Dalton Transactions

RSC Publishing

PAPER

View Article Online
View Journal

Cite this: DOI: 10.1039/c3dt50756d

Synthesis and structural determination of zinc complexes based on an anilido-aldimine ligand containing an O-donor pendant arm: zinc alkoxide derivative as an efficient initiator for ring-opening polymerization of cyclic esters†

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Zinc complexes bearing the anilido-aldiminate $\mathbf{AA^{OMe}}$ ligand ($\mathbf{AA^{OMe}}$-H = (*E*)-2,6-diisopropyl-*N*-(2-(((2-methoxyethyl)imino)methyl)phenyl)aniline) were synthesized in a stepwise method and were structurally characterized. The reaction of $\mathbf{AA^{OMe}}$-H (**1**) with one equivalent of diethyl zinc ($ZnEt_2$) furnishes a three-coordinated and mononuclear zinc complex [($\mathbf{AA^{OMe}}$)ZnEt] (**2**). Further reaction of **2** with a stoichiometric amount of benzyl alcohol (BnOH) affords a four-coordinated and dinuclear zinc benzylalkoxide complex $[(\mathbf{AA^{OMe}})Zn(\mu\text{-OBn})]_2$ (**3**). In the presence of two equivalents of $\mathbf{AA^{OMe}}$-H with $ZnEt_2$, a homoleptic and four-coordinated zinc complex $[(\mathbf{AA^{OMe}})_2Zn]$ (**4**) is formed. The geometry around the zinc centres of **3** and **4** are both distorted tetrahedrals, while **2** adopts a different coordination mode with a slightly distorted trigonal planar geometry. The variable-temperature ^{1}H NMR studies of **3** illustrate that **3** exhibits a dinuclear structure in solution at low temperature as well as in the solid state. While raising the temperature, it drifts towards dissociation to form a mononuclear zinc benzylalkoxide species, which coexists in solution. The ring-opening polymerizations of ε-caprolactone (ε-CL) and β-butyrolactone (β-BL) catalyzed by complexes **3** and **4** are investigated. The ε-CL and β-BL polymerizations initiated by zinc alkoxide **3** were demonstrated to have living characteristics and to proceed in a controlled manner with narrow polydispersity indices (PDIs < 1.12). An efficient catalytic performance for the β-BL polymerization with a high monomer-to-initiator ratio (1200/1) initiated by **3** has also been reported.

Received 20th March 2013,
Accepted 27th May 2013

DOI: 10.1039/c3dt50756d

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Introduction

Using well-defined metal complexes for the evolution of catalytic systems toward ring-opening polymerizations (ROP) has had considerable attention because ROP provides a promising method for producing biodegradable polymers such as poly(ε-caprolactone) (PCL), poly(lactide) (PLA) and poly(β-butyrolactone) (PHB), as well as their copolymers.[1] Among them, PHB is a kind of thermoplastic polymer with specific properties ($T_m \sim 180$ °C and $T_g \sim 2$ °C)[2] which has a stretchable behavior similar to a BOPP film, whilst performing in an elastomeric manner resembling polyurethane.[3] As a result, systems which introduce a single-active site into metal complexes supported by a variety of ancillary ligands such as Schiff base, β-diketiminate, bisphenolate, amino-bis(phenolate),[4] pyrazolone ketiminate,[5] benzotriazole phenolate,[6] and many other ligands have been reported to achieve high catalytic activities in a well-controlled fashion. In particular, the anilido-aldiminate (**AA**) system attracts increasing attention due to the easily achievable single-site catalysts.[7] For instance, rare-earth metal complexes bearing the *N*,*N*,*N*-tridentate **AA** ligand and introducing the pendant arm of the quinolinyl group on the amido nitrogen have demonstrated a single active site nature which efficiently initiates the polymerization of ε-caprolactone (ε-CL).[7b]

Based on the inspiration of the efficient catalytic systems supported by **AA** ligands, our current focus has been to develop such ligands with a pendant arm attached *via* the imine nitrogen and to complex these to aluminium, magnesium and zinc precursors as catalysts for CO_2/epoxide

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† Electronic supplementary information (ESI) available. CCDC 928698–928701. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt50756d

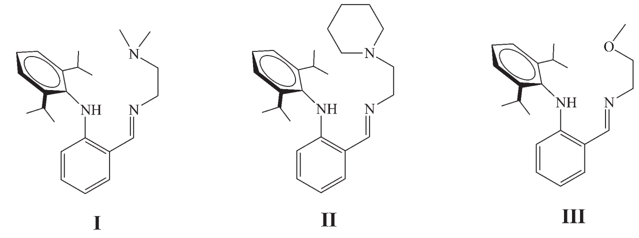
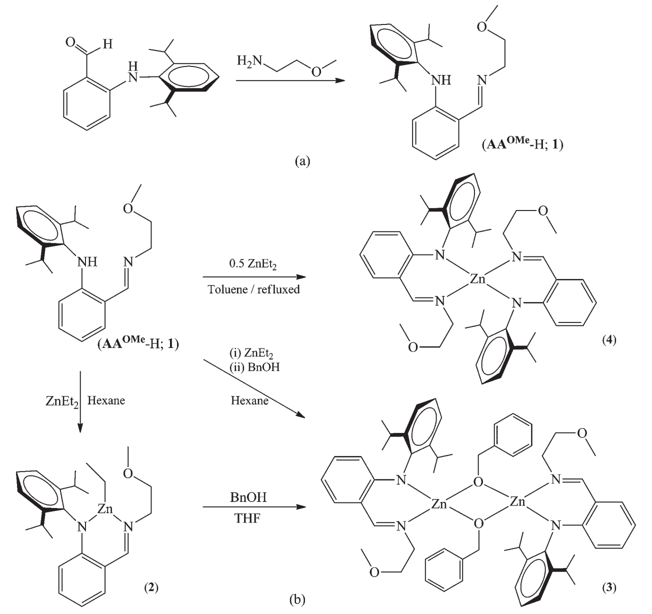


Chart 1 Several types of anilido-aldimine ligands containing N- or O-donor pendant arms.

coupling and ROP of cyclic esters. Recently, a useful synthetic route for the preparation of bi-, tri- or multi-dentate **AA** was established[8] and the purification method is simple in that the products are readily obtained *via* only a recrystallization and without any chromatographic technique. Moreover, we have synthesized and characterized several magnesium and zinc complexes derived from *N*,*N*,*N*-tridentate anilido-aldimine (**AA**) ligands (type **I–II**, Chart 1).[9] The ROPs of L-lactide, ε-CL and β-butyrolactone in the presence of alcohol catalyzed by these complexes have illustrated a high performance with a living characteristic, furnishing polyesters with narrow polydispersity indices (PDIs < 1.30). To extend the investigations into **AA** derivatives and to compare differences in the polymerization efficiency, a new anilido-aldimine ligand containing an O-donor pendant arm (type **III**, Chart 1) has been designed and synthesized. We envisaged that the minor changes in the pendant arm of the O-donor functional group might lead to differences in the bonding modes and the synthesis of well-defined ROP metal alkoxide initiators, [(**AA**)M(OR)]$_n$ (M = Zn or Mg; OR = alkoxy; n = 1 or 2). In this article, we describe the synthesis, structure, and ROP catalytic studies of zinc derivatives bearing the anilido-aldimine ligand of this kind. We also report the use of an effective zinc alkoxide derivative to prepare PHB with a large molecular weight.



Scheme 1 Synthetic routes of (a) the ligand **AA**$^{\mathbf{OMe}}$-H (**1**) and (b) the complexes (**2**)–(**4**).

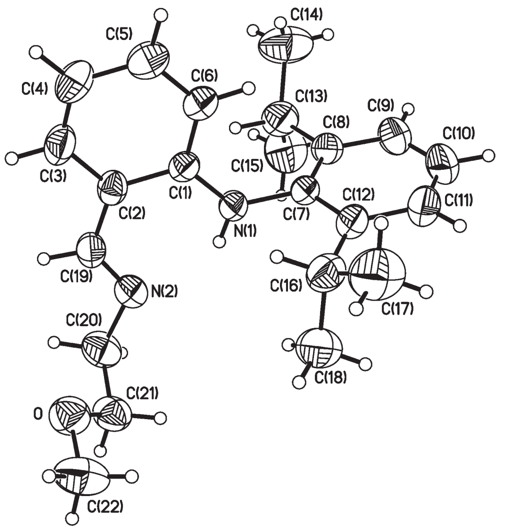


Fig. 1 ORTEP drawing of **AA**$^{\mathbf{OMe}}$-H (**1**) with probability ellipsoids drawn at the 30% level. Selected bond lengths (Å) and angles (°): N(1)–C(1) 1.357(3), N(1)–C(7) 1.422(3), N(2)–C(19) 1.266(3), N(2)–C(20) 1.465(4), N(1)⋯N(2) 2.704(3).

Results and discussion

Syntheses and crystal structure

The new anilido-aldimine ligand containing the O-donor functional group, (*E*)-2,6-diisopropyl-*N*-(2-(((2-methoxyethyl)imino)-methyl)phenyl)aniline (**AA**$^{\mathbf{OMe}}$-H, **1**), was synthesized in an 84% yield based on methods from the literature[8] as shown in Scheme 1(a). Compound **1** was isolated as a crystalline solid and was characterized by ^{1}H and ^{13}C NMR spectra. The ^{1}H NMR spectrum of the ligand exhibited signals at 8.46 ppm for the aldimine proton of HC=N, and the corresponding ^{13}C NMR signal was around 165.76 ppm, indicating the formation of the desired **AA**$^{\mathbf{OMe}}$-H ligand. The downfield N–H signal at 10.48 ppm implies a hydrogen bond exists between the N–H and the N(imine), which was further verified by X-ray structural determination. Suitable crystals for X-ray diffraction analysis of **1** were obtained from a saturated *n*-hexane solution, as shown in Fig. 1. The molecular structure of **1** reveals that the distance between N(1)⋯N(2) (2.704(3) Å) is shorter than that of the sum of the van der Waals radii (3.10 Å), probably suggesting a hydrogen bond exists between the N–H(aniline) and the N(imine). The mean planes of two phenyl rings are approximately perpendicular to each other with a dihedral angle equal to 86.7(5)°. As shown in Scheme 1(b), the reaction of compound **1** with one equivalent of diethyl zinc (ZnEt$_2$) in *n*-hexane gave a yellow crystalline solid, [(**AA**$^{\mathbf{OMe}}$)ZnEt] (**2**) in a good yield (85%). Complex **2** was also characterized by spectroscopic studies. The disappearance of the N–H signal of **1** and the appearance of the resonance of Zn–Et (0.85 and 0.12 ppm) reveals that complex **2** was successfully synthesized. To prepare the well-defined ROP Zn initiator [(**AA**)Zn(OR)]$_n$ (OR = alkoxy; n = 1 or 2), the presence of **2** and a stoichiometric amount of benzyl alcohol in THF afforded the zinc benzylalkoxide complex [(**AA^{OMe}**)Zn(μ-OBn)]$_2$ (**3**). It was mainly identified by the disappearance of the aniline group (10.48 ppm), the upfield shift from 8.46 to 7.90 ppm of the aldimine proton and the appearance of two doublet resonances of the methylene protons from the benzylalkoxy group (4.52 and 4.30 ppm). Alternatively, **3** could also be prepared directly by the reaction of **AA^{OMe}**-H with 1.0 mol equiv. of ZnEt$_2$, followed by the addition of BnOH (one equiv.) in a good yield. Furthermore, treatment of **1** and half an equivalence of ZnEt$_2$ in refluxing toluene solution produced a bis-adduct zinc complex [(**AA^{OMe}**)$_2$Zn] (**4**). The spectroscopic verification showed the disappearance of the aniline proton (10.48 ppm) and the methyl protons of the isopropyl group had split from the signal at 1.13 ppm into four doublet signals (1.10, 0.94, 0.77 and 0.39 ppm). All Zn complexes were isolated as yellow crystalline solids and were characterized by microanalysis as well as X-ray diffraction.

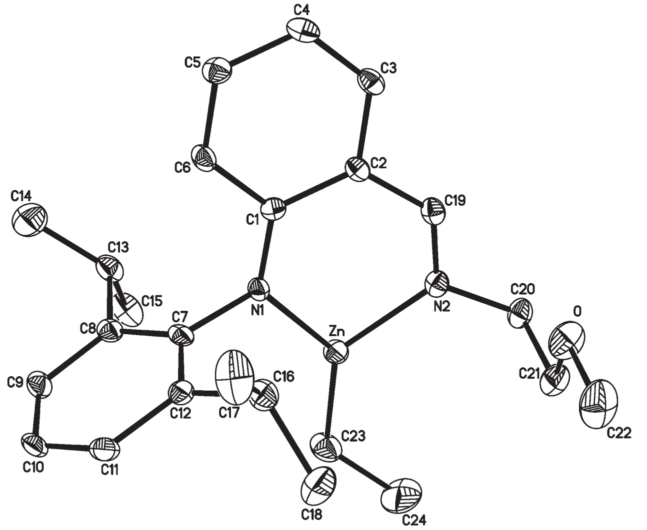


Fig. 2 ORTEP drawing of complex **2** with probability ellipsoids drawn at the 50% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Zn–N(1) 1.938(2), Zn–N(2) 1.996(2), Zn–C(23) 1.965(2), N(2)–C(19) 1.290(3), N(1)–Zn–N(2) 94.62(7), N(1)–Zn–C(23) 134.55(9), C(23)–Zn–N(2) 130.52(9).

Oak Ridge Thermal Ellipsoid Plot (ORTEP) drawings illustrating selected bond lengths and angles of the molecular structures of **2**, **3** and **4** are shown in Fig. 2–4, respectively. The crystal structure of **2** displays that it is a three-coordinate monomeric complex and has a slightly distorted trigonal planar geometry around the Zn atom (*ca.* 359.7(2)°). The zinc atom slightly diverges from the mean plane of the six-membered ring composed of Zn/N(1)/C(1)/C(2)/C(19/)N(2) by about 0.107 Å. It also slightly deviates from the triangle mean plane (N(1)/N(2)/C(23)) by about 0.061 Å. The bond lengths around the Zn centre (Zn–N(1) = 1.938(2) Å and Zn–N(2) = 1.996(2) Å) are shorter than the related distances in the three-coordinate complex [(**AA^{Bn}**)ZnEt][10] (Zn(1)–N(1) = 1.950(3) Å and Zn(1)–N(2) = 2.015(3) Å), which might disclose the stronger bonding between the zinc and the ancillary ligand owing to the less steric hindrance of the methoxy group. On the basis of the

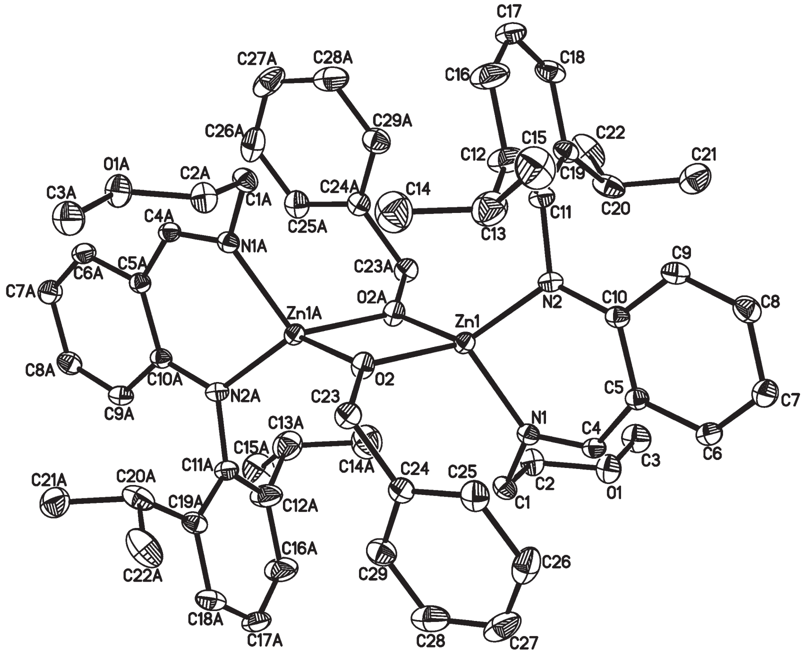


Fig. 3 ORTEP drawing of complex **3** with probability ellipsoids drawn at the 50% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Zn(1)–N(1) 2.005(2), Zn(1)–N(2) 1.959(2), Zn(1)–O(2) 1.984(2), Zn(1)–O(2A) 1.951(2), N(2)–Zn(1)–N(1) 95.77(6), N(2)–Zn(1)–O(2) 123.49(6), O(2A)–Zn(1)–N(1) 114.40(6), O(2A)–Zn(1)–N(2) 129.24(6), O(2A)–Zn(1)–O(2) 79.82(5), O(2)–Zn(1)–N(1) 115.84(5).

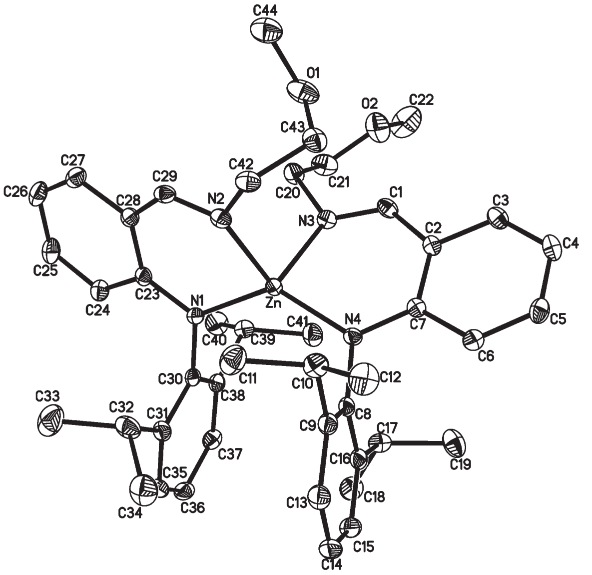


Fig. 4 ORTEP drawing of complex **4** with probability ellipsoids drawn at the 50% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Zn–N(1) 1.967(2), Zn(1)–N(2) 2.068(2), Zn–N(3) 2.034(2), Zn–N(4) 1.965(2), N(1)–Zn–N(2) 94.19(5), N(1)–Zn–N(3) 113.45(5), N(1)–Zn–N(4) 132.40(5), N(2)–Zn–N(3) 97.16(5), N(2)–Zn–N(4) 119.45(5), N(3)–Zn–N(4) 95.81(5).

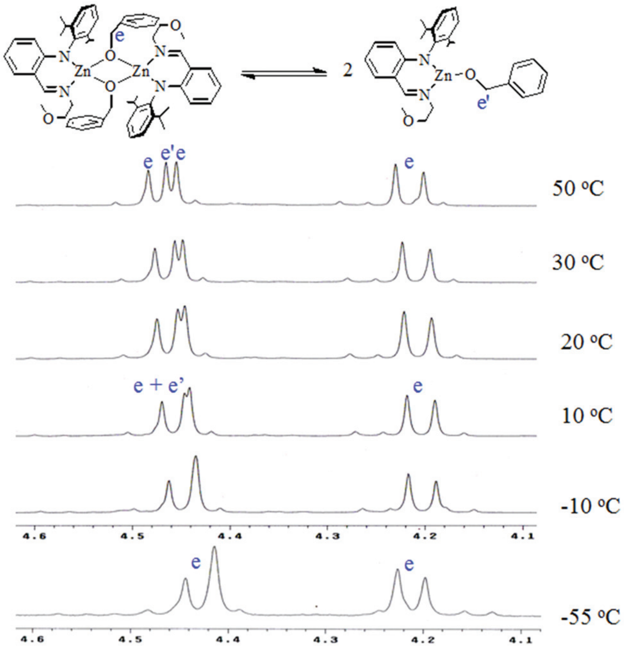


Fig. 5 Variable-temperature ^{1}H NMR studies of complex **3** in $CDCl_3$.

single crystal X-ray analysis for **3**, the complex has been constructed as a symmetric structure bearing two bridging benzylalkoxy groups and two ancillary ligands with an inversion centre between two zinc atoms. Complex **3** demonstrates a four-coordinate dimmeric zinc benzylalkoxide complex and a distorted tetrahedral geometry around the zinc atoms with the two included angles, O(2A)–Zn(1)–N(2) = 129.24(6)° and O(2A)–Zn(1)–O(2) = 79.82(5)°. Notably, the different bond distances between the zinc and nitrogen atoms were observed as Zn(1)–N(2) = 1.959(2) Å and Zn(1)–N(1) = 2.005(2) Å. Because of the resonance effect of the aniline substituent on the phenyl ring with respect to the lack of electronic density, the bond strength of Zn(1)–N(2) is slightly stronger than Zn(1)–N(1). This differs from the chelating mode of the zinc complex reported by Coates *et al.*, $[(\mathrm{BDI\text{-}3})\mathrm{Zn}(\mu\text{-}\mathrm{O^iPr})]_2$,[11] with the corresponding bond lengths of Zn(1)–N(1) = 2.008(2) Å and Zn(1)–N(2) = 1.996(2) Å. Furthermore, recrystallization from a saturated toluene solution generates complex **4** as transparent yellow crystals. Crystallographic analysis indicates that **4** is a homoleptic and a four-coordinate complex lying on a distorted tetrahedral geometry around the zinc centre with the bond angles ranging from 94.15(9)° to 132.44(9)°. The Zn-containing bond lengths, Zn–N(1) = 1.967(2) Å, Zn–N(2) = 2.069(2) Å, Zn–N(3) = 2.034(2) Å and Zn–N(4) = 1.963(2) Å, show that **4** is built of two covalent bonds and two dative bonds around the zinc centre, suggesting an iso-structure compared with $[(\mathbf{AA^{Bn}})_2\mathrm{Zn}]$.[10] Notably, two six-membered rings consisting of a Zn centre bonded to bidentate $\mathbf{AA^{OMe}}$ ligands in **4** are formed in twisted conformations. It is interesting to note that all $\mathbf{AA^{OMe}}$ ligands in complexes **2–4** assume a *N*,*N*-bidentate bonding mode with the amido and imine nitrogen atoms coordinated to the metal centre, and the pendant oxygen atom does not coordinate to the zinc centre.

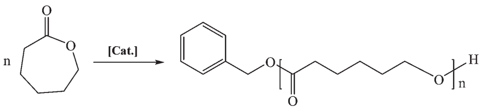
Variable-temperature ^{1}H NMR studies of complex 3

On the basis of the ^{1}H NMR spectrum of complex **3** (Fig. S1, ESI†), the signal pattern demonstrates the existence of two different conformations in solution at 20 °C. To figure it out, a variable-temperature ^{1}H NMR experiment was accomplished in $CDCl_3$ as shown in Fig. 5. One set of splitting peaks (4.18–4.46 ppm) for **3** at −55 °C was found since the two methylene protons of the benzylalkoxy group were fixed and were chemically non-equivalent at the lower temperature. As the temperature was raised (~10 °C), the signal at 4.42–4.48 ppm (e + e′) began to broaden gradually. As the temperature was raised to 50 °C, these resonances split significantly, while the peak of the benzyl group (e′) shows a singlet peak at *ca.* 4.45 ppm, indicating another species has appeared. The new species can be attributed to a mononuclear zinc alkoxide complex dissociated from the dimeric Zn complex **3** in the solution state. It is also believed that this mononuclear zinc complex is the active species during the ring-opening polymerization of cyclic esters. These results are similar to those previously reported for zinc and magnesium complexes with *N*,*N*,*O*-tridentate Schiff base ligands.[12]

Ring-opening polymerization of ε-caprolactone and β-butyrolactone

The ring-opening polymerization (ROP) of ε-caprolactone (ε-CL) was generally executed in toluene under a dry nitrogen atmosphere and was systematically studied as listed in Table 1. As shown in entries 1–3, the optimized ε-CL polymerization conditions initiated by **3** with a monomer-to-initiator ratio of

Table 1 Ring-opening polymerization of ε-caprolactone initiated by **3** and **4**/BnOH



Entry	Cat.	[ε-CL]$_0$/[Zn]$_0$/[BnOH]$_0$	t (min)	Conv.[c] (%)	M_n (calcd)[d]	M_n (obsd)[e]	M_n (NMR)[f]	PDI[e]
1[a]	**3**	200/1/0	180	85	19 500	25 000 (14 000)	23 700	1.05
2[b]	**3**	200/1/0	50	87	20 000	29 100 (16 300)	25 200	1.05
3[b]	**3**	200/1/0	70	99	22 700	33 900 (19 000)	26 400	1.07
4[b]	**3**	25/1/0	70	99	2900	5700 (3200)	3400	1.09
5[b]	**3**	50/1/0	70	99	5800	10 200 (5700)	7200	1.04
6[b]	**3**	100/1/0	70	99	11 400	18 300 (10 200)	14 100	1.05
7[b]	**4**/BnOH	200/1/1	120	99	22 700	19 600 (11 000)	28 800	1.27

[a] [Zn]$_0$ = 5 mM, 10 mL toluene, 30 °C. [b] [Zn]$_0$ = 5 mM, 10 mL toluene, 55 °C. [c] Obtained from ^{1}H NMR determination. [d] Calculated from the molecular weight of ε-caprolactone (114.14 g mol^{-1}) multiplied by [ε-CL]$_0$/[Zn]$_0$ multipled by the conversion yield plus the molecular weight of benzyl alcohol (108.14 g mol^{-1}). [e] Obtained from GPC analysis and calibrated by a polystyrene standard. Values in parentheses are the values obtained from GPC multiplied by 0.56.[15] [f] Obtained from ^{1}H NMR analysis.

200 were found to be [Zn]$_0$ = 5 mM in toluene at 55 °C, and the conversion yields proceed to completion within 70 min. The experimental results of entries 3–6 demonstrate that the complex **3** has good catalytic performances in a range of monomer/initiator molar ratios, [ε-CL]$_0$/[Zn]$_0$, from 25 to 200. The linear relationship between M_n *versus* [ε-CL]$_0$/[Zn]$_0$ and the low polydispersity indices (<1.10), as shown in Fig. S2, ESI,† exhibit a living characteristic and a well-controlled manner for the polymerization process. The ^{1}H NMR spectrum of PCL-25 displays that the polymer chain end was capped with a benzyl ester and a hydroxyl group with the integration ratio close to 5 : 2 : 2 between H$_a$, H$_b$ and H$_d$ (Fig. 6). Moreover, based on the successful ROP of lactones polymerized by the [(**AA**$^{\mathbf{Bn}}$)$_2$Zn]/9-AnOH catalytic system,[10] the bis-adduct Zn **4** was expected to be an active catalyst for the ε-CL polymerization in the presence of alcohol. With the addition of a stoichiometric amount of BnOH under the similar conditions of the previously described entries, **4** can also perform with a good catalytic activity toward the polymerization of ε-CL. It was found that 99% monomer conversion was achieved within 120 min, however, with a slightly larger PDI (~1.27) than **3**. This may be due to the larger steric hindrance around the zinc centre in complex **4**, retarding the coordination of the monomers to the zinc atoms, which further decreases the rate of propagation. It was believed that the **4**/BnOH system might undergo an "activated-monomer" route, where ε-CL or BnOH was activated by the Zn complex **4** and BnOH behaved as a nucleophile.[6b]

As a result of the good performance in the ROP of ε-CL, **3** has been further applied to catalyze the ring-opening polymerization of β-butyrolactone (β-BL) in order to produce poly(3-hydroxybutyrate) (PHB). All polymerizations were also performed under a dry N$_2$ atmosphere in toluene. As depicted by entries 1–2 in Table 2, the Zn complex **3** can polymerize β-BL in toluene with ~94% conversion yields within 8 h at 55 °C, yielding PHB with a very low PDI (<1.10). Under these optimal conditions, the polymerization of β-BL was then systematically studied to explore the catalytic properties (Table 2, entries 3–6). As illustrated in Fig. S3, ESI,† a linear relationship between M_n *versus* [β-BL]$_0$/[**3**]$_0$ and narrow polydispersity indices ranging from 1.05 to 1.11 also indicate a "controlled" manner during the ROP of β-BL. The end group determination from the ^{1}H NMR spectrum of PHB-25 (Fig. 7) revealed that the polymer chain end was capped with a benzyl ester and a hydroxyl group with the integration ratio close to 5 : 2 : 1 between H$_a$, H$_c$ and H$_d$. It is worth noting that **3** demonstrates excellent catalytic activity up to a 1200-fold ratio, [β-BL]$_0$/[**3**]$_0$ = 1200, generating a high molecular weight of PHB (M_n = 49 200 g mol^{-1}), and its PDI remains narrow (~1.08). The catalytic performance of the β-BL polymerizations by zinc alkoxide **3** seems to be better than that of our previously reported tridentate anilido-aldimine zinc ethyl catalyst [(**AA**$^{\mathbf{Pip}}$)ZnEt], in which a 5-fold equiv. of catalyst loading towards alcohol is required to reach a high conversion yield and a large M_n under the higher monomer-to-initiator ratio (>500).[9b]

Based on the aforementioned results, the mechanism of ROP catalyzed by **3**, as shown in Scheme 2, could be proposed as the following: the dissociation of **3** affords the active species, the mononuclear zinc benzylalkoxide complex (**A**), followed by the coordination of the cyclic ester to the zinc centre forming an intermediate (**B**). Thereby, the insertion of the Zn–OBn to the carbonyl group of the monomers forms a ring-opening species (**C**). Finally, proceeding with the propagation generates the polyester (**D**), end-capped by a benzylalkoxy and a hydroxyl group.

Conclusions

A new anilido-aldimine ligand, **AA**$^{\mathbf{OMe}}$-H (**1**), modified by an O-donor pendent-arm substituent, and three novel zinc complexes **2–4** bearing such **AA** ligands have been synthesized and fully characterized by spectroscopic studies as well as microanalysis. All compounds were also structurally confirmed by single crystal X-ray diffraction determination. Variable-

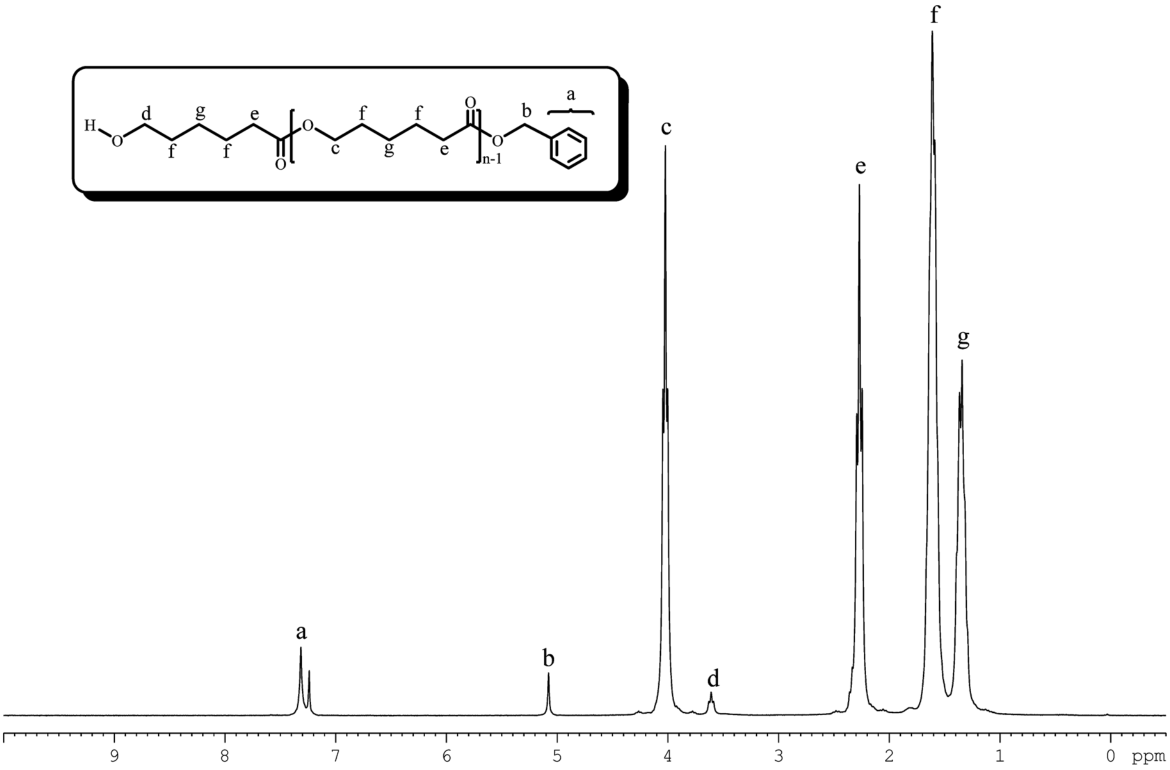
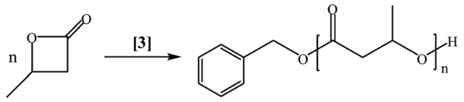


Fig. 6 ^{1}H NMR spectrum of PCL-25 (Table 1, entry 4) initiated by **3**.

Table 2 Ring-opening polymerization of β-butyrolactone initiated by **3**



Entry	[β-BL]$_0$/[**3**]$_0$	*t* (h)	Conv.^{c} (%)	M_n (calcd)^d	M_n (obsd)^e	M_n (NMR)^f	PDI^e
1^a	400/1	28.5	63	11 000	10 700	9100	1.06
2^b	400/1	8	94	16 300	15 400	21 100	1.08
3^b	50/1	8	98	2200	3800	3000	1.11
4^b	100/1	8	99	4400	6000	5400	1.09
5^b	200/1	8	99	8600	11 000	11 300	1.05
6^g	1200/1	8	98	50 700	49 200	—^{h}	1.08

[a] [**3**]$_0$ = 5 mM, 5 mL toluene, 30 °C. [b] [**3**]$_0$ = 5 mM, 5 mL toluene, 55 °C. [c] Obtained from ^{1}H NMR determination. [d] Calculated from the molecular weight of β-butyrolactone (86.09 g mol^{-1}) multiplied by [β-BL]$_0$/2·[**3**]$_0$ multiplied by the conversion yield plus the molecular weight of benzyl alcohol (108.14 g mol^{-1}). [e] Obtained from GPC analysis and calibrated by a polystyrene standard. [f] Obtained from ^{1}H NMR analysis. [g] Condition: [**3**]$_0$ = 10 mM in 10 mL toluene, 55 °C. [h] Not determination.

temperature ^{1}H NMR studies of **3** display it has a dissociative behavior in the solution state as the temperature is raised from −55 to 50 °C. **3** is a four-coordinate dinuclear Zn alkoxide complex at low temperatures, and dissociates to form a three-coordinate monomeric zinc alkoxide complex, which is considered as an active species during the ROP process, at relatively high temperatures. Experimental results illustrate that the zinc benzylalkoxide **3** initiates the ROP of ε-CL and β-BL in a living fashion, furnishing PCL and PHB with controlled molecular weights and very narrow PDIs. The excellent catalytic activity of complex **3** also enabled the preparation of a high molecular weight of atactic-PHB with a very narrow PDI (<1.1).

Experimental

General considerations

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

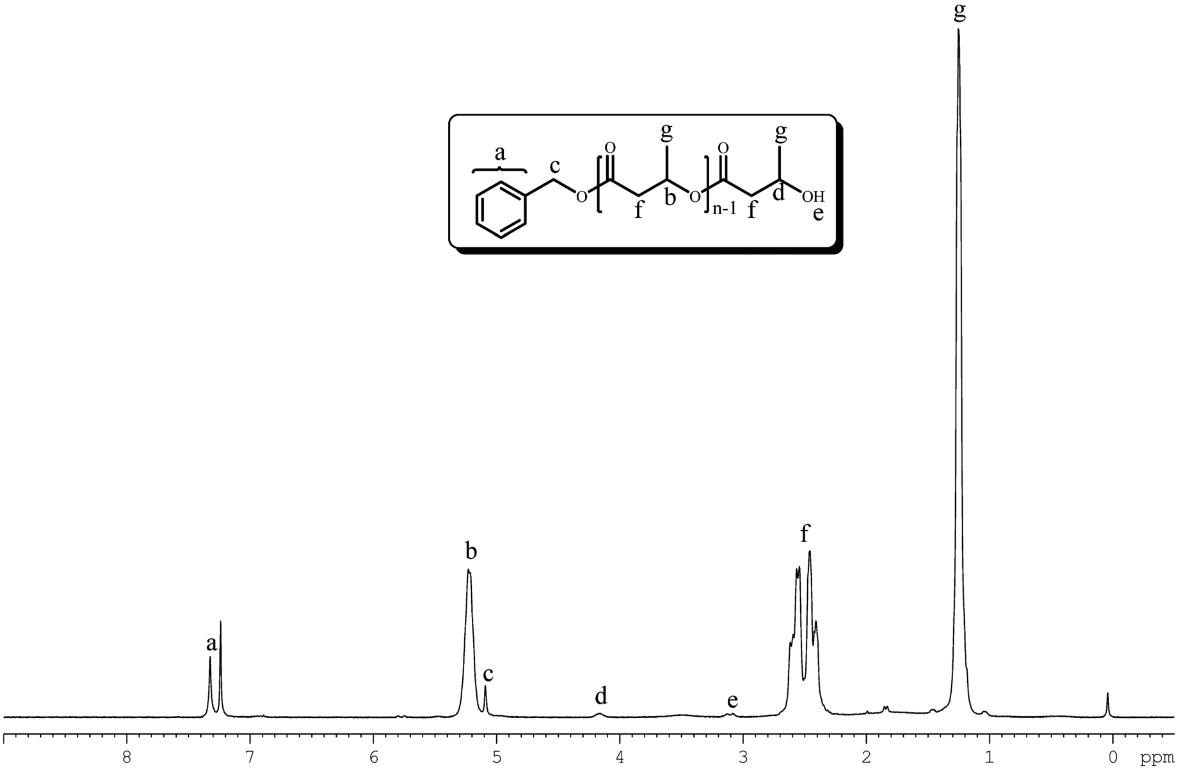
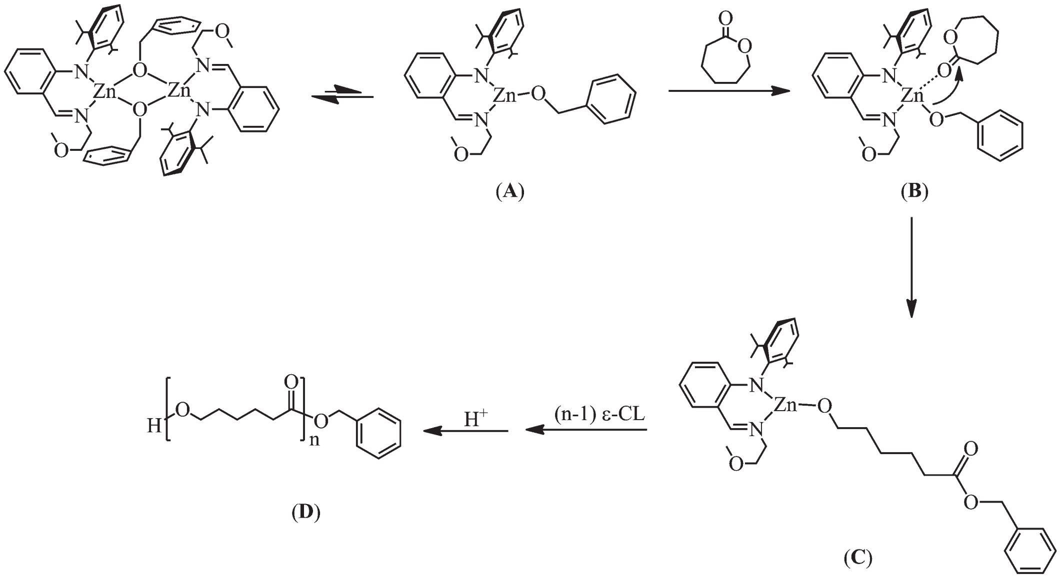


Fig. 7 ^{1}H NMR spectrum of PHB-25 (Table 2, entry 3) initiated by **3**.



Scheme 2 Proposed mechanism of ROP initiated by **3**.

at least 24 h over sodium/benzophenone (hexane, toluene, tetrahydrofuran (THF)), or over phosphorus pentoxide (CH_2Cl_2). β-BL and benzyl alcohol were mixed with CaH_2 and filtered, followed by distillation under reduced pressure. Deuterated solvents and ε-caprolactone (ε-CL) were dried over 4 Å molecular sieves. $ZnEt_2$ (1.0 M in hexane) (Aldrich), 2-bromobenzaldehyde (Acros), ethylene glycol (Acros), *p*-toluenesulfonic acid (Acros), $Pd(OAc)_2$ (Lancaster), sodium *tert*-butoxide (Acros), 2,6-diisopropylaniline (Acros), trifluoroacetic acid (Acros), and 2-methoxyethylamine (Acros) were purchased and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Aveance (300 and 400 MHz) spectrometers with chemical shifts given in parts per million from the peak of the internal TMS. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument. Gel permeation chromatography (GPC) measurements were performed on a Jasco PU-2080 plus system equipped with a RI-2031 detector using THF (HPLC grade) as an eluent. The chromatographic column was Phenomenex Phenogel 5μ 103 Å and the calibration curve used to calculate M_n(GPC) was produced from polystyrene standards. The GPC results were calculated using the Scientific Information Service Corporation (SISC) chromatography data solution 3.1 edition.

Synthesis of (*E*)-2,6-diisopropyl-*N*-(2-(((2-methoxyethyl)imino)methyl)phenyl)aniline (AA^{OMe}-H, 1)

A mixture of 2-methoxyethylamine (0.36 g, 3.4 mmol) and 2-(2,6-diisopropyl-phenylamino)benzaldehyde (0.95 g, 3.4 mmol) were stirred in refluxing methanol (30 mL) for 12 h. The solution was condensed to *ca.* 10 mL, and then 40 mL of *n*-hexane was introduced to precipitate the crude product. Volatile materials were removed under vacuum to give brown solids. Suitable crystals for X-ray diffraction analysis were obtained from a saturated *n*-hexane solution. Yield: 0.96 g (84%). Anal. calc. for $C_{22}H_{30}N_2O$: N, 8.28; C, 78.06; H, 8.93. Found: N, 7.99; C, 77.82; H, 9.08%. ^{1}H NMR ($CDCl_3$, ppm): δ 10.48 (1H, s, PhN*H*), 8.46 (1H, s, *H*C=N), 7.29–6.18 (7H, m, Ph*H*), 3.78 (2H, t, NCH_2CH_2O), 3.64 (2H, t, NCH_2CH_2O), 3.34 (3H, s, OCH_3), 3.10 (2H, m, $CH(CH_3)_2$), 1.13 (12H, m, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, ppm): δ 165.76 (*H*C=N), 149.48, 147.54, 135.24, 133.64, 131.10, 127.17, 123.68, 116.62, 114.92, 111.66 (*Ar*), 72.74 (NCH_2CH_2O), 61.12 (NCH_2CH_2O), 58.97 (OCH_3), 28.35 ($CH(CH_3)_2$), 24.88, 22.84 ($CH(CH_3)_2$).

Synthesis of [(AA^{OMe})ZnEt] (2)

To an ice cold solution of **1** (0.68 g, 2.0 mmol) in 30 mL *n*-hexane was slowly added $ZnEt_2$ (2.20 mL, 1.0 M in *n*-hexane, 2.20 mmol) under a dry nitrogen atmosphere. The mixture was then stirred for 6 h while the temperature was slowly increased to ambient temperature. Volatile materials were removed under vacuum and the residues were recrystallized from a saturated *n*-hexane solution to give yellow crystals suitable for X-ray diffraction analysis. Yield: 0.73 g (85%). Anal. calc. for $C_{24}H_{34}N_2OZn$: N, 6.49; C, 66.73; H, 7.93. Found: N, 6.99; C, 66.50; H, 7.54%. ^{1}H NMR ($CDCl_3$, ppm): δ 8.32 (1H, s, *H*C=N), 7.23–7.18 (4H, m, Ph*H*), 7.01 (1H, t, Ph*H*), 6.40 (1H, t, Ph*H*), 6.22 (1H, d, Ph*H*), 3.88 (2H, t, NCH_2CH_2O), 3.66 (2H, t, NCH_2CH_2O), 3.35 (3H, s, OCH_3), 3.00 (2H, m, $CH(CH_3)_2$), 1.10 (6H, d, $CH(CH_3)_2$), 1.03 (6H, d, $CH(CH_3)_2$), 0.85 (3H, t, $ZnCH_2CH_3$), 0.12 (2H, q, $ZnCH_2CH_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 170.21 (*H*C=N), 157.23, 144.83, 143.67, 137.16, 133.56, 124.80, 123.65, 116.05, 113.99, 112.35 (*Ar*), 72.54 (NCH_2CH_2O), 60.73 (NCH_2CH_2O), 59.08 (OCH_3), 27.08 ($CH(CH_3)_2$), 24.20, 24.03 ($CH(CH_3)_2$), 11.88 ($ZnCH_2CH_3$), −2.08 ($ZnCH_2CH_3$).

Synthesis of [(AA^{OMe})Zn(μ-OBn)]$_2$ (3)

To an ice cold solution of **1** (0.68 g, 2.0 mmol) in 30 mL *n*-hexane was slowly added $ZnEt_2$ (2.20 mL, 1.0 M in *n*-hexane, 2.20 mmol) under a dry nitrogen atmosphere. The mixture was then stirred for 6 h while the temperature was slowly increased to ambient temperature. Volatile materials were removed under vacuum to give yellow solids. The residues were redissolved in 30 mL of tetrahydrofuran and thence benzyl alcohol (0.21 mL, 2.0 mmol) was added slowly to this ice cold THF solution. The mixture was then stirred for another 6 h while the temperature was slowly increased to ambient temperature. Volatile materials were removed under vacuum and the residues were recrystallized from 20 mL of *n*-hexane to give a yellow crystalline solid. Yield: 0.69 g (68%). Suitable crystals for X-ray diffraction analysis were obtained from a saturated toluene solution. Anal. calc. for $C_{58}H_{72}N_4O_4Zn_2$: N, 5.49; C, 68.29; H, 7.11. Found: N, 5.22; C, 67.64; H, 7.09%. ^{1}H NMR ($CDCl_3$, 223 K, ppm): δ 7.93 (1H, s, *H*C=N), 7.29–5.87 (12H, m, Ph*H*), 4.45 (1H, d, OCH_2Ph), 4.22 (1H, d, OCH_2Ph), 3.13 (3H, s, OCH_3), 3.03–3.10 (2H, m, $CH(CH_3)_2$), 3.00 (2H, t, NCH_2CH_2O), 2.54 (2H, t, NCH_2CH_2O), 1.05 (6H, d, $CH(CH_3)_2$), 0.83 (6H, d, $CH(CH_3)_2$).

Synthesis of [(AA^{OMe})$_2$Zn] (4)

To an ice cold solution of **1** (0.68 g, 2.0 mmol) in 30 mL toluene was slowly added $ZnEt_2$ (1.20 mL, 1.0 M in *n*-hexane, 1.20 mmol) under a dry nitrogen atmosphere. The mixture was then stirred for 36 h in refluxing toluene. Volatile materials were removed under vacuum and the residues were recrystallized from *n*-hexane to give a yellow crystalline solid. Suitable crystals for X-ray diffraction analysis were obtained from a saturated toluene solution. Yield: 0.58 g (79%). Anal. calc. for $C_{44}H_{58}N_4O_2Zn$: N, 7.57; C, 71.38; H, 7.90. Found: N, 7.34; C, 71.62; H, 8.15%. ^{1}H NMR ($CDCl_3$, ppm): δ 8.11 (1H, s, *H*C=N), 7.12–6.95 (4H, m, Ph*H*), 6.83 (1H, t, Ph*H*), 6.30 (1H, t, Ph*H*), 6.01 (1H, d, Ph*H*), 3.64 (1H, m, NCH_2CH_2O), 3.39–3.27 (3H, m, NCH_2CH_2O, NCH_2CH_2O), 3.21 (3H, s, OCH_3), 3.17–2.96 (2H, m, $CH(CH_3)_2$), 1.10, 0.94, 0.77, 0.39 (12H, d, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, ppm): δ 170.99 (*H*C=N), 160.26, 147.10, 145.16, 143.96, 137.28, 132.37, 124.24, 124.21, 123.66, 119.65, 115.59, 111.85 (*Ar*), 71.56 (NCH_2CH_2O), 58.55 (NCH_2CH_2O), 57.96 (OCH_3), 28.21, 27.44 ($CH(CH_3)_2$), 25.43, 24.77, 24.17, 22.77 ($CH(CH_3)_2$).

Polymerization of ε-caprolactone catalyzed by 3

A typical polymerization procedure was exemplified by the synthesis of PCL-200 (the number 200 indicates the designed $[\varepsilon\text{-CL}]_0/[Zn]_0$). To a rapidly stirring solution of [($\mathbf{AA^{OMe}}$)Zn(μ-OBn)]$_2$ (**3**) (0.051 g, 0.050 mmol) in toluene (10 mL) was added ε-caprolactone (2.20 mL, 20.0 mmol) under a dry nitrogen atmosphere. The reaction mixture was then stirred at 55 °C for 70 min. The conversion yield (99%) of PCL-200 was analyzed by ^{1}H NMR spectroscopic studies. After the reaction was quenched by the addition of excess water (1.0 mL), the polymer was precipitated into *n*-hexane (100 mL). The final polymer was then dissolved in THF (5.0 mL) and purified on precipitation again in methanol (50 mL), collected, and dried under vacuum. Yield: 2.09 g (92%).

Table 3 Crystallographic data of complexes **1–4**

	1	2	3	4
Empirical formula	$C_{22}H_{30}N_2O$	$C_{24}H_{34}N_2OZn$	$C_{58}H_{72}N_4O_4Zn_2$	$C_{44}H_{58}N_4O_2Zn$
Formula weight	338.48	431.90	1019.94	740.31
Temp (K)	296(2) K	100(2) K	100(2) K	100(2) K
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$C2/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	31.4201(10)	10.0897(3)	9.4830(3)	10.6979(2)
b (Å)	8.0500(3)	21.5824(7)	12.5950(4)	13.3403(2)
c (Å)	8.0500(3)	10.7341(4)	12.6403(4)	14.2243(2)
α (°)	90	90	104.2100(10)	92.6920(10)
β (°)	90.222(2)	102.916(2)	108.1830(10)	96.9920(10)
γ (°)	90	90	103.9290(10)	104.5650(10)
V (Å^3)	4157.0(3)	2278.32(13)	1305.32(7)	1943.78(5)
Z	8	4	1	2
D_{calc} (Mg m^{-3})	1.082	1.259	1.297	1.265
μ (Mo Kα) (mm^{-1})	0.066	1.094	0.968	0.673
F(000)	1472	920	540	792
Reflections collected	14 550	20 551	23 060	32 685
No. of parameters	227	253	312	460
Indep. reflns (R_{int})	4091 (0.0634)	5609 (0.0432)	6458 (0.0197)	9617 (0.0242)
R_1 [$I > 2\sigma(I)$]	0.0788	0.0393	0.0359	0.0312
wR_2 [$I > 2\sigma(I)$]	0.1831	0.0827	0.0942	0.0735
Goodness-of-fit on F^2	1.023	1.008	1.050	1.032

Polymerization of ε-caprolactone catalyzed by 4 in the presence of BnOH

A typical polymerization procedure was exemplified by the synthesis of PCL-200 (the number 200 indicates the designed [ε-CL]$_0$/[BnOH]$_0$). To a rapidly stirring solution of [(**AA**$^{\mathbf{OMe}}$)$_2$Zn] (**4**) (0.037 g, 0.050 mmol) and benzyl alcohol (0.05 mL, 0.05 mmol, 1 M in toluene) in toluene (10 mL) was added ε-caprolactone (1.10 mL, 10.0 mmol) under a dry nitrogen atmosphere. The reaction mixture was then stirred at 25 °C for 120 min. The conversion yield (99%) of PCL-200 was analyzed by ^{1}H NMR spectroscopic studies. After the reaction was quenched by the addition of excess water (1.0 mL), the polymer was precipitated into *n*-hexane (100 mL). The final polymer was then dissolved in THF (5.0 mL) and purified on precipitation again in methanol (50 mL), collected, and dried under vacuum. Yield: 0.97 g (85%).

Synthesis of polyhydroxybutyrate with benzylalkoxy chain-end group catalyzed by 3

A typical polymerization procedure was exemplified by the synthesis of PHB-200 (the number 200 indicates the designed [ε-CL]$_0$/[Zn]$_0$). To a rapidly stirring solution of [(**AA**$^{\mathbf{OMe}}$)-Zn(μ-OBn)]$_2$ (**3**) (0.051 g, 0.050 mmol) in toluene (5 mL) was added ε-caprolactone (2.20 mL, 20.0 mmol) under a dry nitrogen atmosphere. The reaction mixture was then stirred at 55 °C for 8 h. The conversion yield (94%) of PHB-200 was analyzed by ^{1}H NMR spectroscopic studies. After the reaction was quenched by the addition of excess water (1.0 mL), the polymer was precipitated into *n*-hexane (100 mL). The final polymer was then dissolved in dichloromethane (5.0 mL) and purified on precipitation again in *n*-hexane (50 mL), collected, and dried under vacuum to give a yellow colloid. Yield: 1.51 g (93%).

X-ray crystallographic studies

Suitable crystals of **1** was sealed in thin-walled glass capillaries and mounted on a Bruker APEX2 diffractometer to collect the diffraction data at 296 K. Suitable crystals of complexes **2–4** were mounted onto glass fiber using perfluoropolyether oil and cooled rapidly in a stream of cold nitrogen gas to collect the diffraction data at 100 K using a Bruker APEX2 diffractometer. Intensity data were collected in 1350 frames with increasing *w* (width of 0.5° per frame). The absorption correction was based on the symmetry-equivalent reflections using the SADABS program.[13a] The space group determination was based on a check of the Laue symmetry and systematic absence, and was confirmed by the structure solution. The structures were solved with direct methods using a SHELXTL package.[13b,c] All non-H atoms were located from successive Fourier maps, and hydrogen atoms were treated as a riding model on their parent C atoms. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H-atoms. Drawing of the molecules was done using Oak Ridge Thermal Ellipsoid Plots (ORTEP).[14] Crystallographic data of complexes **1–4** are summarized in Table 3.

Acknowledgements

We gratefully acknowledge the financial support from the National Science Council, Taiwan (NSC101-2113-M-005-020-MY3 to B.-T. Ko and NSC101-2113-M-005-010-MY3 to C.-C. Lin).

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