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Well-defined sterically hindered zinc aryloxides: Excellent catalysts for ring-opening polymerization of ε-caprolactone and L-lactide

Bor-Hunn Huang, Chien-Nan Lin, Mao-Lin Hsueh, Taimur Athar, Chu-Chieh Lin*

Department of Chemistry, National Chung Hsing University, 250 Kuo Kuang Road, Taichung 402, Taiwan, ROC

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Abstract

Three novel sterically hindered zinc aryloxides have been prepared and well characterized. Their catalytic activities toward ring-opening polymerization (ROP) of ε-caprolactone and L-lactide have been investigated. The reaction of 2,2′-ethylidene-bis(4,6-di-*tert*-butylphenol) (EDBP-H_2), 2,2′-(2-methoxybenzylidene)bis(4-methyl-6-*tert*-butylphenol) (MEBBP-H_2) and 2,2′-(2-methoxybenzylidene)bis(4,6-di(1-methyl-1-phenylethyl)phenol) (MEMPEP-H_2) with $ZnEt_2$ in THF yields dimeric zinc complexes $[(\mu\text{-EDBP})Zn(THF)]_2$ (**1**), $[(\mu\text{-MEBBP})Zn(THF)]_2$ (**2**) and $[(\mu\text{-MEMPEP})Zn(THF)]_2$ (**3**), respectively. Experimental results show that all three compounds are good catalysts for ROP of ε-caprolactone and L-lactide yielding polymer in a controlled fashion with low polydispersity indexes.

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Keywords: Zinc; Catalyst; L-lactide

1. Introduction

Biodegradable polyesters such as poly(ε-caprolactone) (PCL), polylactide (PLA) and their copolymers have been attracting considerable attention owing to their potential applications in biomedical fields such as absorbable sutures and delivery medium for controlled release of drugs [1]. The ring-opening polymerization (ROP) of cyclic esters (e.g., ε-caprolactone (CL) and L-lactide (LA)) is a major and convenient method for the synthesis of these polyesters. $Al(OR)_3$ [2] and $Sn(Octoate)_2/ROH$ [3] have been used as initiators for ROP of lactone/lactides. However, in many cases, backbiting reaction/transesterification takes place as side reactions resulting in the formation of macrocycles or chain redistribution with wide range of molecular weight distribution. The undesired backbiting/transesterification reactions can be minimized by using a bulky ligand coordinatively attached with active metal center which provides a steric barrier for prevention of undesired side reactions. Recently, various sterically ligand coordinated main group metal complexes, such as aluminum [4], magnesium [5], stannous [6], lithium [7], calcium [8] as well as transition metal complexes [9] have been reported to be efficient initiators or catalysts for ROP of cyclic esters giving polymers with low molecular distribution.

Zinc complexes with sterically hindered ligands have attracted considerable attention in recent years as catalysts/initiators for the ROP of CL and LA [10]. Most recently, a series of novel aluminum [4f,h,i], lithium [7a,d] and magnesium [5c] complexes with a bulky ligand, 2,2′-ethylidene-bis(4,6-di-*tert*-butylphenol) (EDBP-H_2) have been synthesized and these complexes have shown great reactivity toward ROP of L-lactide in our laboratory. These bulky ligands are designed to provide a steric barrier around active metal ions for minimizing the side reaction. We report herein the synthesis and characterization of three novel sterically hindered zinc complexes. Experimental results show that these zinc compounds are good catalysts for the ROP of ε-caprolactone and L-lactide yielding polyesters with low polydispersity indexes (PDIs) in a wide range of monomer-to-initiator ratios.

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* Corresponding author. Tel.: +886 4 22840412; fax: +886 4 22862547.
E-mail address: cchlin@mail.nchu.edu.tw (C.-C. Lin).

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2. Results and discussion

2.1. Synthesis and spectroscopic studies

Except for the commercially available ligand 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) (EDBP-H_2), the sterically bulky bisphenol ligands, 2,2′-(2-methoxybenzylidene)bis(4-methyl-6-*tert*-butylphenol) (MEBBP-H_2) [11] and 2,2′-(2-methoxybenzylidene)bis(4,6-di(1-methyl-1-phenylethyl)phenol) (MEMPEP-H_2) [12] are synthesized according to the method reported previously. Further reactions of these bisphenol ligands with 1.1 molar equiv of $ZnEt_2$ in THF produce four-coordinated dimeric zinc complexes $[(EPBP)Zn(THF)]_2$ (**1**) $[(MEBBP)Zn(THF)]_2$ (**2**) and $[(MEMPEP)Zn(THF)]_2$ (**3**) in moderate yields as shown in Scheme 1. All of these compounds were isolated as colorless crystalline solids and have been characterized by spectroscopic studies as well as X-ray structural determination.

Suitable crystals for structural determination of **1**–**3** were obtained from a toluene or a mixture of hexane/tetrahydrofuran solution, and the molecular structures of **1** and **2** are shown in Figs. 1 and 2. The structure of **1** shows a dimeric feature containing a Zn_2O_2 core bridging through one of the phenoxy oxygen atoms with the center of the Zn_2O_2 core sitting on the crystallographic center. The geometry around Zn is a distorted tetrahedron bound to one phenoxy oxygen, a THF, and two bridging phenoxy oxygen atoms with the Zn–O(2) bond distance of 1.847(3) (phenoxy) and Zn–O(3) bond distance of 2.057(3) (THF). The bridging oxygen atom bonded to two Zn atoms are asymmetric with the Zn–O(1) bond distance of 1.979(2), and Zn–O(1A) bond distance of 1.986(2) (bridging oxygen). The molecular structures of **2**–**3** are similar to that of **1**. The geometry around Zn in **2** is also distorted from tetrahedron and the bridging oxygen atom bond distances are asymmetric to the two Zn centers with the mean bond distances of Zn–O(1) 1.985(2) (bridging oxygen), Zn–O(1A) 1.990(2) (bridging oxygen), Zn–O(2) 1.847(2) (phenoxy), Zn–O(3) 2.030(2) (THF).

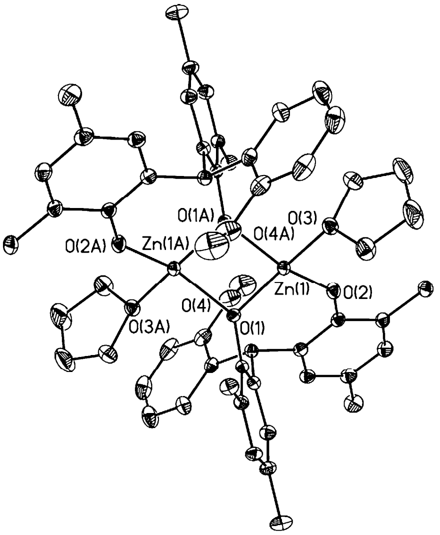
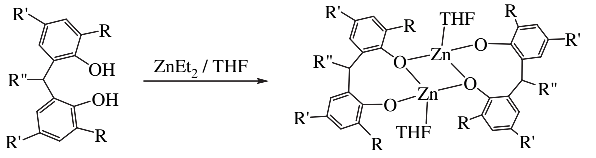


Fig. 2. Molecular structure of **2** as 20% ellipsoids. Methyl carbons of the *tert*-butyl groups and all hydrogen atoms are omitted for clarity.



1. R = R' = *t*-Bu, R'' = Me
2. R = *t*-Bu, R' = Me, R'' = o-(OMe)C_6H_4
3. R = R' = $C(CH_3)_2Ph$, R'' = o-(OMe)C_6H_4

Scheme 1.

2.2. Ring-opening polymerization of ε-caprolactone catalyzed by **1**–**3**

In general, polymerization was performed as the following procedures. CL (0.26 mL, 2.5 mmol) and BnOH (1 mL, 0.10 mmol) were added to a rapidly stirred solution of catalysts **1**, **2** or **3** in toluene. The reaction mixture of **1** was stirred and

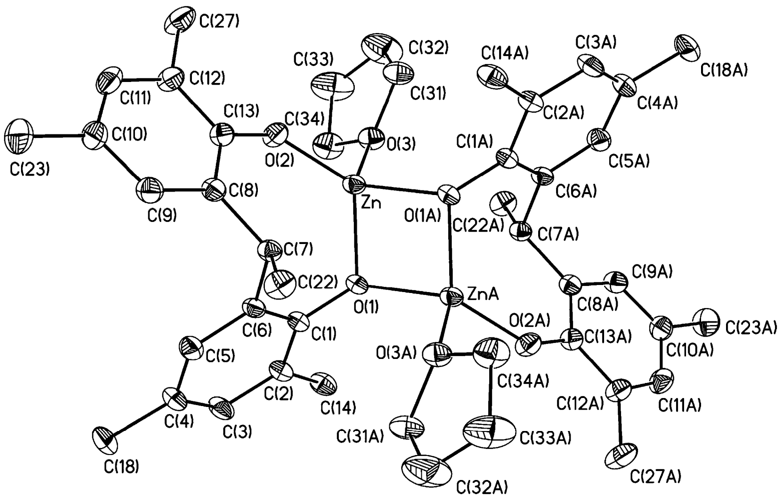


Fig. 1. Molecular structure of **1** as 20% ellipsoids. Methyl carbons of the *tert*-butyl groups and all hydrogen atoms are omitted for clarity.

slowly heated to 50 °C, **2** was stirred and slowly heated to 50 °C, and **3** was stirred at 25 °C for 1 h, during which the increase in viscosity of the solution was observed. After the reaction was quenched by the addition of an excess 0.35 N aqueous acetic acid solution, the polymer was precipitated out in *n*-heptane. Polymerizations of CL under different reaction conditions have been systematically studied as shown in Table 1 (entries 1–22). It was found that the polydispersity indexes (PDIs) of PCL catalyzed by **1–3** range from 1.05 to 1.17. A linear relationship between number-average molecular weight (Mn) and monomer-to-initiator ratio ($[M]_0/[BnOH]_0$) exists as shown in Fig. 3 [13], implying the "living" character of the polymerization process. The "living" character of the active polymer chain end was further confirmed by the sequential ROP of CL. In the resumption experiment (Table 1, entries 6, 14 and 21), another portion of CL monomer ($[M]_0/[BnOH]_0 = 50$ for **1**; $[M]_0/[BnOH]_0 = 100$ for **2**, **3**) was added after polymerization of first addition ($[M]_0/[BnOH]_0 = 50$ for **1**; $[M]_0/[BnOH]_0 = 100$ for **2**, **3**) had gone to completion. Furthermore, **1** has demonstrated that as many as 20-fold of [BnOH]/[**1**] can be used. This is very important for biomedical purpose in which a small amount of zinc complex can be used to initiate a substantial amount of polymer. The ^{1}H NMR spectrum of PCL-50 (the number 50 indicates the designed $[CL]_0/[BnOH]_0$ ratio) (Fig. 4) indicates the polymer chain should be capped with one benzyl ester and one hydroxyl group. While comparing the reactivity of **1–3** toward the ring-opening polymerization of ε-caprolactone, it has been found that the reactivity of **3** is somewhat larger than that of **2**. For instance, ROP of CL in the same condition, up to 91% conversion can be achieved within 2 h using **3** as catalyst (Table 1, entry 18). However, it takes 3.5 h when **2** is used as catalyst (Table 1, entry 15). The polymerization activity with **3** > **1** and **2** > **1** can be concluded by the comparison of (Table 1, entry 17/ entry 1) and (Table 1, entry 10/entry 3), respectively. These results indicate that an increase in sterically bulky substituents on the bisphenol ligand increases the polymerization rate. This order is consistent with the observation for aluminum and magnesium complexes [4f,g,12].

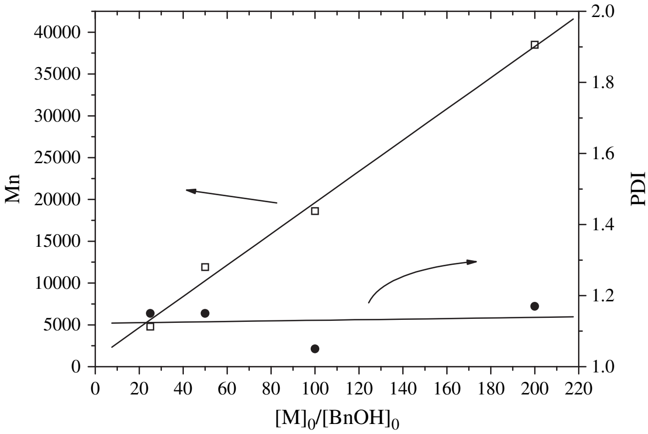


Fig. 3. Polymerization of CL catalyzed by **1** in 1,2-dichloroethane at 50 °C. The relationship between Mn (□), PDI (●) of polymer and the initial mole ratio $[M]_0/[BnOH]_0$ is shown.

2.3. Ring-opening polymerization of L-lactide

ROP of L-lactide was carried out by employing **1–3** (0.05 mmol) as catalysts and the reaction was systematically examined in 1,2-dichloroethane (10 mL) at 50 °C or 83 °C as

Table 1
Ring-opening polymerization of ε-caprolactone catalyzed by complexes **1–3** in toluene

Entry	[Zn]	$[M]_0/[Zn]_0/[BnOH]_0$	Temp (°C)	Time (h)	Mw/Mn	Mn[a] (obsd)	Mn[b] (calcd)	Mn[c] (NMR)	Conv[c] (%)
1	**1**	100/1/2	25	7	1.12	11,000 (6200)	4900	5400	92
2	**1**	50/1/2	50	1	1.15	4800 (2700)	2600	2500	95
3	**1**	100/1/2	50	2	1.15	11,900 (6700)	5300	4900	99
4	**1**	200/1/2	50	2	1.05	18,600 (10,400)	9800	10,100	93
5	**1**	400/1/2	50	3	1.17	38,500 (21,600)	20,100	22,300	96
6	**1**	50 (50)/1/2	50	1 (1)	1.13	10,400 (5800)	5300	5700	99
7	**1**	400/1/10	50	1	1.10	8400 (4700)	4200	4500	99
8	**1**	400/1/20	50	1	1.07	4100 (2300)	2200	2400	99
9	**2**	50/1/2	50	0.5	1.10	5100 (2900)	2900	3400	97
10	**2**	100/1/2	50	0.5	1.10	9000 (5000)	5500	6000	95
11	**2**	200/1/2	50	1	1.12	21,900 (12,300)	10,800	12,900	94
12	**2**	300/1/2	50	1	1.13	31,600 (17,700)	16,400	16,100	95
13	**2**	400/1/2	50	1	1.12	39,900 (22,300)	22,000	23,100	96
14	**2**	100 (100)/1/2	50	0.5 (0.5)	1.10	24,100 (13,500)	11,400	12,300	99
15	**2**	200/1/2	25	3.5	1.10	25,300 (14,200)	11,300	13,400	98
16	**3**	50/1/2	25	1	1.07	5600 (3100)	2900	3400	97
17	**3**	100/1/2	25	1.5	1.10	10,300 (5800)	5600	5900	96
18	**3**	200/1/2	25	2	1.08	21,000 (11,800)	10,500	12,500	91
19	**3**	300/1/2	25	3	1.08	27,500 (15,400)	15,500	16,300	90
20	**3**	400/1/2	25	4	1.08	39,100 (21,900)	20,600	21,500	90
21	**3**	100 (100)/1/2	25	1.5 (1.5)	1.13	19,400 (13,500)	11,400	12,900	99
22	**3**	200/1/4	25	2	1.10	13,600 (7600)	5800	8600	99

Values in parentheses are the values obtained from GPC × 0.56 [14].

[a] Obtained from GPC analysis and calibrated by a polystyrene standard.

[b] Calculated from the molecular weight of ε-caprolactone × $[M]_0/[BnOH]_0$ × the conversion yield.

[c] Obtained from ^{1}H NMR analysis.

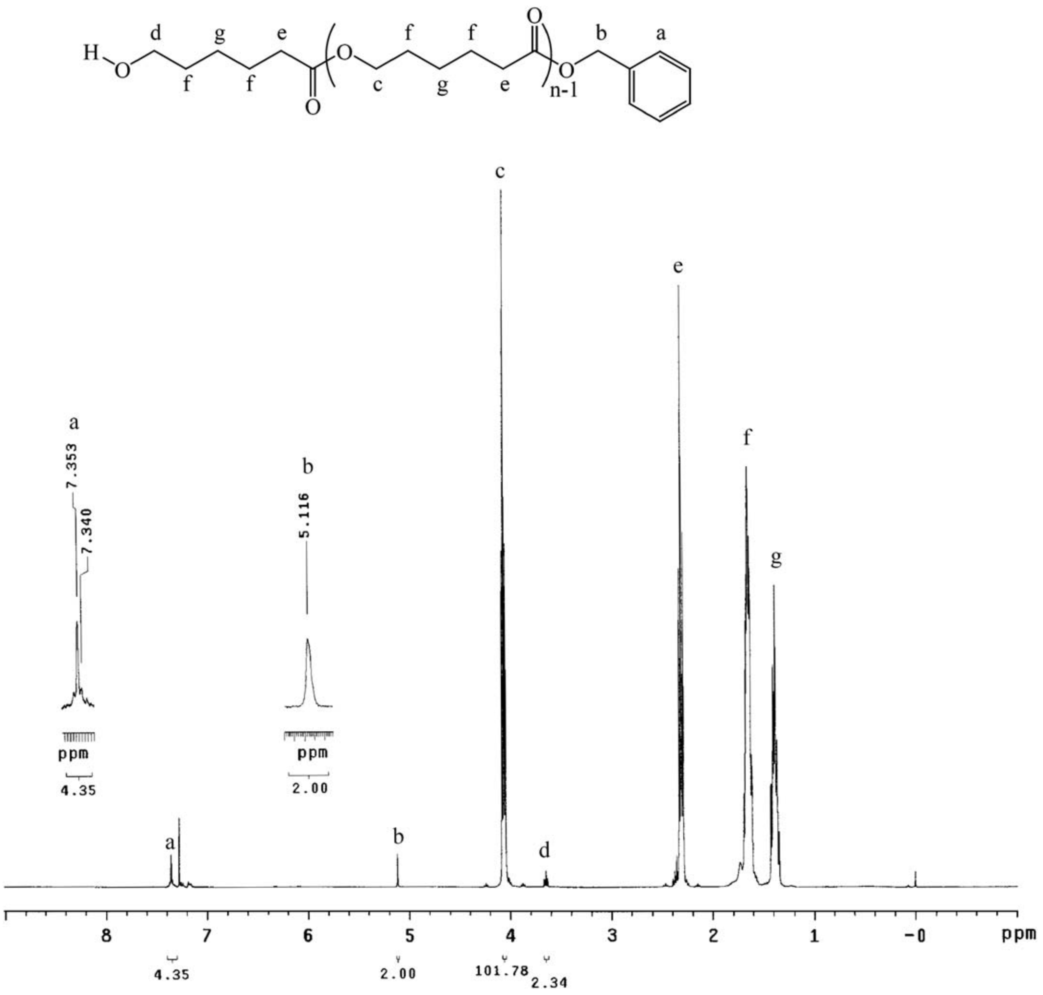


Fig. 4. ^{1}H NMR spectrum of PCL-50 catalyzed by **1**.

shown in Table 2. It was found that **1**–**3** are efficient catalysts for the ROP of L-lactide and the reaction gets completed within 9 h for **2** (Table 2, entry 7) and 5 h for **3** (Table 2, entry 11) at 50 °C, respectively. However, the conversion goes only to 61% at the same condition in 16 h when using **1** as catalyst (Table 2, entry 1). The experimental result reveals the reactivity is in the order $\mathbf{3} > \mathbf{2} > \mathbf{1}$ which is consistent with that observed for CL polymerization. The PDIs of poly(L-lactide)s obtained are low, ranging from 1.09 to 1.20, and a linear relationship between Mn and $[M]_0/[BnOH]_0$ exists (Fig. 5). The ^{1}H NMR spectrum of PLA-50 (Fig. 6) indicates that the polymer chain should be capped with one benzyl ester at one end and with a hydroxyl group at the other end. These results suggest that the polymerization occurs through insertion of a benzyl alkoxy group into the lactide.

*2.4. Proposed mechanism for ROP of L-lactide catalyzed by **1***

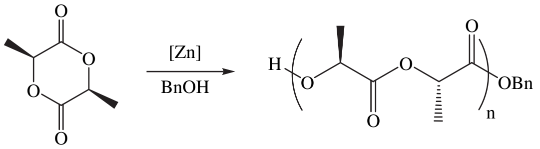
Both Zn atoms of **1** are equivalent and can act as Lewis acids which are similar to its magnesium analogues [16]. In the presence of an excess of L-LA, dissociation of THF occurs followed by the coordination of L-lactide on both Zn and Zn(A) atoms giving intermediate (**A**) as shown in Scheme 2. The insertion of benzyl alcohol, which is activated by the formation of a hydrogen bond through the terminal oxygen atom of EDBP^{2-} (**B**), to the carbonyl group of L-LA leads to the ring-opening polymerization. Activation of benzyl alcohol by the formation of hydrogen bond has been verified by the isolation of a lithium complex in which a hydrogen bond between benzyl alcohol and the oxygen atom of EDBP^{2-} ligand has been observed [12]. Further evidence can be found by the theoretical calculation of a magnesium system [16].

3. Experimental section

3.1. General

All manipulations were carried out under a dry nitrogen atmosphere. All glasswares were flame-dried under vacuum before use. Solvents were dried by refluxing at least for 24 h over sodium/benzophenone (hexane, toluene and tetrahydrofuran), phosphorus pentoxide (CH_2Cl_2), or over anhydrous magnesium sulphate (benzyl alcohol) and freshly distilled prior to use. Deuterated solvents and ε-caprolactone were dried over 4 Å molecular sieves. L-lactide is purified from the recrystallization

Table 2
Ring-opening polymerization of L-lactide catalyzed by complexes **1–3** in 1,2-dichloroethane



Entry	[Zn]	$[M]_0/[Zn]_0/[BnOH]_0$	Temp (°C)	Time (h)	Mw/Mn	Mn[a] (obsd)	Mn[b] (calcd)	Mn[c] (NMR)	Conv[c] (%)
1	**1**	100/1/2	50	16	1.08	5600 (3200)	4500	3300	61
2	**1**	100/1/2	83	4	1.14	9900 (5700)	7200	5900	>99
3	**1**	200/1/2	83	4	1.09	21,200 (12,300)	14,100	12,100	97
4	**1**	300/1/2	83	4	1.10	29,800 (17,300)	20,800	18,500	96
5	**1**	400/1/2	83	4	1.16	42,100 (24,400)	28,300	25,100	98
6	**2**	50/1/2	50	9	1.20	6300 (3700)	3400	3700	92
7	**2**	100/1/2	50	9	1.17	13,500 (7800)	7000	6700	96
8	**2**	150/1/2	50	9	1.16	19,300 (11,200)	10,600	11,500	97
9	**2**	200/1/2	50	9	1.09	24,500 (14,200)	14,200	13,400	98
10	**3**	50/1/2	50	5	1.18	6300 (3700)	3400	3400	91
11	**3**	100/1/2	50	5	1.17	13,400 (7800)	6900	6800	95
12	**3**	150/1/2	50	5	1.20	18,500 (10,700)	10,500	11,100	96
13	**3**	200/1/2	50	5	1.20	25,100 (14,600)	14,100	13,800	97

Values in parentheses are the values obtained from GPC × 0.58 [14,15].

[a] Obtained from GPC analysis and calibrated by a polystyrene standard.

[b] Calculated from the molecular weight of ε-caprolactone × $[M]_0/[BnOH]_0$ × the conversion yield.

[c] Obtained from ^1H NMR analysis.

of the toluene solution. $ZnEt_2$ (1.0 M in hexane), 2,2′-Ethylidenebis(4,6-di-*tert*-butylphenol), 2,4-bis(α,α-dimethylbenzyl)phenol, 2-*tert*-butyl-4-methylphenol, formaldehyde, *o*-anisaldehyde, acetic acid and benzenesulfonic acid were purchased and used without further purification. ^1H NMR spectra were recorded on a Varian Mercury-400 (400 MHz) spectrometer with chemical shifts given in ppm from the internal TMS. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument.

*3.2. [(μ-EDBP)Zn(THF)]$_2$ (**1**)*

A diethylzinc solution (1.1 mL, 1.0 M in hexane, 1.1 mmol) was added slowly to an ice cold solution (0 °C) of 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) (0.88 g, 2.0 mmol) in tetrahydrofuran (20 mL). The mixture was stirred for 3 h at room temperature and evaporated to dryness under vacuum. The residue was dissolved in hot THF (60 mL) and filtered through celite. Colorless crystals were obtained from a mixture of hexane and tetrahydrofuran at room temperature after overnight. Yield: 1.78 g (78%). Anal. Calcd for $C_{68}H_{104}O_6Zn_2$: C, 71.12; H, 9.13%. Found: C, 71.72; H, 9.48%. ^1H NMR ($CDCl_3$, ppm) δ 7.24–6.83 (m, 8H, Ph); 6.05 (s, 1H, CH); 3.69 (br, 4H, OCH_2CH_2); 3.45 (s, 3H, OCH_3); 2.17 (s, 6H, $PhCH_3$); 1.80 (br, 4H, OCH_2CH_2); 1.35 (s, 18H, $C(CH_3)_3$).

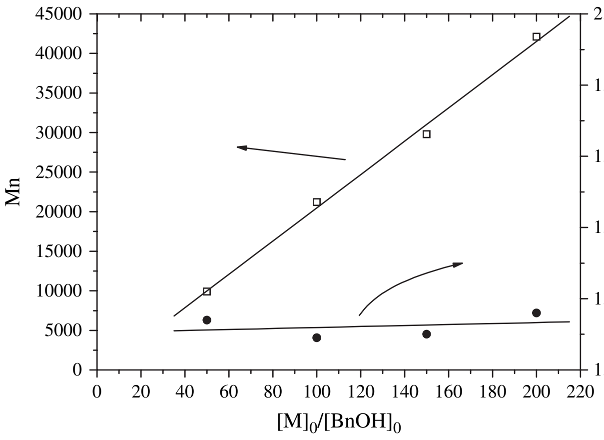


Fig. 5. Polymerization of L-LA catalyzed by **1** in 1,2-dichloroethane at 83 °C. The relationship between Mn (□), PDI (●) of polymer and the initial mole ratio $[M]_0/[BnOH]_0$ is shown.

*3.3. [(μ-MEBBP)Zn(THF)]$_2$ (**2**)*

To an ice cold solution (0 °C) of 2,2′-(2-methoxybenzylidene)bis(4-methyl-6-*tert*-butylphenol) (0.446 g, 1.0 mmol) in tetrahydrofuran (20 mL) was added slowly diethylzinc solution (1.20 mL, 1.0 M in hexane, 1.20 mmol). The mixture was stirred at room temperature for 3 h, during which a white precipitate was formed and the volatile materials were removed under vacuum. The residue was dissolved in hot THF (70 mL) and filtered through celite. Colorless crystals were obtained from a mixture of hexane and tetrahydrofuran (2:7) at room temperature after three days. Yield: 0.89 g (76%). Anal. Calcd for $C_{68}H_{88}O_8Zn_2$: C, 70.15; H, 7.62%. Found: C, 69.74; H, 8.02%. ^1H NMR ($CDCl_3$, ppm): δ 7.25–6.84 (m, 16H, Ph); 6.40 (s, 2H, C*H*); 3.79 (br, 8H, OC*H*$_2$); 3.68 (s, 6H, OCH_3); 2.16 (s, 12H, $PhCH_3$); 1.75 (br, 8H, OCH_2C*H*$_2$); 1.36 (s, 36H, $C(CH_3)_3$). Mp: 162–164 °C.

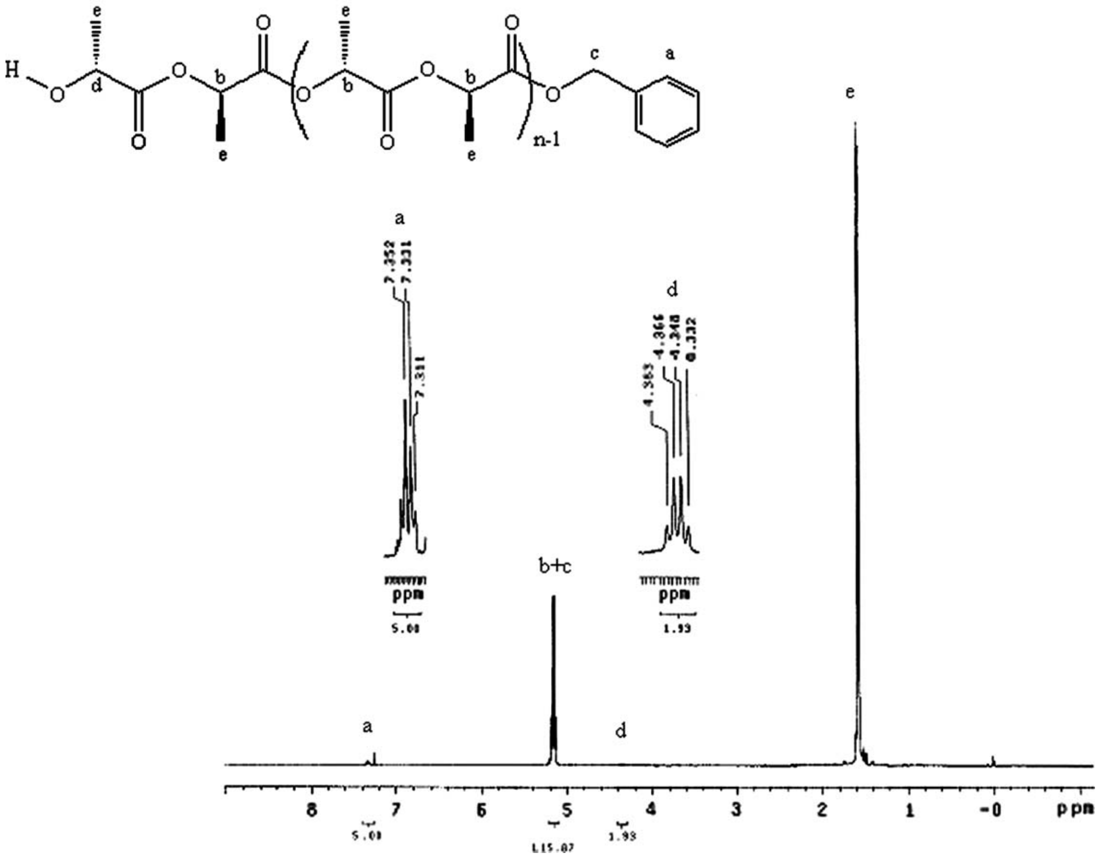


Fig. 6. ^{1}H NMR spectrum of PLA-50 catalyzed by **1**.

3.4. [(μ-MEMPEP)Zn(THF)]$_2$ (3)

To an ice cold solution (0 °C) of 2,2′-(2-methoxybenzylidene)-bis(4,6-di(1-methyl-1-phenylethyl)phenol) (1.56 g, 2.0 mmol) in tetrahydrofuran (20 mL) was added slowly diethylzinc solution (2.40 mL, 1.0 M in hexane, 2.4 mmol). The mixture was stirred at room temperature for 24 h and evaporated to dryness under vacuum. The residue was dissolved in THF (10 mL) and filtered through celite. Colorless crystals were obtained from a mixture of hexane and tetrahydrofuran (1:8) at room temperature. Yield: 1.35 g (74%). Anal. Calcd for $C_{120}H_{128}O_8Zn_2$: C, 78.80; H, 7.05%. Found: C, 78.13; H, 7.13%. ^{1}H NMR ($CDCl_3$, ppm) δ 7.48–6.55 (m, 56H, Ph-*H*); 6.12 (s, 2H, C*H*); 3.36 (s, 6H, OCH_3); 2.69 (br, 8H, OCH_2); 1.41 (br, 8H, OCH_2CH_2); 1.56, 1.26 (s, 48H, $PhC(CH_3)_2$). Mp: 178–180 °C.

3.5. Polymerization of ε-caprolactone catalyzed by 1

A typical polymerization procedure was exemplified by the synthesis of PCL-50 (the number 50 indicates the designed $[CL]_0/[BnOH]_0$) at 50 °C (Table 1, entry 2). The conversion yield (95%) of PCL-50 was analyzed by ^{1}H NMR spectroscopic studies. To a rapidly stirred solution of [(μ-EDBP)Zn(THF)]$_2$ (**1**) (0.057 g, 0.05 mmol) in toluene (5 mL) was added a mixture of ε-caprolactone (0.26 mL, 2.5 mmol) and benzyl alcohol (1.0 mL, 0.10 mmol). The reaction mixture was stirred for 1 h; viscosity of the reaction mixture increases. The reaction was quenched by the addition of an aqueous acetic acid solution (0.35 N, 10 mL), and the polymer was precipitated out as white crystalline solid on pouring the mixture into *n*-hexane (40 mL). Yield: 0.21 g (72%).

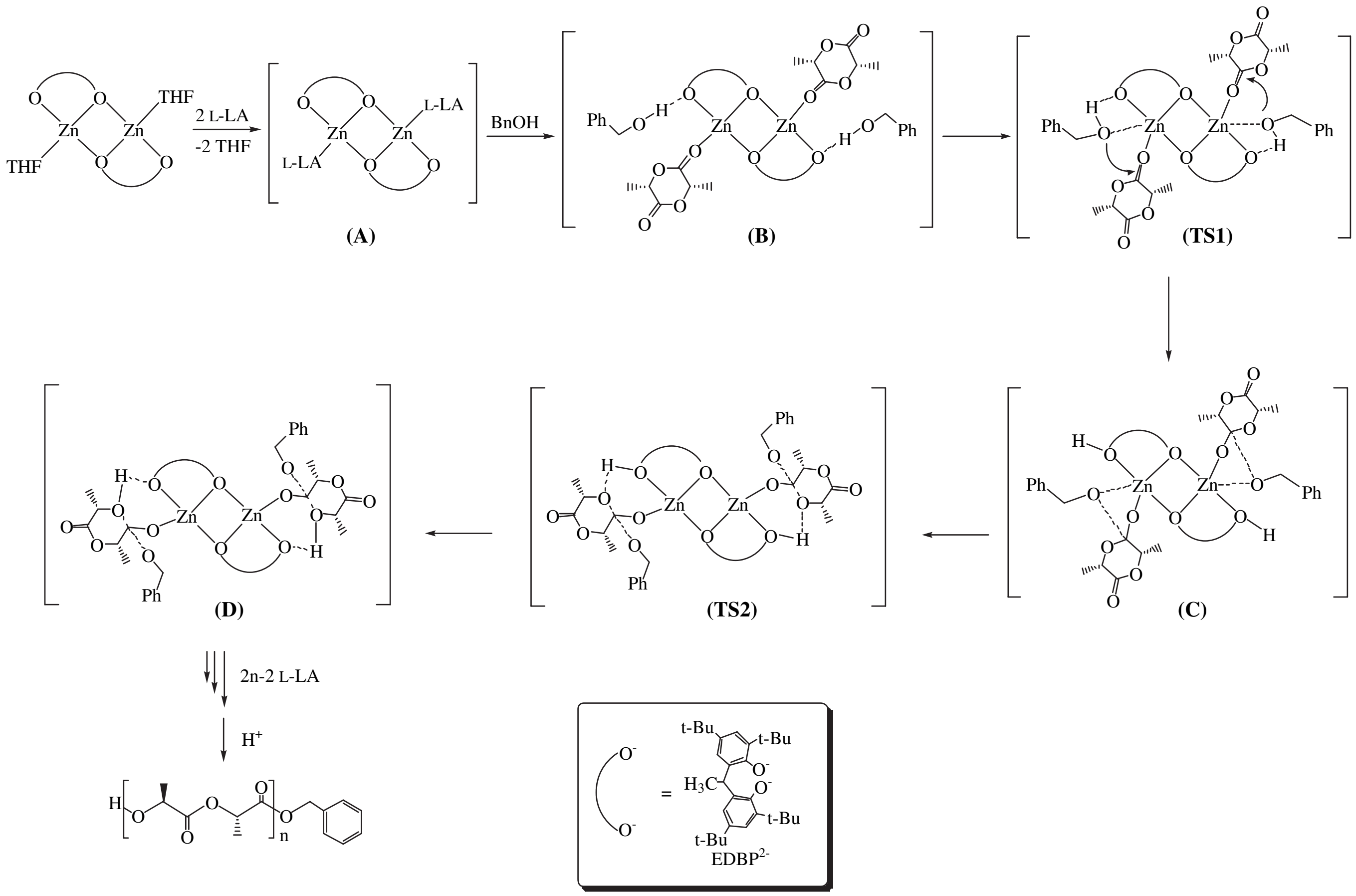
3.6. Polymerization of L-lactide catalyzed by 2

A typical polymerization procedure was exemplified by the synthesis of PLA-50 (the number 50 indicates the designed $[LA]_0/[BnOH]_0$) at 50 °C (Table 2, entry 6). The conversion yield (92%) of PLA-50 was analyzed by ^{1}H NMR spectroscopic studies. To a rapidly stirred solution of [(μ-MEBBP)Zn(THF)]$_2$ (**2**) (0.058 g, 0.05 mmol) in 1,2-dichloroethane (10 mL) was added a mixture of L-lactide (0.36 g, 2.5 mmol) and benzyl alcohol (1.0 mL, 0.10 mmol). After 9 h stirring the increase of viscosity was observed in the reaction mixture. The reaction was quenched by the addition of an aqueous acetic acid solution (0.35 N, 10 mL), and the polymer was precipitated out as white crystalline solid on pouring the mixture into *n*-hexane (100 mL). Yield: 0.32 g (89%).

3.7. Measurement

3.7.1. GPC measurements

The GPC measurements were performed on a Hitachi L-7100 system equipped with a differential Bischoff 8120 RI



Scheme 2.

detector using THF (HPLC grade) as an eluent. The chromatographic column was Phenomenex Phenogel 5 μ 10^3 Å and the calibration curve is made by polystyrene standards to calculate Mn (GPC). A typical GPC measurements description was exemplified by the measurement of PCL-50 (the number 50 indicates $[M]_0/[I]_0$). PCL-50 (0.025 g) was dissolved in 3.975 g THF (HPLC grade) and filtered through a filter (13 mm Millex-HN Filter 0.45 μm NY Nonsterile). Then 25 mL of the solution was injected into the GPC and the flow eluent rate is 1 mL min^{-1} for 15 min. The results were calculated by SISC chromatography data solution 1.0 edition.

3.7.2. X-ray crystallographic studies

Suitable crystals of **1–3** were sealed in thin-walled glass capillaries under a nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. Intensity data were collected in 1350 frames with increasing *ω* (width of 0.3° per frame). The absorption correction was based on the symmetry-equivalent reflections using the SADABS program. The space group determination was based on a check of the Laue symmetry and systematic absences and confirmed by using the structure solution. The structure was solved by direct methods or Patterson methods using an 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

Three novel dimeric zinc aryloxides, $[(\mu\text{-EDBP})Zn(THF)]_2$ (**1**), $[(\mu\text{-MEBBP})Zn(THF)]_2$ (**2**) and $[(\mu\text{-MEMPEP})Zn(THF)]_2$ (**3**) have been synthesized and structurally characterized. Compounds **1–3** have demonstrated efficient catalytic activities toward ROP of ε-caprolactone and L-lactide. As much as 20-fold polymer chains per zinc center can be generated.

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Appendix A. Supporting information

This includes the crystallographic data of **1–4** and Figs. S1–S4. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2006.07.015.

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