A Highly Efficient Initiator for the Ring-Opening Polymerization of Lactides and ϵ-Caprolactone: A Kinetic Study

Hsuan-Ying Chen, Bor-Hunn Huang, and Chu-Chieh Lin*

Department of Chemistry, National Chung-Hsing University, Taichung 402, Taiwan, R.O.C.

Received March 31, 2005; Revised Manuscript Received April 27, 2005

ABSTRACT: A trinuclear zinc alkoxide [{(BDI-OMe)Zn(μ-OBn)}$_2$Zn(μ-OBn)$_2$] (**1**) and a homoleptic zinc complex [(BDI-OMe)$_2$Zn] (**2**) have been prepared by the addition of benzyl alcohol to a mixture of BDI-OMe-H with Et_2Zn. Compound **1** has been employed as an initiator for ring-opening polymerization of lactides and ϵ-caprolactone. The highly efficient initiator of the zinc complex shown in the polymerization process enabled us to synthesize the PLA at ambient temperature, yielding PLA with well molecular control and narrow molecular weight distribution in a very short period of time. The polymerization kinetics were studied with $[LA]_0/[\mathbf{1}] = 200/1$ and $[LA]_0 = 0.5$ M at 25 °C. Experimental results indicate a second-order dependency on [LA] ($k_{obs} = 0.033$ M^{-1} s^{-1}). Moreover, a first-order dependency in [**1**] is indicated of k_{obs} vs [Initiator], with a slope equal to the first-order rate constant $k = 12.2$ M^{-2} s^{-1}. Furthermore, the heterotactic PLA with *Pr* up to 83% can be achieved in a mixed solvent of CH_2Cl_2 and THF at −35 °C. However, according to polymerization kinetic studies of CL, a first-order dependency on [CL] and [**1**] is observed for ROP of ϵ-caprolactone.

Introduction

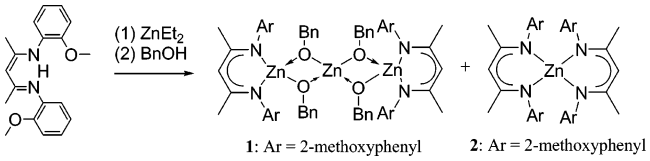
Poly(lactide) (PLA) and poly(ϵ-caprolactone) (PCL) and their copolymers have been studied intensively due to their biodegradability, biocompatibility, and permeable properties and have shown their potential applications in a variety of fields.[1] Though several strategies have been used for the preparation of PLA and PCL, the particular convenient method to synthesize these polymers is the ring-opening polymerization (ROP) of lactides/lactone and their functionally related compounds. Many metal complexes (e.g., Al[2], Li[3], Mg,[4] Fe,[5] Sn,[6] or Zr[7]) have been used as initiator/catalyst in the ROP of cyclic esters. However, when using metal alkoxides as initiators for ROP of lactides, backbiting reactions leading to the formation of macrocycles always occur as side reactions. The undesired backbiting reactions can be eliminated by using a suitable sterically bulky ligand to interact coordinatively with the active center and therefore provide a steric barrier to a certain extent around that metal center to minimize the side reactions.

β-Diketiminato ligands have emerged as one of the most versatile ligands in coordination chemistry for their strong metal−ligand bonds, and these ligands are readily tunable to access derivatives containing a range of substituents around the ligand skeleton.[8] Recently, compounds with sterically bulky substituents on the nitrogen donor atoms of β-diketiminato ligands have been used widely in small molecule activation,[9] olefin polymerization,[10] and ROP of cyclic esters.[11] The side reactions of ROP of cyclic esters, such as transesterification, can be reduced by using a modified β-diketiminato ligand with a methoxy group. We describe herein the complexation chemistry of zinc with a β-diketiminato ligand and to examine the ability of its alkoxide to initiate the ring-opening polymerization of lactides and ϵ-caprolactone.

Results and Discussion

Synthesis and Characterization. The ligand BDI-OMe-H (BDI-OMe-H = 2-(2-methoxyphenyl)amino-4-(2-methoxyphenyl)imino-2-pentene) was prepared by the reaction of 2,4-pentanedione with 2 mol equiv of 2-methoxyaniline in the presence of a catalytic amount of benzenesulfonic acid. In the progress of this research, BDI-OMe-H has been published by Carey et al.[12] Followed by the reaction of BDI-OMe-H with a stoichiometric amount of diethylzinc in hexane for 3 h, 2 mol equiv of benzyl alcohol (BnOH) was added to form a trinuclear zinc alkoxide [{(BDI-OMe)Zn(μ-OBn)}$_2$Zn(μ-OBn)$_2$] (**1**) and a homoleptic complex [(BDI-OMe)$_2$Zn] (**2**) in moderate yield, as shown in Scheme 1. During the reaction of BDI-OMe-H with Et_2Zn, a monomeric [(BDI-OMe)ZnEt] was observed as an intermediate. Unlike other BDI systems in which [(BDI)ZnR] can be isolated,[11c,13] [(BDI-OMe)ZnEt] disproportionates to complex **2** and Et_2Zn slowly at ambient temperature. Therefore, stepwise synthesis of **1** is unsuccessful. It is believed that, in the presence of BnOH, [(BDI-OMe)-ZnEt] and Et_2Zn react with BnOH to yield [(BDI-OMe)-ZnOBn] and Zn(OBn)$_2$, respectively. The combination of 2 equiv of [(BDI-OMe)ZnOBn] with Zn(OBn)$_2$ gives complex **1**. All of BDI-OMe-H, **1**, and **2** were analyzed on the basis of ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, and X-ray structural determination. X-ray structural analysis reveals that complex **1** consists of two [(BDI-OMe)Zn(μ-OBn)] moieties bridging by a Zn-(μ-OBn)$_2$ molecule through the oxygen atoms of benzyl alkoxy groups, as shown in Figure 1. All Zn atoms are distorted tetrahedral, and these two BDI-OMe$^-$ ligands are arranged so that they are nearly perpendicular to each other with the dihedral angle between these two ZnNCCCN planes being 85.1°. The internal Zn atom is a distorted tetrahedron with bond angles of 82.91, 82.89, 119.03, and 126.19°. Both Zn(1)O(7)Zn(2)O(8) and Zn-

Scheme 1



1: Ar = 2-methoxyphenyl **2**: Ar = 2-methoxyphenyl

10.1021/ma050672f CCC: $30.25
Published on Web 05/28/2005

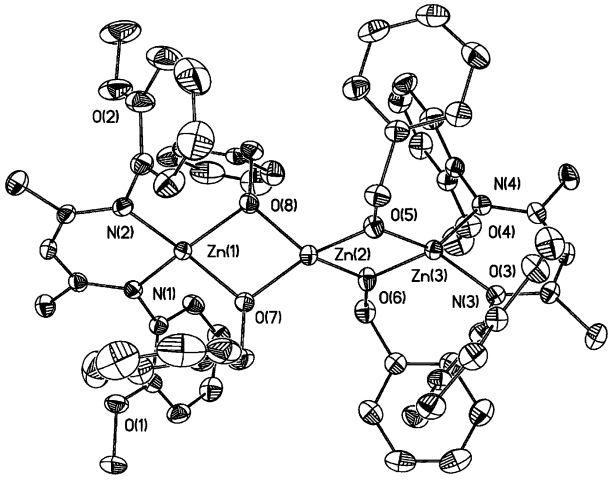


Figure 1. ORTEP drawing of [{(BDI-OMe)Zn(μ-OBn)}$_2$Zn(μ-OBn)$_2$] (non-hydrogen atoms) with thermal ellipsoids drawn at the 20% probability level. Selected bond lengths [Å]: Zn(1)−O(8) 1.923(3), Zn(1)−O(7) 1.961(3), Zn(1)−N(1) 1.965(3), Zn(1)−N(2) 1.953(3), Zn(2)−O(7) 1.929(2), Zn(2)−O(8) 1.923(3), Zn(2)−O(5) 1.920(2), Zn(2)−O(6) 1.923(2), Zn(3)−O(5) 1.952(2), Zn(3)−O(6) 1.966(2), Zn(3)−N(3) 1.952(3), Zn(3)−N(4) 1.960(3).

(2)O(5)Zn(3)O(6) moieties are nearly planar with a dihedral angle between these two planes of 92.9°. The distal Zn atoms are distorted tetrahedral with the average compressed O−Zn−O and N−Zn−N bond angles of 81.20 and 98.95°. Similar results have been found in [{(BDI)Zn(μ-OMe)}$_2$Zn(μ-OMe)$_2$].[13g] The structure of **2** is also verified by X-ray structural analysis. However, the bond distances and bond angles are not reliable because of a serious disordered problem.

ROP of L-Lactide and ϵ-Caprolactone Initiated by 1. Ring-opening polymerization of L-lactide (LLA) and ϵ-caprolactone (CL) employing **1** as an initiator is systematically examined under a dry nitrogen atmosphere. Conversion of LLA and CL is determined on the basis of ^{1}H NMR spectroscopic studies. The molecular weight and polydispersity of poly(L-lactide) (PLLA) and PCL are measured by gel permeation chromatography (GPC). In general, polymerization was carried out at 25 °C in toluene (20 mL) using **1** (0.05 mmol) as the initiator, and the results are listed in Table 1.

Experimental results show that complex **1** is a highly efficient initiator for the polymerization of LLA. Greater than 90% conversion occurred within 10 min at a desired [LLA]$_0$/[**1**] ratio in toluene at room temperature. On the basis of the molecular weight of PLLA and [LLA]$_0$/[**1**] ratio, we believe that all of the four BnO$^-$ groups could be used as initiators. This is further verified by ^{1}H NMR spectroscopic studies. The ^{1}H NMR spectrum (Figure 3) of PLLA prepared using a [LLA]$_0$/[**1**] ratio of 200 shows one benzyl ester and one hydroxy

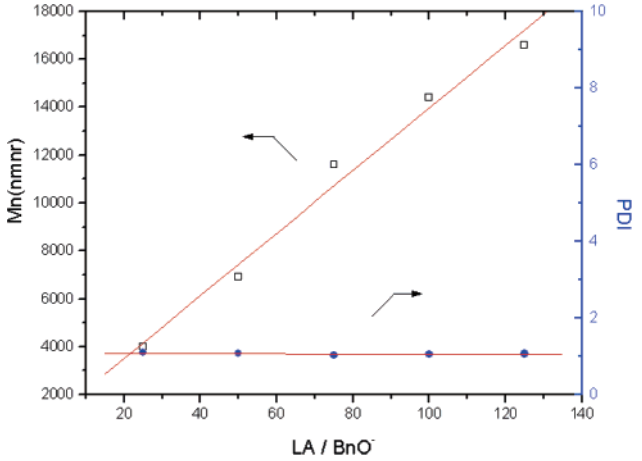


Figure 2. Plot of M_n(NMR) vs[LA]/[BnO$^-$] with polydispersity indices indicated by closed circles (GPC).

chain end with an integral ratio of 5:1 between H$_e$ and H$_c$, suggesting that the initiation occurs through the insertion of the benzyl alkoxy group from compound **1** into L-lactide. The linear increase in M_n with conversion and the low polydispersity indices (PDI, M_w/M_n) of the product polymers (Table 1, Figure 2) show the level of polymerization control is high, and the backbiting reactions do not occur in our condition. If cyclization occurs during polymerization, the PDIs of the resulting PLLA will be much higher. However, the PDIs of the PLLA obtained are in a very narrow range.

Ring-opening polymerization of ϵ-caprolactone employing **1** as an initiator is also investigated, and the linear increase in M_n with conversion and the low polydispersity indices of PCL show the level of polymerization control is high as shown in Table 2 and Figure 4. Experimental results show that the reaction rate of ROP of CL is much slower than that for lactide. However, the conversion up to 95% can be achieved within 2 h and PCL obtained with low polydispersity. It is worth noting that polymerization of CL is always faster than polymerization of lactide initiated by Al,[2a−e] Mg,[14] and Zn[15] stabilized by a diol system. However, in this diketiminate system, the reaction rate of CL is much slower than that of LA. The reason for the difference is probably due to that diketiminate systems are much softer ligands than diol systems. However, a detailed theoretical calculation will be helpful to explicit this result.

Kinetic Studies of Polymerization of L-Lactide and ϵ-Caprolactone by 1. A kinetic study was conducted in order to establish reaction order in monomer and zinc for the polymerization of L-lactide with compound **1**. Conversion of L-lactide with time was monitored by ^{1}H NMR for various concentrations of **1** at 25 °C until monomer consumption was completed ([LA]$_0$/

Table 1. Polymerization of L-Lactide Using Complex 1 as an Initiator at 25 °C

entry	[LA]/[**1**]	t (min)	M_w/M_n	M_n(GPC)[a]	M_n(calcd)[b]	M_n(NMR)[c]	conv (%)[c]
1[d]	100:1	10	1.09	9200	3500	4000	93
2[e]	200:1	10	1.07	13600	7200	6900	97
3[e]	300:1	10	1.02	22000	10400	11600	95
4[d]	400:1	13	1.04	25500	13800	14400	95
5[d]	500:1	10[f]	1.06	29000	17900	16600	99
6[d,g]	200:1	10	1.08	12800	6700	7500	92
7[d,h]	200:1	10	1.16	11300	6600	7200	91

[a] Obtained from GPC analysis and calibrated by polystyrene standard. [b] Calculated from the molecular weight of L-lactide × [M]$_0$/4[**1**]$_0$ × conversion yield plus M_w(BnOH). [c] Obtained from ^{1}H NMR analysis. [d] [**1**] = 2.5 mM. [e] [**1**] = 2.0 mM, rt. [f] Stirred at 25 °C for 5 min and 50 °C for 5 min. [g] Use CH_2Cl_2 as solvent. [h] Use THF as solvent.

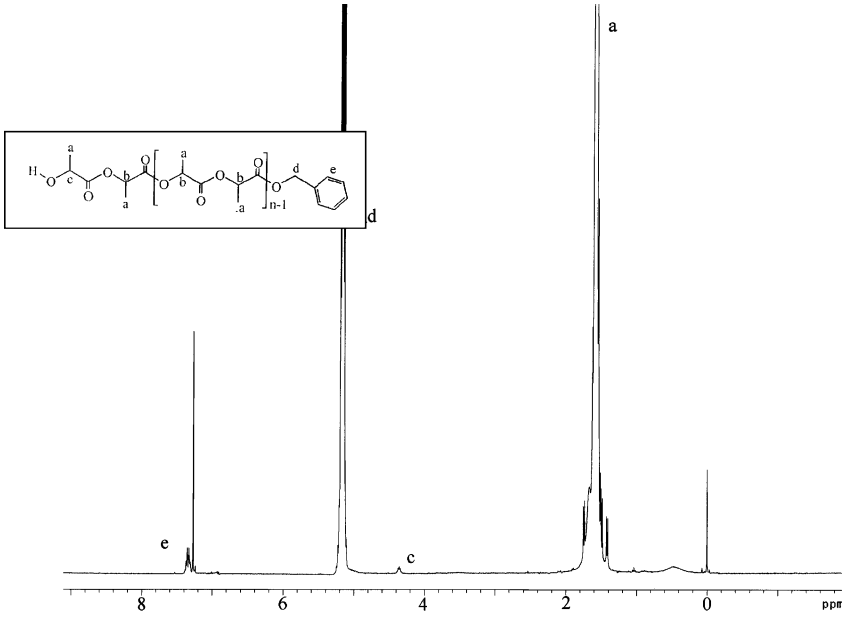


Figure 3. ^{1}H NMR spectrum of PLLA-200 (200 indicates $[LA]_0/[\mathbf{1}]_0 = 200$).

Table 2. Polymerization of ϵ-Caprolactone Using Complex 1 as an Initiator at 25 °C

entry	[M]/[**1**]	t (min)	M_w/M_n	M_n(obsd)[a]	M_n(calcd)[b]	M_n(NMR)[c]	conv (%)[c]
1[d]	128:1[e]	20	1.15	6000	3200	2400	93
2	128:1[e]	60	1.07	7000	3100	3200	91
3	256:1[e]	60	1.07	9100	5900	4800	87
4	400:1[e]	90	1.05	17200	8800	10100	84
5	512:1[e]	105	1.07	19500	12400	13400	92
6	512:1[f]	60	1.05	8445	6100	6400	45
7	256:1[g]	60	1.07	11200	6600	6600	98
8	200:1[h]	25	1.21	10800	4900	5600	92

[a] Obtained from GPC analysis and calibrated by polystyrene standard. [b] Calculated from the molecular weight of CL × $[M]_0/4[\mathbf{1}]_0$ × conversion yield plus M_w(BnOH). [c] Obtained from ^{1}H NMR analysis. [d] Reaction at 50 °C. [e] [**1**] = 5.15 mM. [f] [**1**] = 2.57 mM. [g] [**1**] = 9.89 mM. [h] [**1**] = 17.50 mM.

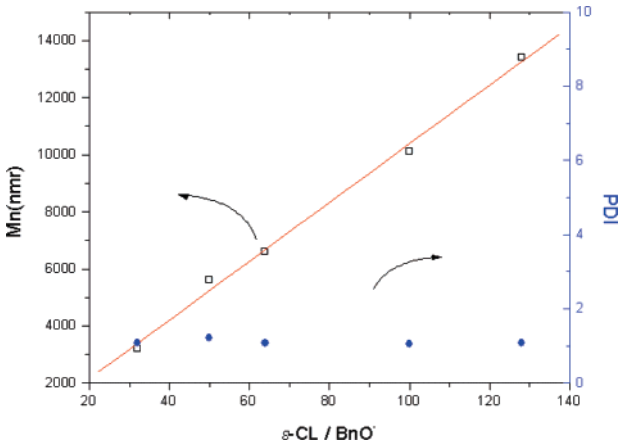


Figure 4. Plot of M_n(NMR) vs[CL]/[BnO$^-$] with polydispersity indices indicated by closed circles (GPC).

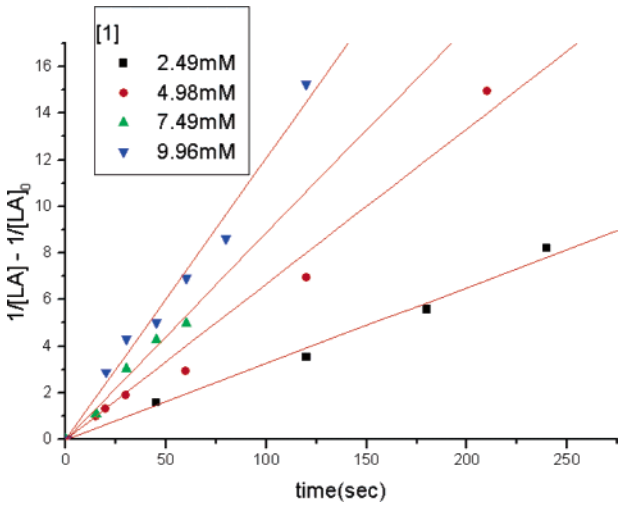


Figure 5. Second-order kinetic plots for L-lactide polymerizations with time in CH_2Cl_2 with different concentration of complex **1** as an initiator.

[**1**] = 200; $[LA]_0$ = 0.5 M in CH_2Cl_2). To determine the kinetic order in [**1**], the dependence of k_{obs} on $[LA]_0$ was analyzed. Plots of $(1/[LA] - 1/[LA]_0)$ vs time in a wide range of $[LA]_0$ are linear, indicating polymerization proceeds with second-order dependence on monomer concentration (Figure 5, $k_{obs} = 0.033$ M^{-1} s^{-1}). Thus, the rate of polymerization can be written as $-d[LA]/dt = k_{obs}[LA]^2$, where $k_{obs} = k[\mathbf{1}]^x$ and k is the rate constant. Plotting ln k_{obs} vs ln[**1**] allows us to determine x, the order in compound **1** concentration. From the slope of the fitted line as shown in Figure 6, the rate constant k is 12.2 M^{-2} s^{-1}. Therefore, on the basis of this analysis, $\chi = 1$. The reaction is first order in compound **1** and second order in monomer concentrations, and the overall rate equation is $-d[LA]/dt = k[LA]^2[\mathbf{1}]^1$. It is interesting to note that the rate law $-d[LA]/dt = k[LA]^2[\mathbf{1}]^1$ is different than the rate law of $-d[LA]/dt = k[LA]^1[ini]^1$ found in the other initiator's system.[13,16]

A kinetic study for the polymerization of CL with compound **1** was also performed. Conversion of CL with time was monitored by ^{1}H NMR for various concentra-

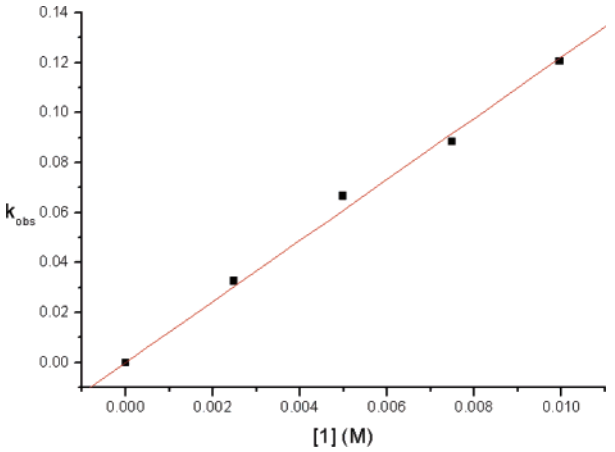


Figure 6. Linear plot of k_{obs} vs [**1**] for the polymerization of L-lactide with $[LA]_0 = 0.5$ M in CH_2Cl_2. $k = 12.2$ M^{-2} s^{-1}.

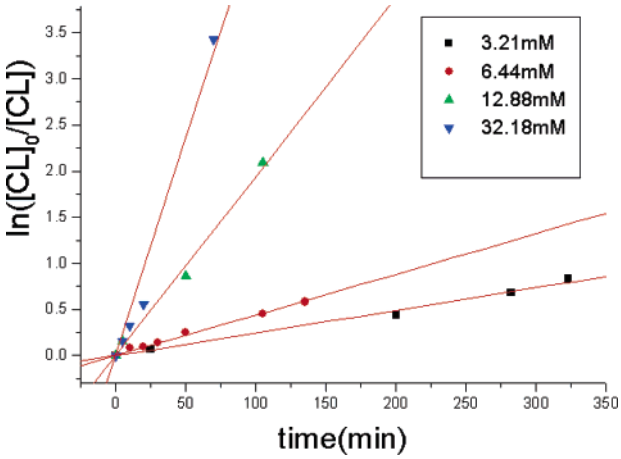


Figure 7. First-order kinetic plots for ϵ-caprolactone polymerizations with time in CH_2Cl_2 with different concentration of complex **1** as an initiator.

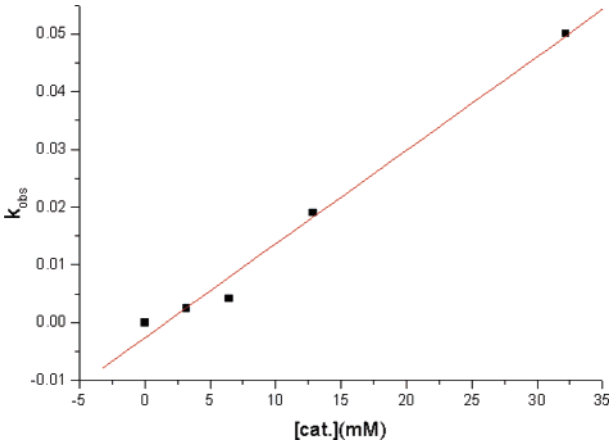


Figure 8. Linear plot of k_{obs} vs [**1**] for the polymerization of ϵ-caprolactone with $[CL]_0 = 3.6$ M in CH_2Cl_2. $k_p = 1.62$ M^{-1} s^{-1}.

tions of **1** at 25 °C until monomer consumption was completed. After careful examination, we found that a linear dependence between $\ln([CL]_0/[CL])$ vs time at several [CL] concentrations was observed, indicating polymerization proceeds with first-order dependence on both ϵ-caprolactone and complex **1** concentration (Figures 7 and 8, $-d[CL]/dt = k_{obs}[CL][\mathbf{1}]$, $k_{obs} = 0.0508$ s^{-1} when [**1**] = 32.18 mM). Experimental results show that the polymerization of L-lactide is much faster than the polymerization of ϵ-caprolactone. This can be explained by the second-order dependency on [LA] compared to the first-order dependency on [CL] and higher k of L-lactide than that of CL. Further studies of the polymerization mechanism are underway.

Stereoselectivity of LA. It has been known that the physical, mechanical, and degradation properties of PLA are dramatically dependent on the stereochemistry of PLA.[17] For example, poly(L-lactide) is a semicrystalline polymer with a melting point around 180 °C. However, poly(*meso*-lactide) is an amorphous polymer. In addition, the same equivalent of PLLA and PDLA forms a crystalline stereocomplex with a melting temperature as high as 230 °C. Kasperczyk et al. have reported that ROP of *rac*-lactide using LiO^tBu gives enriched PLA in a heterotactic sequence.[18] Therefore, the polymerization of *rac*-LA initiated by compound **1** is also performed, and the stereoselectivity is determined by the homonuclear decoupled ^1H NMR spectra. It is worthwhile to note that the tacticity of the polymer is significantly influenced by the solvent and temperature used (Table 3). For instance, changing the solvent from toluene to THF at 25 °C results in an increase in *Pr* (probability of racemic linkages between monomer units)[19] from 57% to 67%. Lowering the temperature from 25 to 0 °C in THF, *Pr* increases from 67% to 72%. However, in a mixed solvent of CH_2Cl_2 and THF at −35 °C, a heterotactic PLA with *Pr* up to 83% can be achieved (Figure 9).

In conclusion, we have prepared and structurally characterized a novel zinc alkoxide which has shown great activity for the controlled polymerization of LLA. Complex **1** also shows good stereoselectivity for ROP of *rac*-lactide in THF/CH_2Cl_2 mixed solvent at low temperature.

Experimental Section

General. All manipulations were carried out under a dry nitrogen atmosphere. Solvents, benzyl alcohol, L-lactide, DL-lactide, and deuterated solvents were purified before use. ^1H and ^{13}C NMR spectra were recorded on a Varian Unity Inova-600 (600 MHz for ^1H and 150 MHz for ^{13}C) or a Varian Mercury-400 (400 MHz for ^1H and 100 MHz for ^{13}C) spectrometer with chemical shifts given in ppm from the internal TMS or the central line of $CHCl_3$. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument. The GPC measurements were performed on a Postnova PN1122 solvent delivery system with TriSEC GPC software using THF (HPLC grade) as an eluent. Molecular weight and molecular weight distributions were calculated using polystyrene as standard.

Synthesis of 2-((2-Methoxyphenyl)amino)-4-((2-methoxyphenyl)imino)-2-pentene (BDI-OMe-H). A mixture of 2-methoxyaniline (12.3 g, 100 mmol), 2,4-pentanedione (5.0 g, 50 mmol), and benzenesulfonic acid (0.30 mL) was refluxed in absolute toluene (30 mL) for 1 day. After being cooled to room temperature, volatile materials were removed under vacuum to give brown oil. Diethyl ether (100 mL) was then added, and the resulting precipitate was extracted by CH_2Cl_2 (30 mL). The orange extraction was dried over $MgSO_4$ and filtered. Removal of the solvent in vacuo afforded BDI-OMe-H as a light yellow solid. Yield: 3.88 g (25%). ^1H NMR ($CDCl_3$, 400 MHz): δ 12.20 (1H, s, N*H*), 6.99 (4H, d, J = 7.2 Hz, MeOArH), 6.87 (4H, m, J = 8 Hz, ArH), 4.92 (1H, s, β-CH), 3.77 (6H, s, CH_3O), 1.98 (6H, s, α-CH_3) ppm. ^{13}C NMR ($CDCl_3$, 400 MHz): δ 160.21 (C=N),151.51 (MeO**C**CN), 135.61 (MeOC**C**N), 123.84, 123.29, 120.74, 111.68 (Ph), 98.16 (β-C), 55.98 (CH_3O), 21.385 ppm (C=**C**HC). Elemental Anal. for $C_{19}H_{22}N_2O_2$: Calcd (found) C 73.52 (72.66), H 7.14 (7.58), N 9.03 (8.40)%.

Synthesis of [{(BDI-OMe)Zn(μ-OBn)}$_2$Zn(μ-OBn)$_2$] (1) and [(BDI-OMe)$_2$Zn] (2). To a suspension of (BDI-OMe-H)

Table 3. Polymerization of *rac*-LA Initiated by Complex 1 Yielded Different Type PLA in Different Solvents (20 mL) at Desired Temperature and Desired $[LA]_0/[1]$ Ratio

entry	solvent	t (min)	T (°C)	PDI	M_n(GPC)	M_n(calcd)	M_n(NMR)	conv (%)	Pr (%)[a]
1[b]	CH_2Cl_2	10	rt	1.03	16700	13500	12400	93	57
2[b]	THF	10	rt	1.09	19000	13600	13900	94	67
3[c]	THF	210	0	1.02	5000	3300	5700	90	72
4[c,d]	THF/CH_2Cl_2	2880	−35	1.01	3900	3000	4100	79	83

[a] *Pr* is the probability of racemic linkages between monomer units and is determined from the methine region of the homonuclear decoupled ^{1}H NMR (600 Hz) spectrum. [b] [LA]/[**1**] = 400. [c] [LA]/[**1**] = 100. [d] In a mixed solvent system with THF/CH_2Cl_2 = 1/1.

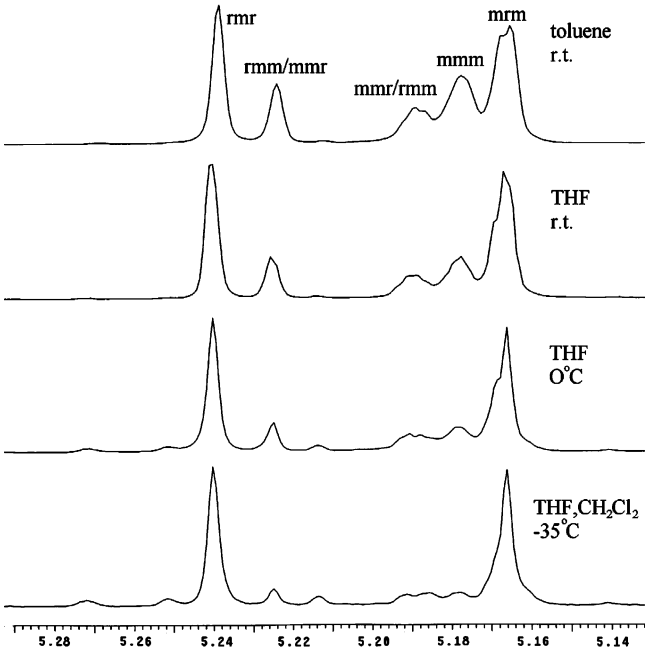


Figure 9. [{(BDI-OMe)Zn(μ-OBn)}$_2$Zn(μ-OBn)$_2$] polymerized *rac*-LA in different solvents at different temperatures.

(2.26 g, 7.3 mmol) in hexane (15 mL) was added diethylzinc (10 mL, 10 mmol). After being stirred at 0 °C for 3 h, a clear yellow solution was obtained. Volatile materials were removed in vacuo to yield an yellow oily compound which was then redissolved in hexane (15 mL). BnOH (1.53 mL, 14.6 mmol) was added to the hexane solution, and the mixture was stirred at 0 °C for 3 h. The resulting yellow powder was collected by filtration and washed with hexane (15 mL) three times.

The light yellow solid [{(BDI-OMe)Zn(μ-OBn)}$_2$Zn(μ-OBn)$_2$] **(1)** was dried in vacuo. Yield: 2.10 g (46%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.16, 6.99, 6.41, 6.10 (20H, s, $C_6\mathbf{H}_5CH_2O$), 6.82 (4H, d, J = 8.0 Hz, MeOArH), 6.65 (4H, m, J = 14.0 Hz, ArH), 4.69 (2H, s, β-CH), 4.13 (8H, s, Ph$\mathbf{CH}_2$O), 3.53 (12H, s, CH_3O), 1.69 (6H, s, α-CH_3) ppm. ^{13}C NMR ($CDCl_3$, 400 MHz): δ 168.20 (C═N),152.62 (MeO**C**CN), 145.49 (MeOC**C**N), 138.56, 128.00, 127.59, 126.16, 125.98, 124.79, 120.71, 110.99 (Ph), 93.45 (β-C),68.52 (Ph$\mathbf{CH}_2$O), 55.08 (CH_3O), 23.00 ppm (C═**C**HC). Anal. Calcd (found) for $C_{66}H_{70}N_4O_8Zn_3$: C 63.75 (63.35), H 5.67 (5.75), N 4.51 (5.05)%.

The filtrate was dried under vacuum to give yellowish powder [(BDI-OMe)$_2$Zn] **(2)**. Yield: 0.624 g (25%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.92, 6.73 (8H, s, MeOArH), 4.39 (1H, s, β-CH), 3.43 (6H, s, CH_3O), 1.63 ppm (6H, s, α-CH_3). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 166.991 (C═N), 152.73 (MeO**C**CN), 139.69 (MeOC**C**N), 125.89, 123.72, 120.64, 111.86 (Ph), 93.87 (β-C), 55.42 (CH_3O), 22.69 ppm (C═**C**HC). Anal. Calcd (found) for $C_{38}H_{42}N_4O_4Zn$: C 66.60 (66.71), H 6.19 (5.72), N 8.19 (8.19)%.

Typical Polymerization Procedure of L-Lactide. A typical polymerization procedure was exemplified by the synthesis of PLLA-400 (the number 100 indicates the designed $[LA]_0$/[initiator]) at room temperature. The conversion yield (95%) of PLLA-400 was analyzed by ^{1}H NMR spectroscopic studies. A mixture of complex **1** (0.0622 g, 0.05 mmol) and L-lactide (2.88 g, 20 mmol) in toluene (30 mL) was stirred at room temperature for 13 min. Volatile materials were removed in vacuo, and the residue was dissolved in THF (10 mL). The mixture was then quenched by the addition of an aqueous acetic acid solution (0.35 N, 10 mL), and the polymer was precipitated on pouring into *n*-hexane (40 mL) to give white crystalline solids. Yield: 2.50 g (87%).

Typical Polymerization Procedure of ε-Caprolactone. A typical polymerization procedure was exemplified by the synthesis of PCL-512 (the number 512 indicates the designed $[CL]_0/[1]$) at room temperature. The conversion yield (92%) of PCL-512 was analyzed by ^{1}H NMR spectroscopic studies. A mixture of complex **1** (0.0961 g, 0.077 mmol) and ε-caprolactone (4.40 mL, 40 mmol) in toluene (15 mL) was stirred at room temperature for 105 min. Volatile materials were removed in vacuo, and the residue was redissoved in THF (15 mL). The mixture was then quenched by the addition of an aqueous acetic acid solution (0.35 N, 10 mL), and the polymer was precipitated on pouring into *n*-hexane (40 mL) to give white crystalline solids. Yield: 3.05 g (70%).

Kinetic Studies of Polymerization of L-Lactide by 1. L-Lactide (0.36 g, 2.5 mmol) was added to a solution of **1** (with 2.49, 4.98, 7.49, and 9.96 mM) in methylene chloride (5 mL). The mixture was then stirred at room tempture under N_2. At appropriate time intervals, 0.5 mL aliquots were removed and quenched with methanol (1 drop). The aliquots were then dried to constant weight in vacuo and analyzed by ^{1}H NMR.

Kinetic Studies of Polymerization of ε-Caprolactone by 1. Kinetic studies of CL were examined by two different methods. (a) CL (18 mmol) was added to a solution of **1** (with 3.21, 4.29, 6.44, 12.88, and 32.18 mM) in methylene chloride (5 mL). The mixture was then stirred at room temperature under N_2. At appropriate time intervals, 0.5 mL aliquots were removed and quenched with methanol (1 drop). The aliquots were then dried to constant weight under vacuum and analyzed by ^{1}H NMR. (b) CL (5 mmol) was added to a NMR tube with a solution of **1** (50, 62, and 75 mM) in d_3-chloroform (1 mL). The mixture was analyzed by NMR at appropriate time intervals.

X-ray Crystallographic Studies. Suitable crystals of **1** 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 was confirmed using the structure solution. The structure was solved by 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.

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

Supporting Information Available: Crystallographic data of **1**, kinetic studies of ε-caprolactone polymerization by **1** (NMR studies), and figures comparing second- and first-order

kinetic plots dependency for L-lactide. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Endo, M.; Aida, T.; Inoue, S. *Macromolecules* **1987**, *20*, 2982. (b) Duda, A.; Florjanczyk, Z.; Hofman, A.; Slomkowski, S.; Penczek, S. *Macromolecules* **1990**, *23*, 1640. (c) Kowalski, A.; Duda, A.; Penczek, S. *Macromol. Rapid Commun.* **1998**, *19*, 567. (d) Gan, Z.; Jim, T. F.; Jim, M.; Yuer, Z.; Wang, S.; Wu, C. *Macromolecules* **1999**, *32*, 1218. (e) Chamberlain, B. M.; Sun, Y.; Hagadorn, J. R.; Hemmesch, E. W.; Young, V. G., Jr.; Pink, M.; Hillmyer, M. A.; Tolman, W. B. *Macromolecules* **1999**, *32*, 2400. (f) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **1999**, *121*, 4072. (g) Chen, X.; Gross, R. A. *Macromolecules* **1999**, *32*, 308. (h) Jeong, B.; Bae, Y. H.; Lee, D. S.; Kim, S. W. *Nature (London)* **1997**, *388*, 860. (i) Gref, R.; Minamitake, Y.; Peracchia, M. T.; Trubetskov, V.; Torchilin, V.; Langer, R. *Science* **1994**, *263*, 1600.

(2) (a) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 1316. (b) Huang, C.-H.; Wang, F.-C.; Ko, B.-T.; Yu, T.-L.; Lin, C.-C. *Macromolecules* **2001**, *34*, 356. (c) Liu, Y.-C.; Ko, B.-T.; Lin, C.-C. *Macromolecules* **2001**, *34*, 6196. (d) Chen, H.-L.; Ko, B.-T.; Huang, B.-H.; Lin, C.-C. *Organometallics* **2001**, *20*, 5076. (e) Hsueh, M.-L.; Huang, B.-H.; Lin, C.-C. *Macromolecules* **2002**, *35*, 5763. (f) Zhong, Z.; Dijkstra, P. J.; Feijen, J. *J. Am. Chem. Soc.* **2003**, *125*, 11291.

(3) (a) Kricheldorf, H. R. *Makromol. Chem.* **1993**, *194*, 1665. (b) Ko, B.-T.; Lin, C.-C. *J. Am. Chem. Soc.* **2001**, *123*, 7973. (c) Chisholm, M. H.; Lin, C.-C.; Galluccia, J. C.; Ko, B.-T. *Dalton Trans.* **2003**, 406.

(4) (a) Kricheldorf, H. R.; Berl, M.; Scharnagl, N. *Macromolecules* **1988**, *21*, 286. (b) Chisholm, M. H.; Eilerts, N. W.; Huffman, J. C.; Iyer, S. S.; Pacold, M.; Phomphrai, K. *J. Am. Chem. Soc.* **2000**, *12*, 11845. (c) Chisholm, M. H.; Gallucci, J.; Phomphrai, K. *Inorg. Chem.* **2002**, *41*, 2785. (d) Chisholm, M. H.; Phomphrai, K. *Inorg. Chim. Acta* **2003**, *350*, 121.

(5) (a) O'Keefe, B. J.; Breyfogle, L. E.; Hillmyer, M. A.; Tolman, W. B. *J. Am. Chem. Soc.* **2002**, *124*, 4384. (b) Duda, A.; Penczek, S. In *Polymers from Renewable Resources: Biopolyesters and Biocatalysis*; Scholz, C., Gross, R. A., Eds.; *ACS Symp. Ser. 764*. (c) *J. Am. Chem. Soc.* **2000**, 160. (d) Dobrzynski, P.; Kasperczyk, J.; Janeczek, M.; Bero, M. *Polymer* **2002**, *43*, 2595.

(6) Kricheldorf, H. R.; Sumbbl, M. V.; Saunders, I. K. *Macromolecules* **1991**, *24*, 1944.

(7) (a) Schwach, G.; Coudane, J.; Engel, R.; Vert, M. *Polym. Int.* **1998**, *46*, 177. (b) Bero, M.; Kasperczyk, J.; Jedliński, Z. *Macromol. Chem*. **1990**, *191*, 2287. (c) Bero, M.; Kasperczyk, J.; Adamus, G. *Macromol. Chem*. **1993**, *194*, 907.

(8) (a) Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. *Chem. Rev.* **2002**, *102*, 3031 and references therein.

(9) Lewiński, J.; Ochal, Z.; Bojarski, E.; Tratkiewicz, E.; Justyniak, I.; Lipkowski, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 4643.

(10) Shaviv, E.; Botoshansky, M.; Eisen, M. S. *J. Organomet. Chem.* **2003**, *683*, 165.

(11) (a) Chisholm, M. H.; Gallucci, J.; Phomphrai, K. *Inorg. Chem.* **2004**, *43*, 6717. (b) Chisholm, M. H.; Gallucci, J.; Phomphrai, K. *Chem. Commun.* **2003**, 48. (c) Dove, A. P.; Gibson, V. C.; Marshall, E. L.; White, A. J. P.; Williams, D. J. *Dalton Trans.* **2004**, 570.

(12) Carey, D. T.; Cope-Eatough, E. K.; Vilaplana-Mafe, E.; Mair, F. S.; Pritchard, R. G.; Warren, J. E.; Woods, R. J. *Dalton Trans.* **2003**, 1083.

(13) (a) Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **1998**, *120*, 11018. (b) Cheng, M.; Attygalle, A. B.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **1999**, *121*, 11583. (c) Chamberlain, B. M.; Cheng, M.; Moore, D. R.; Ovitt, T. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 3229. (d) Cheng, M.; Moore, D. R.; Reczek, J. J.; Chamberlain, B. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 8738. (e) Rieth, L. R.; Moore, D. R.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 15239. (f) Moore, D. R.; Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2003**, *125*, 11911. (g) Allen, S. D.; Moore, D. R.; Lobkovsky, E. B.; Coates, G. W. *J. Organomet. Chem.* **2003**, *683*, 137. (h) Chamberlain, B. M.; Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 3229.

(14) Shueh, M.-L.; Wang, Y.-S.; Huang, B.-H.; Kuo, C.-Y.; Lin, C.-C. *Macromolecules* **2004**, *37*, 5155.

(15) (a) Yu, T.-L. Ph.D. Dissertation, 2005. (b) Lin, C.-N. M.S. Thesis, 2005. (c) Liu, P.-C. M.S. Thesis, 2005.

(16) Williams, C. K.; Breyfogle, L. E.; Choi, S. K.; Nam, W.; Yong, V. G., Jr.; Hillmyer, M. A.; Tolman, W. B. *J. Am. Chem. Soc.* **2003**, *125*, 11350.

(17) (a) MacDonald, R. T.; McCarthy, S. P.; Gross, R. A. *Macromolecules* **1996**, *29*, 7356. (b) Stevels, W. M.; Ankone, M. J. K.; Dijkstra, P. J.; Feijen, J. *Macromolecules* **1996**, *29*, 6132. (c) Sarasua, J.-R.; Prud'homme, R. E.; Wisniewski, M.; Le Borgne, A.; Spassky, N. *Macromolecules* **1996**, *31*, 3895.

(18) Kasperczyk, J. E. *Macromolecules* **1995**, *28*, 3937.

(19) (a) Nakano, K.; Kosaka, N.; Hiyama, T.; Nozaki, K. *Dalton Trans.* **2003**, 4039. (b) Kricheldorf, H. R. *Polymer* **1992**, *33*, 2817. (c) O'Keefe, B. J.; Hillmyer, M. A.; Tolman, W. B. *Dalton Trans.* **2001**, 2215. (d) Cabaret, O. D.; Martin-Vaca, B.; Bourissou, D. *Chem. Rev.* **2004**, *104*, 6147.

MA050672F