



Ring opening polymerization of L-lactide by an electron-rich Schiff base zinc complex: An activity and kinetic study

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ABSTRACT

A zinc complex with the Schiff base $[(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}=\text{CHC}_6\text{H}_3(\text{OH})(\text{OMe})]$, LH, derived from 2-dimethylaminoethylamine and *o*-vanillin $[\text{Zn}_2\text{L}_2(\text{OBn})_2]$, has been synthesized and its structure has been established by X-ray crystallography and NMR spectroscopy. This zinc complex efficiently initiated the ring-opening polymerization (ROP) of L-lactide (L-LA), and the polymerization runs were well controlled, giving polylactide end-capped with benzyl ester and hydroxyl groups. The structure of the ancillary ligands showed some influence on the catalytic activity, the introduction of electron-rich methoxy at *ortho*-phenoxy substituent resulted in a decrease of the polymerization rate. In addition, we also have found that the overall rate expression is $d[\text{lactide}]/dt = k_p[\text{lactide}]^1[\text{Zn}_2\text{L}_2(\text{OBn})_2]^1$ in the kinetic study with the ROP of L-LA.

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1. Introduction

Poly(lactide) (PLA), prepared from natural renewable resources has recently gained much attention due to its biodegradable and biocompatible nature, and its wide use in the biomedical, pharmaceutical and environmental fields as a potential alternative to polyolefins [1–12]. Nowadays, the major chemical synthetic methods for preparing high molecular weight polylactides generally rely on the controlled ring opening polymerization (ROP) of lactides initiated by well-defined metal complexes of aluminium [13–18], calcium [19–24], magnesium [22,25–28], rare-earth metals [29–31] and zinc derivatives [22,32–37].

The industrial scale production of PLA relies on the use of Sn(II) initiators. However, these are difficult to remove from the resultant polymer and there are concerns over the toxicity of tin [38]. Therefore, numerous zinc, magnesium and calcium complexes have been used as “benign” polymerization initiators in the ROP processes. At the same time, the development of new ancillary (mainly N- and O-containing) ligand systems with the low toxicity is currently attracting growing attention. As a result, many zinc complexes, supported by steric hindrance trispyrazolylborate [39], diketiminate [32,40,41], Schiff base [36,42–44], aminophenolate [22,33–35] and many other ligands [37,45–47] have been used for the polymer-

ization of cyclic esters and have exhibited highly active and living properties.

As Lin et al. [42] reported that a series of NNO-tridentate Schiff base zinc alkoxides are good initiators for the ring opening polymerization of lactide, they also pointed out that the *para*-position electron-donating groups on the phenol ring of NNO-tridentate Schiff base ligand can increase the polymerization progress and the bulky group at the *ortho*-position of phenol can decrease the activity of the initiator. Therefore, there is an interesting question about the activities of these kinds of initiators when the *ortho*-position of phenol is an electron donor group. In this context, a new electron-rich Schiff base $[(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}=\text{CHC}_6\text{H}_3(\text{OH})(\text{OMe})]$ zinc complex $[\text{Zn}_2\text{L}_2(\text{OBn})_2]$ (Scheme 1) has been prepared and characterized by X-ray crystallography and NMR spectroscopy. Experimental results show that this complex is an excellent initiator toward the controlled polymerization of L-LA and its activity decrease by the introduction of electron-rich methoxy at *ortho*-phenoxy substituent to the ancillary ligand. To extend the deepness of our polymerization studies, herein we also report that the overall rate expression is $d[\text{lactide}]/dt = k_p[\text{lactide}]^1[\text{Zn}_2\text{L}_2(\text{OBn})_2]^1$ in the kinetic study with the ROP of L-LA.

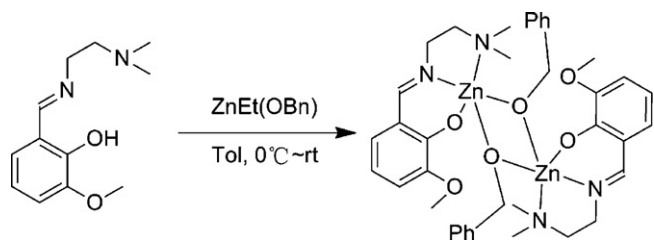
2. Experimental

2.1. General considerations

All manipulations were carried out under a dry nitrogen atmosphere. Solvents were dried by refluxing for at least

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Scheme 1. Synthesis of $[Zn_2L_2(OBn)_2]$.

24 h over sodium/benzophenone (n-hexane, toluene, and THF), phosphorus pentoxide (CH_2Cl_2) and calcium hydride (benzyl alcohol). L-Lactide (Jinan Daigang Co., Ltd.) was recrystallized in toluene twice for using. *o*-Vanillin was purchased from Acros. Others reagents were purchased from Tianjin Chemical Reagent Co., Ltd. and used without further purification. Schiff base $[(CH_3)_2NCH_2CH_2N=CHC_6H_3(OH)(OMe)]$ [HL] was synthesized according to the literature [48]. 1H and ^{13}C NMR spectra were recorded on a Bruker ADVANCE DRX-200 (200 MHz for 1H and 50 MHz for ^{13}C) or a Bruker AVANCE III (400 MHz for 1H and 100 MHz for ^{13}C) spectrometer. Chemical shifts are reported in δ (ppm) using residual proton impurities in $CDCl_3$ as a reference. Monomer conversion was determined from the relative intensities of the OCH_2 signals for the monomer (multiplet at δ 5.05 ppm) and polymer (multiplet at δ 5.25 ppm). Mass Spectra were obtained from the Trace DSQ GC-MS(EI) or the LC-MS(EI). Elemental analyses were carried out on an Elementar Vario EL element analyzer. X-ray structural analyses were carried out on a Bruker SMART APEX II diffractometer, using graphite monochromated $Cu K\alpha$ or $Mo K\alpha$ radiation. The molecular weight and polydispersity of PLA were measured by the Waters gel permeation chromatograph (GPC) using THF (HPLC grade) as an eluent and calculated using polystyrene as a standard reference. The GPC system was equipped with a Waters 2707 plus autosampler, a Waters 1515 isocratic HPLC pump, a Waters 2414 refractive index detector. THF was used as eluent at a flow rate of 1.0 mL/min. The temperatures of the columns and detector were both $30^\circ C$. Mn values of PLAs were corrected with a Mark-Houwink factor of 0.58 [49].

2.2. Preparation of Schiff base zinc complex $[Zn_2L_2(OBn)_2]$

$ZnEt_2$ (2.2 mL, 2.2 mmol) was slowly added to an ice cold toluene (20 mL) solution of benzyl alcohol (0.23 mL, 2.2 mmol) under a N_2 atmosphere. After the mixture was stirred for 1 h at $0^\circ C$, this mixture was transferred to HL (0.44 g, 2 mmol), and then the mixture was stirred for 12 h at room temperature. The solvent was removed under vacuum to afford a yellow solid, and the residue was recrystallized from a toluene-THF solution. Yield 0.38 g (48%). 1H NMR (400 MHz, $CDCl_3$, $25^\circ C$, ppm): δ 8.16, 7.94 (s, 1H, $N=CH$), 7.34–7.32, 7.18–6.99 (m, 5H, $ArH-OBn$), 6.83–6.78, 6.71–6.67, 6.66–6.42 (m, 3H, $ArH-L$), 4.85 (br, 2H, OCH_2Ph), 3.80 (s, 3H, OCH_3), 3.64 (br, 2H, $C=NCH_2$), 3.24 (t, 2H, $C=NCH_2$, $J=5.6$ Hz), 2.55 (br, 2H, $C=NCH_2CH_2$), 2.40 (t, 2H, $C=NCH_2$, $J=5.6$ Hz), 2.06 (s, 6H, $N(CH_3)_2$). ^{13}C NMR (100 MHz, $CDCl_3$, $25^\circ C$, ppm): δ 170.69 ($C=N$), 162.46, 152.66, 127.89, 127.39, 126.86, 117.87, 113.94, 112.21 (ArC), 59.42, 59.18 (OCH_2Ph), 57.77 (OCH_3), 55.90 ($C=NCH_2$), 45.94 ($C=NCH_2CH_2$), 45.43 ($N(CH_3)_2$). Anal. calc. for $C_{38}H_{48}N_4O_6Zn_2$: C, 57.95; H, 6.14; N, 7.11. Found: C, 54.94; H, 6.30; N, 6.56.

2.3. Typical polymerization procedures

A typical polymerization procedure was exemplified by the synthesis of PLA (the number 100 indicates the designed $[LA]_0/[complex]_0$) at $60^\circ C$ (Table 1, entry 1). The

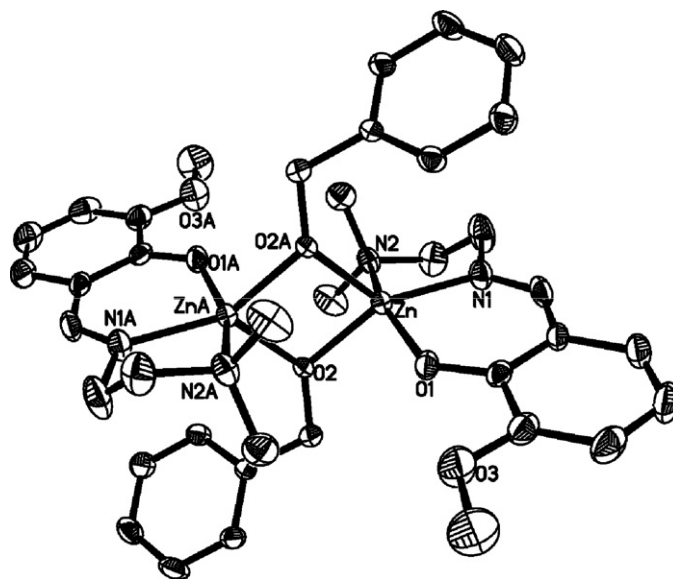


Fig. 1. ORTEP drawing of $[Zn_2L_2(OBn)_2]$ with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (\AA) and bond angles (deg): $Zn-O(1)$ 2.041(2), $Zn-O(2)$ 2.001(2), $Zn-O(2A)$ 1.977(2), $Zn-N(1)$ 2.057(3) and $Zn-N(2)$ 2.369(3). $O(1)-Zn-N(2)$ 158.44(10), $O(2)-Zn-N(1)$ 147.06(10), $O(2A)-Zn-N(1)$ 129.14(10) and $(2A)-Zn-O(2)$ 83.03(8).

polymerization conversion was analyzed by 1H NMR spectroscopic studies. L-Lactide (0.216 g, 1.5 mmol) was added to a solution of $[Zn_2L_2(OBn)_2]$ (0.012 g, 0.015 mmol) in toluene (10 mL). After the solution was stirred at $60^\circ C$ for 2 h, the reaction was then quenched by the addition of water. Hexane (40 mL) was then added to the above mixture to give a white crystalline solid. The resulting solid was washed with hexane twice and then dried under vacuum. Yield: 0.132 g (62%). 1H NMR (400 MHz, $CDCl_3$, $25^\circ C$, ppm): δ 7.37–7.34 (m, 5H, $ArH-OBn$), 5.16 (q, 2H, OCH_2Ph and nH, $CH-PLA$, $J=7.2$ Hz), 4.35 (dd, 1H, $CH-PLA$, $J=5.6$ Hz), 1.98 (s, 1H, $OH-PLA$) and 1.58 (d, 3H, CH_3-PLA , $J=7.2$ Hz).

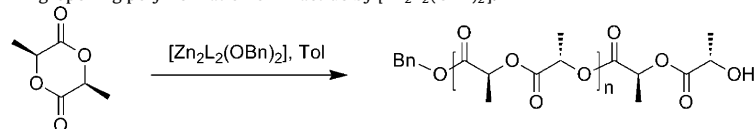
2.4. Kinetic study of L-lactide polymerization with $[Zn_2L_2(OBn)_2]$ 1

A kinetic study [50] was conducted to establish the reaction order with respect to monomer and initiator **1**. L-Lactide (0.216 g, 1.5 mmol) was added to a solution of **1** (1.50, 1.88, 2.39 or 2.78 mM) in toluene (10 mL). The solution was then stirred at $60^\circ C$ under an atmosphere of nitrogen. At the indicated time intervals, 0.05 mL aliquots were removed, trapped with liquid N_2 , stripped of solvent, and analyzed by 1H NMR in $CDCl_3$. The lactide concentration $[LA]$ was determined by integrating the quartet methine peak of lactide at 5.00 ppm and the quartet methine peak of polylactic acid at 5.25 ppm.

2.5. X-ray crystallographic studies

Suitable crystal of $[Zn_2L_2(OBn)_2]$ complex were sealed in thin-walled glass capillaries under a nitrogen atmosphere and was mounted on a Bruker AXS SMART 1000 diffractometer. Intensity data were collected in 1350 frames with increasing w (width of 0.3° per frame). The absorption correction was based on the symmetry-equivalent reflections using the program SADABS [51]. The space group determination was based on a check of the Laue symmetry and systematic absence and was confirmed using the structure solution. The structures were solved by direct methods using the SHELXTL package [52,53]. All non-H atoms were located from successive Fourier maps, and hydrogen atoms were refined using a

Table 1
Ring-opening polymerization of L-Lactide by $[\text{Zn}_2\text{L}_2(\text{OBn})_2]$.^a



Entry	Solvent	$[\text{M}]_0/[\text{Cat}]_0$	Temperature (°C)	Time (h)	Conv ^b . (%)	$\text{Mn}(\text{cal})^c$ (g mol ⁻¹)	$\text{Mn}(\text{obs})^d$ (g mol ⁻¹)	PDI ^d
1	Toluene	100/1	60	2	94.0	6876	5644	1.21
2	Toluene	200/1	60	4	92.3	13,399	10,045	1.14
3	Toluene	300/1	60	8	97.6	21,190	21,255	1.26
4	Toluene	400/1	60	10	99.5	28,764	24,908	1.12
5	Toluene	100/1	25	16	89.3	6538	6145	1.14

^a Conditions: $[\text{Zn}_2\text{L}_2(\text{OBn})_2]$ (0.015 mmol), toluene (10 mL), 60 °C.

^b Determined by ¹H NMR.

^c Calculated from $\text{Mn}(\text{cal}) = [\text{M}]/2[\text{I}] \times \text{M}[\text{M}] \times \text{conv}(\%) + \text{M}(\text{BnOH})$.

^d Observed by GPC in THF using polystyrene standards and a correction factor of 0.58 [49].

riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms.

3. Results and discussion

3.1. Synthesis and structural characterization of $[\text{Zn}_2\text{L}_2(\text{OBn})_2]$

The Schiff base [HL] was synthesized according to the literature [48] $[\text{Zn}_2\text{L}_2(\text{OBn})_2]$ was obtained via the reaction of HL and ZnEt(OBn) in 1:1.1 molar ratio in toluene at room temperature (Scheme 1). Single crystals of $[\text{Zn}_2\text{L}_2(\text{OBn})_2]$ suitable for X-ray structural determination was obtained from toluene and THF solution. As depicted in Fig. 1, in the solid state $[\text{Zn}_2\text{L}_2(\text{OBn})_2]$ [54] has a dimeric structure with two symmetrical pentacoordinated zinc centre bridging through the oxygen atom of the benzyl alkoxy group. And the geometry around Zn atoms were distorted trigonal bipyramidal with an average compressed axial O(1)–Zn–N(2) 158.44(10)° and equatorial O(2)–Zn–N(1) 147.06(10)°, O(2A)–Zn–N(1) 129.14(10)° and

O(2A)–Zn–(2) 83.03(8)°. The distances from the Zn atom to O(1), O(2), O(2A), N(1), and N(2) were 2.041(2), 2.001(2), 1.977(2), 2.057(3) and 2.369(3) Å. These bond lengths and bond angles are all within a normal range for zinc Schiff base complexes [42,43].

The stoichiometric structure of $[\text{Zn}_2\text{L}_2(\text{OBn})_2]$ was further confirmed on the basis of ¹H and ¹³C NMR spectroscopy. In the ¹H NMR spectrum of this complex (Fig. 2) in CDCl₃ at room temperature, two sets of resonance peaks (N=CH, δ 8.16, 7.94 ppm; N–(CH₃)₂, δ 2.02, 1.87 ppm) indicate the existence of both dimeric and monomeric species instead feature in solution at this temperature. Furthermore, monomeric species is more than dimeric species [42].

3.2. Ring-opening polymerization of L-lactide

As can be seen from the data compiled in Table 1, $[\text{Zn}_2\text{L}_2(\text{OBn})_2]$ (1.5 mM) is active initiators for the ring opening polymerization of L-lactide. Experimental results show that the polymerization can reach to completion within 10 h at 60 °C in the monomer-to-initiator ratio ($[\text{M}]_0/[\text{I}]_0$) range of 100–400. The polymerization is

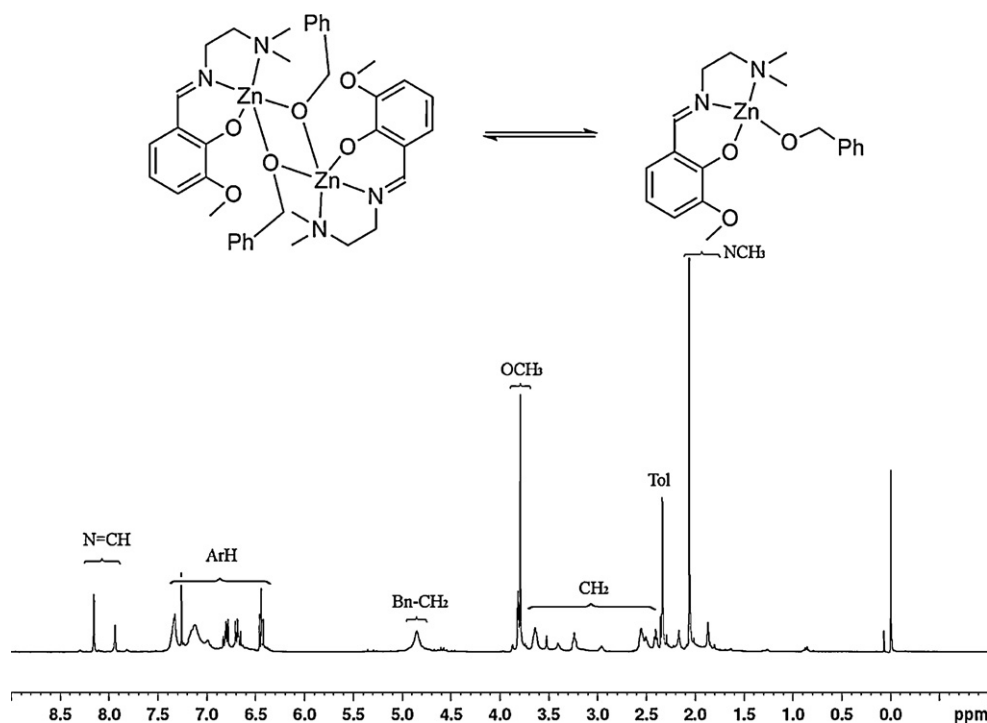


Fig. 2. The ¹H NMR spectrum of $[\text{Zn}_2\text{L}_2(\text{OBn})_2]$.

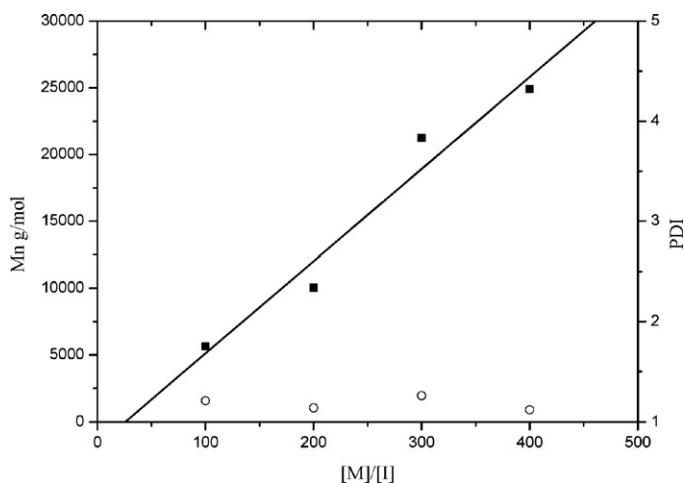


Fig. 3. (A) Ring-opening polymerization of L-LA initiated by $[Zn_2L_2(OBn)_2]$ under different $[LA]_0/[initiator]_0$, ■: plot of Mn vs. L-LA to initiator ratio, and ○: PDI.

well controlled and the “living” character is demonstrated by the low polydispersity index (PDIs) ranging from 1.12 to 1.26 of the polymers and by the linear relationship between Mn and $[M]_0/[I]_0$ ratio (Fig. 3). In order to realize the initiating process, 1H NMR studies on the PLLA-100 (Table 1, entry 1) indicates that the polymer chain is capped with a benzyl ester group on one end and a hydroxyl group on the other end (Fig. 4) According to the integration ratio close to 5:1 between Ha and He, it is suggested that the initiation occurred through the insertion of the benzyl alkoxy group from **1** into L-lactide, giving a zinc alkoxide intermediate, which further reacts with excess of L-LA yielding polyesters [42,43].

Compared with the zinc analogue complexes (A–E) (Fig. 5) reported by Lin et al. [42] the reactivity of initiator **1** toward the ROP of L-lactide is lower than that of complexes A–E (except for C). Polymerization goes to completion within 960 min at 25 °C for **1** (Table 1, entry 5), and the polymerization conversion only reaches to 10% within 80 min at 25 °C for **1**. For instance, complete

polymerization takes 30–80 min at 25 °C while using complexes (A and E) as an initiator, but the polymerization reaction completed within 240 min at 80 °C for C. It is found that the presence of substituent, at *ortho*-position of the phenoxide unit of the ligand, plays an important role in determining the polymerization rate. When the *ortho*-hydrogen of phenoxide is replaced by sterically hindered *tert*-butyl group and electron-donating methoxyl group, the polymerization rate both decreases dramatically as compared to the reaction rate of **1**, A and E, and the polymerization rate decreases more for **1** than A and E. It is revealed that electron-donating effect combined with steric effect plays an important role in decreasing the reactivity of zinc alkoxide. It attributes to the bond intensity of zinc and oxygen atom of the alkoxy group (**1** > A, E) in their single crystal structure, such as Zn–O(2) 2.001(2), Zn–O(2A) 1.977(2) for **1**, Zn–O(2) 2.016(1), Zn–O(2A) 1.978(2) for A and Zn–O(2) 1.989(3), Zn–O(2A) 2.089(3) for E. And the stronger these bonds intensity is, the more difficultly the coordination insertion occurs.

3.3. Kinetic studies of polymerization of L-lactide by $[Zn_2L_2(OBn)_2]$ **1**

A kinetic study [50] was conducted to establish the reaction order with respect to monomer and initiator **1**. L-Lactide (0.216 g, 1.5 mmol) was added to a solution of **1** (1.50, 1.88, 2.39, or 2.78 mM) in toluene (10 mL). The solution was then stirred at 60 °C under an atmosphere of nitrogen. At the indicated time intervals, conversion of L-lactide was analyzed by 1H NMR in $CDCl_3$.

As expected, plots of $\ln([lactide]_0/[lactide])$ vs. time for a wide range of **1** are linear, indicating the usual first order dependence on monomer concentration (Fig. 6). Thus, the rate expression can be written as $d[lactide]/dt = k_p[lactide]^1[1]^n = k_{obs}[lactide]^1$, where $k_{obs} = k_p[1]^n$. A plot of k_{obs} vs. **1** (Fig. 7) allows the determination of k_p and n . The linear relationship between k_{obs} vs. **1** indicates the first-order in initiator. The slope of the best fit line (75.97) equals k_p and thus the polymerization rate constant, k_p , is $75.97 M^{-1} min^{-1}$. Therefore, the overall rate expression is $d[lactide]/dt = k_p[lactide]^1[1]^1$.

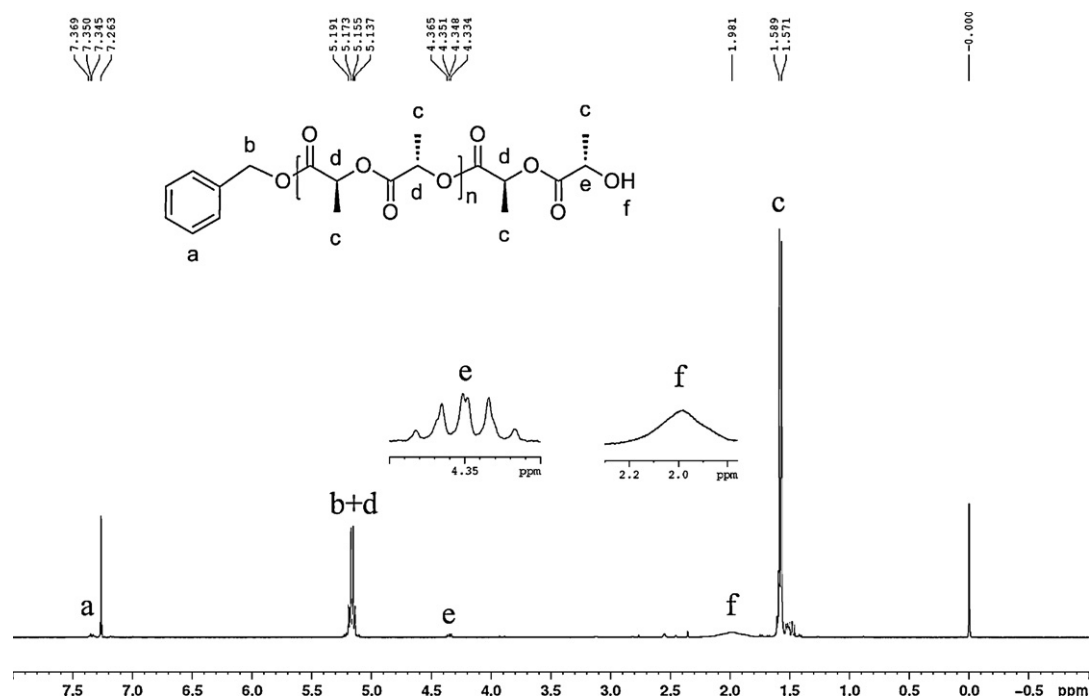


Fig. 4. 1H NMR spectrum of PLLA-100 (Table 1, entry 1).

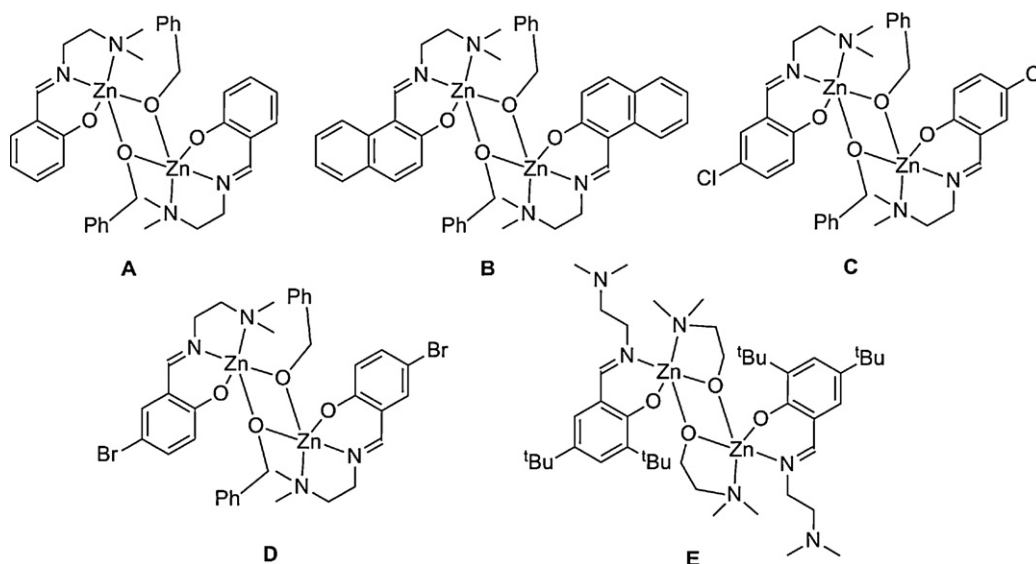


Fig. 5. The structure of zinc alkoxides (A–E).

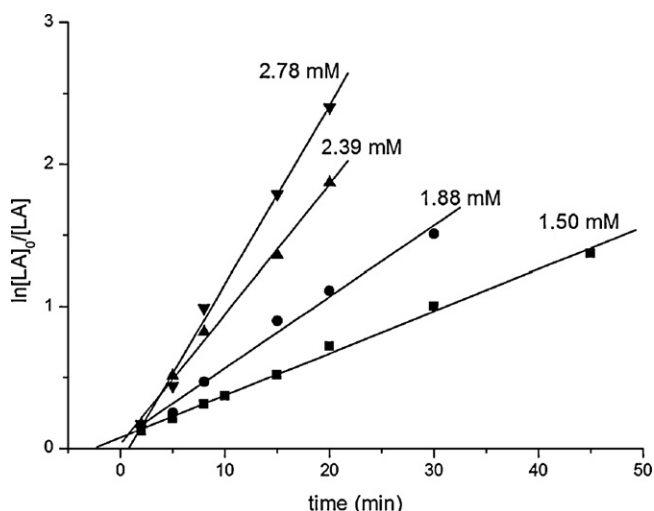


Fig. 6. First-order kinetic plots for L-lactide polymerizations with time in toluene with different concentration of $[Zn_2L_2(OBn)_2]$ as an initiator.

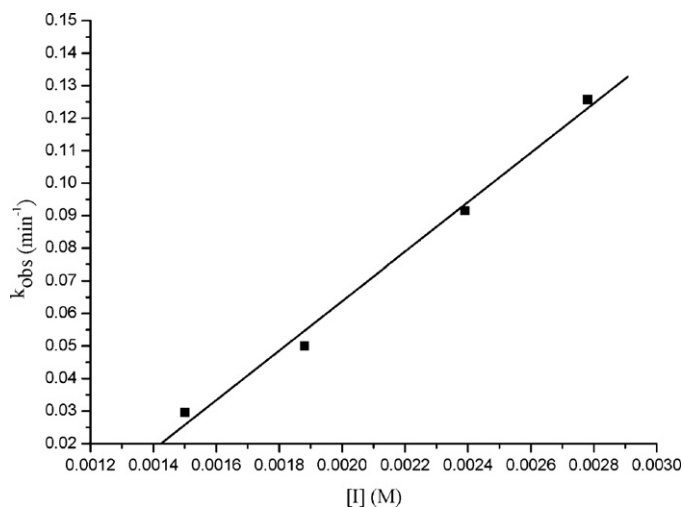


Fig. 7. Linear plot of k_{obs} vs. $[I]$ for the polymerization of L-lactide with $[LA]_0 = 0.15$ M in toluene. $k_p = 75.97$ M⁻¹ min⁻¹.

4. Conclusion

A zinc complex with the Schiff base, derived from 2-dimethylaminoethylamine and *o*-vanillin $[Zn_2L_2(OBn)_2]$, has been synthesized and its structure has been established by X-ray crystallography and NMR spectroscopy. This zinc complex efficiently initiated the ROP of L-LA, and the polymerization runs were better controlled. The structure of the ancillary ligands showed some influence on the catalytic activity, the introduction of electron-rich methoxy at *ortho*-phenoxy substituent resulted in a decrease of the polymerization rate. In addition, we also have found that the polymerization reaction proceeds with first-order rate in both monomer and initiator.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.molcata.2011.10.012](https://doi.org/10.1016/j.molcata.2011.10.012).

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