Preparation and characterization of bisphenolato magnesium derivatives: an efficient catalyst for the ring-opening polymerization of ε-caprolactone and L-lactide†

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A series of magnesium complexes have been prepared and characterized, in which [(EDBP-Me)Mg(μ-OBn)]$_2$ (**4**) has shown high activity toward the ring-opening polymerization (ROP) of ε-caprolactone and L-lactide. 2,2′-Ethylidene-bis(4,6-di-*tert*-butylphenol)-monomethyl ether ([EDBP-(Me)H]) is prepared by the reaction of 2,2′-ethylidene-bis(4,6-di-*tert*-butylphenol) (EDBP-H$_2$) with dimethyl sulfate. The reaction of [EDBP-(Me)H] with ^{n}Bu$_2$Mg yields [(EDBP-Me)Mg^{n}Bu]$_2$, which further reacts with benzyl alcohol and N,N-dimethylethylenediamine giving complexes [(EDBP-Me)Mg(μ-OBn)]$_2$ (**4**) and {[EDBP(Me)]Mg(μ-Me$_2$NCH$_2$CH$_2$NH)}$_2$ (**5**), respectively. Experimental results indicate that the activity of complex **4** toward cyclic esters is higher than that of [(μ-EDBP)Mg]$_2$/(BnOH).

Introduction

Currently, polyesters such as polylactide (PLA) and poly(ε-caprolactone) (PCL) are of great interest due to their wide biomedical, pharmaceutical and environmental applications.[1] The most effective method for the preparation of PLA and PCL is the ring-opening polymerization (ROP) of related cyclic esters,[2] where metal alkyls,[3] amides,[4] thiolates,[5] aryl oxides,[6] alkoxides[7] and enolates[8] in the presence or absence of alcohol have been used as initiators. Among them, single-site metal alkoxides have the highest activity with a good control over the polymer molecular weight.[7]

Metal complexes supported by a variety of ligands such as *β*-diketiminate, salen, and many others have been developed and used as catalytic/initiating systems for ROP of lactide. In addition, bisphenolate system is also attracting considerable attention, because it is easily modified and functionalized. As a result, many bisphenolato ligands (Chart 1a) have been introduced through a link of various functional groups and their metal complexes have been proven to be effective initiators.[9] Recently, many lithium, sodium, magnesium, zinc and aluminium bulky bisphenolato complexes have been used as initiators/catalysts for ROP of lactide in our laboratory.[2d,10] Among these metals, magnesium is non-toxic and essential for human life,[11] therefore, magnesium complexes are good candidates as catalysts/initiators in the preparation of biomedical grade PLA. However, the reactivity of magnesium complexes [LMg(THF)]$_2$ derived from these bisphenol ligands show only moderate activity in the ROP of LA in the presence of additional alcohols.[12] In order to enhance the activity of magnesium, modification of EDBP-H$_2$ [EDBP-H$_2$: 2,2′-ethylidene-bis(4,6-di-*tert*-butylphenol)] has been investigated. As a result, a series of EDBP-H$_2$ derivatives, EDBP-RTs-H (Chart 1b), have been prepared from the reaction of EDBP-H$_2$ with the related thionyl chloride.[13] Experimental results indicate that the activity of the magnesium complexes can be dramatically increased by the modification of the bisphenol system. In this research, a different approach is used in which [EDBP-(Me)H] derived from EDBP-H$_2$ is synthesized. The catalytic activity of its magnesium complex, [(EDBP-Me)Mg(μ-OBn)]$_2$ towards ROP of LA and e-CL is investigated. The mechanism for the polymerization of e-CL initiated by [(EDBP-Me)Mg(μ-OBn)]$_2$ will also be discussed.

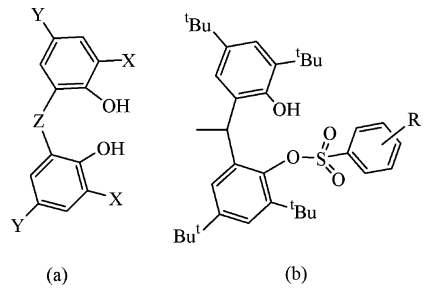

Chart 1 Structure of (a) bisphenol ligands and (b) EDBP-RTs-H.

Results and discussion

Synthesis and characterization

The monovalent bisphenolato ligand, [2-(2-methoxy-3,5-di-*tert*-butylphenyl)-2′-ethylidene(4,6-di-*tert*-butylphenol), EDBP-(Me)H, **1**] was prepared in high yield (84%) by the reaction of 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) (EDBP-H$_2$) with one molar equivalent of potassium carbonate in acetone followed by the addition of a stoichiometric amount of dimethyl sulfate (Scheme 1). Due to the replacement of one of the phenol protons to the methyl group, two aryl rings of compound **1** are chemically non-equivalent; this phenomenon has been verified by

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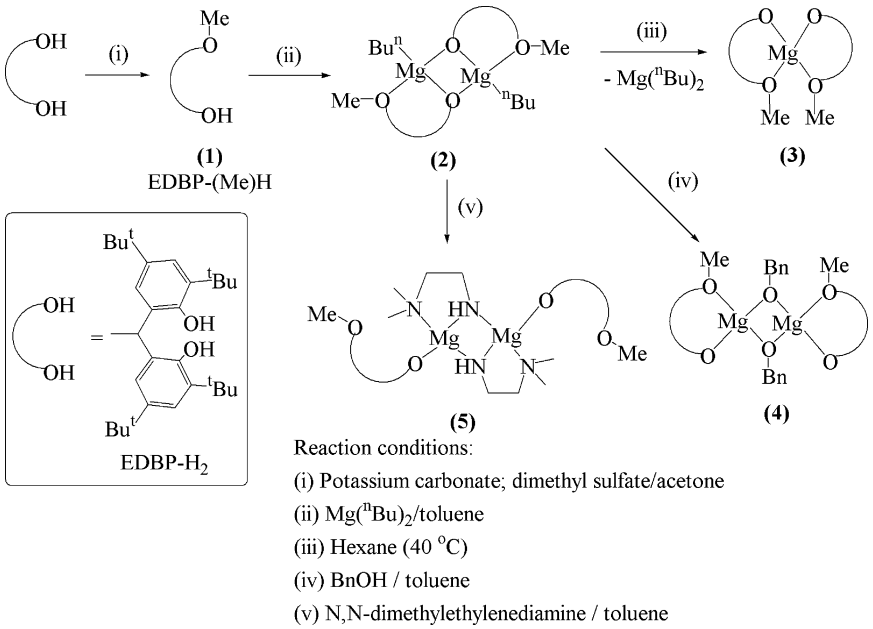


Scheme 1 Preparation of EDBP-(Me)H and its magnesium complexes.

^{1}H NMR spectroscopic studies. For instance, four resonance peaks corresponding to aromatic protons ($\delta = 7.28, 7.19, 7.13, 7.12$ ppm, 1H each) and four peaks arising from *tert*-butyl groups ($\delta = 1.38, 1.36, 1.34, 1.23$ ppm, 9H each) were observed.

Further reaction of compound **1** with a stoichiometric amount of ^{n}Bu$_2$Mg in toluene produces $\{[\mu\text{-EDBP(Me)}]Mg^nBu\}_2$ (**2**) in near quantitative yield. Compound **2** is verified by spectroscopic studies as well as elemental analysis. Attempts to grow suitable crystals of **2** for X-ray structure determination were unsuccessful. Like many other magnesium complexes, compound **2** is rather thermally unstable and ligand exchange of compound **2** occurs in a warm hexane (40 °C) solution yielding [(EDBP-Me)$_2$Mg] (**3**) as crystalline solids. However, compound **3** can also be prepared in high yield from the reaction of ^{n}Bu$_2$Mg with two molar equivalents of [EDBP-(Me)H]. The molecular structure of compound **3** (Fig. 1) shows, it is a homoleptic complex with a tetra-coordinated Mg atom supported by the oxygen atoms of the EDBP(Me)$^-$ ligand in which there is a 2-fold axis passing through the Mg atom. The Mg–O(2) bond length of 2.091(2) Å is longer than the Mg–O(1) distance 1.865(2) Å, attributed to the neutral coordination bonding from the methoxy group.

Treatment of compound **2** with two molar equivalents of benzyl alcohol in toluene at ambient temperature generates a magnesium benzyl alkoxide, $\{[\text{EDBP(Me)}]Mg(\mu\text{-OBn})\}_2$ (**4**) in moderate yield (47%). ^{1}H NMR spectroscopic studies reveal the formation of a trace amount of **3** along with **4**. Compound **3** can be removed by crystallization of the mixture. Compound **4** is relatively more thermally stable than complex **2**. It is stable even in a warm (40 °C) hexane solution for 6 h. Single crystals of **4** suitable for X-ray structural determination were obtained from a toluene solution. The molecular structure shows that complex **4** (Fig. 2) is dimeric in which each Mg atom adopts a distorted tetrahedral geometry coordinated to one phenoxy oxygen, one methoxy oxygen and two bridged oxygen atoms of the benzyl alkoxy groups. The complex is a C_2 symmetric compound which has a 2-fold axis through

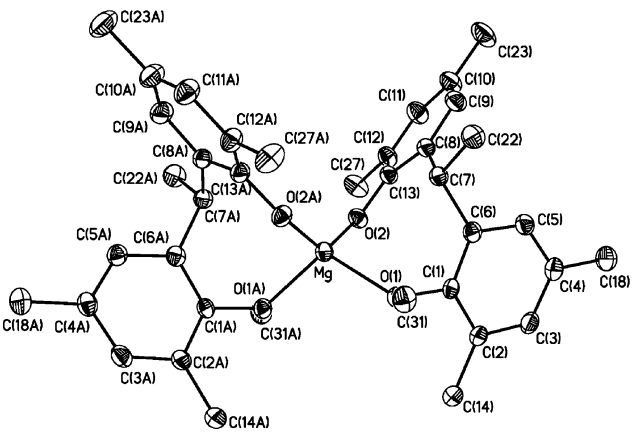


Fig. 1 Molecular structure of **3** as 20% ellipsoids. All the hydrogen atoms and methyls at the *t*-butyl groups of the EDBP-Me$^-$ ligand are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mg–O(1) 1.865(2), Mg–O(2) 2.091(2), O(1)–Mg(1)–O(2) 100.40(10), O(2)–Mg–O(2A) 129.27(17), O(1)–Mg–O(1A) 110.94(14), O(2)–Mg–O(1A) 107.77(9).

the Mg(1)–O(3)–Mg(1A)–O(3A) plane. The longer Mg–O(2) bond length [2.080(2) Å] than the Mg–O(1) bond length [1.852(2)] is as expected because of a dative bonding feature of Mg–O(2) similar to the results found in **3**.

$\{[\text{EDBP(Me)}]Mg(\mu\text{-}Me_2NCH_2CH_2NH)\}_2$ (**5**) is prepared from the reaction of $\{[\mu\text{-EDBP(Me)}]MgBu\}_2$ with N,N-dimethylethylenediamine in a 1:2 ratio with a similar procedure to that of **4**. Single crystals of **5** suitable for structure determination were obtained from a CH_2Cl_2 solution. The molecular structure of compound **5** (Fig. 3) reveals a dimeric feature with 5,4,5 rings in which each of the magnesium atoms coordinates with the nitrogen atom of the amino group, a nitrogen atom of the -NMe$_2$ group and the phenoxy oxygen atom. These 5,4,5 rings form a ladder structure. There is an inversion center lying at

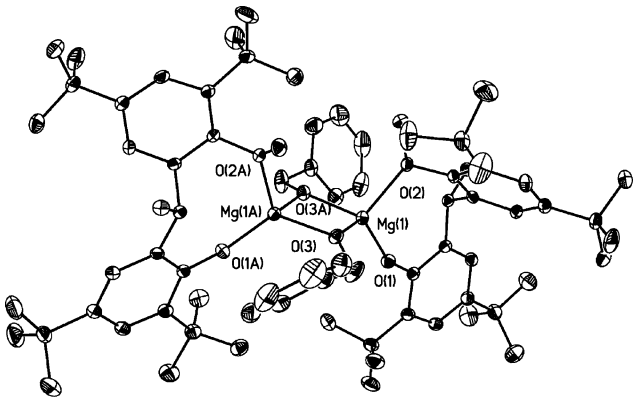


Fig. 2 Molecular structure of **4** as 20% ellipsoids. All of the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mg(1)–O(1) 1.852(2), Mg(1)–O(2) 2.080(2), Mg(1)–O(3) 1.959(2), Mg(1)–O(3A) 1.943(2). O(1)–Mg(1)–O(2) 110.97(8), O(1)–Mg(1)–O(3) 117.59(9), O(1)–Mg(1)–O(3A) 124.40(9), O(2)–Mg(1)–O(3) 108.35(8), O(2)–Mg(1)–O(3A) 108.08(8), O(3)–Mg(1)–O(3A) 84.27(9).

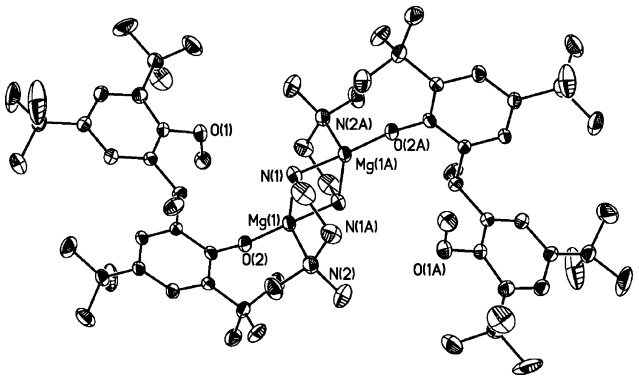


Fig. 3 Molecular structure of **5** as 20% ellipsoids. All the hydrogen atoms and methyls at the *t*-butyl groups of the EDBP-Me$^-$ ligand are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mg(1)–O(2) 1.836(2), Mg(1)–N(1) 2.076(3), Mg(1)–N(2) 2.167(3), Mg(1)–N(1A) 2.090(3); N(1)–Mg(1)–N(2) 85.65(13), N(1)–Mg(1)–N(1A) 90.81(12), O(2)–Mg(1)–N(2) 111.97(12), O(2)–Mg(1)–N(1A) 121.90(12), Mg(1)–N(1)–Mg(1A) 89.19(12).

the Mg(1)–N(1)–Mg(1A)–N(1A) plane, hence the complex is an *I* symmetric compound. The coordinated behavior of EDBP(Me)$^-$ in complex **5** differs from the situation found in complex **4**. The molecular structure of **5** shows that in the presence of the stronger coordination group (-NMe_2), the methoxy group of the EDBP(Me)$^-$ ligand swings away from the Mg atom. The result reveals the hemilabile property of the EDBP(Me) ligand. By combining the structure studies of compounds **5** and **4**, we present evidence for the hemilabile property of the reduced bisphenolato (EDBP(Me)) ligand. For a specific requirement, the application of the hemilabile property in catalyst design would be a good consideration.[14]

ROP of ε-caprolactone and L-lactide initiated by {[EDBP(Me)]Mg(μ-OBn)}$_2$

The catalytic activities of complex **4** towards ROP of ε-caprolactone (CL) and L-lactide (LLA) have been systematically studied and the experimental results are listed in Table 1. Conversion of CL and L-LA is determined based on the ^{1}H NMR spectroscopic studies. The molecular weight and polydispersity of poly(L-lactide) (PLLA) and PCL are measured by both gel-permission chromatography (GPC) and ^{1}H NMR spectroscopy. In the case of CL, conversion up to 96% can be achieved within 1 h at 25 °C. The number average molecular weight (M_n) of the polymer increases linearly with the increase of the [M]/[**4**] ratio, implying a living character of complex **4** (Table 1, entries 1–4; Fig. 4).

The polydispersity indices (PDIs) of these polymers are quite low ranging from 1.07 to 1.08. The molecular weight of PCL and the chemical nature of the structure chain ends are established by ^{1}H NMR studies. For example, the ^{1}H NMR spectrum of PCL-50 (the number 50 indicates the designed $[M]_0$/[**4**] ratio) gave an integral ratio close to 2:2:48 for H_b (-OCH_2Ph from PCL at the benzyl ester chain end), H_g (-CH_2 from PCL at the hydroxy end) and H_f ({-$CH_2OC(O)$-}$_n$), respectively (Fig. 5). The result indicates that the polymerization is initiated by the insertion of the benzyl alkoxy group to ε-caprolactone. By comparing the molecular weight of PCL and the [M]/[**4**] ratio, it can be concluded that both benzyl alkoxy groups act as initiators in the polymerization.

ROP of L-lactide (L-LA) initiated by **4** was also performed. Experimental results show that complex **4** is a highly efficient initiator for the polymerization of L-LA. Conversion up to 99% can be achieved within 10 min at 0 °C. Linearity between the molecular weight of PLLA and the monomer/initiator ratio is

Table 1 Ring-opening polymerization of ε-caprolactone and L-lactide initiated by **4**

entry	Monomer	[M]:[**4**]	M_n (Calc.)[a]	M_n (NMR)[b]	M_n (GPC)[c]	PDI[c]	t (min)	T (°C)	Conv. (%)
1	ε-CL	50:1	2800	3000	6100	1.07	60	25	94
2	ε-CL	100:1	5500	6200	12800	1.07	60	25	95
3	ε-CL	150:1	7800	8700	17000	1.08	60	25	90
4	ε-CL	200:1	11000	13000	23500	1.08	60	25	96
5	L-LA	50:1	3700	9300	13800	1.09	10	0	>99
6	L-LA	100:1	7200	15900	28400	1.07	10	0	>99
7	L-LA	150:1	9800	22000	38000	1.06	10	0	90
8	L-LA	200:1	14400	—[d]	50000	1.18	15	0	>99
9	L-LA	50(50):1	7200	16300	29900	1.17	10(10)	0	>99

[a] Calculated from the molecular weight of monomer times $[M]_0/2[\mathbf{4}]_0$ times the conversion plus the molecular weight of BnOH. [b] Obtained from ^{1}H NMR analysis. [c] Obtained from GPC analysis which were calibrated with a polystyrene standard. The differences between theoretical calculated and GPC analyzed values could be illustrated in the literature. The corrected M_n of PLLA would be obtained by multiplying the value obtained from GPC by 0.58 and 0.62 for PCL.[15] [d] Not available.

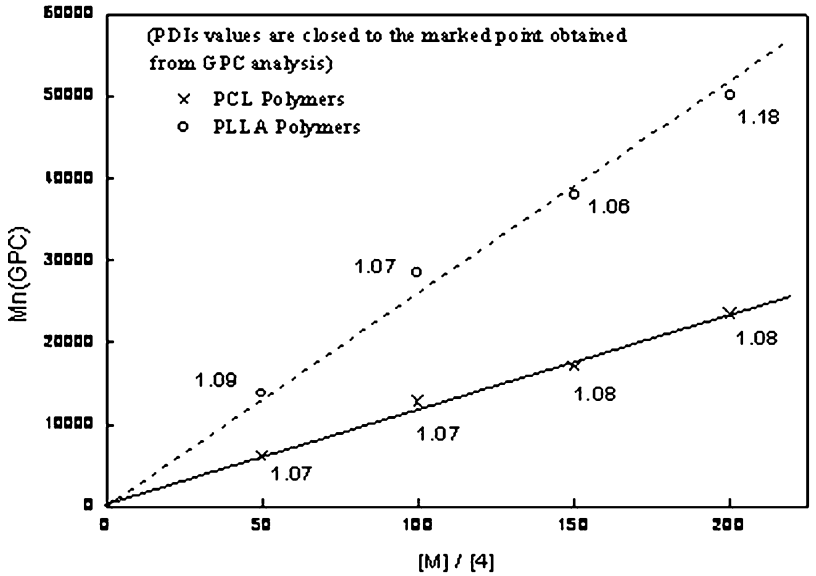


Fig. 4 Polymerization of cyclic esters initiated by **4**.

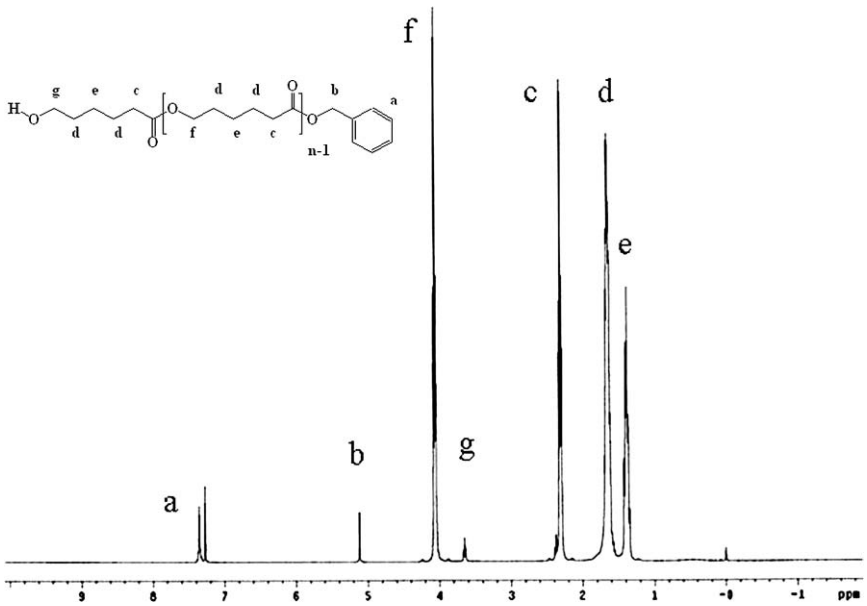
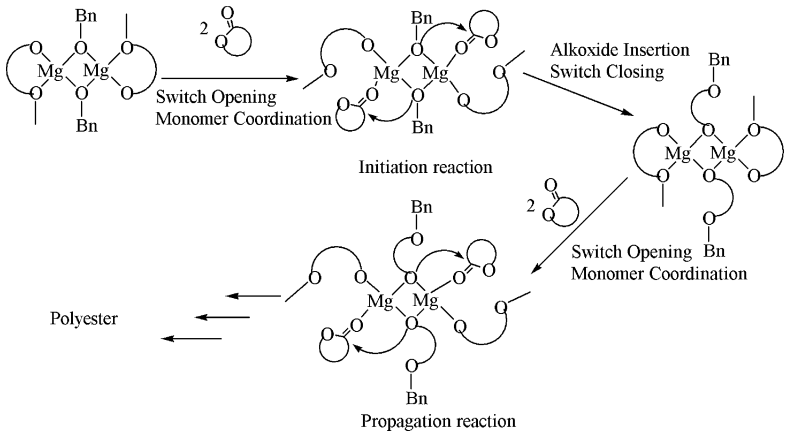


Fig. 5 ^{1}H NMR spectrum of PCL-50 in $CDCl_3$.

observed (Table 1, entries 5-8; Fig. 4). The living character can be further verified by the stepwise addition of L-lactide (entry 9). It is interesting to note that the molecular weight of PLLA is twice that expected indicating that only one of the two benzyl alkoxy groups are active in the polymerization. A similar result has been observed in the $[(EDBP\text{-}RTs)Mg(OBn)]_2$ system. However, the reason for the difference between the polymerization of CL and L-LA is still unknown. By comparing the activity of complex **4** with our earlier reported $[(\mu\text{-}EDBP)Mg]_2$/BnOH system,[12] the activity of **4** is highly enhanced by the modification of the divalent $EDBP^{2-}$ ligand to a monovalent EDBP-Me^- ligand. This difference is probably attributed to two situations. One cause is the higher activity of the BnO^- group than that of the BnOH, the other is the weak coordination ability of the methoxy group to act as a switch during polymerization, therefore, stabilizing the intermediate.

Proposed mechanism for the ROP of ε-caprolactone initiated by $\{$[EDBP(Me)]Mg(μ-OBn)$\}_2$

With the previous illustrations, the methoxy group of [EDBP-$(Me)^-$] leaves the Mg atom when a stronger coordination ligand is in the environment. By considering this hemilabile property of EDBP(Me) in complex **4**, we propose the mechanism of the ROP process of PCL as shown in Scheme 2. In the first step, the methoxy group of EDBP(Me) dissociates from the Mg atom, and then the oxygen atom of the carbonyl group of the cyclic ester coordinates to the Mg atom. Secondly, the alkoxide attacks the carbon atom of the carbonyl group via an insertion reaction, opening the ring and forming a new alkoxide that contains the benzyl group in the end chain. Finally, in the third step, the methoxy group of EDBP(Me) re-coordinates to the Mg atom, stabilizing the



Scheme 2 Proposed mechanism for the ROP of ε-caprolactone.

complex. Repeating the cycle, propagation continues until all of the monomer is consumed, producing a polyester pendant on the Mg atom. Polyester would be obtained by terminating the reaction.

Conclusions

Three novel magnesium complexes of a monovalent bisphenolato ligand have been synthesized and fully characterized by spectroscopic methods as well as XRD structural determination. The result of the catalytic ROP reaction indicates that complex **4** is a better complex than $[(EDBP)Mg(THF)]_2$ for this purpose. Combining the characterization of complexes **4** and **5** reveals the hemilabile property of the ligand EDBP(Me). This property enables the complex to act as a switch for controlled ligand coordination and stabilizes the intermediate.

Experimental

General conditions

All manipulations were carried out under a dry nitrogen atmosphere and all glassware was flame-dried under vacuum before use. Solvents were dried by refluxing for at least 24 h over sodium/benzophenone (hexane, toluene and tetrahydrofuran) or phosphorus pentoxide or anhydrous magnesium sulfate (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 of the toluene solution. Mg^nBu_2 (1.0 M in heptane), N,N-dimethylethylenediamine, 2,2′-ethylidenebis(4,6-di-*tert*-butyl phenol) (EDBP-H_2), potassium carbonate, dimethyl sulfate and acetic acid were purchased and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury-400 (400 MHz for ^{1}H, 100 MHz for ^{13}C) spectrometer with chemical shifts given in ppm referenced to TMS as internal standard. Infrared spectra were obtained from a Bruker Equinox 55 spectrometer. Microanalyses were performed using a Heraeus CHN-OS-RAPID instrument. The electron impact mass spectrum (EIMS) was obtained using a JEOL JMS-SX/SX 102A mass spectrometer. GPC measurements were performed on a Hitachi L-7100 system equipped with a differential Bischoff 8120 RI detector using THF (HPLC grade) as an eluent. The chromatographic column was Phenomenex Phenogel 5 μ 103 Å and the calibration curve used to calculate M_n (GPC) was produced from polystyrene standards. The GPC results were calculated using the SISC chromatography data solution 1.0 edition.

Preparation of 2,4-di-*tert*-butyl-6-(1-(3,5-di-*tert*-butyl-2-methoxyphenyl)ethyl)phenol [EDBP-(Me)H] (1)

A mixture of EDBP-H_2 (0.88 g, 2 mmol) and potassium carbonate (0.28 g, 2 mmol) in acetone (40 mL) was stirred at room temperature for 0.5 h. Dimethyl sulfate (0.38 g, 3 mmol) was then added and the resulting mixture was stirred for another 48 h. The mixture was filtered and the filtrate was dried in *vacuo* giving white powder. The white powder was redissolved in hot hexane (50 mL) and dried over $MgSO_4$. The hexane solution was then concentrated to *ca.* 30 mL and was cooled to −20 °C. White crystalline solid was obtained after 1 day at −20 °C. Yield: 0.76 g (84%). Anal. Cacld for $C_{31}H_{48}O_2$: C, 82.24; H, 10.69%. Found: C, 82.00; H, 9.92%.^{1}H NMR ($CDCl_3$, ppm): δ 7.28, 7.19, 7.13, 7.12 (s, 4H, Ph-*H*); 4.52 (q, 1H, *H*CCH$_3$ J = 7.2 Hz); 3.96 (s, 3H, OC*H*$_3$); 1.76 (d, 3H, HCC*H*$_3$, J = 7.2 Hz); 1.38, 1.34, 1.36 1.23 (s, 36H, C(C*H*$_3$)$_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 152.7, 150.5, 146.9, 141.6, 141.4, 137.9, 135.5, 131.4, 123.0, 122.3, 119.9, 114.8 (*Ph*); 63.7 (O*C*H$_3$); 35.3, 35.0, 34.6, 34.4 (C(*C*H$_3$)$_3$); 31.7, 31.4, 30.3, 29.7 (C(*C*H$_3$)$_3$); 29.9 (Ph$_2$*C*CH$_3$); 20.3 (Ph$_2$*C*CH$_3$). Mass spectrum (EI, m/z): 452.6 (M^+). Mp: 169–171 °C. IR (KBr, cm^{-1}): 3510(s), 2963(s), 2868(s), 1767(m), 1599(m), 1456(s), 1427(s), 1392(m), 1361(s), 1321(m), 1289(s), 1224(s), 1154(m), 1133(m), 1108(m), 1065(m), 988(s), 932(m), 904(m), 881(m), 811(m), 799(br), 769(br).

Synthesis of [μ-(EDBP-Me)MgBu]$_2$ (2)

Mg^nBu_2 (2.20 mL, 1.0 M in heptane, 2.20 mmol) was added slowly to an ice cold (0 °C) toluene solution (15 mL) of EDBP-(Me)H (0.905 g, 2.0 mmol). The mixture was stirred for 8 h while the temperature was increased to room temperature slowly. The volatile materials were removed under vacuum yielding white solid. The residue was then dissolved in toluene (10 mL) and filtered through Celite®. The filtrate was concentrated to *ca.* 5 mL. Colorless crystals were obtained at −20 °C after 24 h. Yield: 0.981 g (92%). Anal. Calcd for $C_{70}H_{112}Mg_2O_4$: C, 78.85; H, 10.59%. Found: C, 77.35; H, 9.64%. ^{1}H NMR (C_6D_6, ppm):

δ 7.95, 7.79, 7.51, 7.41 (s, 8H, Ph-*H*); 5.25 (q, 2H, *H*CCH$_3$ J = 6.8 Hz); 3.63 (s, 6H, OC*H*$_3$); 1.61 (d, 6H, HCC*H*$_3$, J = 6.8 Hz); 1.72, 1.44, 1.36, 1.35 (s, 72H, C(C*H*$_3$)$_3$); 0.63–1.38 (m, 14H, C*H*$_2$C*H*$_2$C*H*$_3$); –0.34 (m, 4H, MgC*H*$_2$). ^{13}C NMR (C_6D_6, ppm): δ 154.1, 149.9, 149.1, 141.0, 140.9, 139.7, 139.5, 133.9, 126.5, 124.4, 123.4, 122.4 (*Ph*); 66.28 (O*C*H$_3$); 36.5, 35.7, 34.9, 34.6 (*C*(CH$_3$)$_3$); 33.3, 32.5, 32.0, 31.6 (C(*C*H$_3$)$_3$); 31.3 (*C*CH$_3$); 30.2 (C*C*H$_3$); 26.3 (MgCH$_2$CH$_2$CH$_2$*C*H$_3$); 14.6 (MgCH$_2$CH$_2$*C*H$_2$); 13.9 (MgCH$_2$*C*H$_2$); 1.4 (Mg*C*H$_2$). Mp: 183-185 °C.

Synthesis of [EDBP-Me]$_2$Mg (3)

Method A. [μ-EDBP(Me)]MgBu}$_2$ (0.958 g, 1.8 mmol) was dissolved in hot (40 °C) hexane (50 mL) and was filtered through Celite®. The resulting solution was then kept in room temperature. Colorless thin crystals were obtained after 45 days. Yield: 0.684 g (82%). **Method B.** Mg(^{n}Bu)$_2$ (1.1 mL, 1.0 M in heptane, 1.1 mmol) was added slowly to an ice cold toluene (15 mL) solution of [EDBP-(Me)H] (**1**) (0.905 g, 2.0 mmol). The mixture was stirred for 1 h while the temperature was increased slowly to room temperature and the mixture was stirred for another 7 h. The volatile materials were removed under vacuum giving a colorless solid. The residue was recrystallized from a mixed hexane (50 mL) and diethyl ether (2 mL) solution. Yield: 0.751 g (90%). Anal. Calcd for $C_{62}H_{94}MgO_4$: C, 80.27; H, 10.21%. Found: C, 80.38; H, 9.99%. ^{1}H NMR ($CDCl_3$, ppm): δ 7.59–6.81 (m, 8H, Ph-*H*); 4.90 (q, 2H, *H*CCH$_3$ J = 7.2 Hz); 4.48 (s, 6H, OC*H*$_3$); 1.65 (d, 6H, HCC*H*$_3$, J = 7.2 Hz); 1.59, 1.55, 1.31, 1.25 (s, 72H, C(C*H*$_3$)$_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 159.1, 149.5, 149.3, 141.0, 140.9, 136.1, 134.5, 131.4, 126.2, 124.4, 121.1, 119.4 (*Ph*); 65.65 (O*C*H$_3$); 36.2, 34.8, 34.0, 33.9 (*C*(CH$_3$)$_3$); 32.9, 31.9, 31.7, 31.4 (C(*C*H$_3$)$_3$); 29.4 (Ph$_2$*C*CH$_3$); 22.7 (Ph$_2$C*C*H$_3$). Mp: 256–258 °C.

Synthesis of {[EDBP(Me)]Mg(μ-OBn)}$_2$ (4)

Benzyl alcohol (0.21 mL, 2.0 mmol) was added slowly to an ice cold solution (0 °C) of {[μ-EDBP(Me)]MgBu}$_2$ (1.06 g, 1.0 mmol) in toluene (15 mL). After the ice bath was removed, the mixture was stirred at room temperature for 6 h and was then evaporated to dryness under vacuum. The residue was dissolved in warm toluene (40 °C, 10 mL) and filtered through Celite®. Colorless crystals were obtained from concentrated solution (5 mL) at room temperature after three days. Yield: 0.543 g (46.6%). Anal. Calcd for $C_{76}H_{108}Mg_2O_6$: C, 78.27; H, 9.33%. Found: C, 77.86; H, 8.74%. ^{1}H NMR (C_6D_6, ppm): δ 7.62–6.97 (m, 18H, Ph-*H*); 5.12, 5.06 (dd, 4H, OC*H*$_2$Ph, J = 14 Hz); 3.74 (q, 2H, *H*CCH$_3$ J = 7.2 Hz); 3.63 (s, 6H, OC*H*$_3$); 1.63 (d, 6H, HCC*H*$_3$, J = 7.2 Hz); 1.82, 1.71, 1.37, 0.97 (s, 72H, C(C*H*$_3$)$_3$). ^{13}C NMR (C_6D_6, ppm): δ 159.3, 150.4, 149.2, 144.0, 141.0, 139.7, 135.9, 135.24, 132.8, 129.0, 127.1, 126.1, 126.0, 124.0, 121.5, 120.0 (*Ph*); 66.6 (O*C*H$_2$Ph); 63.6 (O*C*H$_3$); 35.9, 35.8, 35.7, 34.5 (*C*(CH$_3$)$_3$); 32.8, 32.6, 31.0, 30.8 (C(*C*H$_3$)$_3$); 30.6 (Ph$_2$*C*CH$_3$); 22.9 (Ph$_2$C*C*H$_3$). Mp: 202–204 °C (dec.).

Synthesis of {[EDBP(Me)]Mg[μ-(CH$_3$)$_2$NCH$_2$CH$_2$NH]}$_2$ (5)

N,N-Dimethylethylenediamine (0.22 mL, 2.0 mmol) was added slowly to {[μ-EDBP(Me)]MgBu}$_2$ (1.06 g, 1.0 mmol) in toluene (20 mL) at 0 °C. The ice bath was removed and the solution was warmed to room temperature and stirred for 8 h. All volatile materials were removed under vacuum, and the residue was dissolved in CH_2Cl_2 (10 mL) and filtrated through Celite®. The resulting solution was concentrated to *ca.* 5 mL and kept at room temperature. After 5 days, colorless crystals were obtained. Yield: 0.521 g (46%). Anal. Calcd for $C_{31}H_{48}O_2$: C, 82.24%; H, 10.69%. Found: C, 82.00%; H, 9.92%. ^{1}H NMR ($CDCl_3$, ppm): δ 7.44–6.86 (m, 8H, Ph-*H*); 4.71 (q, 2H, *H*CCH$_3$ J = 6.4 Hz); 3.96 (s, 6H, OC*H*$_3$); 2.64 (br, 4H, C*H*$_2$CH$_2$NMe$_2$); 2.32 (br, 4H, CH$_2$C*H*$_2$NMe$_2$); 2.15 (br, 12H, CH$_2$CH$_2$N(C*H*$_3$)$_2$); 1.76 (d, 6H, CC*H*$_3$, J = 6.4 Hz); 1.38, 1.33, 1.30, 1.13 (s, 72H, C(C*H*$_3$)$_3$); 0.88 (br, 2H, N*H*).

Polymerization of ε-caprolactone initiated by 4

A typical polymerization procedure was exemplified by the synthesis of PCL-50 (the number 50 indicates the designed [CL]$_0$/[**4**]$_0$) at 25 °C (Table 2, entry 1). The conversion (94%) of PCL-50 was analyzed by ^{1}H NMR spectroscopy. ε-Caprolactone (0.263 mL, 2.5 mmol) was added to a rapidly stirred solution of {[EDBP(Me)]Mg(μ-OBn)}$_2$ (**4**) (583 mg, 0.05 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred at 25 °C for 1 h during which the viscosity of the reaction mixture increases. The reaction was then quenched by the addition of an aqueous acetic acid solution (0.35 N, 10 mL), and PCL was precipitated out as a white solid on pouring the mixture into n-hexane (100 mL). The resulting solid was filtered and washed twice with hexane and then dried under vacuum. Yield: 0.249 g (92%).

Polymerization of L-lactide initiated by 4

A typical polymerization procedure was exemplified by the synthesis of PLA-50 (the number 50 indicates the designed [LA]$_0$/[**4**]$_0$) at 0 °C (Table 2, entry 5). The conversion (>99%) of PLA-50 was analyzed by ^{1}H NMR spectroscopy. To a rapidly stirred solution of {[EDBP(Me)]Mg(μ-OBn)}$_2$ (**4**) (583 mg, 0.05 mmol) in CH_2Cl_2 (20 mL) was added a mixture of L-lactide (0.36 g, 2.5 mmol) and benzyl alcohol (1.0 mL, 0.10 mmol). After 10 minutes 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 solid on pouring the mixture into *n*-hexane (100 mL). Yield: 0.257 g (71%).

X-ray crystallographic studies

Suitable crystals of **3**, **4** and **5** 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. One solvated ether molecule, one solvated toluene molecule and two CH_2Cl_2 molecules were observed to co-recrystallize with complexes **3**, **4** and **5**, respectively. Due to the

Table 2 Crystallographic data of complexes **3–5**[a]

	3·Et_2O	**4**·$2C_7H_8$	**5**·$2CH_2Cl_2$
Empirical formula	C_{66} H_{104} Mg O_5	C_{90} H_{124} Mg_2 O_6	C_{72} H_{120} Cl_4 Mg_2 N_4 O_4
FW	1001.8	1350.51	1296.4
Temp (K)	293	293	293
Cryst. syst.	Monoclinic	Monoclinic	Triclinic
Space group	*C*2/*c*	*C*2/*c*	*P*-1
a/Å	26.224(4)	18.354(3)	10.566(2)
b/Å	14.652(2)	14.909(3)	10.567(2)
c/Å	18.448(3)	30.879(5)	18.362(4)
α/deg	90	90	84.166(5)
β/deg	105.519(3)	100.342(4)	80.160(4)
γ/deg	90	90	77.437(5)
Volume/Å^3	6829.5(19)	8313(2)	1967.3(8)
Z	4	4	1
Density (calcd)/Mg/m^3	0.974	1.079	1.094
Abs. coeff./mm^{-1}	0.067	0.079	0.211
F(000)	2208	2944	704
No. of reflns collected	19352	21853	10833
No. of indep reflns	6754 [*R*(int) = 0.1032]	8057 [*R*(int) = 0.0683]	7631 [*R*(int) = 0.0272]
No. of data/restraints/params	6754/5/313	8057/1/430	7631/1/389
*R*1[b]	0.0786	0.0755	0.0766
*wR*2[c]	0.2071	0.2081	0.2167
GoF[d]	1.022	1.152	1.050
Min., max. residual density e Å^{-3}	0.377 and –0.310	0.338 and –0.272	0.394 and –0.564

[a] With disordered solvent contribution. [b] $R1 = \|\sum(|F_o| - |F_c|)/\sum|F_o|\|$. [c] $R2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[W(F_o^2)^2]\}^{1/2}$, $w = 0.10$. [d] $\mathrm{GoF} = [\sum w(F_o^2 - F_c^2)^2/(N_{\mathrm{reflns}} - N_{\mathrm{papams}})]^{1/2}$.

disorder of these solvent molecules, their bond distances and bond angles are not reliable. Crystallograhic data of complexes **3–5** are summarized in Table 2.

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