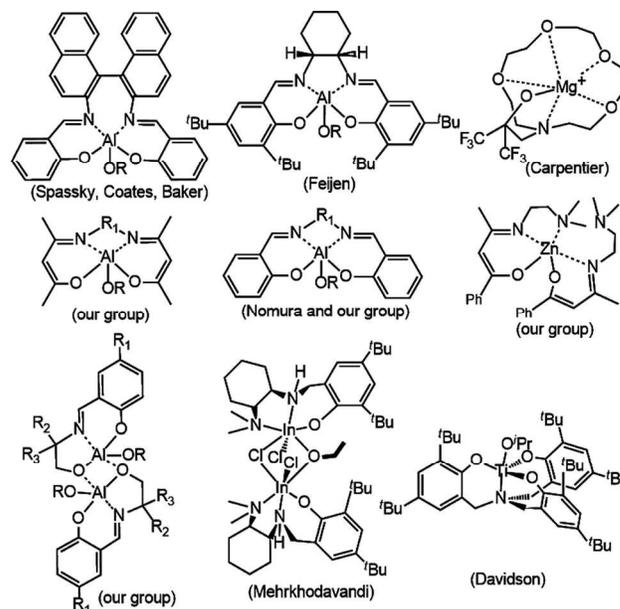


Figure 2. Initiators for stereoselective ROP of lactide.

Based on the efficient uses of titanium complexes,<sup>16,17</sup> we speculate this type of titanium complexes bearing N, N-bidentate diamido ligands might be potential catalysts for the ROP of *rac*-LA. In this work, we report the preparation of a numbers of titanium complexes bearing phenanthrene derivatives and their activities toward the ROP of lactide.

## Experimental

### General

All experimental operations were performed using Schlenk line techniques. Elemental analysis was accomplished by a Varian EL microanalyzer;  $^1\text{H}/^{13}\text{C}$  NMR spectra were recorded on a Bruker 300 MHz or 400 MHz spectrometer  $\text{CDCl}_3$  for compounds and polymers. Gel permeation chromatography measurements were performed on a Waters 515 GPC with  $\text{CHCl}_3$  as the eluant (flow rate: 1 mL/min, at 35 °C). The molecular weight was adjusted through PS standard. Crystallographic data were gathered and analyzed by according to the experiments of references.<sup>23a, 34</sup> 2,2'-biphenyldicarboxaldehyde, isopropylamine, aniline, 2,6-disisopropyl aniline, Ytterbium(III) trifluoromethanesulfonate, Samarium(II) iodide and dichlorotitanium diisopropoxide were purchased from J&K Scientific company.

### Synthesis of pro-ligands

General procedure: under a nitrogen atmosphere, a mixture of amine (10 mmol), 2,2'-biphenyldicarboxaldehyde (5 mmol) and  $\text{MgSO}_4$  (1.0 g) in hexane (20 mL) was refluxed for 3–5 h. The insoluble substance was removed by hot filtration and then the solvent was removed under vacuum. The yellow residue was dissolved in dry THF (10 mL),  $\text{SmI}_2$  (20 mmol) and  $\text{Yb}(\text{OTf})_3$  (10 mmol) in dry THF (200 mL) was added dropwise at 0 °C, then the reaction was allowed to stand at rt for ca. 18 h, then quenched with saturated aqueous  $\text{NaHCO}_3$  and filtered. The two phases were separated, and the aqueous layers extracted twice with  $\text{CHCl}_3$ . The solvent was removed under vacuum. The product was isolated as colorless solid by silica-gel column chromatography ( $V_{\text{petroleum}} : V_{\text{ethyl acetate}} = 10 : 1$ ) in 52.5–63.4% yields.

**L<sub>1</sub>**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298K)  $\delta$  7.81 (d,  $J = 7.2$  Hz, 1H, ArH), 7.55 (d,  $J = 7.3$  Hz, 1H, ArH), 7.39 – 7.24 (m, 6H, ArH), 3.86 (s, 2H, CHN), 3.83 – 3.66 (m, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 3.42 (bs, 1H, ArNH), 3.25 (bs, 1H, RNH), 1.03 (d,  $J = 6.6$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 0.96 ppm (d,  $J = 6.6$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298K)  $\delta$  137.01, 136.90, 136.52, 136.22, 134.60, 133.44, 132.63, 131.50, 129.00, 128.93, 127.64, 127.51, 50.2 (s, CHN), 49.9 (s, CHN), 45.04 (CH(CH<sub>3</sub>)<sub>2</sub>), 44.78 (CH(CH<sub>3</sub>)<sub>2</sub>), 18.13 (CH(CH<sub>3</sub>)<sub>2</sub>), 17.92 (CH(CH<sub>3</sub>)<sub>2</sub>). Anal. Calcd for  $\text{C}_{20}\text{H}_{26}\text{N}_2$  (%): C, 81.59; H, 8.90; N, 9.51. Found: C, 81.55; H, 8.85; N, 9.46. HRMS ( $m/z$ ): calcd for  $\text{C}_{26}\text{H}_{22}\text{N}_2$ : 294.2. Found: 294.1

**L<sub>2</sub>**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298K):  $\delta$  7.29 (d,  $J = 7.8$  Hz, 2H, ArH), 7.26 – 7.05 (m, 8H, ArH), 6.95 (t,  $J = 7.3$  Hz, 2H, ArH), 6.80 – 6.43 (m, 6H, ArH), 5.01 (s, 2H, CHN), 4.72 (s, 2H, RNH).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298K):  $\delta$  146.5, 139.7, 138.2, 129.4, 128.6, 127.7, 118.5, 118.1, 114.5, 113.9, 64.2 (s, CHN), 62.1 (s, CHN). Anal. Calcd for  $\text{C}_{26}\text{H}_{22}\text{N}_2$  (%): C, 86.15; H, 6.12; N, 7.73. Found: C, 86.18; H, 6.15; N, 7.76. HRMS ( $m/z$ ): calcd for  $\text{C}_{26}\text{H}_{22}\text{N}_2$ : 362.2. Found: 362.2.

**L<sub>3</sub>**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 233K):  $\delta$  7.96 (d,  $J = 7.3$  Hz, 1H, ArH), 7.81 (d,  $J = 7.4$  Hz, 1H, ArH), 7.76 (d,  $J = 7.7$  Hz, 1H, ArH), 7.54 – 7.38 (m, 2H, ArH), 7.28 (t,  $J = 7.5$  Hz, 1H, ArH), 7.19 (d,  $J = 7.7$  Hz, 2H, ArH), 6.98 (dt,  $J = 15.5$ , 7.6 Hz, 4H, ArH), 6.76 (s, 1H, ArH), 6.50 (d,  $J = 7.5$  Hz, 1H, ArH), 5.02 (s, 2H, CHN), 4.21 (d,  $J = 11.6$  Hz, 1H, RNH), 3.56 – 3.50 (m, 2H, 1H, RNH and 1H,  $\text{CH}(\text{CH}_3)_2$ ), 3.34 – 3.29 (m, 3H,  $\text{CH}(\text{CH}_3)_2$ ), 1.23 (dd,  $J = 10.8$ , 6.7 Hz, 18H,  $\text{CH}(\text{CH}_3)_2$ ), 0.65 (s, 3H,  $\text{CH}(\text{CH}_3)_2$ ), 0.36 ppm (s, 3H,  $\text{CH}(\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 233K)  $\delta$  142.97, 142.79, 142.59, 141.83, 139.83, 137.00, 136.61, 136.08, 133.61, 132.35, 128.44, 128.20, 128.14, 127.94,

127.85, 127.28, 127.04, 126.72, 123.86, 123.82, 123.52, 123.47, 123.09, 123.05, 120.42, 120.05, 61.30 (s, CHN), 61.16 (s, CHN), 60.86 – 60.54 (m,  $\text{CH}(\text{CH}_3)_2$ ), 60.20 (s,  $\text{CH}(\text{CH}_3)_2$ ), 60.17 (s,  $\text{CH}(\text{CH}_3)_2$ ), 28.10 (d,  $J = 18.3$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 24.42 – 23.30 (m,  $\text{CH}(\text{CH}_3)_2$ ) ppm. Anal. Calcd for  $\text{C}_{38}\text{H}_{46}\text{N}_2$  (%): C, 85.99; H, 8.74; N, 5.28. Found: C, 85.96; H, 8.72; N, 5.27. HRMS ( $m/z$ ): calcd for  $\text{C}_{38}\text{H}_{46}\text{N}_2$ : 530.4. Found: 530.3.

### 70 Synthesis of titanium complexes

General procedure: under a nitrogen atmosphere, a solution of *n*-BuLi (4 mmol) was slow added to a solution of pro-ligand **L<sub>n</sub>** (2 mmol) in toluene (15 mL) at –78 °C. The reaction mixture was allowed to warm to rt and stirred for 3 h. Then the solution was slow added to a solution of  $\text{TiCl}_2(\text{O}^i\text{Pr})_2$  (2 mmol) in toluene (50 mL) at –20 °C. The reaction was allowed to warm to rt and stirred for ca. 4 h. The insoluble substance was filtered off, and the solvent was removed to give a red solid. The product as a red crystal was attained by crystallization from *n*-pentane (yield: 79.3–85.7%).

**1**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298K)  $\delta$  7.81 (d,  $J = 7.2$  Hz, 1H, ArH), 7.55 (d,  $J = 7.3$  Hz, 1H, ArH), 7.39 – 7.24 (m, 6H, ArH), 4.98 (s, 2H, CHN), 3.62 (sept,  $J = 7.5$  Hz, 1H,  $\text{OCH}(\text{CH}_3)_2$ ), 3.54 – 3.47 (m, 1H,  $\text{OCH}(\text{CH}_3)_2$ ), 3.42 (m, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 3.34 (m, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 1.10 (d,  $J = 6.9$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 1.05 (d,  $J = 7.0$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 0.77 (s, 6H,  $\text{OCH}(\text{CH}_3)_2$ ), 0.62 ppm (s, 6H,  $\text{OCH}(\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298K)  $\delta$  140.55, 139.87, 137.82, 137.50, 130.22, 129.99, 128.00, 127.94, 128.03 – 127.68 (m), 118.43 (d,  $J = 19.6$  Hz), 60.20 (s,  $\text{OCH}(\text{CH}_3)_2$ ), 59.72 (s,  $\text{OCH}(\text{CH}_3)_2$ ), 59.17 (s, CHN), 59.14 (s, CHN), 30.46 (s,  $\text{CH}(\text{CH}_3)_2$ ), 29.32 (s,  $\text{CH}(\text{CH}_3)_2$ ), 26.27 (d,  $J = 19.1$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 25.97 (br,  $\text{CH}(\text{CH}_3)_2$ ), 24.24 – 23.11 (m,  $\text{OCH}(\text{CH}_3)_2$ ) ppm. Anal. Calcd for  $\text{C}_{26}\text{H}_{38}\text{N}_2\text{O}_2\text{Ti}$  (%): C, 68.11; H, 8.35; N, 6.11. Found: C, 68.09; H, 8.33; N, 6.10.

**2**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298K)  $\delta$  7.99 (d,  $J = 7.4$  Hz, 2H, ArH), 7.67 (m, 2H, ArH), 7.55 – 7.30 (m, 4H, ArH), 6.98 (t,  $J = 7.5$  Hz, 4H, ArH), 6.85 (d,  $J = 7.3$  Hz, 4H, ArH), 5.85 (s, 2H, CHN), 4.83 – 4.88 (m, 2H,  $\text{OCH}(\text{CH}_3)_2$ ), 1.19 (s, 6H,  $\text{OCH}(\text{CH}_3)_2$ ), 0.92 ppm (s, 6H,  $\text{OCH}(\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298K)  $\delta$  143.21, 142.85, 142.70, 142.55, 141.97, 140.10, 137.29, 136.83, 136.22, 133.81, 132.50, 128.74, 128.29, 128.08, 127.99, 127.46, 127.33, 126.90, 124.02, 123.66, 123.24, 121.02, 62.54 (s,  $\text{OCH}(\text{CH}_3)_2$ ), 62.03 (s,  $\text{OCH}(\text{CH}_3)_2$ ), 60.81 (s, CHN), 60.78 (s, CHN), 24.77 – 23.53 (m,  $\text{OCH}(\text{CH}_3)_2$ ) ppm. Anal. Calcd for  $\text{C}_{32}\text{H}_{34}\text{N}_2\text{O}_2\text{Ti}$  (%): C, 73.00; H, 6.51; N, 5.32. Found: C, 73.02; H, 6.54; N, 5.35.

**3**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 308K)  $\delta$  7.60 (d,  $J = 7.9$  Hz, 1H, ArH), 7.30 – 6.77 (m, 13H, ArH), 5.83 (s, 2H, CHN), 4.79 – 4.73 (m, 1H,  $\text{OCH}(\text{CH}_3)_2$ ), 4.59 – 4.52 (m, 1H,  $\text{OCH}(\text{CH}_3)_2$ ), 4.38 (td,  $J = 12.2$ , 6.1 Hz, 2H,  $\text{OCH}(\text{CH}_3)_2$ ), 4.11 – 3.97 (m, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 3.89 – 3.66 (m, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 3.10 (dt,  $J = 13.8$ , 6.9 Hz, 2H,  $\text{CH}(\text{CH}_3)_2$ ), 1.41 (d,  $J = 6.2$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 1.31 (d,  $J = 6.2$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 1.23 (dd,  $J = 6.9$ , 4.0 Hz, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 1.14 (d,  $J = 6.9$  Hz, 6H,  $\text{OCH}(\text{CH}_3)_2$ ), 0.87 ppm (d,  $J = 6.9$  Hz, 6H,  $\text{OCH}(\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 308K):  $\delta$  138.29, 134.43, 131.00, 129.39 (br), 128.83, 128.38 (br), 128.22 (br), 127.91 (br), 127.59 (br), 126.47, 125.20, 124.50, 124.26, 123.76, 123.18, 122.99, 77.8 ( $\text{OCH}(\text{CH}_3)_2$ ), 76.0 ( $\text{OCH}(\text{CH}_3)_2$ ), 69.1 (CHN), 31.64 (br,  $\text{CH}(\text{CH}_3)_2$ ), 31.49 (br,  $\text{CH}(\text{CH}_3)_2$ ), 28.03 (br,  $\text{CH}(\text{CH}_3)_2$ ), 26.6 (s,  $\text{CH}(\text{CH}_3)_2$ ), 26.3 (s,  $\text{CH}(\text{CH}_3)_2$ ), 26.0 (br,  $\text{CH}(\text{CH}_3)_2$ ), 25.80 (br,  $\text{CH}(\text{CH}_3)_2$ ), 23.11 (s,  $\text{OCH}(\text{CH}_3)_2$ ), 22.57 ppm (s,  $\text{OCH}(\text{CH}_3)_2$ ). Anal. Calcd for  $\text{C}_{44}\text{H}_{58}\text{N}_2\text{O}_2\text{Ti}$  (%): C, 76.06; H, 8.41; N, 4.03. Found: C, 76.09; H, 8.44; N, 4.06. Crystal of **3** suitable for X-ray structural analysis was grown in pentane solution. CCDC: 1035591.

## General procedure for lactide polymerization

### Polymerizations in solution

In a typical polymerization reaction: titanium complex (0.5 mmol) and required quantity of lactide in toluene (100 mL) were added in a flame-dried ampule including a magnetic stir bar. The ampule was placed in an oil bath at 70 °C. The polymer was isolated by precipitating with cold methanol or refrigerated centrifuge, after required quantity of reaction time. The solid was attained and dried *in vacuo* at rt for 36h.

### Solventless polymerization

In a representational melt polymerization reaction, titanium complex (0.1 mmol) and lactide (30 mmol, 4.32 g) were loaded in a flame-dried vessel containing a magnetic stir bar. The ampule was immersed in an oil bath at 140 °C for 5 h before being cooled to rt. Methanol (30 mL) was added and the solid was dissolved in dichloromethane. The solvents were removed *in vacuo* and the solid was washed with methanol (70 mL×3) to remove residual monomer. The solid was collected and dried *in vacuo* at rt for 36h.

## Result and discussion

### Synthesis of pro-ligands and titanium complexes

As is shown in the Scheme 1, pro-ligands **L**<sub>1</sub> – **L**<sub>3</sub> are synthesized easily by the condensation reaction between 2,2'-biphenyldicarboxaldehyde and modified amine and then through intermolecular coupling reactions catalyzed by 4 equivalents of SmI<sub>2</sub> with 2 equivalents of Yb(OTf)<sub>3</sub> in a similar process to **20a** in the Ref. 24 in middling yields (52.5–63.4%).

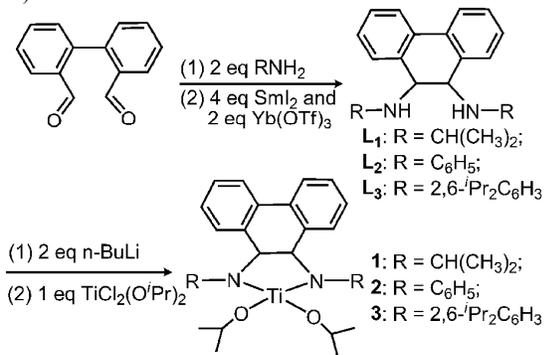


Figure 3. Synthesis of pro-ligands and complexes.

Titanium complexes **1** – **3** were synthesized *via* one-pot synthesis. The lithiation of pro-ligands **L**<sub>1</sub> – **L**<sub>3</sub> with 2 equiv of n-BuLi produced the corresponding lithium salt. The lithiation reaction was proceed at –78 °C to restrict the generation of byproduct because this kind of reaction is generally rapid and exothermic. Then the reactions of TiCl<sub>2</sub>(O<sup>*i*</sup>Pr)<sub>2</sub> with lithium salt were carried out at –20 °C, and titanium complexes **1** – **3** were attained as red solid in good yields (79.3 – 85.7%). All three complexes were sensitive to moisture.

Complexes **1** – **3** were characterized by <sup>1</sup>H/<sup>13</sup>C NMR in CDCl<sub>3</sub> and elemental analysis. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of complexes **1** – **3** showed one ligand and two isopropoxy groups were coordinated to titanium atoms. They showed similar resonances in the high field of δ 4.88 – 3.47 ppm, which attributed to the two secondary protons of –OCH(CH<sub>3</sub>)<sub>2</sub> groups and δ 1.19 – 0.77 and 0.92 – 0.62 ppm for the primary protons of

–OCH(CH<sub>3</sub>)<sub>2</sub> groups in the <sup>1</sup>H NMR spectra. Meanwhile the disappearance of the signals (δ 4.72 – 3.25 ppm) attributed to the diamide –RNH– protons with contrasting to pro-ligands, which suggested the nitrogen atoms from N, N-bidentate ligands were coordinated to the Ti atoms. They were consistent with the single crystal structure of **3** in solid state. The geometry of complex **3** in solid state was confirmed *via* X-ray diffraction analysis. The molecular structure is depicted in Fig. 4. The selected bond distances and angles and other crystallographic data are depicted in Table S1 and Table S2 (see supporting information), respectively. X-ray structural analysis revealed that complex **3** was mononuclear and the central titanium atom was coordinated by two N atoms from N, N-bidentate ligands and two O atoms from isopropoxy groups. In complex **3** (see Table 1), the Ti1–N2 bond length, 1.919(4) Å, is the longest among these Ti–X bond lengths (Ti1–N1: 1.893(4) Å, Ti1–O1: 1.798(4) Å, Ti1–O2: 1.856(4) Å, which were in normal range found in related titanium complexes<sup>25–27</sup>); O1–Ti1–O2, O1–Ti1–N1, O2–Ti1–N1, O1–Ti1–N2, O2–Ti1–N2 and N1–Ti1–N2 angles are 107.53(7), 116.34(7), 109.62(8), 116.34(7) 117.23(7) and 89.09(6) °, respectively. Obviously, the titanium atom was in a distorted tetrahedral geometry in complex **3**.

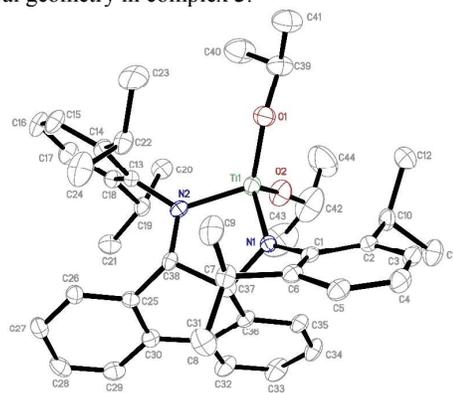


Figure 4. Perspective view of **3** with thermal ellipsoids drawn at 30% probability level. Hydrogens are omitted for clarity.

### Lactide Polymerization

All titanium complexes were researched as catalysts for the ROP L-LA or *rac*-LA. The polymerizations were performed in toluene, and the representative data were recorded in Table 1. These titanium complexes showed low to high activities (71.9 – 95.6% monomer conversion) in toluene at 70 °C. <sup>1</sup>H NMR and GPC were applied to calculate the *M*<sub>n</sub> index of the PLA. All the polymers had the number-averaged molecular weights (analyzed through GPC<sup>28</sup>) near theoretical ones (calculated from the monomer/catalyst molar ratio). The molecular weight (*M*<sub>n</sub>) of the polymers propagated almost linearly depending on the raise of the monomer transformation rate and the polydispersity index (PDI) of these polymers were relatively low (1.08 – 1.31, Entries **1** – **8**, e.g. Fig. 6, Table 1, Entry 3). It revealed that the polymerizations in toluene solution were well controlled. It was note that the activities of these complexes reduced with the raise of substituent's bulk. Complex **1** showed the highest activity (95.6% monomer conversion Table 1, Entry 1) at the same polymerization parameters among these complexes (Table 1, Entries 1, 2 and 3). It was possibly attributed to **1** possess the least steric hindrance among these complex. Similar situations also appeared in Al complexes in the previous reports.<sup>29</sup>

Furthermore, the ligands had certain ability to influence the PDI of the polymer, and this ability varied with bulk of ligands. For instance, the PDI decreased from 1.31 to 1.11 with the raise

of the volume of the substitutes on “R” from *i*-propyl to 2,6-di-*i*-propylphenyl (see Table 1, Entries 1, and 3). Complex **3** with bulky ligand attained the least monomer conversion and lowest PDI, a similar situation also appeared in the previous report.<sup>30</sup>

### 5 Kinetics of lactide polymerization

The representative kinetics of ROP of L-LA (monomer/cat.**3** ratio = 100/1) was researched in toluene at 70 °C. The molecular weight ( $M_n$ ) of the polymers increased linearly with increasing monomer conversion. The PDI values of these polymers remain low (1.07 – 1.11) (Fig. 6). The plots of  $\ln([LA]_0/[LA]_t)$  versus time was linear illustrating the polymerization rate has a first-order dependency on monomer employing **3** for ROP of L-LA (Fig. 7).

### Stereoselective polymerization

15 Moreover, the poly(*rac*-LA) (Table 1, Entry 8) with the homonuclear decoupled <sup>1</sup>H NMR spectrum of the methane fragment<sup>31</sup> (see Fig. 5) were also investigated. The  $P_r$ <sup>32</sup> value, 0.63, demonstrated that these polymer chains were partially heterotactic. The results showed that the  $P_r$  selectivities increased from 0.52 to 0.59 with the raise of the bulk of the substitutes on ligands at 70 °C (see Table 1, Entries 5, 6, 7). For complex **3**, reducing the temperature from 70 to 50 °C, the  $P_r$  value increased from 0.59 to 0.63 (Table 1, Entries 7, 8).

### Solventless polymerization

25 In addition, solventless polymerization (melt polymerization) more and more aroused people’s attentions due to less pollution. So we tried to polymerize *rac*-LA in melt polymerization at 140 °C. Under melting condition, these complexes showed higher activity than those of the polymerization in toluene solution (e.g. Table 1, Entries 1, 9 and 13). The highest monomer conversion reached 96.7%.

### Mechanism of lactide polymerization

For studying the mechanism of initiation, end analysis of the oligo(lactide), which was synthesized *via* the ROP of the LA ([LA] : [I] = 20 : 1) was measured by <sup>1</sup>H NMR (Fig. 8). It revealed that the integral ratio of the two peaks at  $\delta$  1.24 ppm, which was attributed to the methyl protons on the isopropoxycarbonyl end, and  $\delta$  4.34 ppm, which was attributed to the methine proton connected to the hydroxyl end, was close to 6/1. This meant the propagating chains were end-capped by an isopropyl ester and a hydroxyl group, the ROP selected a coordination insertion mechanism.<sup>33</sup>

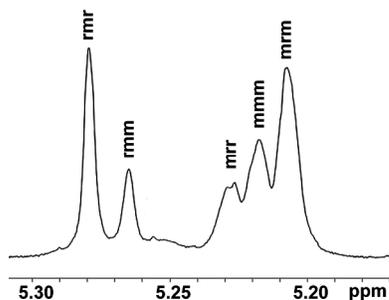


Figure 5. Homonuclear decoupled <sup>1</sup>H NMR spectrum of the methine part of poly(*rac*-LA) using **3** at 50 °C,  $P_r = 0.63$ , in CDCl<sub>3</sub> (Table 1, Entry 8).

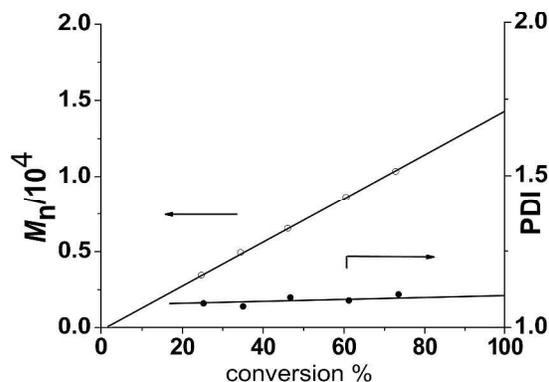


Figure 6. Plots of PLA's  $M_n$  and PDI versus L-LA conversion employing **3**,  $[LA]_0/[cat. \mathbf{3}]_0 = 100$ , at 70 °C in toluene.

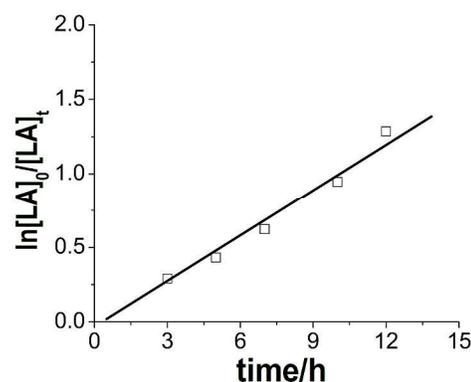


Figure 7. Kinetics of the ROP of L-LA *via* cat. **3** at 70 °C in toluene with  $[LA]_0 = 0.5 \text{ mol L}^{-1}$ ,  $[cat.]_0 = 5 \times 10^{-3} \text{ mol L}^{-1}$ ,  $[LA]_0/[cat.]_0 = 100$ .

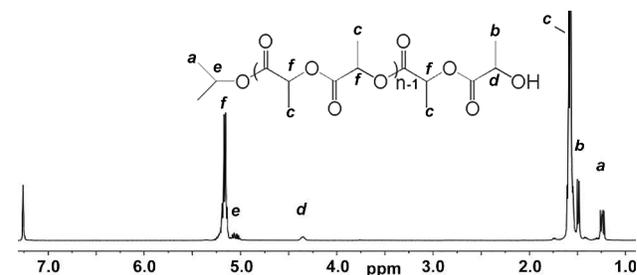


Figure 8. <sup>1</sup>H NMR spectrum of oligomer of LA ( $[LA]_t : [I]_t = 20 : 1$ , Table 1, Entry 4) in CDCl<sub>3</sub>.

### Conclusion

In summary, a number of titanium complexes **1** – **3** were synthesized in good yields. X-ray diffraction analysis revealed that the titanium atom was in a distorted tetrahedral geometry in complex **3**. These complexes were employed as catalysts for the polymerization of L-LA and *rac*-LA. Microstructural analyses of the polymers catalyzed by these complexes revealed that the substituent on the ligand influenced the steric regularity of the polymer and this ability varied with the volume of ligand. Kinetic studies uncovered that polymerization of lactide by complex **3** was first-order as to monomer. In addition, these complexes were turned out to be efficient catalysts for the ROP of lactides in the melt polymerization.

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## Notes and references

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**Table 1.** Representative polymerization data of LA using titanium complexes **1** – **3**.<sup>[a]</sup>

| Entry             | Cat.     | Monomer        | T (°C) | t (h) | [LA] <sub>0</sub> /[Ti] <sub>0</sub> | Conv. <sup>[b]</sup> (%) | $M_{n(\text{calcd})}^{[c]} \times 10^{-4}$ | $M_{n\text{GPC}}^{[d]} \times 10^{-4}$ | PDI <sup>[d]</sup> | $P_r$ |
|-------------------|----------|----------------|--------|-------|--------------------------------------|--------------------------|--|--|--------------------|-------|
| 1                 | <b>1</b> | L-LA           | 70     | 12    | 100                                  | 95.6                     | 1.38                                       | 2.31                                   | 1.31               | –     |
| 2                 | <b>2</b> | L-LA           | 70     | 12    | 100                                  | 89.4                     | 1.29                                       | 2.09                                   | 1.25               | –     |
| 3                 | <b>3</b> | L-LA           | 70     | 12    | 100                                  | 73.5                     | 1.06                                       | 1.80                                   | 1.11               | –     |
| 4                 | <b>1</b> | L-LA           | 70     | 5     | 20                                   | 94.3                     | 0.27                                       | 0.46                                   | 1.08               | –     |
| 5                 | <b>1</b> | <i>rac</i> -LA | 70     | 12    | 100                                  | 94.0                     | 1.35                                       | 2.28                                   | 1.33               | 0.52  |
| 6                 | <b>2</b> | <i>rac</i> -LA | 70     | 12    | 100                                  | 90.2                     | 1.30                                       | 2.20                                   | 1.27               | 0.55  |
| 7                 | <b>3</b> | <i>rac</i> -LA | 70     | 12    | 100                                  | 71.9                     | 1.04                                       | 1.71                                   | 1.17               | 0.59  |
| 8                 | <b>3</b> | <i>rac</i> -LA | 50     | 17    | 100                                  | 83.6                     | 1.20                                       | 2.02                                   | 1.12               | 0.63  |
| 9 <sup>[e]</sup>  | <b>1</b> | L-LA           | 140    | 3     | 100                                  | 96.7                     | 1.39                                       | 2.29                                   | 1.49               | –     |
| 10 <sup>[e]</sup> | <b>2</b> | L-LA           | 140    | 5     | 100                                  | 92.4                     | 1.33                                       | 2.21                                   | 1.40               | –     |
| 11 <sup>[e]</sup> | <b>3</b> | L-LA           | 140    | 5     | 100                                  | 82.3                     | 1.19                                       | 2.00                                   | 1.32               | –     |
| 12 <sup>[e]</sup> | <b>3</b> | <i>rac</i> -LA | 140    | 5     | 100                                  | 81.0                     | 1.17                                       | 1.18                                   | 1.37               | 0.53  |
| 13 <sup>[e]</sup> | <b>1</b> | L-LA           | 140    | 7     | 300                                  | 91.7                     | 3.96                                       | 6.51                                   | 1.86               | –     |
| 14 <sup>[e]</sup> | <b>2</b> | L-LA           | 140    | 7     | 300                                  | 80.2                     | 3.46                                       | 5.54                                   | 1.51               | –     |
| 15 <sup>[e]</sup> | <b>3</b> | L-LA           | 140    | 7     | 300                                  | 67.3                     | 2.91                                       | 4.92                                   | 1.35               | –     |

[a] The polymerizations were performed in toluene solution, [LA]<sub>0</sub> = 0.5 mol L<sup>-1</sup>. [b] Measured by <sup>1</sup>H NMR spectroscopy. [c] Calculated from the molecular weight of LA × [LA]<sub>0</sub>/[Ti]<sub>0</sub> × conversion +  $M_w^{\text{isopropanol}}$ . [d] Attained from GPC analysis and calibrated against polystyrene standard. The veritable value of  $M_{n(\text{calcd})}$  could be calculated according to formula  $M_n = 0.58M_{n\text{GPC}}$ . [e] Melt polymerization.