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Polymer 46 (2005) 9784–9792
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Ring-opening polymerization of lactide initiated by magnesium and zinc alkoxides

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Received 31 May 2005; received in revised form 28 July 2005; accepted 3 August 2005
Available online 25 August 2005

Abstract

A mono methylether Salen-type ligand, SalenMe-H (**1**) is prepared in a one flask reaction by condensation of *trans*-1,2-diaminocyclohexane with 2-methoxybenzenaldehyde and followed by the addition of 2,4-di-*tert*-butylsalicylaldehyde. Further reaction of **1** with $Mg(OBn)_2$ in THF produces a magnesium alkoxide, $[(SalenMe)Mg(OBn)]_2$ (**2**). Compound **1** reacts with $ZnEt_2$ yields monomeric complex (SalenMe)ZnEt (**3**), which further reacts with 1 molar equiv of benzyl alcohol giving $[(SalenMe)Zn(OBn)]_2$ (**4**). Experimental results show that complexes **2** and **4** efficiently initiate the ring-opening polymerization of L-lactide and *rac*-lactide in a controlled fashion, yielding polymers with very low polydispersity indexes. Kinetic studies show a second-order dependency on [LA] and a first-order on [**2**] with magnesium complex **2** as an initiator. While zinc complex **4** is used as an initiator, the polymerization rate has a first order dependency on both [LA] and [**4**].

Keywords: Magnesium; L-lactide; Ring opening polymerization

1. Introduction

It has been of great interest in development of new catalytic/initiating systems for the ring-opening polymerization (ROP) of lactide (LA), because polylactide (PLA) is important biodegradable material derived from renewable feed stocks [1]. The mechanical and thermal properties of PLA dramatically rely on its microstructure, and hence, the stereocontrolled polymerization of lactide has become a focus of attention recently [2]. The most significant advances in stereocontrolled polymerization have been observed by using zinc alkoxides stabilized by β-diketiminate ligands [3] and using aluminum alkoxides stabilized by Salen [4] or Salan [5] base ligands as initiators. In Salen and Salan aluminum systems, excellent isotactic and heteroatactic stereocontrol in ROP of lactide can be achieved, but they suffered from inherently low activity. Therefore, reasonable conversions are generally attained only at high temperatures ($>70\,^{\circ}C$) over a long period of time. It has been known that the activity toward ROP of L-lactide is $Mg > Zn > Al$ [6]. Because Salen and Salan-type ligands are bi-charged, their magnesium and zinc complexes would be neutral which would lead to low activity. For instance, in the case of diol systems, the activity of neutral $[(EDBP)Mg(THF)]_2$ in the presence of alcohol toward polymerization of lactide is only somewhat faster than that of $[(EDBP)Al(OBn)]_2$ [7]. In order to introduce highly active magnesium and zinc alkoxides into this potential system [3,8], a mono methylether Salen-type ligand, SalenMe-H is prepared. The preparation, characterization and catalytic activities toward ROP of lactides of its zinc and magnesium alkoxides will also be presented.

2. Results and discussion

2.1. Syntheses and crystal structure determination

The mono methylether Salen-type ligand, SalenMe-H (**1**), was prepared in 70% yield by condensation of *trans*-1,2-diaminocyclohexane with 1.2 equiv of 2-methoxybenzenaldehyde in the presence of $MgSO_4$, followed by the addition of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde. The

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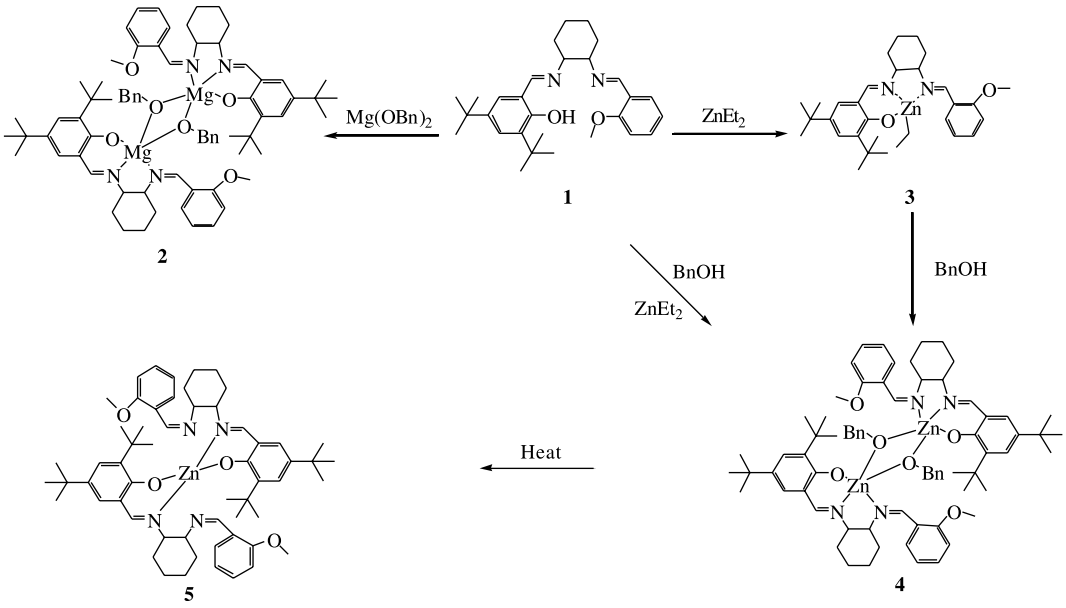
doi:10.1016/j.polymer.2005.08.009



Scheme 1.

reaction of **1** with $Mg(OBn)_2$, prepared in situ from $Mg(^nBu)_2$ with BnOH, produces $[(SalenMe)Mg(OBn)]_2$ (**2**) in 75% yield as shown in Scheme 1. Compound **2** can also be prepared by the addition of $Mg(^nBu)_2$ into a mixture of SalenMe-H and BnOH under low temperature. However, the yield is low because of a side reaction between C=N group and $Mg(^nBu)_2$. To the best of our knowledge, no metal alkoxides supported by a mono methylether Salen-type ligand have been reported, though several Salen coordinated zinc amides and phenoxides have been synthesized by Chisholm et al. [9]. While **1** reacts with $ZnEt_2$, a four-coordinated zinc complex (SalenMe)ZnEt (**3**) can be obtained in almost quantitative yield. Further mixing **3** with a stoichiometric amount of BnOH in toluene, a zinc alkoxide $[(SalenMe)Zn(OBn)]_2$ (**4**) can be produced. Compound **4** can also be prepared by the addition of

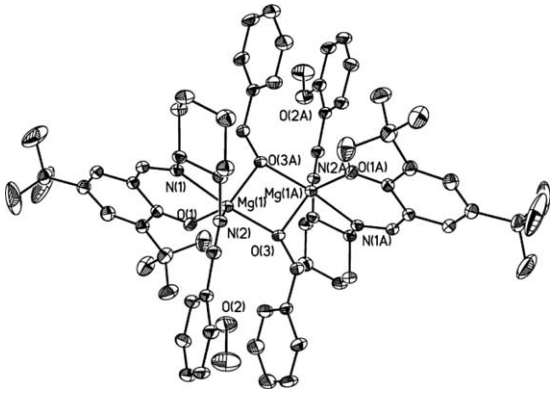


Fig. 1. ORTEP drawing of complex **2** with thermal ellipsoids drawn at the 20% level. Hydrogen atoms are omitted for clarity. Selected bond distances: Mg(1)–Mg(1A) 2.999(9) Å, O(3)–Mg(1), 1.976(6) Å, O(3A)–Mg(1) 1.979(8) Å, Mg(1)–O(1) 1.929(1) Å. Mg(1)–N(1) 2.161(2) Å, Mg(1)–N(2) 2.260(2) Å.

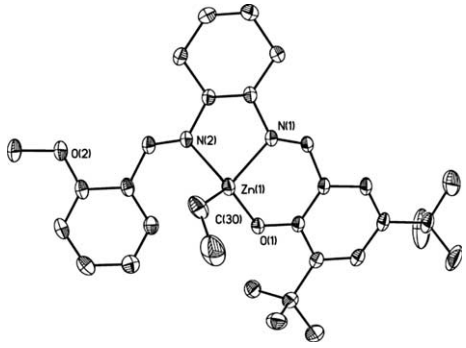


Fig. 2. ORTEP drawing of complex **3** with thermal ellipsoids drawn at the 20% level. Hydrogen atoms are omitted for clarity. Selected bond distances: Zn(1)–N(1) 2.200(9) Å, Zn(1)–N(2) 2.012(7) Å, Zn(1)–O(1) 1.954(8) Å, Zn(1)–C(30) 1.969(3) Å.

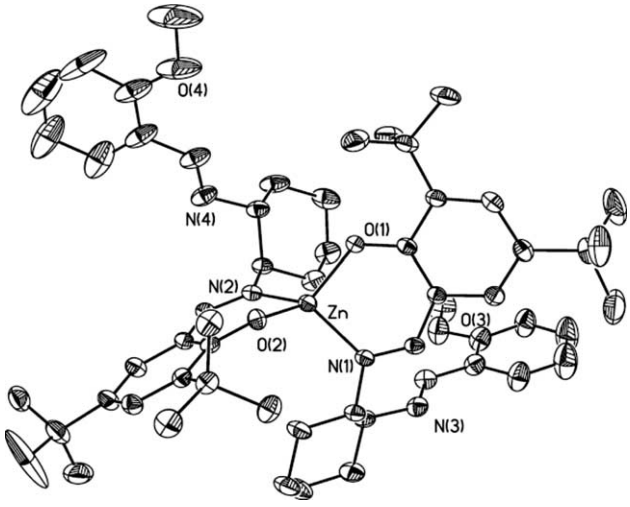
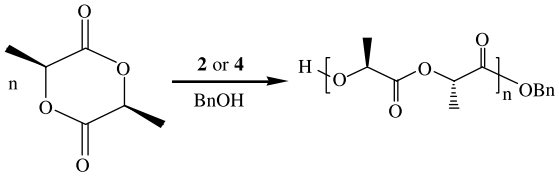


Fig. 3. ORTEP drawing of complex **5** with thermal ellipsoids drawn at the 20% level. Hydrogen atoms are omitted for clarity.

Table 1
Ring-opening polymerization of L-lactide initiated by complexes **2** and **4** in toluene



Entry	Complex	$[M]_0/[I]_0$	T (°C)	t (h)	PDI	M_n (GPC)[a]	M_n (NMR)[b]	M_n (calcd)[c]	Conv (%)
1	**2**	25:1	25	0.75	1.10	6600 (3800)	3700	3600	98
2	**2**	50:1		0.75	1.07	11,400 (6600)	6600	7100	98
3	**2**	75:1		0.75	1.05	20,800 (12,000)	11,000	10,200	94
4	**2**	100:1		0.75	1.09	27,300 (15,800)	15,500	13,900	96
5	**4**	25:1	60	3.5	1.09	7000 (4100)	4100	3400	93
6	**4**	50:1		3.5	1.05	10,900 (6300)	7300	6600	90
7	**4**	100:1		4	1.03	25,800 (15,000)	12,600	13,800	95
8	**4**	150:1		4.5	1.03	34,100 (19,800)	19,000	19,300	89

[a] Obtained from GPC analysis and calibrated by polystyrene standard. Values in parentheses are the values obtained from GPC times 0.58 [12].
[b] Obtained from ^{1}H NMR analysis.
[c] Calculated from the molecular weight of L-lactide times $[M]_0/2[I]_0$ times conversion yield plus the molecular weight of BnOH.

$ZnEt_2$ to the mixture of **1** and benzyl alcohol in toluene. Unlike its magnesium analogue **2**, complex **4** is thermally unstable and decomposed to complex $Zn(SalenMe)_2$ (**5**) upon heating to about 80 °C in acetonitrile.

Single crystals suitable for X-ray structural determination were obtained from cooling a toluene solution (**2** and **3**) or an acetonitrile solution (**1** and **5** [10]). An ORTEP drawing of the molecular structure of **2** is given in Fig. 1. Complex **2** packed as a dimer in the solid state bridging through the oxygen atoms of benzyl alkoxides. The geometry around magnesium is a distorted trigonal bipyramid with N(1) and O(3) at the axial positions and N(2), O(1) and O(3A) on the equatorial positions. This is verified by the N(1)–Mg(1)–O(3) angle of 163.88(8)° and the sum of the N(2)–Mg(1)–O(1), O(1)–Mg(1)–O(3a) and O(3a)–Mg(1)–N(2) angles of 357°. The bond distances between Mg and bridging oxygen atoms are Mg–O(3)1.976(6) and Mg–O(3A) 1.979(8) Å, respectively, well within the range for a bridging Mg–O bond [11]. The Mg(1)–N(2) bond distance, 2.260(2) Å, is ca. 0.1 Å longer than the Mg(1)–N(1) distance 2.161(2) Å, suggesting that N(2) is only weakly coordinated to magnesium.

The ORTEP of **3** is depicted in Fig. 2 and its molecular structure reveals a monomeric form in which zinc ion is distorted from a tetrahedral structure. The Zn(1)–N(1) bond distance, 2.200(9), is 0.19 Å shorter than the Zn(1)–N(2) distance 2.012(7) Å, which also proves N(2) weakly coordinates to zinc ion. The structure of complex **5** is shown in Fig. 3. Trying to grow single crystal of **4** failed, however, its molecular structure is assumed to be similar to

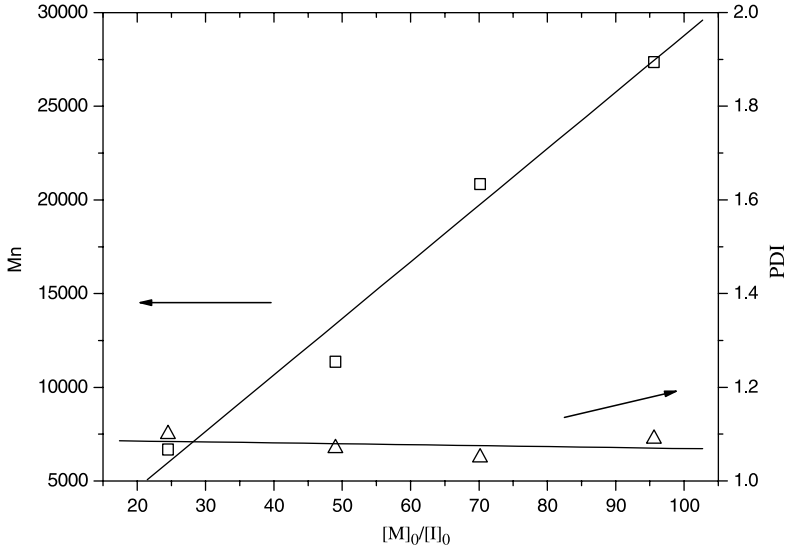


Fig. 4. Polymerization of L-LA catalyzed by **2** in toluene at 25 °C. The relationship between M_n (□) (PDI (△)) of polymer and the initial mole ration $[M]_0/[I]_0$ is shown.

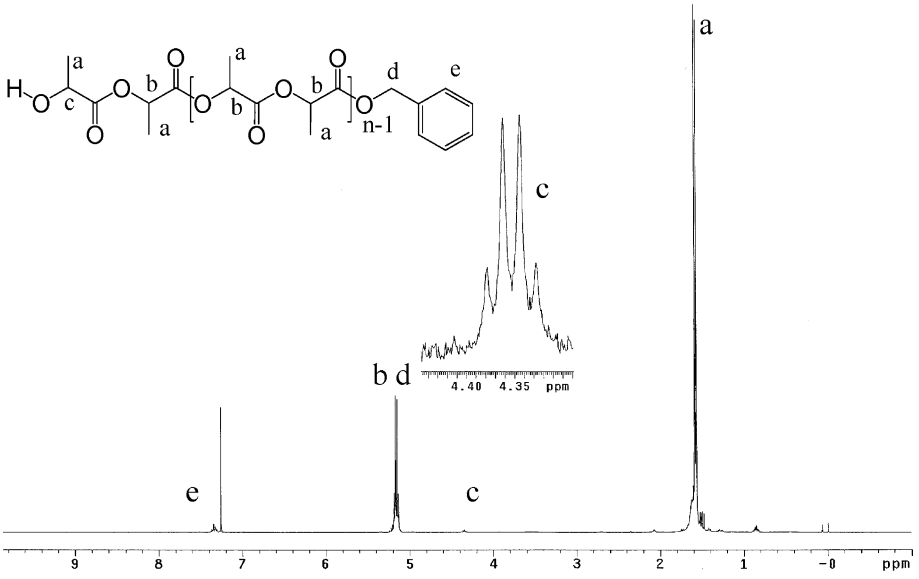


Fig. 5. ^{1}H NMR PLLA 25:1 from entry **1** in $CDCl_3$.

its magnesium analogous **2** based on the ^{1}H NMR spectroscopic studies.

2.2. Ring-opening polymerization of L-lactide

ROP of L-lactide (LLA) employing **2** and **4** as an initiator has been systematically examined in toluene or dichloromethane as shown in Table 1. Experimental results indicate that both complexes **2** and **4** are efficient initiators for ring-opening polymerization of L-lactide. The conversion can reach to 98% using **2** as an initiator in 45 min at room temperature when $[M]_0/[I]_0$ ratio is 50 (Table 1, entry 2). The good polymerization control is demonstrated by the linear relationship between M_n and $[M]_0/[I]_0$ (Fig. 4) and the polymers with very low PDIs, ranging from 1.05 to 1.10. The ^{1}H NMR spectrum of PLLA indicates that the polymer chain should be capped with one benzyl ester and one hydroxyl end with a ratio of 5:1 (Fig. 5). Furthermore, epimerization of the chiral centers in PLLA does not occur as observed by the homonuclear decoupled ^{1}H NMR studies in the methine region [13]. When using **4** as an initiator, conversion higher than 90% can be achieved within 3.5 h at 60 °C in the case of monomer-to-metal ratio ($[M]_0/[I]_0$) of 50 (Table 1, entry 6). As evidenced by the linear relationship between the $[M]_0/[I]_0$ and number-average molecular masses (M_n) (Fig. 6), a good control of polymerization is also accomplished. Moreover, the PDIs of polylactides obtained are quite low, ranging from 1.03 to

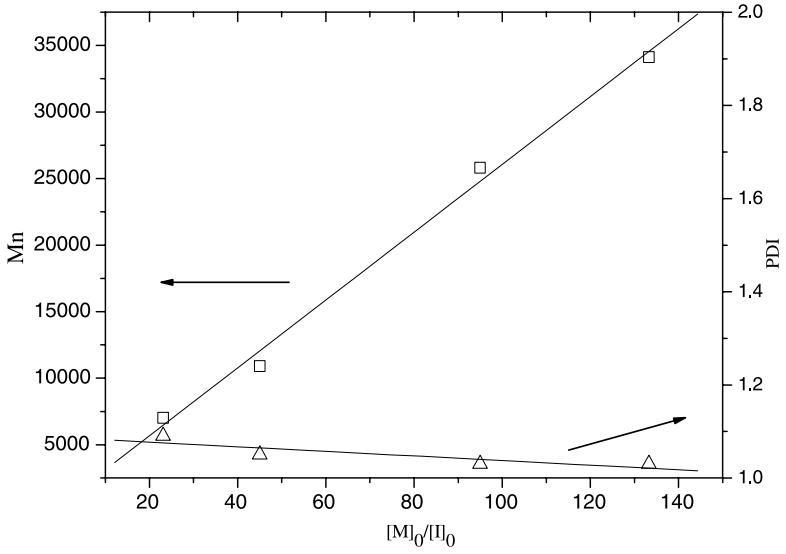
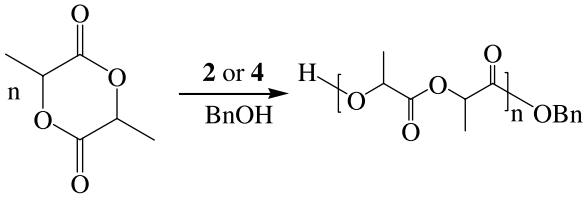


Fig. 6. Polymerization of L-LA catalyzed by **2** in toluene at 60 °C. The relationship between M_n (□) (PDI (△)) of polymer and the initial mole ration $[M]_0/[I]_0$ is shown.

Table 2
Ring-opening polymerization of *rac*-lactide initiated by complexes **2** and **4**



Entry	Complex	Solvent	T (°C)	t (h)	PDI	M_n (GPC)[a]	M_n (NMR)[b]	M_n (calcd)[c]	Conv (%)	Selectivity
1	**2**	THF	25	1	1.06	6300 (3600)	4400	4400	59	Pr = 0.57
2	**2**	Toluene	25	0.75	1.09	11,900 (6900)	5700	7200	98	Pm = 0.54
3	**2**	CH_2Cl_2	0	12	1.05	13,600 (7900)	8900	6700	92	Pm = 0.58
4	**2**	CH_2Cl_2	−30	48	1.09	6000 (3500)	4000	3700	50	Pm = 0.67
5	**4**	CH_2Cl_2	25	24	1.05	9900 (5700)	7400	6900	95	Pr = 0.75

$[M]_0/[I]_0 = 50$, $[I]_0 = 0.05$ mM.
[a] Obtained from GPC analysis and calibrated by polystyrene standard. Values in parentheses are the values obtained from GPC times 0.58 [12].
[b] Obtained from ^{1}H NMR analysis.
[c] Calculated from the molecular weight of L-lactide times $[M]_0/2[I]_0$ times conversion yield plus the molecular weight of BnOH.

1.09. From the comparison of activities of **2** to **4**, we conclude that magnesium alkoxides are more active than its zinc analogous which is consistent with that observed by Chisholm et al. [6].

2.3. Ring-opening polymerization of rac-lactide

Polymerizations of *rac*-lactide by complexes **2** and **4** are also performed. The homonuclear decoupled ^{1}H NMR spectrum at the methine region of the PLA derived from **2** is isotactic predominance (Table 2 entries 2–4). The probability of racemic linkages, Pr, were estimated from the relative intensity of the *rmr* and *mrm* tetrads versus other tetrads (*rmm*/*mmr*, *mmm*) [3,6,14]. The selectivity of **2** is significantly related to solvents. For instance, heterotactic polymer (Pr = 0.57) can be produced in THF, and isotactic polymer (Pm = 0.54) is obtained at room temperature in toluene. While using CH_2Cl_2 as solvent, isotatic polymer with Pm = 0.58 is acquired at 0 °C. When decreased the temperature to −30 °C, Pm up to 0.67 can be accomplished (entry 4). Interestingly, PLA derived from **4** reveals heterotactic predominance with Pr = 0.75 (Table 2, entry 5).

2.4. Kinetic studies of polymerization of L-lactide with complexes 2 and 4

Kinetic studies of L-lactide polymerization with complex **2** and **4** as initiators were conducted in order to establish

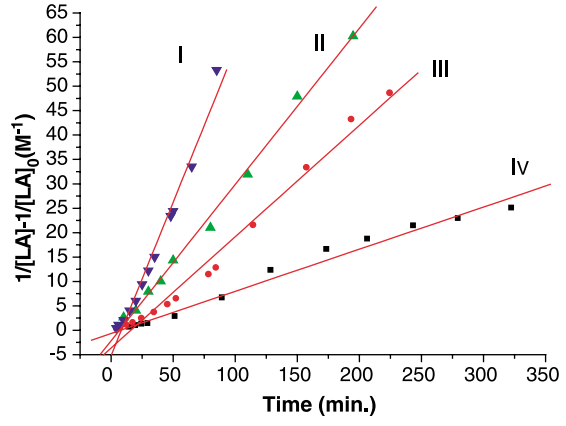


Fig. 7. Plots of $1/[LA] - 1/[LA]_0$ versus time for the polymerization of L-lactide by **2** at 25 °C. ($[LA]_0 = 0.2083$ M; **I**, $[Mg] = 14$ mM; **II**, $[Mg] = 8$ mM; **III**, $[Mg] = 4$ mM; **IV**, $[Mg] = 2$ mM).

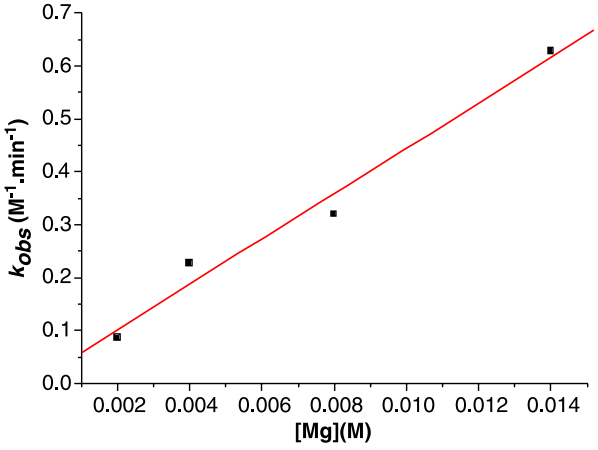


Fig. 8. Polts of k_{obs} versus [Mg] for the polymerization of L-lactide with **2** as an initiator ($CDCl_3$, 25 °C, $[LA]_0 = 0.2083$ M).

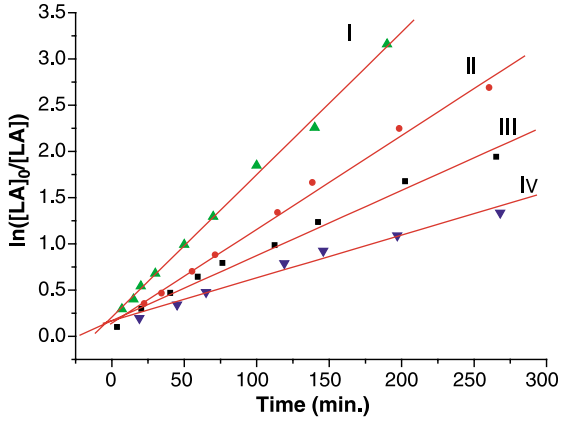


Fig. 9. Plots of $\ln([LA]_0/[LA])$ versus time for the polymerization of L-lactide by **4** at 25 °C. ($[LA]_0 = 0.2083$ M; **I**, [Zn] = 12 mM; **II**, [Zn] = 8 mM; **III**, [Zn] = 6.67 mM; **IV**, [Zn] = 5 mM).

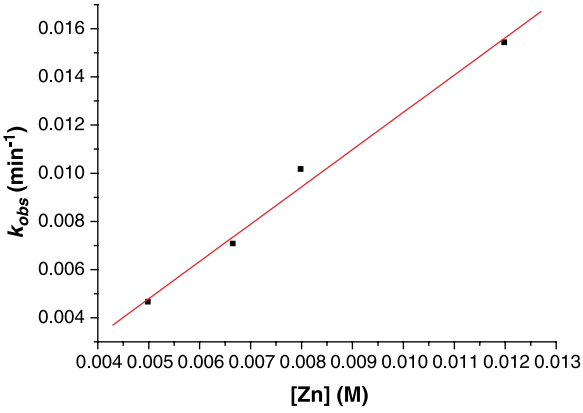


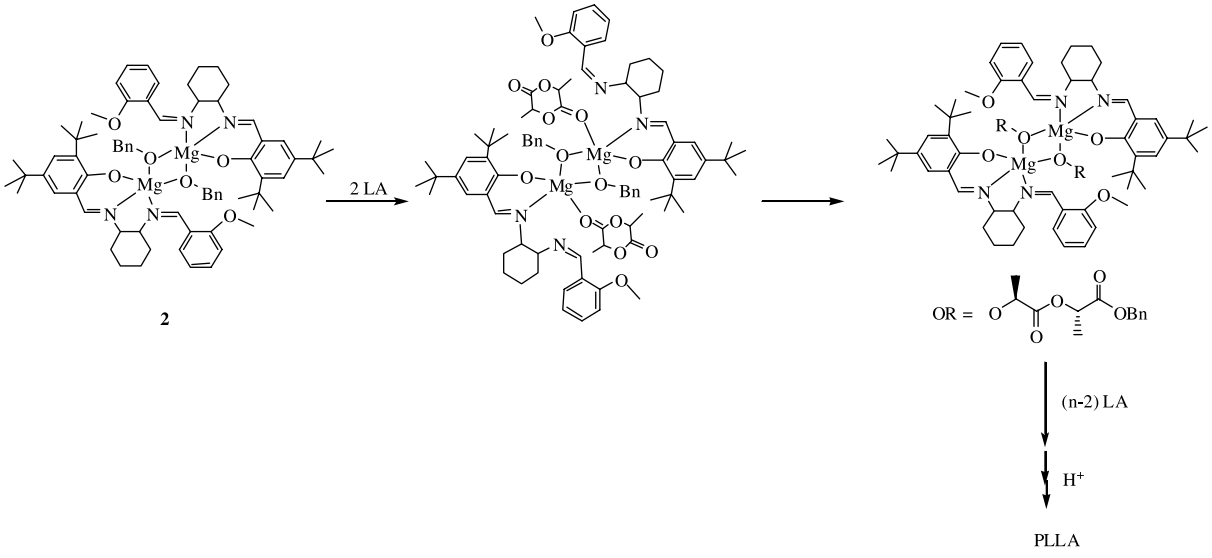
Fig. 10. Polts of k_{obs} versus [Zn] for the polymerization of L-lactide with **4** as initiator ($CDCl_3$, 25 °C, $[LA]_0 = 0.2083$ M).

reaction order in monomer and metal concentration. Conversion of L-lactide with time at various concentrations ($[LA]_0 = 0.2083$ M; $[LA]_0/[Mg]_0$ ranges from 14.86 to 104) of complex **2** in $CDCl_3$ were monitored by a ^{1}H NMR spectrometer at 20 °C. In each case, a significant down deviation was observed for the first-order plots between $\ln[LA]_0/[LA]$ versus time (min) [15]. However, plots of $(1/[LA] - 1/[LA]_0)$ versus time are linear indicating polymerization proceeds with second-order dependence on monomer concentration (Fig. 7, $k_{obs} = 0.1141$ M^{-1} min^{-1}, [LA]/[Mg] = 42, [Mg] = 4.0 mM). Thus, the rate of polymerization can be written as $-d[LA]/dt = k_{obs}[LA]^2$, where $k_{obs} = k[Mg]^x$ and k is the rate constant. The linear relationship between k_{obs} versus [Mg] (Fig. 8) reveals a first-order in initiator. Therefore, the overall rate equation is $-d[LA]/dt = k[LA]^2[Mg]^1$ ($k = 28.53$ M^{-2} min^{-1}, [LA]/[Mg] = 42, [Mg] = 4.0 mM). The rate law $-d[LA]/dt = k[LA]^2[Mg]^1$ is the same as the one found in [{(BDI-OMe)Zn(μ-OBn)}$_2$Zn(μ-OBn)$_2$] system [16], but is different to the rate law of $-d[LA]/dt = k[LA]^1[ini]^1$ found in other initiator's system [3b,5,8a].

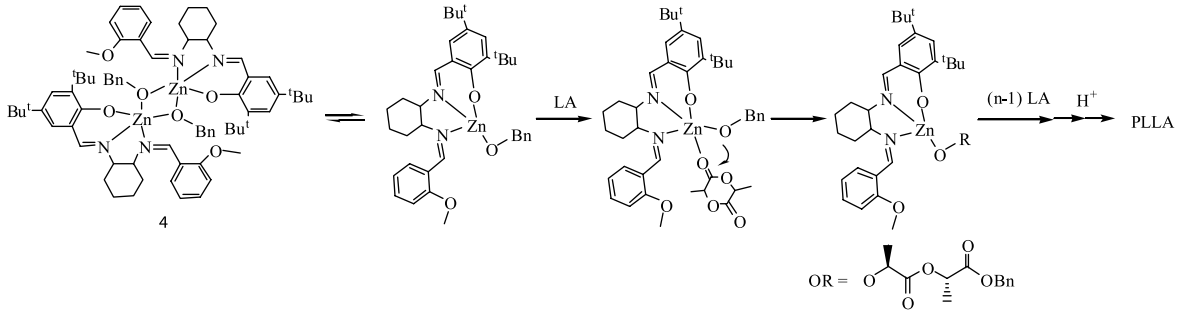
Conversion of L-lactide with time at various concentrations of complex **4** ($[LA]_0 = 0.2083$ M; [Zn] = 5.0–12.0 mM; $[LA]_0/[Zn]_0 = 17.36$ to 41.66) in CD_3Cl at 20 °C were also examined. In this system, plots of $(\ln[LA]_0/[LA])$ versus time (min) are linear indicating polymerization proceeds with first-order dependence on monomer concentration (Fig. 9, $k_{obs} = 0.046$ min^{-1}, [LA]/[Zn] ≈ 42, [Zn] = 5.0 mM). The linear relationship between k_{obs} versus [Zn] (Fig. 10) indicates the first-order in initiator. Therefore, the overall rate equation is $-d[LA]/dt = k[LA]^1[Zn]^1$ ($k = 9.26$ M^{-1} min^{-1}, [LA]/[Zn] ≈ 42, [Zn] = 5.0 mM).

2.5. Proposed mechanism for polymerization of L-lactide

^{1}H NMR studies of compounds **2** and **4** at both low temperature (−60 °C) and ambient temperature (20 °C)



Scheme 2. Proposed mechanism for ring-opening polymerization of L-lactide initiated by complex **2**.



Scheme 3. Proposed mechanism for ring-opening polymerization of L-lactide initiated by complex **4**.

have been undertaken. Experimental results show there is no difference between low temperature and room temperature for both compounds. However, the polymerization kinetic studies show a second-order dependency on [LA] and a first order dependency on [**2**] when using complex **2** as an initiator. While complex **4** is used as an initiator, the polymerization rate has a first order dependency on both [LA] and [Zn]. Based on the spectroscopic studies and kinetic results of complex **2** and **4**, we conclude that the intermediate structure of these two complexes should be different during polymerization. Polymerization intermediate of initiated by complex **2** maybe exists as a dimmer as shown in Scheme 2. The formation of compound **5** suggests us that the C=N group away from the phenoxy oxygen should be the weaker ligand and should be replaced by L-lactide during polymerization. However, the polymerization intermediate for zinc complex **4** is a monomer (Scheme 3).

3. Experimental section

3.1. General

All experiments were carried out under a dry nitrogen atmosphere. Solvents were dried by refluxing at least for 24 h over sodium/benzophenone(toluene, and tetrahydrofuran), phorsphorus pentaoxide (CH_2Cl_2), or over magnesium sulfate (benzyl alcohol) and freshly distilled prior to use. Deuterated solvents was dried over molecular sievents. L-lactide (98%, Aldrich) and *rac*-lactide (99%, Bio-Invigor) were recrystallized from toluene twice and stored in a dry box. 2-Methoxybenzenaldehyd, 2,4-di-*tert*-butylsalicylaldehyde, $Mg(^nBu)_2$ (1.0 M in heptane) and diethylzinc (1.0 M in hexane) were purchased from Aldrich and used as received. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury-400 (400 MHz) or a Unity Inova-600 (600 MHz) spectrometer with chemical shifts given in parts per million from the peak of internal TMS. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument.

3.2. SalenMe (*1*)

To a solution of *trans*-1,2-diaminocyclohexane (3.4 g, 30 mmol) in 150 mL of dichloromethane was added $MgSO_4$ (10 g) and the system was cooled to 0 °C. 2-Methoxybenzenaldehyde (4.9 g, 36 mmol) in dichloromethane (75 mL) was slowly added. After completion of addition, the mixture was stirred for 24 h at room temperature. Cooling the mixture to 0 °C again, 2,4-di-*tert*-butylsalicylaldehyde (5.6 g, 24 mmol) in 75 mL of dichloromethane was added slowly and the solution was stirred for another 24 h at room temperature. After filtration of $MgSO_4$, the solution was concentrated. The residue was recrystallized from acetonitrile twice to give yellow crystalline solid. Yield: 7.5 g (70%) Anal. Calcd (found) for $C_{29}H_{40}N_2O_2$: N, 6.24 (6.08); C, 77.64 (77.34); H 8.99 (8.56)%. ^1H NMR ($CDCl_3$, ppm): δ 8.59 (s, 1H, C*H*=N), 8.24 (s, 1H, C*H*=N), 7.81 (d, 1H, J= 8 Hz, Ar*H*), 7.29 (m, 2H, Ar*H*), 6.94 (m, 2H, Ar*H*), 6.78 (d, 1H, J=8 Hz, Ar*H*), 3.66 (s, 3H, OMe), 3.37 (m, 2H, C*H*N=C), 1.85 (m, 8H, –CH_2–), 1.42 (s, 9H, C(CH_3)$_3$), 1.24 (s, 9H, C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 165.52, 158.74, 158.19, 157.53, 139.54, 136.24, 131.48, 127.27, 126.38, 125.77, 124.90, 120.50, 117.86, 110.96, 74.25, 71.95, 55.35, 34.89, 33.98, 33.23, 32.99, 31.42, 29.39, 24.48, 24.36.

3.3. [(SalenMe)Mg(OBn)]$_2$ (*2*)

To a solution of benzyl alcohol (0.42 mL, 4 mmol) in 20 mL of THF at 0 °C, was slowly added $Mg(^nBu)_2$ (2 mL, 1 M in hexane, 2 mmol) and the mixture was stirred for 12 h at room temperature. The mixture was cooled to 0 °C again and a solution of ligand **1** (0.896 g, 2 mmol) in 10 mL of THF was added slowly. The generate solution was stirred for another 12 at room temperature and volatile materials were removed under vacuum. The residue recrystallized in hot toluene to give yellow crystalline solid. Yield: 0.87 g (75%) yield. Anal. Calcd (found) for $C_{72}H_{92}Mg_2N_4O_6$: N, 4.84 (4.82); C, 74.67 (74.40); H, 8.01 (8.00)%. ^1H NMR ($CDCl_3$, ppm): δ 7.91 (s, 1H, C*H*=N), 7.89 (s, 1H,C*H*=N), 6.7–7.45 (m, 11H, Ar*H*), 4.58 (b, 2H, OCH_2Ph), 3.59 (s, 3H, OMe), 3.46 (b, 1H, C*H*–N=), 2.82 (b, 1H, C*H*–N=), 1.39–2.35 (m, 8H, –CH_2–),1.64 (s, 9H, C(CH_3)$_3$), 1.23 (s, 9H, C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 171.17, 167.51, 158.09, 157.58, 146.40, 132.77, 131.44, 129.50, 129.19, 128.20, 127.76, 127.55, 126.04, 125.12, 124.88, 120.95,

119.46, 112.59, 70.92, 68.95, 65.61, 57.29, 35.44, 33.63, 31.55, 31.40, 30.54, 29.86, 24.92, 24.06 ppm.

3.4. (SalenMe)ZnEt (**3**)

To a solution of Ligand **1** (0.896 g, 2.00 mmol) in 20 mL toluene at 0 °C was added diethyl zinc (2.2 mL, 1 M in hexane, 2.2 mmol). The mixture was stirred at room temperature overnight and was then filtered through celite. The filtrate was dried in vacuo to give yellow solid. Yield: 1.03 g (95%). Crystals suitable for X-ray diffraction were grown from toluene. Anal. Calcd (found) for $C_{31}H_{44}N_2O_2Zn$: N, 5.17 (5.26); C, 68.69 (68.89); H 8.18 (8.32)%. ^{1}H NMR ($CDCl_3$, ppm): δ 8.65 (s, 1H, C*H*=N), 8.179 (s, 1H, C*H*=N), 7.81 (m, 1H, Ar*H*), 7.37 (d, 1H, J= 2.4 Hz, Ar*H*), 7.25 (m, 2H, Ar*H*), 6.85 (m, 2H, Ar*H*), 6.83 (d, 1H, J=2.4 Hz, Ar*H*), 3.75 (s, 3H, OMe), 3.53 (m, 2H, C*H*N=C), 1.8 (m, 8H, –CH_2–), 1.42 (s, 9H, C(CH_3)$_3$), 1.28 (t, 3H, J=8 Hz, ZnCH_2CH_3), 1.26 (s, 9H, C(CH_3)$_3$), 0.42 (q, 2H, J=8 Hz, ZnCH_2) ^{13}C NMR ($CDCl_3$, ppm): δ 170.30, 167.64, 158.78, 158.04, 140.69, 135.41, 131.91, 129.43, 129.06, 127.37, 124.47, 120.65, 117.18, 110.94, 73.93, 73.51, 55.45, 35.43, 33.76, 33.50, 33.00, 31.33, 29.37, 24.75, 24.36, 12.20, 0.07.

3.5. [(SalenMe)Zn(OBn)]$_2$ (**4**)

To a solution of complex **3** (1.08 g, 2 mmol) in toluene (20 mL) at 0 °C, was slowly added benzyl alcohol (0.21 mL, 2 mmol). The mixture was stirred for 12 h at room temperature and then filtered through celite. The filtrate was dried in vacuo to give pale yellow solid. The residue was dissolved in 5 mL of CH_2Cl_2. Followed by the addition of 30 mL hexane, yellow precipitate was obtained. Yield: 0.81 g (65%). Anal. Calcd (found) for $C_{72}H_{92}N_4O_6Zn_2$: N 4.52 (4.16); C, 69.72 (69.25); H, 4.52 (4.51)%. ^{1}H NMR ($CDCl_3$, ppm): δ 8.09 (s, 1H, C*H*=N), 7.91 (s, 1H, C*H*=N), 7.71 (d, 1H, J=6.4 Hz, Ar*H*), 7.36 (d, 1H, J=2.4 Hz, Ar*H*), 7.21–7.30 (m, 3H, Ar*H*), 7.00 (m, 3H, Ar*H*), 6.84 (m, 1H, Ar*H*), 6.67 (d, 1H, J=6.4 Hz, Ar*H*), 6.63 (d, 1H, J=2.4 Hz, Ar*H*), 4.85 (dd, 2H, J=12 Hz, OCH_2Ph), 3.44 (s, 3H, OMe), 3.28 (m, 1H, C*H*N=C), 2.90 (m, 1H, C*H*N=C), 1.53–2.0 (m, 8H, –CH_2–), 1.58 (s, 9H, C(CH_3)$_3$), 1.98 (s, 9H, C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 173.68, 169.01, 158.75, 158.61, 140.38, 134.38, 131.49, 130.06, 129.11, 127.99, 127.01, 126.29, 124.92, 120.44, 116.50, 110.95, 73.31, 72.69, 68.86, 55.14, 35.54, 33.64, 33.57, 32.13, 31.33, 29.64, 24.67, 24.05.

3.6. Zn(SalenMe)$_2$ (**5**)

Complex **4** (0.618 g, 0.5 mmol) was dissolved in acetonitrile (20 mL) under a hot water bath (80 °C) for 1 h and then cooled to room temperature. **5** can be obtained as yellow crystals. Yield: 0.41 g (85%). Anal. Calcd (found) for $C_{58}H_{78}N_4O_4Zn$: N, 5.73 (5.80); C, 70.02 (70.21); H, 8.04 (8.14)%. ^{1}H NMR ($CDCl_3$, ppm): δ 8.57 (s, 1H, C*H*=N), 8.51 (s, 1H, C*H*=N), 8.23 (s, 1H, C*H*=N), 7.94 (m, 2H, C*H*=N+ Ar*H*), 7.76 (d, 1H, J=7.6 Hz, Ar*H*), 7.24–7.37 (m, 4H, Ar*H*), 6.84–6.98 (m, 4H, Ar*H*), 6.72 (d, 1H, J= 7.6 Hz, Ar*H*), 6.64 (m, 1H, Ar*H*), 3.77 (s, 3H, OMe), 3.55 (m, 1H, C*H*N=C), 3.54 (s, 3H, OMe), 3.98 (m, 1H, C*H*N=C), 3.32 (m, 1H, C*H*N=C), 3.11 (m, 1H, C*H*N=C), 1.52–1.99 (m, 16H, –CH_2–), 1.42 (s, 9H, C(CH_3)$_3$), 1.33 (s, 9H, C(CH_3)$_3$), 1.25 (s, 9H, C(CH_3)$_3$), 1.15 (s, 9H, C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 173.92, 173.32, 168.46, 168.35, 159.44, 158.97, 158.62, 157.93, 140.83, 140.57, 134.35, 133.92, 131.85, 131.46, 129.97, 129.68, 129.23, 129.05, 126.98, 126.80, 125.18, 124.53, 120.68, 120.49, 117.12, 116.35, 111.54, 111.09, 74.52, 72.45, 72.29, 72.24, 55.73, 55.31, 35.38, 35.28, 34.55, 33.91, 33.71, 33.55, 33.43, 32.25, 31.36, 31.28, 31.24, 29.61, 29.57, 24.81, 24.37, 24.10, 24.02.

3.7. Typical polymerization procedures

A typical polymerization procedure was exemplified by the synthesis of PLLA-50 (the number 50 indicates the designed $[M]_0/[I]_0$) at room temperature (Table 1, entry 2). The conversion yield (98%) of PLLA-50 was analyzed by ^{1}H NMR spectroscopic studies. To a mixture of complex **2** (0.029 g, 0.05 mmol) and L-lactide (0.36 g, 2.5 mmol) was added toluene (10 mL) at 25 °C. After the solution was stirred for 45 min, the reaction was then quenched by the addition of an aqueous acetic solution (0.35 N, 10 mL), and the polymer was precipitated on pouring the mixture into *n*-hexane (40 mL) to give white crystalline solids. The solid was filtered and washed with cold ethanol (10 mL) twice and was then dried under vacuum.

3.8. General kinetic studies

To a solution of L-lactide (0.18 g, 1.25 mmol) in $CDCl_3$ (3 mL) was added a different concentration solution of **2** or **4** in $CDCl_3$ (3 mL). The conversion yield of polymerization was analyzed by a Varian Mercury-400 NMR spectrometer in a period of time interval.

3.9. Measurement

3.9.1. GPC measurements

The GPC measurements were performed on a Hitachi L-700 system equipped with a differential Bischoff 8120 RI detector using THF (HPLC grade) as an eluent. The chromatographic column was Phenomenex Phenogel 5 10∼3A and the calibration curve is made by polystyrene standards to calculate M_n (GPC). A typical GPC measurements description was exemplified by the measurement of PLA-25 (the number 25 indicates $[M]_0/[I]_0$). 0.025 g PLA-25 was dissolved by 3.975 g THF (HPLC grade) and filter through a filter (13 mm Millex-HN Filter 0.45 μm NY Non-sterile). Then 25 μL of the solution were injected into the

GPC and the flow eluent rate is 1 mL min^{-1}. Full study was be finished in 15 min. The results were calculated by SISC chromatography data sation 1.0 edition.

3.9.2. NMR measurements

PLA-25 (ca. 0.01 g) was dissolved in $CDCl_3$ (ca. 0.5 mL) in a NMR tube and was determined by a Mercury-400 (400 Hz) spectrometer. The spectrum was obtained from at least 10 Fid files. M_n (NMR) for PLA was calculated based on the comparison of integral between peaks at 7.27–7.37 (–CH_2*Ph*), 5.18 (–OC*H*MeC(O)), 4.36 (–C*H*MeOH) ppm.

3.9.3. X-ray crystallographic studies

Single crystals suitable for X-ray structural determination of **2** and **3** were sealed in thin-walled glass capillaries under nitrogen atmosphere and were mounted on Brucker 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 SADABS program. 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 direct methods using a SHELXTL package. All non-H atoms were located from successive Fourier maps, and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H-atoms.

4. Conclusion

The first examples of mono methylether Salen supported magnesium and zinc alkoxides have been synthesized. These complexes efficiently initiate ROP of lactides in good controlled manner. It is interesting to note that magnesium complex **2** initiates ROP of *rac*-LA giving mostly isotactic PLA, while zinc complex **4** yields mostly heterotactic PLA. The polymerization kinetic studies show a second-order dependency on [LA] and a first order dependency on [**2**] when using complex **2** as an initiator. While complex **4** is used as an initiator, the polymerization rate has a first order dependency on both [LA] and [Zn].

Acknowledgements

Financial support from the National Science Council of the Republic of China is greatly acknowledged.

Supporting information

Crystallographic data of **2**, **3** and **5** are available at doi:10.1016/j.polymer.2005.08.009

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