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ORIGINAL PAPER

The novel $[(dME)_2(HIM)P]_2Ti(IV)$ complex: synthesize, characterization, and its utility in ROP of D,L-lactide

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Abstract The novel {2,4-bis(1,1-dimethylethyl)-6-{[(2-hydroxyethyl)imino]methyl} phenoxy}$_2$ titanium(IV) complex {$[(dME)_2(HIM)P]_2Ti(IV)$} had been synthesized and characterized by EA, XRF, IR, and NMR methods. The $[(dME)_2(HIM)P]_2Ti(IV)$ complex was reactive and promoted ring-opening polymerization (ROP) of D,L-lactide in the presence of benzyl alcohol (BnOH). And the results showed that ROP of D,L-lactide were produced upon addition of an excess (1–8 equiv.) of external BnOH. The complex showed a living and controlled fashion ($M_w/M_n = 1.15$–1.32) for ROP of D,L-lactide and could produce the poly(D,L-lactide) with average molecular weight (M_n) up to 8.87×10^4 g mol^{-1}. The mechanism study by ^{1}H NMR spectrum of poly(D,L-lactide) with terminal benzyl ester group and $[(dME)_2(HIM)P]_2Ti(IV)$ complex revealed that the polymerization proceeded through the traditional activated monomer mechanism and the acyl-oxygen bond cleavage mode of monomer. And the ^{13}C NMR spectra and TG/DSC analysis showed that poly(D,L-lactide) was essential atactic and thermal stable polymer.

Keywords Titanium complex · ROP · D,L-Lactide · Atactic

Introduction

In recent years, the massive use and disposal of petroleum-based plastics had been seriously caused the environmental hazards. To address these problems, people should develop the renewable, degradable, and recyclable "green materials" as the replacements for the petroleum-based materials [1]. The most popular and important

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biodegradable aliphatic polyesters, such as polylactic acid or polylactide (PLA), polyethylene oxide (PEO), poly(ε-caprolactone) (PCL), poly(3-hydroxybutyrate) (PHB), and polyglycolic acid (PGA) had drawn much attention.

PLA was biodegradable and biocompatible polyester that had been used for decades, and it was suitable for a variety of application for its excellent mechanical and physical properties, such as packaging materials, surgical sutures, drug delivery systems, and scaffolds for tissue engineering [2–4]. The commercial PLA were usually synthesized by polycondensation method from lactic acid. However, the polycondensation route had inherent drawbacks like poor kinetic control and difficulty in removal of liberated byproduct water, so it was difficult to give the high molecular weight PLA. The PLA was usually prepared by ring-opening polymerization (ROP) of L-lactide or D,L-lactide, thus the metal alkoxides were known to be efficient catalysts or initiators for the ROP of the L-lactide or D,L-lactide. Most recently, an important task for developing new catalytic system was to make metal complexes afford well-controlled polymerization of D,L-lactide, therefore, these metal complexes, such as tin [5, 6], aluminum [7–9], lithium [10], magnesium [11], zinc [12, 13], iron [14, 15], and other transition metal complexes [16–19], seemed to be suitable for this purpose.

Phenoxy-imines were a versatile class of ligands that displayed the ranges of diverse application spanning from bioinorganic chemistry [20] to coordination chemistry [21], chemical catalysis [22, 23], and materials-related application [24, 25]. Such as, the Al complex catalysts [8] containing a series of phenoxy-imine ligands had showed the catalytic activity for ROP of various cyclic esters. Recently, it was reported that the phenoxy-imine Ti(IV) and Zr(IV) complexes were active for lactide polymerization [26], as well, Jones and co-workers [27–29] also observed that a serious of phenoxy-imine Ti(IV) complexes were extremely active for the polymerization of D,L-lactide. In the case of D,L-lactide, Jones's complexes as catalysts produced atactic PLA. However, the literature [30] reported that the titanium alkoxides as initiators could produce heterotactic-biased poly(D,L-lactide), and increased heterotactic-biased poly(D,L-lactide) was formed as the number of chlorine atoms increased in $TiCl_x(O\text{-}i\text{-}Pr)_{4-x}$.

Therefore, we stimulated similarly to explore the ROP of D,L-lactide because of the poly(D,L-lactide) eco-friendly feature. One of our core programs was to design novel catalyst with phenoxy-imine ligand for well-controlled ROP of D,L-lactide. In this contribution, we described the preparation and characterization of a novel $[(dME)_2(HIM)P]_2Ti(IV)$ complex with phenoxy-imine ligands. The catalytic activity of the $[(dME)_2(HIM)P]_2Ti(IV)$ complex in the ROP of D,L-lactide was further discussed, and theoretical polymerization mechanism was also discussed.

Experimental section

Materials

All the experiments were performed in the condition of dry and purified nitrogen (99.99%). The D,L-lactide was synthesized by polycondensation and depolymerization reactions from D,L-lactic acid in our laboratory and purified by crystallizing with ethyl acetate, then dried in vacuum at 35 °C for 48 h. The dehydration of toluene and *n*-hexane was performed with calcium hydride (CaH_2) and phosphorus pentoxide (P_2O_5), respectively. All other materials were of analytical grade and used as received.

Measurements

The elemental analysis (EA) was carried out from a Vario EL III elemental analysis instrument (Elementar, Germany). The infrared spectra (IR) and X-ray fluorescence (XRF) spectroscopy were recorded on a Perkin-Elmer GX spectrometer (Perkin-Elmer, USA) and a XRF 1800 CCDE spectrometer (Shimadzu, Japan) in KBr disc, respectively. The ^1H and ^{13}C NMR spectra were obtained from an AVANCE-500 NMR spectrometer (Bruker, Switzerland) in deuterated chloroform ($CDCl_3$) using tetramethylsilane (TMS) as an internal standard. Number averaged molecular weight (M_n), weight averaged molecular weight (M_w), and polydispersity indexes (PDIs) of these poly(D,L-lactide)s were determined by gel permeation chromatographic (GPC) instrument equipped with multi angle laser light scattering detector (MALS). Molecular weights were calibrated according to polystyrene standards. Tetrahydrofuran (THF) was used as an eluent at a flow rate of 1.0 ml min^{-1} at 40 °C. Thermogravimetric (TG) and differential scanning calorimetric (DSC) analysis were carried out using with STA449C instrument (Netzsch, Germany) under argon atmosphere at a heating rate of 10 °C min^{-1}.

Synthesis of 2,4-bis(1,1-dimethylethyl)-6-{[(2-hydroxyethyl)imino]methyl}phenol [$(dME)_2(HIM)P\text{-}H_2$] ligand

3,5-di-*tert*-Butylsalicylaldehyde (9.37 g, 40 mmol) and ethanolamine (2.5 ml, 40 mmol) were refluxed for 3 h in ethanol (60 ml). The solvent was evaporated and the residue was purified by crystallizing using *n*-hexane (20 ml) at −20 °C to afford the Schiff base ligand as a yellow solid in 84% (9.30 g) yield. Anal. calcd for $C_{17}H_{27}NO_2$ (277.40): C 73.61, H 9.81, N 5.05; Found: C 73.68, H 9.83, N 5.07.

Synthesis of the {2,4-bis(1,1-dimethylethyl)-6-{[(2-hydroxyethyl)imino]methyl}phenoxy}$_2$ Ti(IV) complex {$[(dME)_2(HIM)P]_2Ti(IV)$}

2,4-Bis(1,1-dimethylethyl)-6-{[(2-hydroxyethyl)imino]methyl}phenol Schiff base ligand (5.55 g, 20 mmol) and tetraethyl titanate (2.1 ml, 10 mmol) were stirred in toluene (20 ml) for 24 h at ambient temperature. The solvent was evaporated and the residue was purified by crystallizing using *n*-hexane (10 ml) at −20 °C to afford the {2,4-bis(1,1-dimethylethyl)-6-{[(2-hydroxyethyl)imino]methyl} phenoxy} Ti(IV) complex {$[(dME)_2(HIM)P]_2Ti(IV)$} as yellow crystal in 82% (4.88 g) yield. Anal. calcd for $C_{34}H_{50}N_2O_4Ti$ (598.27): C 68.21, H 8.42, N 4.68; Found: C 68.28, H 8.39, N 4.63.

ROP of D,L-lactide using $[(dME)_2(HIM)P]_2Ti(IV)$ complex as catalyst

Bulk polymerizations of D,L-lactide were carried out in vacuum-sealed glass ampoules. The glass ampoules were first charged with the designed monomer (D,L-lactide) and benzyl alcohol ($[M]_0/[BnOH]_0$, M = D,L-lactide, BnOH = benzyl alcohol) in Table 1, subsequently, $(dME)_2(HIM)P]_2Ti(IV)$ complex was dissolved in dichloromethane and then added keeping with the designed $[M]_0/[Ti]_0/[BnOH]_0$ (Ti = $(dME)_2(HIM)P]_2Ti(IV)$ complex) by a syringe, as shown in Table 1. The ampoules were heated at 40 °C under vacuum to remove the dichloromethane and purged with dry nitrogen. Then these ampoules were sealed under high vacuum and immersed in an oil bath. Polymerizations were carried out at 160 °C. After a predetermined time, the glass ampoules were cooled in liquid nitrogen, and the sealed ampoules were broken and the poly(D,L-lactide) samples were removed by dissolving in chloroform and precipitating in ethanol. The obtained poly(D,L-lactide) were separated by filtration, dried under reduced pressure, and characterized by ^1H and ^{13}C NMR spectra, gel permeation chromatography, and TG/DSC analysis.

Results and discussion

Characterization of $(dME)_2(HIM)P\text{-}H_2$ ligand and $[(dME)_2(HIM)P]_2Ti(IV)$ complex

X-Ray fluorescence (XRF) spectroscopy was a powerful method to assay most of chemical compositions of solid and liquid samples [31]. Figure 1 shows the XRF spectrum of the complex, and two peaks corresponded to the Ti Kα line and Ti Kβ line shown at 86° and 77°, respectively, which indicated that there was titanium (Ti) in the complex sample and the complex might had been prepared through alcohol exchange reaction between $(dME)_2(HIM)P\text{-}H_2$ ligand and tetraethyl titanate. In the presence of KBr, three peaks of bromine (Br) shown at different degree in the Fig. 3, and they were coincident with two Br Kα lines and a Br Kβ line. But the peaks of other elements were out of the scanning degree.

Figure 2 shows IR spectra of $(dME)_2(HIM)P\text{-}H_2$ ligand (a) and $[(dME)_2(HIM)P)]_2Ti(IV)$ complex (b). In the IR spectrum (a in Fig. 2) of the $(dME)_2(HIM)P\text{-}H_2$ ligand, the peak at 3,326 cm^{-1} represented the stretching vibration of alcohol hydroxyl (–OH), and two peaks at 1,471 and 1,441 cm^{-1} represented deformation vibration of phenol hydroxyl. However, these peaks had disappeared in the IR spectrum (b in Fig. 2) of $[(dME)_2(HIM)P]_2Ti(IV)$ complex, and other two peaks that were ascribed to the stretching vibration of N → Ti coordination bond and O–Ti covalent bond occurred at 579 and 559 cm^{-1}, respectively. On the other hand, the stretching vibration peak of imino group (–CH=N) in $(dME)_2(HIM)P\text{-}H_2$ ligand showed at 1,634 cm^{-1}(a in Fig. 2), however, it shifted to 1,623 cm^{-1} in $[(dME)_2(HIM)P]_2Ti(IV)$ complex (b in Fig. 2) due to the nitrogen coordination with Ti, which revealed that the $(dME)_2(HIM)P\text{-}H_2$ ligand had reacted with tetraethyl titanate following the alcohol exchange protocol.

Table 1 ROP of D,L-lactide catalyzed by a binary catalyst $[(dME)_2(HIM)P]_2Ti(IV)/BnOH$ in bulk phase

Entries	$[M]_0$/ $[Ti]_0$/ $[BnOH]_0$	Time (h)	M_w^a (obsd) (g/mol)	M_n^a (obsd) (g/mol)	M_n^b (calcd) (g/mol)	M_n^c (NMR) (g/mol)	Conversion[c] (%)	Yield[d] (%)	PDI[e]
1	400/1/1	6	49,200	39,700	37,500	43,200	65	55	1.24
2	400/1/2	8	29,000	23,000	21,700	24,400	75	67	1.26
3	400/1/4	12	16,100	13,200	11,300	14,500	78	70	1.22
4	800/1/1	8	91,700	76,400	85,300	78,700	74	66	1.20
5	800/1/2	12	62,300	51,100	49,100	57,700	85	74	1.22
6	800/1/4	16	31,200	26,400	23,100	21,700	80	70	1.18
7	1,200/1/1	12	90,600	77,400	120,900	82,300	70	64	1.17
8	1,200/1/2	16	82,100	68,300	73,500	63,300	85	77	1.19
9	1,200/1/4	20	40,600	34,700	30,600	33,400	85	81	1.17
10	1,600/1/1	10	100,900	76,500	149,900	67,700	65	55	1.30
11	1,600/1/2	14	102,800	87,100	110,700	84,500	96	91	1.18
12	1,600/1/4	18	66,600	57,400	54,300	51,200	94	90	1.16
13	1,600/1/8	22	28,900	24,500	26,300	22,300	91	85	1.18
14	2,200/1/2	14	97,300	77,200	125,200	76,400	79	37	1.26
15	2,200/1/4	18	73,500	58,300	55,500	52,400	70	61	1.26
16	2,200/1/8	22	36,700	27,800	25,500	38,400	64	52	1.32
17	1,000/1/2	12	74,100	62,300	64,200	63,300	89	78	1.19
18	1,200/1/2	12	91,600	78,200	82, 200	77,900	95	91	1.17
19	1,400/1/2	12	96,900	84,300	96,800	85,700	96	94	1.15
20	1,600/1/2	12	100,300	86,500	109,600	87,700	95	92	1.16
21	1,800/1/2	12	10,000	84,800	124,600	86,500	96	91	1.18
22	2,000/1/2	12	99,300	82,100	120,900	84,200	84	76	1.21
23	2,400/1/2	12	89,300	72,600	129,700	73,200	75	70	1.23
24	1,600/1/2	4	87,800	73,200	85,300	76,200	74	70	1.20
25	1,600/1/2	6	92,300	78,100	98,000	80,500	85	81	1.18
26	1,600/1/2	8	98,500	84,200	107,200	82,500	93	90	1.17
27	1,600/1/2	12	100,300	86,500	109,500	87,700	95	92	1.16
28	1,600/1/2	16	102,000	88,700	111,900	90,200	97	94	1.15
29	1,600/1/2	20	103,400	86,900	111,900	90,800	98	95	1.19

Polymerization performed in bulk phase with $[M]_0 = 0.1$ mol at 160 °C

[a] Determined by gel permeation chromatography (GPC) and calibrated by a polystyrene standard [M_n^a(obsd) $= 0.56$ M_n(GPC)] [33]

[b] Calculated from the molecular weight of D,L-lactide × $[M]_0/[BnOH]_0$ × the conversion yield + M_{BnOH}, with $M_{BnOH} = 108$ g mol^{-1} [34, 35]

[c] Determined by ^{1}H NMR spectrum

[d] Obtained from weight of polymer obtained/weight of monomer used

[e] Obtained from M_w(obsd)/M_n(obsd)

Figure 3A, and B shows the ^{1}H NMR and ^{13}C NMR spectra of $(dME)_2(HIM)P\text{-}H_2$ ligand, respectively, their proton and carbon peaks were in good agreement with the structure of phenoxy-imine ligand. Figure 4A and B also shows the ^{1}H NMR

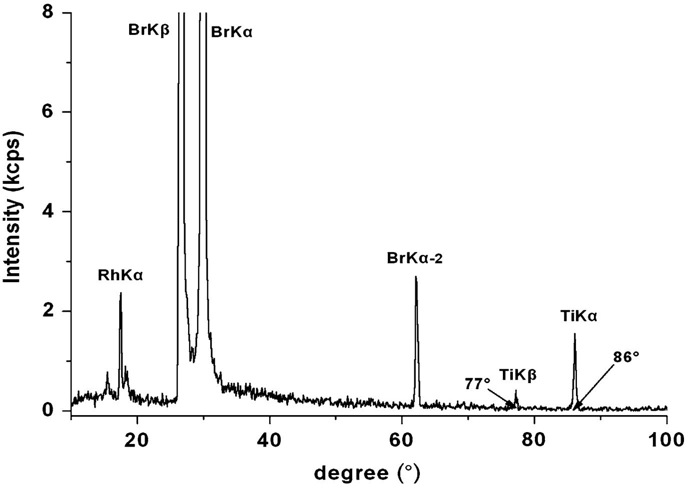


Fig. 1 XRF spectroscopy of $[(dME)_2(HIM)P)]_2Ti(IV)$ complex

and ^{13}C NMR spectra of $[(dME)_2(HIM)P]_2Ti(IV)$ complex, respectively. Compared to $(dME)_2(HIM)P\text{-}H_2$ ligand (Fig. 3A), two methylene ($-CH_2$) proton peaks (c and d in Fig. 4A) of $[(dME)_2(HIM)P]_2Ti(IV)$ complex had shifted to the lower field. Especially, the methylene ($-CH_2$) protons peak (c in Fig. 3A) had been split to two symmetrical quartet peaks (c in Fig. 4A) in $[(dME)_2(HIM)P]_2Ti(IV)$ complex for the deshielding, which revealed that the electron cloud density of nitrogen atom in imine group ($-CH=N$) was decreased due to its coordination with Ti. And also, the chemical shift distance of two carbon peaks (c and d in Fig. 4B) was wider than that of two carbon peaks (c and d in Fig. 3B). These observations indicated that $[(dME)_2(HIM)P]_2Ti(IV)$ complex was prepared successfully and its structure is shown in Fig. 4.

ROP and proposed mechanism of D,L-lactide catalyzed by a binary catalyst $[(dME)_2(HIM)P]_2Ti(IV)/BnOH$

ROP of D,L-lactide were carried out by employing $[(dME)_2(HIM)P]_2Ti(IV)$ complex and BnOH as a binary catalyst and the polymerization reactions were systematically examined in bulk phase at 160 °C, as well as molar ratio of $[M]_0/[Ti]_0/[BnOH]_0$ and reaction time were investigated, which is summarized in Table 1. When the temperature of the mixture samples reached 160 °C, the polymerizations were visually indicated by a distinct color change and formation of dark-brown viscous mass in case of the $[(dME)_2(HIM)P]_2Ti(IV)$ complex, and the change of viscosity was also clearly noticed. However, the color change was not apparent but a change of viscosity was clearly noticed for the ROP of D,L-lactide in the presence of Sn(II) catalyst [32]. The polymers precipitated in ethanol solution leaded to the polymers having light brown to pale yellow coloration, but repeated reprecipitation was found essential to decolorize the polymers to acceptable levels for further characterization. The number average molecular weight (M_n) and polydispersity indexes (PDIs) of poly(D,L-lactide) samples based on GPC were determined.

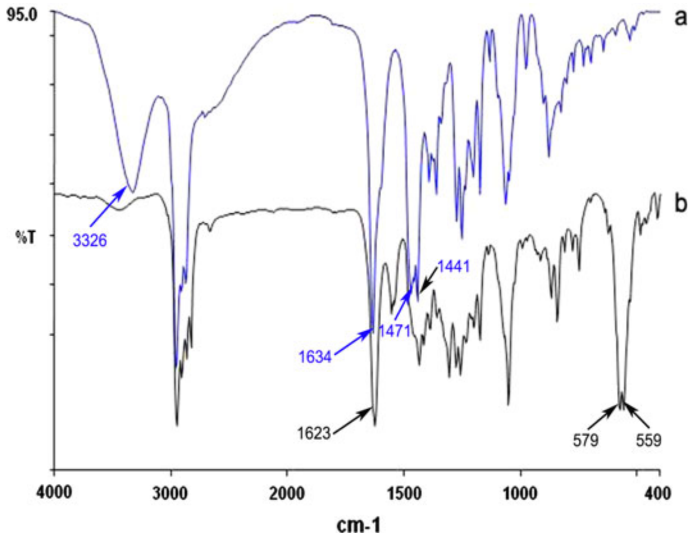


Fig. 2 The comparison of FTIR spectra for $(dME)_2(HIM)P\text{-}H_2$ ligand (*a*) and $[(dME)_2(HIM)P)]_2Ti(IV)$ complex (*b*)

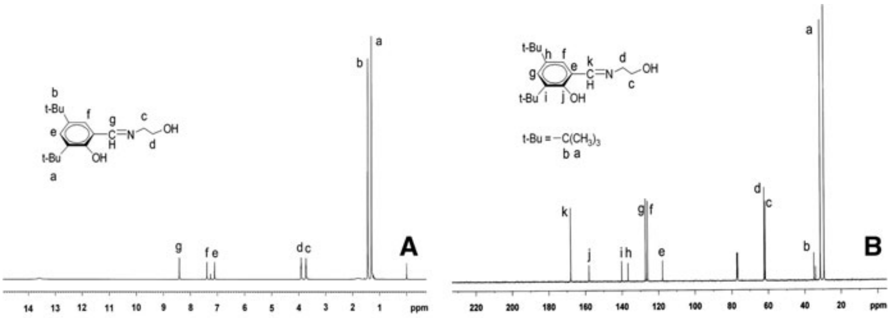


Fig. 3 ^{1}H NMR (**A**) and ^{13}C NMR (**B**) spectra of $(dME)_2(HIM)P\text{-}H_2$ ligand

In Table 1, all observed molecular weights based on GPC with $[(dME)_2(HIM)P]_2Ti(IV)$ complex as catalyst were above 1×10^4 g mol^{-1}. The ROP of D,L-lactide in bulk phase at 160 °C were produced upon of addition of an excess (1–8 equiv.) of external benzyl alcohol (BnOH). There the $[(dME)_2(HIM)P]_2Ti(IV)$ complex/BnOH as a binary catalyst, most of agreements between experimental andTable 1, entries 2, 5, and 17–20). However, an increase of the $[M]_0/[Ti]_0/[BnOH]_0$ molar ratios ranging from 1,800/1/2 to 2,400/1/2 showed a decrease in polymer molecular weights (Table 1, entries 21–23), which revealed that the M_n was consistent with $[M]_0/[Ti]_0/[BnOH]_0$ molar ratios under same polymerization temperature and reaction time, and the higher molecular weight (M_n) was up to 8.65×10^4 g mol^{-1}

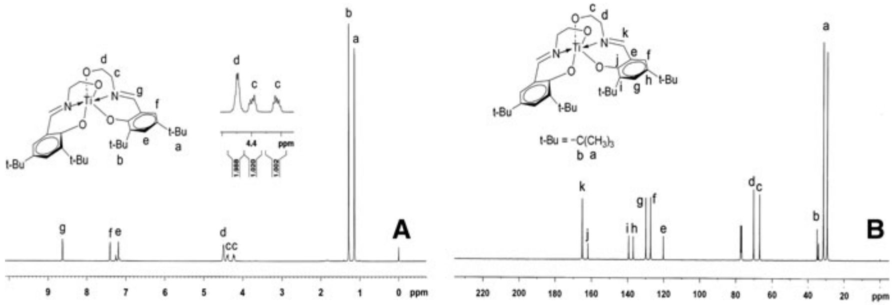


Fig. 4 ^{1}H NMR (**A**) and ^{13}C NMR (**B**) spectra of [(dME)$_2$(HIM)P]$_2$Ti(IV) complex

(Table 1, entry 20). Similarly, the reaction time also showed a positive effect on overall conversion of D,L-lactide (Table 1, entries 24–28). With the variation of reaction time (Table 1, entries 24–27), the conversion of D,L-lactide increases quickly (74–95%), then went temperedly (95–98%) from 16 to 20 h (Table 1, entries 27–29). Therefore, there were no obvious changes with prolonged reaction time to the conversion, and the yield of poly(D,L-lactide) was similar tendency with the conversion. Here, there was a linear relationship between the M_n and conversion at the $[M]_0/[Ti]_0/[BnOH]_0$ molar ratios ranging from 400/1/2 to 1,600/1/2 (Table 1, entries 24–28) after 12 h at 160 °C, and the molecular weight distribution was relatively narrow ($M_w/M_n = 1.15$–1.20), which indicated that a living and controlled fashion of polymerization was also accomplished (in Fig. 5).

Worth was the comparison of the [(dME)$_2$(HIM)P)]$_2$Ti(IV) complex as catalyst with the reported similar systems catalyst, such as titanium biphenoxy-alkoxide [32] and titanium bis(aryloxo) complexes [Ti$_2$(μ-OEt)$_2$(edbp)$_2$(OEt)$_2$ and Ti(edbp)(O^{i}Pr)$_2$ complex, edbp-H$_2$ = 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol] catalysts [36]. In our study, the higher molecular weight PLA polymers were consistently obtained at the [M]:[Ti] ratio 1,600:1 after 4–20 h at 160 °C (Table 1, entries 24–29). Though the obtained higher monomer conversion and yields within 2.5 h at much catalyst loadings, the molecular weights of obtained PLA polymers with titanium biphenoxy-alkoxide and titanium bis(aryloxo) complexes as catalysts were below 2×10^4 g mol^{-1}, yielding the PLAs with wide molecular weight distribution. As well other similar catalysts systems, Salen–Na$_2$ complex [37] [Salen = *N*,*N*′-bis(3,5-di-*tert*-butyl-salicylidene)-1,3-propanediamine] showed higher catalytic activity for ROP of L-lactide at the [M]:[Cat] ratio 500:1 after 18.5 h at 30 °C, the number averaged molecular weight (M_n) of obtained PLA was close to 7×10^4 g mol^{-1} and the monomer conversion was above 95%. However, the polydispersity index (PDI) of the PLA was above 1.40. Therefore, it revealed that the [(dME)$_2$(HIM)P]$_2$Ti(IV) complex showed higher catalytic activity for ROP of D,L-lactide and a well-controlled manner at 160 °C, and the obtained polymers had a controlled molecular weight and low polydispersity indexes (PDIs).

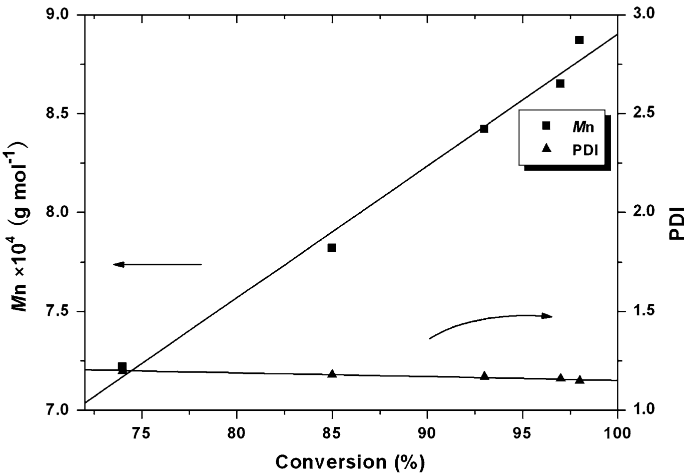


Fig. 5 Plot of M_n (■) and PDI (▲) versus monomer conversion for ROP of D,L-lactide catalyzed by a binary catalyst $[(dME)_2(HIM)P]_2Ti(IV)$/BnOH (bulk phase, 160 °C, $[M]_0/[Ti]_0/[BnOH]_0 = 1{,}600$, here M: D,L-lactide monomer, Ti: $[(dME)_2(HIM)P]_2Ti(IV)$ complex, BnOH: benzyl alcohol)

The formation of alkoxide species was monitored by ^1H NMR spectroscopy in CD_3Cl, and Fig. 6 shows ^1H NMR spectrum of poly(D,L-lactide) in the presence of the binary catalyst $[(dME)_2(HIM)P]_2Ti(IV)$/BnOH. When D,L-lactide was added to the Ti(IV) alkoxide generated by reacting $[(dME)_2(HIM)P]_2Ti(IV)$ complex with benzyl alcohol in 1:2 ratio, the polymerization started instantaneously. Then the poly(D,L-lactide) with terminal benzyl ester group and $[(dME)_2(HIM)P]_2Ti(IV)$ complex could be obtained by dissolving in chloroform and precipitating in ethanol and identified (Fig. 6). The ^1H NMR spectrum analysis of the obtained poly(D,L-lactide) clearly showed the existence of Ti(IV) alkoxide and terminal benzyl ester group. Furthermore, no free benzyl alcohol and lactide monomer could be observed in the polymerization, showing that the mechanism for the ROP of D,L-lactide agreed with the traditional-activated monomer mechanism.

From the previous ^1H NMR spectrum (Fig. 6), we concluded that the proposed mechanism for ROP of D,L-lactide was catalyzed by the binary catalyst $[(dME)_2(HIM)P]_2Ti(IV)$/BnOH. On the basis of the $[(dME)_2(HIM)P]_2Ti(IV)$ complex, which should be a prominent feature in an activated monomer mechanism, where the D,L-lactide monomers were activated by the metal center of the complex (Scheme 1). In the presence of benzyl alcohol, the titanium alkoxide complex with activated monomers was nucleophilic attacked of hydroxy group of benzyl alcohol, then the poly(D,L-lactide) oligomers with terminal benzyl ester group were obtained by the exchange/transfer reactions. Subsequently, the polymerization of other activated monomers proceeded by the nucleophilic attack of hydroxy group of the poly(D,L-lactide) oligomers to the monomer activated by coordination of titanium. The similar mechanism was proposed in the literature [38, 39].

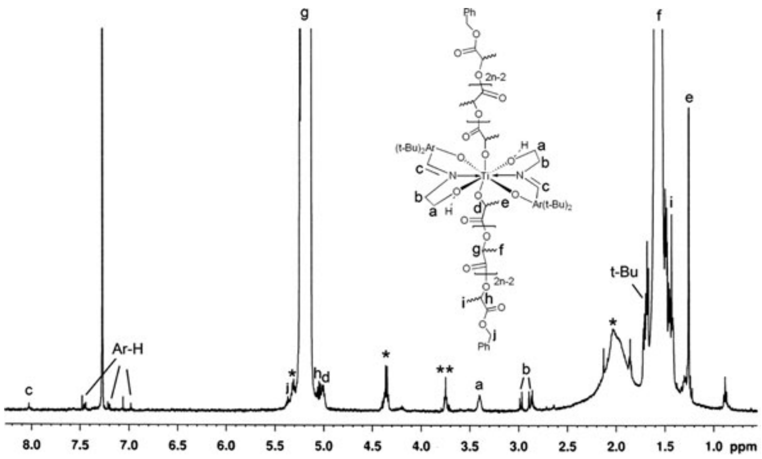
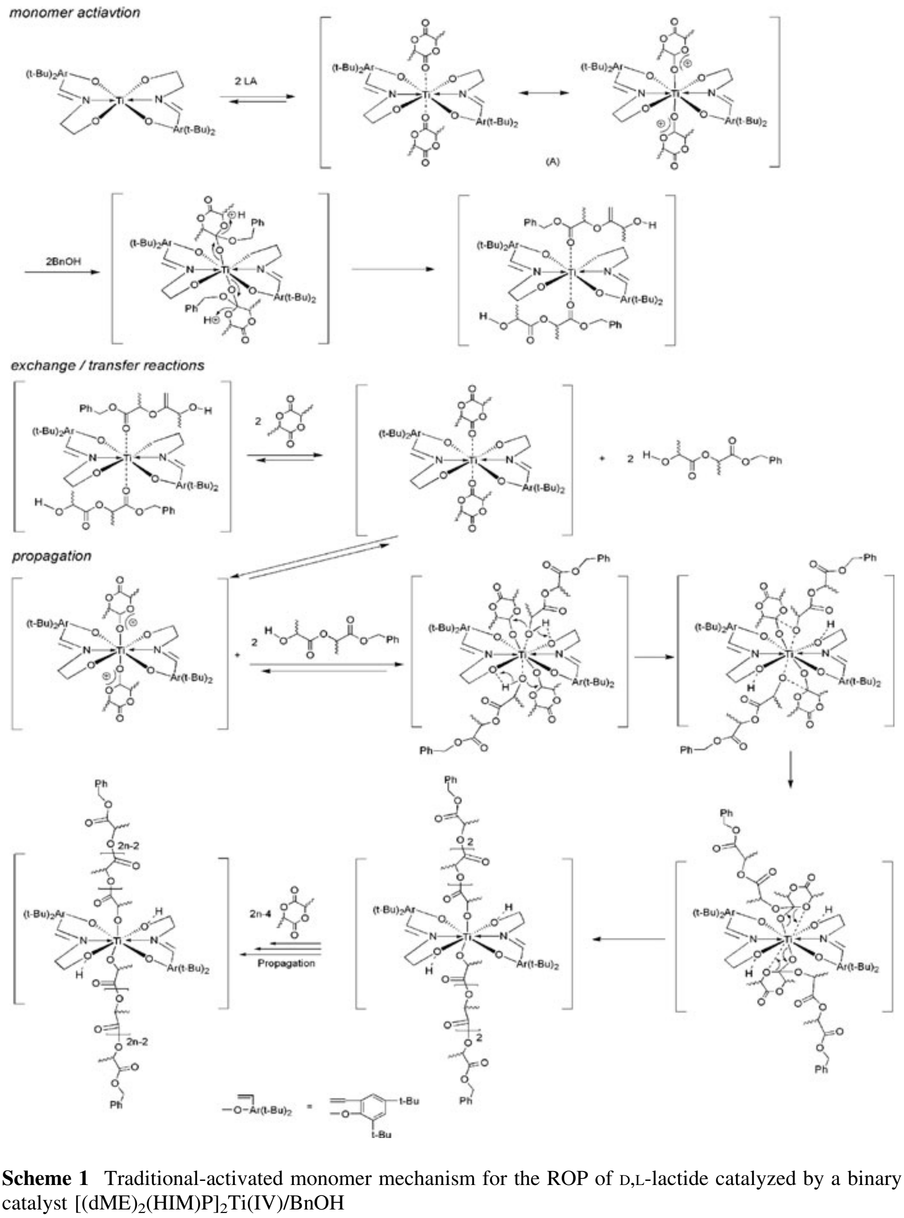


Fig. 6 ^{1}H NMR spectrum of poly(D,L-lactide) with terminal benzyl ester group and $[(dME)_2(HIM)P]_2Ti(IV)$ complex [*a few poly(D,L-lactide)s with terminal benzyl ester group; **methylene proton peaks of rudimental ethanol; $[M]_0/[Ti]_0/[BnOH]_0 = 400:1:2$, at 160 °C for 12 h]

The ^{13}C NMR spectrum and thermal analysis of PLA

It was reported that carbonyl (–C=O) and methine (–CH) carbons were the stereosensitive groups leading to hexad and tetrad sequences, respectively [40]. Figure 7 shows the ^{13}C NMR spectrum of poly(D,L-lactide) with $[(dME)_2(HIM)P]_2Ti(IV)$/BnOH as a binary catalyst. The peaks due to methyl carbon, methine carbon, and carbonyl carbon were observed at 16.6–17.7, 68.9–69.2, and 169.1–169.2 ppm, respectively. The carbon peak assignment to the corresponding carbon atoms was in good agreement with the chemical structure of PLA, and they were different from the single peak of the corresponding carbon atoms of poly(L-lactide). On the other hand, the presence of syndiotactic dyad at 69.4 ppm could be ascribed to the methine protons resonance absorption peak in iss stereosequence, which indicated that there was intermolecular transesterification in ROP of lactide [41]. However, there is no visible peak of iss stereosequence at 69.4 ppm in Fig. 7, and it revealed that no notable intermolecular transesterification leaded to the formation of iss stereosequence structures. Therefore, we could infer that the transesterification was very poor during ROP of D,L-lactide employing the $[(dME)_2(HIM)P]_2Ti(IV)$ complex as catalyst and the molecular weight distributions of poly(D,L-lactide) should be narrow, which could be proved from the lower PDIs in Table 1. In Fig. 7, there were clearly two resonances at 69.2 and 69.0 ppm, and the resonance at 69.2 ppm was for the isi tetrad and the resonance at 69.0 ppm was for the sis, iii, iis, and sii tetrads, otherwise, the two resonances had not the same intensities, which were consistent with the reported microstructure of poly(D,L-lactide) [42, 43] and indicated that obtained poly(D,L-lactide) was atactic polymer. Thus, the results showed that $[(dME)_2(HIM)P]_2Ti(IV)$ complex could efficiently catalyze the ROP of D,L-lactide in the presence of benzyl alcohol and showed a well-controlled manner,



Scheme 1 Traditional-activated monomer mechanism for the ROP of D,L-lactide catalyzed by a binary catalyst $[(dME)_2(HIM)P]_2Ti(IV)/BnOH$

and the obtained polymer with controlled molecular weight and low PDI was an essential atactic polymer.

Figure 8 shows the thermogravimetric (TG) and differential scanning calorimetry (DSC) analysis of the obtained poly(D,L-lactide). According to the TG curve, there was 5% weight loss, ranging from 260 to 280 °C, which might be the lower molecular weight polymers and some monomers were lost. Therefore, an increase of

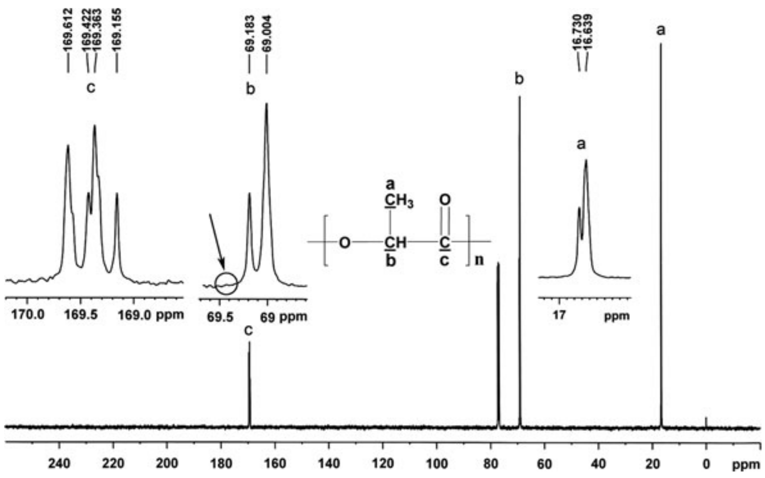


Fig. 7 ^{13}C NMR spectrum of obtained poly(D,L-lactide) with $[(dME)_2(HIM)P]_2Ti(IV)/BnOH$ as a binary catalyst (no visible peak of iss stereosequence at 69.4 ppm)

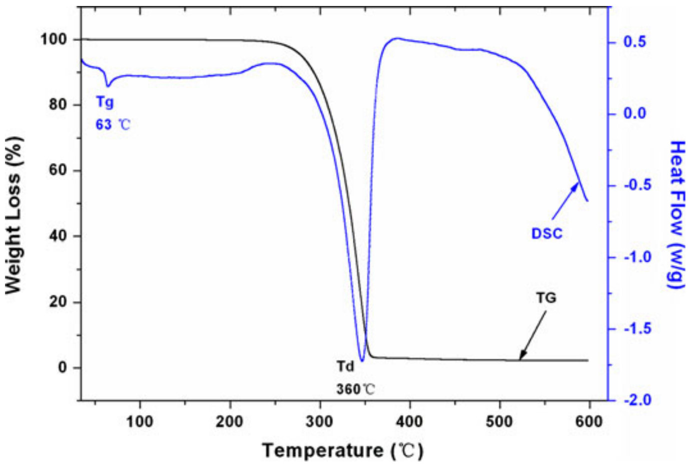


Fig. 8 TG and DSC analysis of the poly(D,L-lactide) with $[(dME)_2(HIM)P]_2Ti(IV)/BnOH$ as a binary catalyst

temperature resulted in the lower molecular weight polymers and some monomers decomposition and these minor samples lost easily on the onset decomposition temperature. The 93% weight loss was visible from 380 to 600 °C and accompanied with the most output of heat at 347 °C, and it indicated that high molecular weight poly(D,L-lactide) began to run complicated decomposition reaction. The results demonstrated that the poly(D,L-lactide) was thermal stable polymer and had similar thermal stability of poly(D,L-lactide) prepared using the stannous octoate ($Sn(Oct)_2$) as catalyst [44, 45].

However, no crystallization temperature (T_c) was observed from the DSC curve in Fig. 8, and it indicated that the obtained poly(D,L-lactide) was an amorphous polymer and the $[(dME)_2(HIM)P]_2Ti(IV)$ complex did not show stereoselective ROP of D,L-lactide. The trend of glass transition temperature (T_g) was in relation to molecular weight, in general, T_g of PLA was linearly dependent on the molecular weight until it reached its maximum [46, 47]. According to Fig. 8, the T_g was 63 °C, and it was important to point out that T_g of the obtained PLA in our study was higher than that of the reported poly(D,L-lactide) prepared using the similar aluminum Half–Salen complexes [48], and zinc lactate [49] and other compound [50] as catalyst, which was consistent with obtained poly(D,L-lactide) with high M_n (8.87×10^4 g mol^{-1}) and the results showed that $[(dME)_2(HIM)P]_2Ti(IV)$ complex in the presence of BnOH was an effective catalyst for ROP of D,L-lactide.

In conclusion, these results indicated that the $[(dME)_2(HIM)P]_2Ti(IV)$ complex was catalytic active for ROP of D,L-lactide, and the obtained poly(D,L-lactide) was essential atactic and thermal stable polymer. The crystal structure of the $[(dME)_2(HIM)P]_2Ti(IV)$ complex and kinetic of D,L-lactide polymerization would be reported further.

Conclusions

We had demonstrated that the synthesis of a novel $[(dME)_2(HIM)P]_2Ti(IV)$ complex, and its molecular structure was confirmed by EA, XRF, IR and ^1H NMR and ^{13}C NMR methods. Notably, the complex was an effective catalyst for ROP of D,L-lactide in the presence of BnOH, and the results revealed that the complex showed a well-controlled manner for ROP of D,L-lactide in bulk phase to give poly(D,L-lactide) with average molecular weight (M_n) up to 8.87×10^4 g mol^{-1} and a narrow molecular weight distribution ($M_w/M_n = 1.15$–1.32), and the poly(D,L-lactide) was essential atactic and thermal stable polymer.

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