

New Titanium Complex bearing O, N, N, O-tetradentate Ligands: Synthesis, Characterization and Catalysis on the Ring-opening Polymerization of D, L-lactide

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Abstract. Poly (lactic acid) has become a hot topic in biomedical field due to good biocompatibility and biodegradability. As an important method for synthesis of poly lactic acid materials, ring-opening polymerization of lactide catalyzed by metal complexes can achieve the controllable polymerization of lactide by selecting appropriate ligand and metal. The metal complex of (LTi-O)₂ (L=3, 5-Di-tert-butylsalicylaldehyde-ethylenediamine) has been synthesized and characterized via element analysis and ¹H NMR spectroscopy. Furthermore, X-ray single crystal diffraction analysis has been used to determine the molecule structure of the complex (C₂/c, Z=4, a=25.495(8), b=16.189(4), c=17.559(5) Å, β=110.209(3) °, V=6801(3) Å³). The catalytic experimental results show that this Schiff-base complex has relatively high catalytic activity and controllability of molecular weights (PDI=1.09-1.24) in catalyzing ring-opening polymerization of D, L-lactide.

Introduction

Polylactide (PLA) has been widely used in textile, package, and biomedical field for its biocompatibility and biodegradability [1-5]. These degradable polyesters can be synthesized either by polycondensation of lactic acid or through ring-opening polymerization (ROP) of the cyclic dimer, namely lactide [6].

Ring-opening polymerization of lactide initiated by metal complexes is an efficient way to produce PLA. This method can enable control of polymer molecular weight and polymer architecture and can yield macromolecular samples with narrow molecular weight distributions [7]. The choice of supporting ligands on central metals is very important to the catalytic behavior of the complexes. Recently, various sterical ligands coordinated main group metal complexes, such as aluminium, magnesium, stannous, lithium; calcium had been reported to be effective catalysts or initiators for ROP of lactide [8-12].

Most recently, an important task for developing new catalytic systems is to make the catalysts or initiators more biocompatible and less toxic with a view to use in biomedical application [13]. Some metal complexes such as magnesium, calcium, zinc, aluminum, and tin (II) are attractive due to their low toxicity and have been reported to be effective catalysts for the ROP of lactide [14].

In the past decades, titanium (Ti) complexes have exhibited unique activity in producing poly ethylene (PE) with controlled molecular weights and microstructure [15, 16]. The catalytic activity of the titanium complexes could promote people to explore them further as catalysts for bulk and solution phase polymerization of lactide. Recently, titanium complexes featured bis(aryloxo), bis(trimethylsilyl)amides and biphenoxy ligands showed also catalytic activity for ROP of lactide [15-17]. However, the main drawback with the use of these catalysts is poor control in molecular weight and with broad polydispersity (PDI) due to high reactivity towards most organic solvents and the collocation ligands lack the protective obstacle.

We describe herein the preparation of a new Schiff-base titanium complex. The catalytic behaviours of the complex on the ROP of D, L-lactide were investigated. The results show that this complex can effectively catalyze polymerization of D, L-lactide.

Experimental

General Procedures

D, L-lactide was synthesized in our laboratory and was purified by repeated crystallization from ethyl acetate and dried under vacuum at 35°C for 24 h. The dehydration of toluene was performed by calcium hydride. Tetraethyl titanate, 3, 5-Di-tert-butylsalicylidene, ethanol, 1, 2-ethylenediamine and tetrahydrofuran (THF) of analytical reagent grade were purchased and used without purification.

Instrumentation

The elemental analysis (EA) of L and (LTi-O)₂ were carried out from a Vario EL III elemental analysis instrument (Elementary, Germany) with ICP-atomic emission spectroscopy performed.

¹H NMR spectra were obtained from a VANCE-500 NMR spectrometer (Bruker, Switzerland) using TMS as an internal standard in CDCl₃.

Single crystal diffraction data of (LTi-O)₂ were collected on an AFC10/Saturn724+ diffractometer with Mo K α radiation ($k = 0.71073 \text{ \AA}$). Intensity data were collected with the θ range from 3.04° to 27.51° in the $\omega/2\theta$ scan mode. The diffracted data were corrected for Lorentz polarization effects and empirical absorption corrections. The structure was solved using direct methods and refined by full-matrix least-squares procedures on F² using SHELX-97 program packages [18, 19].

Preparation of Title Complex

Preparation of Ligand (L). The 3, 5-Di-tert-butylsalicylaldehyde (9.4g, 0.04mol) was dissolved in 60ml ethanol at 78°C. After the solution stirred for 1h, 1, 2-ethylenediamine (1.2ml, 0.02mol) was added and the yellow lamellar solid was quickly precipitated. The solid was filtered and washed with heat ethanol, and then dried under vacuum for 24h. Yield: 79.32%. ¹H NMR (CDCl₃, 500 MHz, 25°C): δ =1.338(s, 18H, C(CH₃)₃), 1.493(s, 18H, C(CH₃)₃), 3.951(s, 4H, CH₂), 7.118(d, 2H, J=1.2 Hz, Ar-H), 7.421(d, 2H, J=1.5 Hz, Ar-H), 8.431 (s, 2H, CH), 13.678(s, 2H, OH). Anal. Calcd for C₃₂H₄₈O₂N₂: C, 78.00; H, 9.82; N, 5.69. Found: C, 79.9; H, 9.80; N, 5.66.

Preparation of (LTi-O)₂. The (LTi-O)₂ was prepared via an alcohol exchange method by Ligand, tetraethyl titanate and water in 1:1:1 molar ratio in toluene medium under dry and purified nitrogen. The mixture was stirred for 24h over night at room temperature. The yellow solid was crystallized from the toluene medium. Yield:

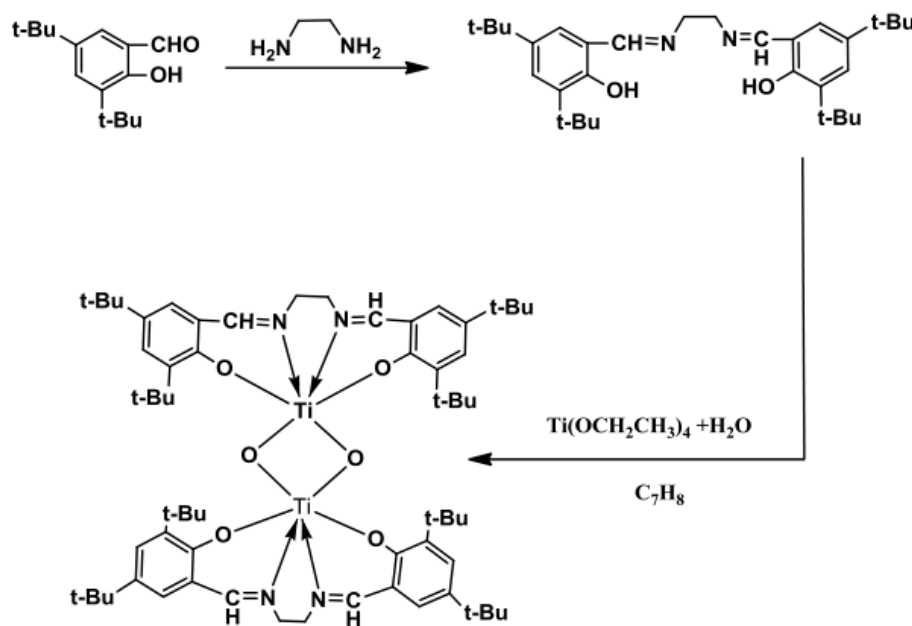
65.11%. ^1H NMR (CDCl_3 , 500 MHz, 25 $^\circ\text{C}$): 1.272 (s, 18H, C (CH_3)₃), 1.363 (s, 18H, C (CH_3)₃), 3.383 (d, 4H, $J=3.6$ Hz, CH_2), 4.418 (d, 4H, $J=3.3$ Hz, CH_2), 6.994 (d, 4H, $J=1.2$ Hz, Ar-H), 7.395 (d, 4H, $J=1.2$ Hz, Ar-H), 8.082 (s, 2H, CH). Anal. Calc. for $\text{C}_{64}\text{H}_{92}\text{N}_4\text{O}_6\text{Ti}_2$: C, 69.30; H, 8.36; N, 5.05. Found: C, 69.29; H, 8.34; N, 5.03

Polymerization Procedure

Bulk polymerizations of D, L-lactide were carried out in vacuum-sealed glass ampoules after all glass ampoules were dried at 180 $^\circ\text{C}$ for 3h in muffle furnace. The glass ampoules were charged with different D, L-lactide monomer to catalyst (LTi-O)₂ molar ratio. Then D, L-lactide was polymerized at 160 $^\circ\text{C}$. After a predetermined time, glass ampoules were removed and quenched to temperature around 25 $^\circ\text{C}$ to stop polymerization. Then the polymers were purified by dissolved in dichloromethane and precipitated from an excess of cold methanol, and the PLA was dried in vacuum at 35 $^\circ\text{C}$ for 24 h. The molecular weight and polydispersion index (PDI) of PLA were obtained from the GPC analysis and calibrated polystyrene standard. Three Agilent 1100 HPLC columns (300 \times 8.0 mm) were used in series with THF as the eluent at a flow rate of 1.0 ml/min at 25 $^\circ\text{C}$.

Results and Discussion

The synthesis route of (LTi-O)₂ is depicted in Scheme1. The Schiff-base ligand was synthesized via classical method which based on the condensation of primary amine (ethylenediamine) and aldehyde group (3, 5-Di-tert-butyl-salicylaldehyde). The (LTi-O)₂ was synthesized by interesterification of Ligand, $\text{Ti}(\text{OCH}_2\text{CH}_3)_4$ and water.



Scheme1 The synthetic route for (LTi-O)₂

Ligand and (LTi-O)₂ were characterized by EA and ^1H NMR spectroscopy. The structure of (LTi-O)₂ was further determined by X-ray single crystal diffraction analysis. The Mn and polydispersion index (PDI) of PLA were detected by GPC.

Crystal Structure

Suitable yellow single crystal was chosen for X-ray single crystal analysis. The crystal structure of (LTi-O)₂ complex is shown in Fig.1. Crystallographic data and selected bond distances and angles are listed in Table 1 and Table 2 respectively.

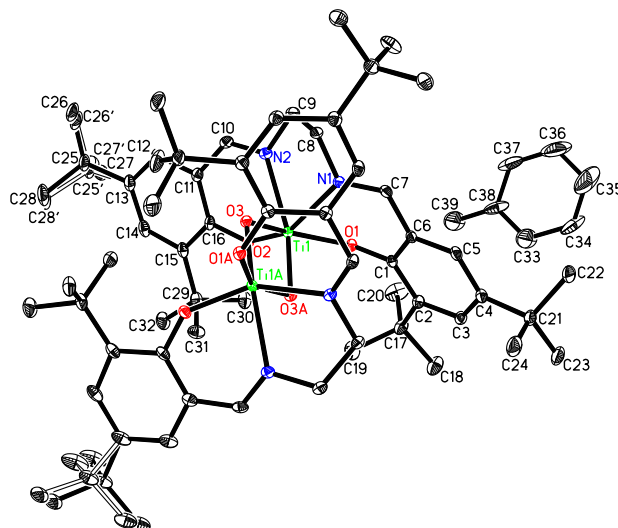


Figure 1. The crystal structure of (LTi-O)₂

As can be seen from the crystallographic data in Table 1, crystal system of (LTi-O)₂ is a monoclinic structure with C2/c space group. According to the Fig.1., there are a (LTi-O)₂ molecule and a toluene molecule in the crystal structure, which attributes to crystallization from toluene. The title complex is in a dimeric structure, i.e. two ligands bind to two titanium ions in an O, N, N, O-tetradentate mode respectively. However, two titanium ions bind each other via four O-Ti bonds. Therefore, there are two bonding manners to two Ti ions, including bridge-linking method of eight O-Ti covalent bonds and chelating method of four N→Ti coordination bonds. The bond lengths between O atom and center Ti are apparent approximate equality, ranging from 1.832(2) Å to 1.976(2) Å and the average bond distance is 1.891 Å. The bond lengths of two Ti-N are 2.187(3) Å and 2.269(2) Å respectively and the average bond length is 2.228 Å. The observed average bond lengths of Ti-O and Ti-N are in consistent with Ti-O single bond and Ti-N single bond character [20]. In addition, the distance of N1-C7(1.281(4) Å) and that of N2-C10 (1.286(4) Å) are in accordance to the lengths of C=N double bonds, such as dC=N=1.272 Å [21], dC=N =1.289 Å and other dC=N in salicylaldimines Schiff base complex. So the distances of N1-C7 and N2-C10 indicate clearly the double bond character.

Table1. Details of the crystallographic data and refinements for (LTi-O)₂

Formula	C ₇₁ H ₁₀₀ O ₆ N ₄ Ti ₂
Formula weight	1201.35
Crystal system	Monoclinic
Space group	C2/c
Temperature (K)	103(2)
Wavelength (Å)	0.71073
Crystal size	0.50 × 0.23 × 0.23 mm
Volume(Å ³)	6801(3)
Unit cell dimensions	
A (Å)	25.495(8)
B (Å)	16.189(4)
C (Å)	17.559(5)
α (°)	90
β (°)	110.209(3)
γ (°)	90
Z	4
Density (calculated)(Mg/m ³)	1.173
Absorption coefficient(mm ⁻¹)	0.287
F(0 0 0)	2584
θ Range for data collection (°)	3.04 -27.51
Index ranges	-31 ≤ h ≤ 33, -21 ≤ k ≤ 21, -22 ≤ l ≤ 17
Reflections collected/unique	26650 / 7755 (R(int) = 0.0480)
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9362 and 0.8700
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	7755 / 15 / 409
Goodness-of-fit on F ²	0.999
Final R indices [I > 2σ(I)]	R ₁ =0.0579, wR ₂ =0.1397
R indices (all data)	R ₁ =0.0805, wR ₂ =0.1551
Largest diff. peak and hole (e Å ⁻³)	0.452 and -0.551

Table 2. Selected bond lengths (Å) and angles (°) of (LTi-O)₂

Bond lengths			
Ti(1)-O(1)	1.976(2)	Ti(1)-N(1)	2.187(3)
Ti(1)-O(2)	1.885(2)	Ti(1)-N(2)	2.269(2)
Ti(1)-O(3)	1.870(2)	O(1)-C(1)	1.327(3)
Ti(1)-O(3)A	1.832(2)	O(2)-C(16)	1.339(3)
Angles			
O(3)A-Ti(1)-O(3)	81.56(9)	O(2)-Ti(1)-O(1)	97.83(9)
O(3)A-Ti(1)-O(1)	88.22(9)	O(3)A-Ti(1)-N(1)	109.97(9)
O(1)-Ti(1)-N(1)	77.99(9)	O(3)-Ti(1)-N(1)	81.85(9)
N(1)-Ti(1)-N(2)	71.85(9)	O(2)-Ti(1)-N(1)	148.12(9)
O(2)-Ti(1)-N(2)	79.91(9)	O(3)A-Ti(1)-N(2)	162.95(9)
O(3)-Ti(1)-O(2)	108.93(9)	Ti(1)A-O(3)-Ti(1)	98.32(9)
O(3)-Ti(1)-N(2)	81.96(9)	O(1)-Ti(1)-N(2)	108.55(9)
O(3)-Ti(1)-O(1)	152.72(9)	O(3)A-Ti(1)-Ti(1)A	41.35(6)
O(3)-Ti(1)-Ti(1)A	40.32(6)	O(2)-Ti(1)-Ti(1)A	112.59(6)
O(1)-Ti(1)-Ti(1)A	123.66(6)	N(1)-Ti(1)-Ti(1)A	95.17(6)
N(2)-Ti(1)-Ti(1)A	122.28(7)		

ROP of D, L-LA

ROP of D, L-LA employing (LTi-O)₂ as catalyst under solvent-free conditions was systematically examined as shown in Table 3.

Table 3. The detail results of ROP

Entry	[M] ₀ /[I] ₀	t(h)	T(°C)	PDI	M _n ^a (×10 ⁴)	Conv (%)
1	2300:1	16	160	1.21	8.980	90.10
2	2600:1	16	160	1.16	9.058	95.21
3	2800:1	16	160	1.14	8.973	88.51
4	3000:1	16	160	1.09	8.762	78.00
5	2600:1	6	160	1.12	8.912	90.21
6	2600:1	12	160	1.15	8.960	94.00
7	2600:1	16	160	1.16	9.058	95.21
8	2600:1	20	160	1.24	9.210	95.00
9	2600:1	16	150	1.13	8.910	91.10
10	2600:1	16	160	1.16	9.058	95.21
11	2600:1	16	170	1.20	8.810	95.19
12	2600:1	16	180	1.21	8.627	95.16

^a Determined from GPC measurements (THF at 1 ml per minute, relative to polystyrene standards).

The experimental results indicate that (LTi-O)₂ is active for the ROP of D, L-LA. The Mn of PDLLA varies from 8.762×10⁴~9.210×10⁴ g/mol with molecular weight distribution of 1.09~1.24. The PDIs of PDLLA are lower than those of the normal

polymer obtained via ROP of LA catalyzed by tin-octanoate. The low PDIs demonstrate a good control of polymerization procedure.

Conclusions

In conclusion, a novel titanium Schiff base complex has been prepared and characterized by NMR and EA analysis. Furthermore, the X-ray crystal structure of $(\text{LTi-O})_2$ was investigated. The results show that the title complex is a binuclear complex formed with two Ti(IV) and two salicylaldehyde Schiff-base ligands. The complex has shown great reactivity for ROP of D, L-LA, under melt conditions, to produce polymer. The new complex reveals the same practically quantitative conversion degrees and produced polymers with lower PDIs with respect to reference tin-octanoate.

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