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LETTER

Titanium Complexes with Octahedral Geometry Chelated by Salen Ligands Adopting β -*cis* Configuration for the Ring-Opening Polymerisation of Lactide

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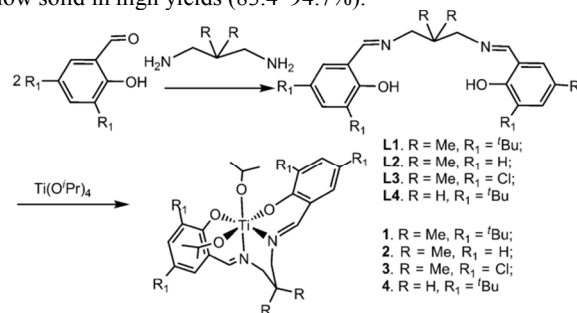
Four titanium complexes based on Salen ligands were prepared and employed for ring-opening polymerisation of lactide. X-ray diffraction analysis revealed the titanium atom was in a distorted octahedral geometry and the quadridentate ligand adopted β -*cis* geometry in complex 1.

Poly(lactide) (PLA) derives from lactic acid as a renewable resource such as corn and sorghum.¹ It is marketed as one of the most promisingly environmentally-friendly polyesters.² Universally polylactide is synthesised by ring-opening polymerisation (ROP) of lactide (LA) which initiated by inorganic initiator such as some complexes of tin,³ aluminum,^{4, 11, 12} zinc,⁵ magnesium,⁶ iron,⁷ titanium,⁸ indium,⁹ rare-earth metal.¹⁰ Over the past few decades, some labs have reported lots of complexes based on Schiff base^{11, 12} 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.^{11a} Coates, Smith and Baker have reported that the racemic aluminum complex polymerized *rac*-LA more efficiently.^{11b, c, d} 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 ~ 14 .^{11e} Davidson^{8a} have reported that some titanium complexes bearing amine tris(phenolate) alkoxides were single-site initiators for the ring-opening polymerization of *rac*-lactide. Verkade^{8b} 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.¹² 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).^{12b} showed high stereo-selectivity 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 complexes¹² chelated by Salen

ligands and the previous reported titanium complexes⁸ 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.^{12a, b} 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.

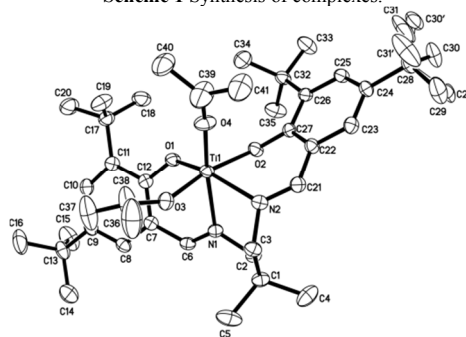


Figure 1. Perspective view of **1** with thermal ellipsoids drawn at 30% probability level. Hydrogens are omitted for clarity.

Entry	Complex	<i>T</i> h	[LA] ₀ /[Ti] ₀	Conv. % ^[b]	<i>M</i> _{n(calcd)} ×10 ^{-4[c]}	<i>M</i> _{n(GPC)} ×10 ^{-4[d]}	PDI ^[d]	<i>P</i> _r
1	1	48	100	10.9	0.16	0.27	1.22	0.67
2	2	48	100	47.8	0.69	1.20	1.41	0.57
3	3	48	100	52.3	0.77	1.31	1.46	0.53
4	4	48	100	14.2	0.21	0.36	1.29	0.59
5	1	96	100	34.2	0.49	0.84	1.27	n.a.
6	2	96	100	87.0	1.25	2.10	1.45	n.a.
7	3	96	100	92.1	1.33	2.14	1.47	n.a.
8	4	96	100	39.3	0.57	0.95	1.31	n.a.
9 ^[e]	1	36	100	78.6	1.13	1.91	1.43	0.59
10 ^[e]	2	36	100	93.4	1.34	2.27	1.74	0.52
11 ^[e]	3	36	100	97.6	1.41	2.39	1.69	0.50
12 ^[e]	4	36	100	80.3	1.16	1.97	1.52	0.55
13 ^[e]	1	72	300	74.0	3.20	5.24	1.48	n.a.
14 ^[e]	2	72	300	89.4	3.86	6.02	1.80	n.a.
15 ^[e]	3	72	300	92.2	3.95	6.25	1.59	n.a.
16 ^[e]	4	72	300	72.8	3.14	5.03	1.55	n.a.

[a] The polymerisation reactions were carried out in toluene solution at 100 °C, [rac-LA]₀ = 0.5 mol L⁻¹, excepting for 150 °C in melt polymerization, [b] Measured by ¹H NMR. [c] Calculated from the molecular weight of LA × [LA]₀/[Ti]₀ × conversion. [d] Obtained from GPC analysis and calibrated against polystyrene standard. The true index of *M*_{n(calcd)} could be calculated according to formula *M*_n = 0.58*M*_{n(GPC)}.¹⁶ [e] Melt polymerization.

Table 1. Representational polymerisation data of LA using complexes **1** – **4**^[a]

All titanium complexes were characterized by ¹H, ¹³C NMR spectroscopy and elemental analysis (see **Experiments in ESI**). The ¹H and ¹³C NMR spectra of **1** – **4** in C₆D₆ showed similar resonances in the high field of δ 5.02 – 5.15 and 4.67 – 4.71 ppm which attributed to the two secondary protons (e.g. ‘c’ and ‘c’ in Fig. S2) of Ti-OC_H(CH₃)₂ groups in the ¹H NMR spectra, respectively, δ 77.63 – 79.23 and 73.07 – 76.51 ppm which attributed to the corresponding two secondary carbons in the ¹³C NMR spectra, respectively. Meanwhile the singlets (δ 14.32 – 14.41 ppm, e.g. ‘a’ in Fig. S3) for hydroxyl’s protons in **1** – **4** disappeared with contrasting to ligands **L1** – **L4**, which indicated the oxygen atoms from Salen ligands were coordinated to the Ti atoms. Interestingly, in addition, other protons attributed to the two isopropoxy groups neighboring Ti atom and two iminophenoxide moieties from the Salen ligand (e.g. two imine, δ 8.24, 8.20 and four ‘Bu methyl resonances, δ 1.23, 1.29, 1.40, 1.51 ppm in complex **1**, see Fig. S2) were also existed in the form of two sets of chemical environments. So it appeared that geometry of **1** in the solution adopted β-*cis*, rather than the *trans* or α-*cis* configuration depicted in Fig. S4,¹³ i.e. the Ti atom in **1** was maybe located in an octahedral geometry and the two N donors occupied axial and equatorial positions, respectively. This configuration was similar with the single crystal structure of compound **5** (see Fig. S5) in solid state.¹⁴ The geometry of **1** in solution state was consistent with the single crystal structure in solid state. Crystal of **1** suitable for X-ray structural determination was grown in benzene solution. The solid geometry of complex **1** was confirmed by X-ray diffraction analysis. The molecular structure was shown in Fig. 1. The selected bond distances and angles and details of crystal data with structure refinements for complex **1** were listed in Table S1 and Table S2 (see **ESI**), respectively. X-ray structural analysis revealed that complex **1** was mononuclear and the central titanium atom was coordinated by two imine N atoms and two O atoms from Schiff base ligand and two O atoms from isopropoxy groups. The solid state structure also displayed the quadridentate ligand adopted β-*cis* geometry (Fig. 1). In complex **1** (see Table S1), the Ti1–N1 bond length, 2.234(3) (Å), is the longest among these Ti–A bond lengths, the O4 and N1 arranged in *trans* position (O4–Ti1–N1: 173.18(14) °). Ti–A bond lengths reflected the donor’s strengths of three different types of coordinated atoms. The Ti–O(iso-propoxide) bonds: Ti1–O1 (1.906(3) Å), Ti1–O2 (1.983(3) Å, which were in normal range

found in related titanium complexes^{15 a, b, c}) were longer than the Ti–O(aryl) bonds: Ti1–O3 (1.828(3) Å), Ti1–O4 (1.795(3) Å). And all Ti–O bonds were shorter than those to the Ti–N: Ti1–N1 (2.234(3) Å), Ti1–N2 (2.182(3) Å, which were close to those in related titanium complexes with Schiff base ligands^{15 d, e, f}). In summary, the titanium located in a distorted octahedral geometry and the quadridentate ligand adopted β-*cis* configuration of complex **1** in the solid state.

All titanium complexes were studied as catalysts for the ROP of *rac*-LA. The monomer was dried 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. ¹H NMR and GPC were applied to calculate the *M*_n index of the PLA. All the polymers had the number-averaged molecular weights (analyzed through GPC and ¹H NMR spectra, e.g. see ‘d’ and ‘f’ in Fig. 4¹⁶) near theoretical ones (calculated from the monomer/catalyst molar ratio). The molecular weight (*M*_n) 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^{8a} and Verkade^{8b}, 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 would resulted in weaker titanium alkoxide bond. Similar situations also appeared in Al complexes in the previous reports.^{12a, 17}

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 ^tBu (see Table 1, Entries 1 and 2).

The poly(*rac*-LA) (Table 1, Entry 16) with the homonuclear decoupled ¹H NMR spectrum of the methane fragment¹⁸ (see Fig. 3) were also researched. The *P*_r¹⁹ value, 0.67, certified that these polymer chains were partially heterotactic. This value was higher than the relevant value (50%) in Ti complex **1** has been reported by Davidson^{8a}. The results showed that the *P*_r selectivities increased from 0.51 to 0.58 with the raise of the bulk of the substitutes on ligands (from hydrogen atoms to *tert*-butyls on phenyl rings) at 100 °C (see Table 1, Entries 10, 12). The *P*_r 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 approximated the corresponding value (96%) about Ti complex **8** which has been reported by Verkade.^{8b}

In order to studying the mechanism of initiation, end analysis of the oligo(lactide), which was synthesised by the ROP of the LA ([LA] : [1] = 14 : 1) was measured by ^1H 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 isopropoxycarbonyl 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,²⁰ the ROP selected a coordination insertion mechanism.²¹

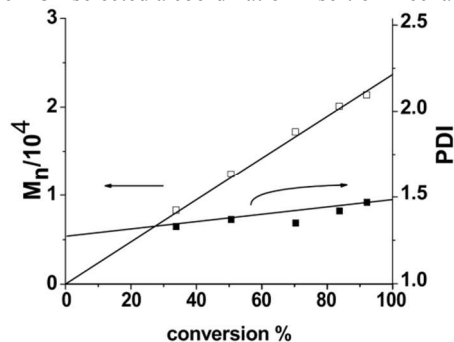


Figure 2. Plots of PLA's M_n and PDI in the light of *rac*-LA conversion employing complex **3**/isopropanol, $[\text{LA}]_0/[\text{cat.}]_0 = 100$, in toluene at 100 °C (Table 1, Entry 7).

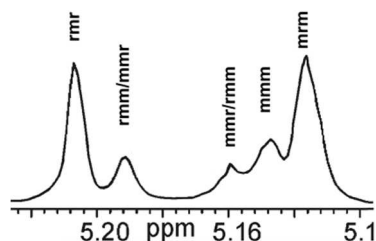


Figure 3. Homonuclear decoupled ^1H NMR spectrum of the methine part of poly(*rac*-LA) by **1** at 100 °C, $P_r = 0.67$, (Table 1, Entry 1, 400 MHz, CDCl_3).

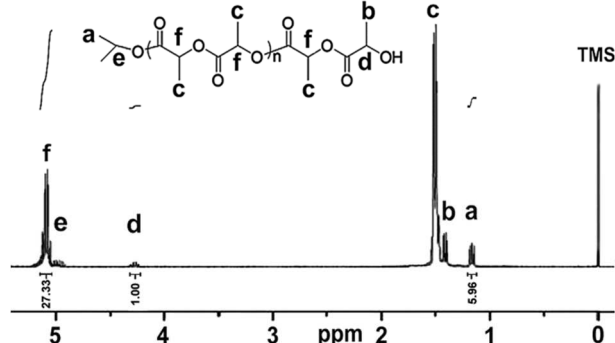


Figure 4. ^1H NMR spectrum of oligo(lactide) prepared by the **1** with $[\text{LA}] : [\text{1}] = 14 : 1$.

In summary, we report four new titanium complexes with octahedral framework chelated by Salen ligands adopting β -*cis* configuration that were employed as initiators for the polymerisation of LA in toluene solution or solventless. These ligands have certain ability to impact the P_r of the polymer, and this ability varies depending on ligands' bulk. Complex **1** showed the highest stereoselectivity for the ROP of *rac*-lactide affording partially heterotactic polylactide. These complexes proved to be efficient initiators for the ROP of lactides in the melt polymerization.

Experimental

3,5-di-*tert*-butylsalicylaldehyde, 1,3-propanediamine, 2,2-dimethyl-1,3-propanediamine, 3,5-dichlorosalicylaldehyde, salicylaldehyde and titanium tetraisopropoxide was obtained from Aldrich.

Ligands **1** – **4** were synthesised by published procedures.^{12a, 12b} 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 (**0.5** mmol) and the required quantity of lactides dried by 4A molecular sieves in advance in toluene (100 mL) 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 \times 3) to remove residual monomer. The solid was collected and dried in vacuo at 35 °C for 40 h.

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[†] Electronic Supplementary Information (ESI) available: X-ray crystallographic datum and refinement for complex **1** in CIF format, Figure S1–S5, Table S1–S2 and Experimental details. See DOI: 10.1039/c000000x/1. (a) K. E. Uhrich, S. M. Cannizzaro, R. S. Langer, K. M. Shakesheff, *Chem. Rev.* 1999, **99**, 3181–3198. (b) R. Langer, J. P. Vacanti, *Science*, 1993, **260**, 920–926. (c) M. J. Stanford, A. P. Dove, *Chem. Soc. Rev.* 2010, **39**, 486–494. (d) X. Song, F. Ling, X. S. Chen, *Acta Polymerica Sinica*, 2013, **1**, 95–101.

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