This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Titanium Complexes with Octahedral Geometry Chelated by Salen Ligands Adopting β-cis Configuration for the Ring-Opening Polymerisation of Lactide

Bo Gao, Xiang Li, Ranlong Duan and Xuan Pang

Four titanium complexes based on Salen ligands were prepared and employed for ring-opening polymerisation of lactide. X-ray diffraction analysis revealed the titanium atom was in a distorted octahedral geometry and the quadridentate ligand adopted β-cis geometry in complex 1.

Poly(lactic acid) (PLA) derives from lactic acid as a renewable resource such as corn and sorghum. It is marketed as one of the most promisingly environmentally-friendly polyesters. Universally poly(lactic acid) is synthesised by ring-opening polymerisation (ROP) of lactide (LA) which initiated by inorganic initiator such as some complexes of tin, aluminum, zinc, magnesium, iron, titanium, indium, rare-earth metal. Over the past few decades, some labs have reported lots of complexes based on Schiff base for the ROP of LA (Fig. S1). Among them, Spassky first used an achiral Salen ligand–aluminium initiator to prepare a stereo-controlled polymerization of isotactic rac-lactide. Coates, Smith and Baker have reported that the racemic aluminium complex polymerized rac-LA more efficiently. Feijen and Zhong have reported (R,R)-CyclohexylSalenAlOiPr [(R,R)-1] polymerized L-lactide significantly faster than D-lactide with a rate constant ratio \( k_L/k_D \) of \( \sim 14 \). Davidson have reported that some titanium complexes bearing amine tris(phenolate) alkoxides were single-site initiators for the ring-opening polymerization of rac-lactide. Verkade reported that some titanatranes show good catalytic activity for the bulk polymerization of L- and rac-LA.

In recent years, our lab have studied many aluminum and zinc metal complexes based on Schiff base ligands. These complexes were turned out to be well efficient initiators in the ROP of lactide (LA). Complex 1 based on Salen ligand L1 (Fig. S1) showed high stereo-seleectiveity for the ROP of rac-LA. However, to the best of our knowledge, few investigations on titanium complexes chelating this types of Salen ligands (see Scheme 1) were researched in the ROP of LA. In consideration of catalytical performances of above aluminum complexes chelated by Salen ligands and the previous reported titanium complexes for the polymerizations of LA, we speculate the titanium complexes supported by the Salen ligands are potential initiators for the ROP of LA. Therefore, we synthesised a number of titanium complexes with this type of Salen ligands and researched catalytic behaviours of them for the ROP of LA in toluene solution or solventless. In this work, we report the preliminary data of these Salen titanium complexes used as initiators for polymerising LA.

Ligands L1 – L4 were synthesized by published procedures. As shown in Scheme 1, titanium complexes 1 – 4 were easily prepared via reacting identical quantity of titanium tetraisopropoxide and correspondent Salen ligands in glovebox and were isolated as yellow solid in high yields (83.4–94.7%).

Scheme 1 Synthesis of complexes.
All titanium complexes were studied as catalysts for the ROP of rac-LA. The monomer was dimer by 4A molecular sieves in advance in toluene. The polymerisations were performed in toluene, and the representational data were depicted in Table 1. These titanium complexes showed low to high activities (10.9 – 92.1% monomer conversion) in toluene at 100 °C. \(^1\)H NMR and GPC were applied to calculate the M<sub>n</sub> index of the PL. All the polymers had the number-averaged molecular weights (analyzed through GPC and \(^1\)H NMR spectra, e.g. “d” and “f” in Fig. 4) 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 PDI index of these polymers were relatively low (1.22 – 1.47, Entries 1 – 8, e.g. Fig. 2, Table 1, Entry 7). These PDI values are close to the corresponding values (1.38 and 1.43) in Ti complexes have been reported by Davidson and Verkade, respectively. It denoted 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 on the phenyl rings, while electron-withdrawing substituent increased polymerisation rate. Complex 3 showed the highest activity (92.1% monomer conversion Table 1, Entry 7) at the same polymerisation conditions among the four complexes (Table 1, Entries 5, 6, 7 and 8). It was possibly attributed to higher electronegativity of the substituent on the ligands which would result in weaker titanium alkoxide bond. Similar situations also appeared in Al complexes in the previous results.

Complex 4 which derived from 1,3-propanediamine was slightly faster than complex 1 which derived from 2,2-dimethyl-1,3-propanediamine as to polymerisation rate (Table 1, Entries 5 and 8). This may attribute to 4 with less steric hindrance.

Moreover, the ligands had certain ability to influence the polydispersity index (PDI) of the polymer, and this ability varied with bulk of ligand. For instance, the PDI values decreased from 1.41 to 1.22 with the raise of the volume of the substitutes on phenyl rings from H to \(^t\)Bu (see Table 1, Entries 1 and 2). The poly(rac-LA) (Table 1, Entry 16) with the homonuclear decoupled \(^1\)H NMR spectrum of the methane fragment was also researched. The P<sub>r</sub> value, 0.67, certified that these polymer chains were partially heterotactic. This value was higher than the relevant value (50%) in Ti complex I which has been reported by Davidson. The results showed that the P<sub>r</sub> selectivities increased from 0.51 to 0.58 with the raise of the bulk of the substituents on ligands (from hydrogen atoms to tert-butyl on phenyl rings) at 100 °C (see Table 1, Entries 10, 12). The P<sub>r</sub> of complex 4, which derived from 1,3-propanediamine, was close to the one of complex 1, which derived from 2,2-dimethyl-1,3-propanediamine (Entries 4, and 6).

In addition, solventless polymerisation (melt polymerization) was more and more aroused people’s attentions due to less pollution. So we tried to polymerize rac-LA in melt polymerization. Under melting conditions, these complexes showed higher activity than those of the polymerisation in toluene solution (e.g. Table 1, Entries 3, 11 and 15), the highest monomer conversion reached 97.6%. This value approached the corresponding value (96%) about Ti complex which has been reported by Verkade.

Table 1. Representational polymerisation data of LA using complexes 1 – 4 (\([e]\))

<table>
<thead>
<tr>
<th>Entry</th>
<th>Complex</th>
<th>(T)</th>
<th>([\text{LA}]_0)</th>
<th>Conv. (%)</th>
<th>M&lt;sub&gt;pecav&lt;/sub&gt; (\times 10^{3})</th>
<th>M&lt;sub&gt;n&lt;/sub&gt; (\times 10^{3})</th>
<th>PDI</th>
<th>P&lt;sub&gt;r&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>48</td>
<td>10.9</td>
<td>0.16</td>
<td>0.27</td>
<td>1.22</td>
<td>0.67</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>48</td>
<td>10.9</td>
<td>0.16</td>
<td>0.27</td>
<td>1.22</td>
<td>0.67</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>48</td>
<td>10.9</td>
<td>0.16</td>
<td>0.27</td>
<td>1.22</td>
<td>0.67</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>48</td>
<td>10.9</td>
<td>0.16</td>
<td>0.27</td>
<td>1.22</td>
<td>0.67</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>96</td>
<td>32.2</td>
<td>0.85</td>
<td>1.41</td>
<td>1.47</td>
<td>1.31</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>96</td>
<td>32.2</td>
<td>0.85</td>
<td>1.41</td>
<td>1.47</td>
<td>1.31</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>7</td>
<td>96</td>
<td>32.2</td>
<td>0.85</td>
<td>1.41</td>
<td>1.47</td>
<td>1.31</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>8</td>
<td>96</td>
<td>32.2</td>
<td>0.85</td>
<td>1.41</td>
<td>1.47</td>
<td>1.31</td>
<td></td>
</tr>
</tbody>
</table>

[a] The polymerisation reactions were carried out in toluene solution at 100 °C. \([\text{rac-LA}]_0 = 0.5\) mol L<sup>-1</sup>, except for 150 °C in melt polymerization. [b] Measured by \(^1\)H NMR. [c] Calculated from the molecular weight of LA \(= [\text{LA}]_0 / [\text{Ti}]_0 \times\) conversion. [d] Obtained from GPC analysis and calibrated against polystyrene standard. The true index of M<sub>pecav</sub> could be calculated according to formula M<sub>n</sub> = 0.5M<sub>r</sub>G<sub>r</sub>GPC. [e] Melt polymerization.
In order to studying the mechanism of initiation, end analysis of the oligo(lactide), which was synthesised by the ROP of the LA ([LA] : [I] = 14 : 1) was measured by H NMR (Fig. 4). It revealed that the integral ratio of the two peaks at δ 1.24 ppm, which was attributed to the methyl protons on the isoproxy carbonyl end, and δ 4.34 ppm, which was attributed to the methine proton connected to the hydroxyl end, was close to 6 : 1. This meant the aggregating chains were end-capped by an isopropyl ester and a hydroxyl group, the ROP selected a coordination insertion mechanism.

Ligands 1 – 4 were synthesized by published procedures. The Ti complexes were prepared by stirring with titanium tetraisopropoxide in toluene at 25 °C. Full details are given in ESI.

In a representational polymerisation reaction, titanium complex (0.05 mmol) and lactides (15 mmol, 2.16 g) were loaded in a flame-dried vessel containing a magnetic bar. The ampulla was immersed in an oil bath at 100 °C. After a certain reaction time, the polymer was isolated by precipitating with cold methanol or refrigerated centrifuge. The solid was collected and dried in vacuo at 35 °C for 40 h.

In a representational melt polymerisation reaction, titanium complex (0.05 mmol) and lactides (15 mmol, 2.16 g) were loaded in a flame-dried vessel containing a magnetic bar. The ampulla was immersed in an oil bath at 150 °C for 2 h before being cooled to RT. Methanol (20 mL) was added and the solid was dissolved in dichloromethane. The solvents were removed in vacuo and the solid was washed with methanol (50 mL × 2) to remove residual monomer. The solid was collected and dried in vacuo at 35 °C for 40 h.

This work was supported by the National Natural Science Foundation of China (Nos. 21204082, 51173183, 51021003, 51233004, 51390484 and 51321062) and the Ministry of Science and Technology of China (No. 2011AA02A2A02).

Notes and references


P. D. Knight, P. Scott, Coord. Chem. Re. 2003, 242, 125.


$P_r$ is the probability of racemic linkages between monomer units and is determined from the methylene region of the homonuclear decoupled 1H NMR spectrum ($P_r + P_n = 1$). The expressions for the tetrad concentrations in terms of $P_r$, assuming Bernoulli statistics and the absence of transesterification, are as follows: 

$$[mmm] = (2(1−P_r)^2 + P_r(1−P_r))/2; [mmr] = (P_r^2 + P_r(1−P_r))/2; [mrm] = (P_r^2 + P_r(1−P_r))/2; [rmm] = (P_r^2 + P_r(1−P_r))/2; [rmr] = (P_r^2 + P_r)/2; [rmm] = (P_r^2 + P_r(1−P_r))/2$$


