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PAPER

Synthesis, characterization and catalytic activity of magnesium and zinc aminophenoxide complexes: Catalysts for ring-opening polymerization of L-lactide†

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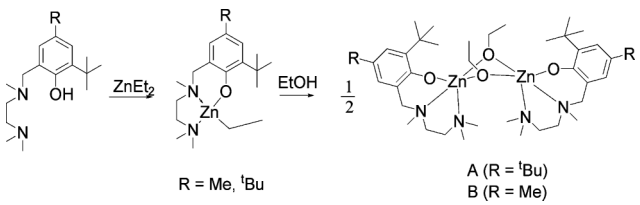
A series of novel magnesium and zinc aminophenoxide complexes were successfully synthesized and one zinc complex was characterized by X-ray crystallography. They were also investigated as initiators for the ring opening polymerization of L-lactide. The complexes are effective in forming polylactides with good conversions. The nature and steric bulk of the ligands coordinated to the central metal ions enormously influenced the polymer properties. Among all the complexes, the zinc aminophenoxide complexes as initiators produced polymers with good molecular weight control and relatively narrow PDIs.

Introduction

Due to their biodegradability, biocompatibility, and permeable properties, aliphatic polyesters, such as poly(ε-caprolactone) (PCL), poly(lactide) (PLA), and their copolymers show potential applications in a variety of fields.[1] Accordingly, the preparation of PCL and PLA has drawn intensive scrutiny recently. The major polymerization method used to synthesize these polymers has been the ring-opening polymerization (ROP) of lactide (LA) and ε-caprolactone (CL) and functionally related compounds. Currently metal alkoxides (*e.g.*, Al,[2] Li,[3] Mg,[4] Fe,[5] Sn,[6] or Zn[7]) are used to initiate the ring-opening polymerization of LA and related cyclic esters.[8] The undesired backbiting/transesterification reactions can be minimized by using a bulky ligand coordinately attached with an active metal center which provides a steric barrier. Recently, many coordinately bulky metal complexes have been synthesized in order to increase the active site of the mononuclear form.[2,6,7]

Schiff base supported metal complexes have been used as catalysts in many applications, due to their diverse forms and ease of preparation.[9] However, their application in ROP was not explored thoroughly. The first Schiff base zinc complex used as an initiator for polymerization of L-lactide was developed by Chisholm *et al.*[7c] The authors changed the Schiff base ligands from bidentate to tridentate and found that the zinc complexes had different variation in their characters and activities towards ROP of LA.[7e] Thus the authors confirmed that changing the coordination numbers of the ligands affects the catalyst character and its activity towards cycloester ROP.

Formerly Tolman *et al.* reported a single-site zinc complex supported by *N*,*N*,*O*-tridentate aminophenol ligands[7d] (Scheme 1) and they exhibit good control in the polymerization of LA to yield high molecular weight PLA at rates faster than other Zn systems reported to till date. Interestingly, the variations occurred by changing ligands from tridentate to bidentate or multidentate type. Herewith we describe the preparation of a series of aminophenol ligands (Scheme 2) with different coordination numbers and sizes of amino group. The catalytic activities of zinc and magnesium alkoxides with different substituents on the amino group of aminophenol ligands were discussed in detail.



Scheme 1

Results and discussion

Synthesis and characterization of Zn and Mg Complexes

All ligands $\mathbf{L^1}$–H–$\mathbf{L^5}$–H were prepared by refluxing a mixture of dialkylamine, *para*-formaldehyde, and 2,4-di-*tert*-butylphenol. Followed by the reaction of $\mathbf{L^1}$–H–$\mathbf{L^5}$–H, a stoichiometric amount of di-n-butylmagnesium in THF was added for 3 h at 0 °C, and then 1 equiv of 2-(dimethylamino)ethanol was added to

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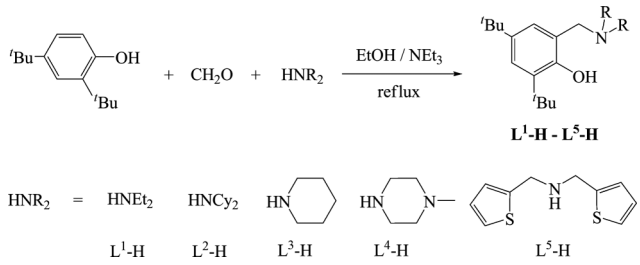
† Electronic supplementary information (ESI) available: Table giving further details of the crystal structure determination, atomic coordinates and isotropic thermal parameters, bond lengths and angles, and anisotropic displacement parameters for **2b**. CCDC reference number 816057. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt11080b



Scheme 2 Preparation of a series of aminophenol ligands.

form magnesium alkoxide compounds (**1a–5a**) in moderate yield (Scheme 3). Similarly, reaction of L **L¹–H–L⁵–H** with $ZnEt_2$ in THF for 3 h at 0 °C and then with benzyl alcohol (BnOH) afforded the benzylalkoxide complexes (**1b–5b**). To compare with zinc benzylalkoxide complexes, the magnesium benzylalkoxide complex (**2c**) with **L²–H** was synthesized. During the reaction of aminophenol with Mg^nBu_2 or $ZnEt_2$, an intermediate was observed as monomeric [LMg^nBu] or [LZnEt]. We also obtained the alkyl magnesium (**2a′**) and zinc (**2b′**) by ligand **L²–H**. The formula and structure are conformed on the basis of ^1H and ^{13}C NMR spectra and X-ray crystal analysis. The single crystal of complex **2b** in Fig. 1 and the supporting information (Table S1, ESI†) shows that the zinc complex is the dimer lying about an inversion centre in the crystal structure with the four-coordinate Zn(II) ion adopting a distorted tetrahedral geometry. The angles between O(1)–Zn–O(2) (123.74(6)°) and O(2)–Zn–O(2A) (82.42(5)°) and the distances between the Zn atom and O(1), O(2), O(2A) and N were 1.9028(13), 1.9766(13), 1.9827(13) and 2.1015(15) Å, confirming the distortion of the structure from an ideal tetrahedral topology.

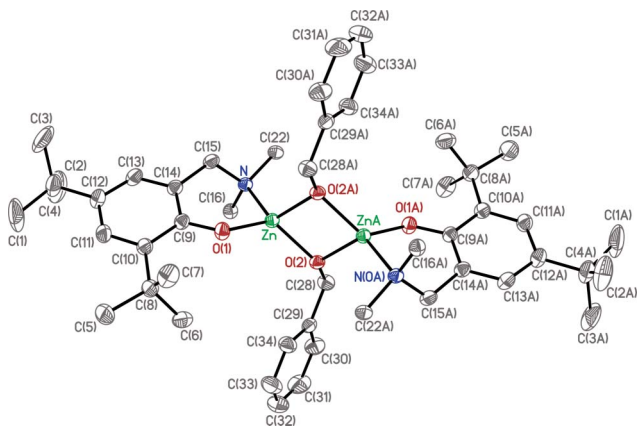
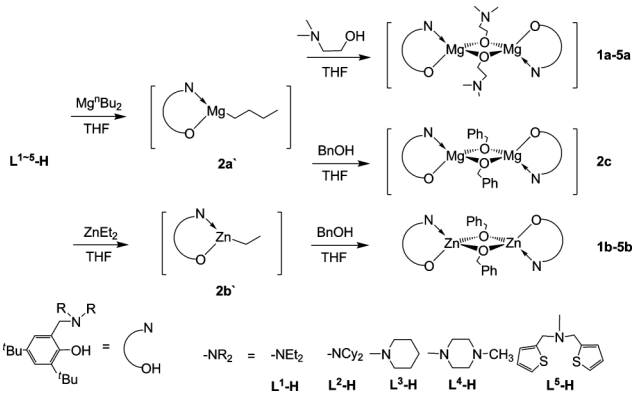


Fig. 1 Molecular structure of [$L^2Zn(\mu\text{-Obn})]_2$ (**2b**) as 20% ellipsoids (hydrogen atoms and four cyclohexyl groups are omitted for clarity). Selected bond lengths (Å) and angles (°): Zn–O(1) 1.9028(13), Zn–O(2) 1.9766(13), Zn–O(2ᵃ)1 1.9827(13), Zn–N 2.1015(15), O(1)–Zn–O(2) 123.74(6), O(1)–Zn–O(2ᵃ)1 108.43(6), O(2)–Zn–O(2ᵃ)1 82.42(5), O(1)–Zn–N 100.07(6), O(2)–Zn–N 124.13(6), O(2ᵃ)1–Zn–N 117.25(6). The symmetry operation implied by the additional "A" letters in the atom labels is (–x, –y, –z).

Melting point depression study of 2b

Although the crystal structure study of **2b** indicates that complex **2b** is a dinuclear species, there are two possible isomers for **2b**



Scheme 3 Synthesis of magnesium and zinc complexes **1b–9b**.

(Chart 1) existing in solution based on the ^1H NMR studies of **2b**. To prove which two isomers are possible, freezing point depression studies of **2b** using naphthalene as the solvent was performed. The dissociation percentage of the dimeric species can be calculated from eqn (1) which ΔT_f is the melting point depressed,

$$\Delta T_f = i \times K_f \times C_m \quad (1)$$

i is the number of particles measured number of particles added, K_f is 6.9 °C mol^{-1} kg for naphthalene, and C_m is the molality of the solute (mol kg^{-1}).

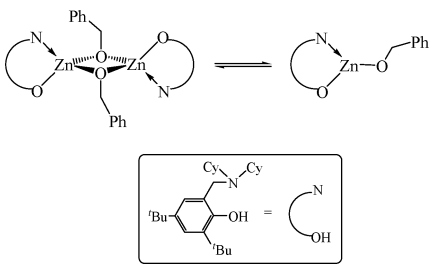


Chart 1 Two possible isomers for **2b**.

Experimental results reveal the activity $i = 1.66 \pm 0.07$, indicating the existence of *ca.* 34% of dinuclear species and 66% of mononuclear species.

Ring-opening polymerization of L-lactide

Polymerization of L-lactide using **1a** (5 mM) as an initiator was systematically investigated in toluene under a dry nitrogen atmosphere (Table 1, entry 1–4). From Table 1, it was found that complex **1a** is an efficient initiator for the polymerization of L-lactide. The polymerization was accomplished within 4 min at room temperature and the scope of these poly(L-lactide)'s (PLLA) polydispersity index (PDI, Mw/Mn) (1.01–1.37) is acceptable. The molecular weight of PLLA was not easy to control due to its high activity. In Fig. 2, the ^1H NMR spectrum of PLLA prepared using a $[LA]_0$/[initiator] ratio of 25 showed one ethyl group and one hydroxy chain end with an integral ratio of 2 : 1 among H_c and H_d, suggesting that the initiation occurred through the insertion of the 2-(dimethylamino)ethanolate group from **1a** into L-lactide. There are no significant influences on the activity of magnesium complexes **2a**–**5a** towards ROP of L-lactide by modifying the steric and coordination number of

Table 1 Polymerization of L-lactide using complexes **1a–5a**, **1b–5b**, and **2c** as initiators at room temperature in toluene (15 mL)

Entry	[M]/ [Init.]	T (min)	Conv (%)[a]	Mn (calcd)[b]	Mn (GPC)[c]	Mn (nmr)[a]	PDI
1	25 (**1a**)	4	94	3400	9400 (5500)	4500	1.37
2	50 (**1a**)	4	88	6400	26 100 (15 100)	12 300	1.22
3	75 (**1a**)	4	98	10 700	33 400 (19 400)	21 600	1.21
4	100 (**1a**)	4	98	14 200	22 700 (13 200)	18 400	1.01
5	100 (**2a**)	3	98	14 200	27 400 (15 900)	—[d]	1.27
6	100 (**3a**)	6	98	14 200	27 300 (15 800)	—[d]	1.31
7	100 (**4a**)	5	93	13 500	34 600 (20 100)	—[d]	1.15
8	150 (**5a**)	3	97	14 200	22 700 (16 100)	—[d]	1.16
9	12.5 (**1b**)	70	95	1600	2900 (1700)	1800	1.07
10	25 (**1b**)	70	87	3000	5400 (3100)	3300	1.09
11	37.5 (**1b**)	70	83	5300	9300 (5400)	5600	1.06
12	50 (**1b**)	70	92	6400	12 900 (7500)	7500	1.05
13	100 (**1b**)	70	92	13 400	25 800 (15 000)	—[d]	1.05
14	100 (**2b**)	9	97	14 100	76 800 (44 500)	—[d]	1.07
15	100 (**3b**)	60	90	13 100	32 500 (18 900)	—[d]	1.02
16	100 (**4b**)	73	95	13 800	28 600 (16 600)	—[d]	1.03
17	100 (**5b**)	24	94	13 600	31 700 (18 400)	—[d]	1.17
18	100 (**2c**)	60	80	13 100	29 800 (17 300)	—[d]	1.17

[a] Obtained from ^{1}H NMR analysis. [b] Calculated from the molecular weight of LA × $[M]_0/[RO^-]_0$ × conversion yield + Mw(ROH). [c] Obtained from GPC analysis and calibrated by a polystyrene standard. Values in parentheses are the values obtained from GPC × 0.58.[10] [d] Not available.

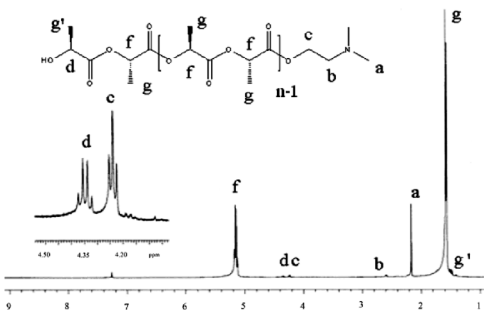


Fig. 2 ^{1}H NMR spectrum of PLLA-25 (25 indicates $[LA]_0/[initiator]_0$ = 25) by **1a**.

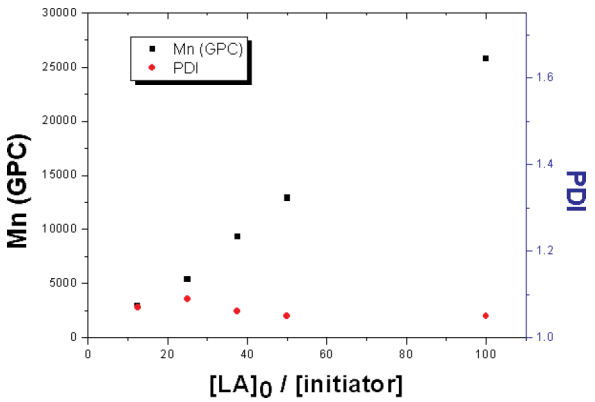


Fig. 3 Polymerization of LA catalyzed by **1b** in toluene at room temperature. The relationship between Mn (■), PDI (●) of polymer and the initial mole ratio $[LA]_0/[initiator]$ is shown.

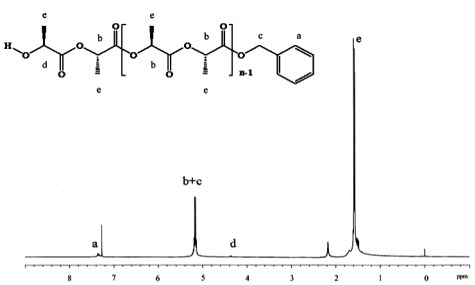


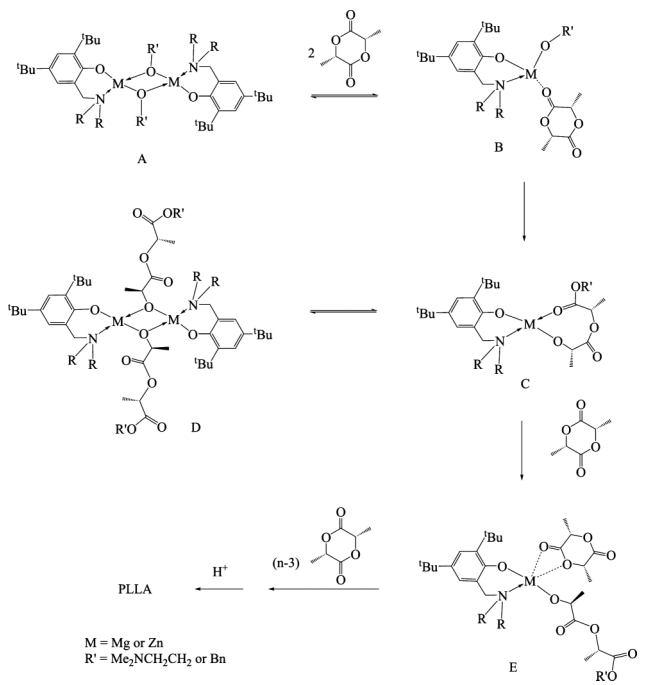
Fig. 4 ^{1}H NMR spectrum of PLLA-25 (25 indicates $[LA]_0/[BnO^-]_0 = 25$) by **1b**.

the ligands (Table 1, entry 5–8). Experimental results show that all these complexes efficiently initiate the polymerization of L-lactide during 3–6 min. Ring-opening polymerization of L-lactide employing zinc complex **1b** as an initiator in toluene completed within 70 min at room temperature. On the basis of the molecular weight of PLLA and the $[LA]_0/[$**1b**$]$ ratio (Table 1, entry 9–13), we conclude that the benzylalkoxides could be used as a good initiators. The linear increase in Mn with conversion and the low PDI of the polymers revealed that the level of polymerization control was high (Fig. 3). The ^{1}H NMR spectrum of PLLA (Fig. 4) indicated that the polymer chain should be capped with one benzyl ester and one hydroxy end; this result suggested that the polymerization occurred through the insertion of a BnO^- group into the L-lactide. When the amino group of the catalysts was substituted to **2b–5b**, the activities were changed (Table 1, entry 14–17). Experimental results showed that all Zn complexes efficiently initiate the polymerization of L-lactide, and PLLA was obtained with the expected molecular weight and with low polydispersity except when using **2b**. The complex **2b** can also polymerize L-lactides with narrow molecular weight distribution and high activity (only 9 min). From Table 1 (entry 13–17), the reactivity order of the catalysts is **2b** > **5b** > **3b** ≥ **1b** ≥ **4b**. The driving force from dimer to monomer is the key factor, presumably the monomer with three coordination numbers were more effective than the dimer with four coordination numbers. It makes the complex **2b** dissociate to be the monomer easily and its own high activity is due to the bulky dicyclohexyl group. The complex **5b** also has a similar cause, as the labile 'sulfur' atom of the ligand can stabilize the intermediate between the monomer and the dimer. When the magnesium benzylalkoxide complex **2c** was used as

the initiator, the L-LA polymerization approached to 80% within 60 min at room temperature (entry 18), which is less effective than **2a** and **2b**. The reason for the activity of **2a** > **2c** was that the amino group of 2-(dimethylamino)ethanolate can stabilize the Mg center during the polymerization with L-LA dissociation and association. The activity of complex **2b** was more than that of **2c**, probably due to Mg–OBn being a stronger bond than Zn–OBn, thus **2c** needs more energy to break the Mg–OBn bond to initiate ROP of L-LA.

Mechanistic studies of polymerization of L-lactide

Although **2b** is a dimeric four-coordinated compound in the solid state, it exists in equilibrium between a dimer and a monomer in solution according to the ^{1}H NMR spectrum. Therefore, the reaction mechanism was proposed as shown in Scheme 4. L-Lactide coordinates to the monomeric three coordinated metal alkoxide a, yielding a penta-coordinated intermediate b, followed by the insertion of an alkoxide group into L-lactide to produce a new initiator c. There exists the equilibrium between the monomer c and dimer d, except that the bulky steric or multi-dentate amino group attached tends to monomer c. When more L-lactides coordinate to the monomer c, this step is the chain propagation step for the production of PLLA and finally PLLA was obtained.



Scheme 4 Proposed mechanism for the ROP of L-lactide by Mg or Zn complexes.

Conclusions

A series of aminophenol ligands (**L^1–H–L^5–H**) and their magnesium and zinc alkoxide complexes were synthesized. Through modifying the amino group with different coordination numbers and size, the activity of the system was adapted for the polymerization of L-LA. For magnesium complexes, there are slight diversities with the different amino groups although the activity dramatically increases by changing the initiator from benzyl oxide to 2-(dimethylamino)ethanolate. However for zinc complexes, the activity increases by changing the amino groups toward huge alkyl or multi-dentate labile group.

Experimental section

General

Standard Schlenk techniques and a N_2-filled glove-box were used throughout the isolation and handling of all the compounds. Solvents, L-lactide, and deuterated solvents were purified prior to use. Naphthalene, diethylamine, 2,4-di-*tert*-butylphenol, dicyclohexylamine, piperidine, 1-methylpiperazine, bis(thiophen-2-ylmethyl)amine, and *para*-formaldehyde were purchased and used without further purification. 2,2′-Methylenebis(4-chloro-6-isopropyl-3-methylphenol) (**L^3–H$_2$**) was prepared by acid-catalyzed condensation following literature procedures.[2d] ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury-400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) spectrometer with chemical shifts given in ppm from the internal TMS or center line of $CDCl_3$. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument.

Synthesis and characterization of ligands (L^1–H–L^5–H)

Synthesis of 2,4-di-*tert*-butyl-6-((diethylamino)methyl)phenol (L^1–H)[11]. Diethylamine (7.31 g, 100.0 mmol), *para*-formaldehyde (3.00 g, 100.0 mmol), and 2,4-di-*tert*-butylphenol (10.31 g, 50 mmol) were dissolved in ethanol (20 mL). The solution was refluxed for 24 h under nitrogen and then cooled to room temperature. Volatile materials were removed under vacuum to yield a light yellow oil. The oil was dissolved in CH_2Cl_2 (100 mL) and the solution was washed with water (2 × 100 ml) and the solvent removed at reduced pressure to give the white powders (10.67 g, 73.2%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.20, 6.82 (s, Ph-*H*, 2H); 3.74 (s, PhCH_2N, 1H); 2.61 (q, N(CH_2CH$_3$)$_2$, J = 7.2 Hz, 4H); 1.42, 1.28 (s, C(CH_3)$_3$, 18H); 1.09 (t, N(CH$_2$CH_3)$_2$, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 154.69, 140.18, 135.42, 123.20, 122.54, 121.44 (*Ph*); 57.86 (Ph*C*H$_2$N); 46.16 (N*C*H$_2$CH$_3$); 34.83, 34.11 (*C*CH$_3$); 31.71, 29.59 (C*C*H$_3$); 11.22 (NCH$_2$*C*H$_3$).

Synthesis of 2,4-di-*tert*-butyl-6-((dicyclohexylamino)methyl)-phenol (L^2–H)[12]. Using a method similar to that for **L^1–H**. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.16, 6.80 (s, Ph-*H*, 2H); 3.91 (s, PhCH_2N, 2H); 2.66 (quintet, CH$_2$N(CH)$_2$, 2H); 1.85–1.58, 1.26–0.99 (m, Cy-*H*, 22H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 155.07, 139.94, 135.19, 123.07, 122.26, 122.04 (*Ph*); 57.74 (Ph*C*H$_2$N); 50.41 (N*C*H$_2$CH$_3$); 34.78, 34.11 (*C*CH$_3$); 30.69, 29.54 (C*C*H$_3$); 31.74, 26.22, 26.04 (*Cy*).

Synthesis of 2,4-di-*tert*-butyl-6-(piperidin-1-ylmethyl)phenol (L^3–H)[11]. Using a method similar to that for **L^1–H**. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.20, 6.81 (s, Ph-*H*, 2H); 3.63 (s, PhCH_2N, 2H); 2.58, 1.62 (m, N(C$_5$H$_{10}$), 10H); 1.42, 1.28 (s, C(CH_3)$_3$, 18H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 154.46, 140.20, 135.34, 123.25, 122.60, 121.00 (*Ph*); 62.87 (Ph*C*H$_2$N); 53.67, 25.78, 24.08 (N(*C*$_5$H$_{10}$)*r*); 34.81, 34.07 (*C*(CH$_3$)$_3$); 31.67, 29.56 (C(*C*H$_3$)$_3$).

Synthesis of 2,4-di-*tert*-butyl-6-((4-methylpiperazin-1-yl)-methyl)phenol (L^4–H)[13]. Using a method similar to that for **L^1–H**. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.22, 6.84 (s, Ph-*H*, 2H); 3.69 (s, PhCH_2N, 2H); 2.54–2.34 (br, N(C_4H_8), 8H); 2.32 (s, NCH_3, 3H); 1.41, 1.28 (s, CCH_3, 18H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 154.13, 140.29, 135.51, 123.45, 122.95, 120.50 (*Ph*); 62.10 (Ph*C*H_2N); 54.90, 52.25 (N(C_4H_8)N); 45.82 (N*C*H_3); 34.84, 34.12 (*C*CH_3); 31.67, 29.59 (C*C*H_3).

Synthesis of 2-((bis(thiophen-2-ylmethyl)amino)methyl)-4,6-di-*tert*-butylphenol (L^5–H). Using a method similar to that for **L^1–H**. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.22, 6.87 (s, Ph-*H*, 2H); 7.30 (d, Ar-*H*, 2H); 7.01–6.80 (m, Ar-*H*, 4H); 3.88 (s, NCH_2, 2H); 3.82 (s, PhCH_2N, 2H); 1.45, 1.28 (s, CCH_3, 18H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 154.07, 140.77, 138.70, 135.84, 123.13, 120.71 (*Ph*); 127.80, 126.76, 125.75 (*Ar*); 57.49 (Ph*C*H_2N); 49.95 (N*C*H_2); 34.94, 34.15 (*C*CH_3); 31.68, 29.65 (C*C*H_3). Anal. Calc. for ($C_{25}H_{33}NOS_2$): C, 70.21%; H, 7.78%; N, 3.28%; S, 15.00%. Found: C, 70.21%; H, 7.49%; N, 3.19%; S, 14.80%

Synthesis of magnesium complexes

Synthesis of $L^1MgOC_2H_4NMe_2$ (1a). Mg^{n}Bu$_2$ (5.5 mL, 1.0 M in hexane, 5.50 mmol) was added slowly to an ice cold (0 °C) solution of **L^1–H** (1.45 g, 5.00 mmol) in THF (15 mL). The mixture was stirred for 3 h and then 2-(dimethylamino)ethanol (0.6 mL, 10.0 M, 6.0 mmol) was added and stirred for 3 h at room temperature. Volatile materials were removed under vacuum to yield yellow oil. The oil was washed with hexane (20 mL) and a white powder was obtained after filtration. Yield: 1.45 g (72%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.17, 6.79 (s, Ph-*H*, 2H); 3.79–3.56 (br, PhCH_2NEt$_2$, OCH_2CH$_2$, 4H); 2.73 (t, OCH$_2$CH_2NMe$_2$, *J* = 14 Hz, 2H); 2.33 (br, N(CH_2CH$_3$)$_2$, N(CH_3)$_2$, 10H); 1.47, 1.28 (s, C(CH_3)$_3$, 18H); 1.09 (t, N(CH$_2$CH_3)$_2$, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 164.7, 135.6, 131.8, 125.6, 123.3, 121.0 (*Ph*); 62.7 (O*C*H$_2$CH$_2$NMe$_2$); 59.4 (OCH$_2$*C*H$_2$NMe$_2$); 57.4 (Ph*C*H$_2$N); 45.0 (N*C*H$_2$CH$_3$); 43.2 (N*C*H$_3$); 35.1, 33.6 (*C*CH$_3$); 32.0, 30.0 (C*C*H$_3$); 29.5 (NCH$_2$*C*H$_3$). Anal. Calc. for ($C_{23}H_{42}MgN_2O_2$): C, 68.56%; H, 10.51%; N, 6.95%. Found: C, 67.94%; H, 9.86%; N, 6.81%. Mp: 177–178 °C.

Synthesis of $L^2MgOC_2H_4NMe_2$ (2a). Using a method similar to that for **1a**. Yield: 1.20 g (47.1%). ^{1}H NMR (400 MHz, C_6D_6, ppm): 7.49, 6.98 (s, Ph*H*, 2H); 3.73 (s, PhCH_2N, 2H); 3.41 (br, OCH_2, 2H); 2.08 (br, CH_2NMe$_2$, 2H); 1.89 (s, N(CH_3)$_2$, 6H); 2.58–2.54, 1.73–1.53, 1.18–0.29 (m, Cy-*H*, 22H); 1.76, 1.38 (s, C(CH_3)$_3$, 18H). ^{13}C NMR (100 MHz, C_6D_6, ppm): 155.88, 140.38, 135.84, 123.34, 122.80, 122.54 (*Ph*); 57.80, 32.04, 26.34, 26.18 (*Cy*); 50.77 (N*C*H$_3$); 35.31 (*C*H$_2$N); 34.35 (O*C*H$_2$CH$_2$N); 31.90 (OCH$_2$*C*H$_2$N); 30.87, 30.00 (C(*C*H$_3$)$_3$); 22.98, 14.26 (*C*(CH$_3$)$_3$). Anal. Calc. for ($C_{31}H_{54}MgN_2O$): C, 72.85%; H, 10.65%; N, 5.48%. Found: C, 57.11%; H, 9.44%; N, 9.52%. Mp: 173–174 °C.

Synthesis of $L^3MgOC_2H_4NMe_2$ (3a). Using a method similar to that for **1a**. Yield: 1.39 g (70%). ^{1}H NMR (400 MHz, C_6D_6, ppm): 7.63, 7.07 (s, Ph*H*, 2H); 3.32 (s, PhCH_2N, 2H); 2.93 (br, OCH_2, 2H); 2.10 (br, CH_2NMe$_2$, 2H); 2.05 (s, N(CH_3)$_2$, 6H); 2.05–1.87, 1.87–1.51, 1.51–1.22 (m, N(C_5H_{10}), 10H); 1.87, 1.22 (s, C(CH_3)$_3$, 18H). ^{13}C NMR (100 MHz, C_6D_6, ppm):165.37, 136.74, 132.94, 125.64, 124.14, 121.33 (*Ph*); 64.99 (O*C*H$_2$CH$_2$N); 63.46 (N*C*H$_3$); 57.36 (OCH$_2$*C*H$_2$N); 54.99 (Ph*C*H$_2$N), 45.77, 35.82, 34.11 (N(C_5H_{10})); 32.62, 32.56 (C(*C*H$_3$)$_3$); 32.48, 30.02 (*C*(CH$_3$)$_3$). Anal. Calc. For ($C_{24}H_{42}MgN_2O_2$): C, 69.47%; H, 10.20%; N, 6.75%. Found: C, 70.51%; H, 9.92%; N, 7.25%. Mp: 170–172 °C.

Synthesis of $L^4MgOC_2H_4NMe_2$ (4a). Using a method similar to that for **1a**. Yield: 1.76 g (82.%). ^{1}H NMR (400 MHz, C_6D_6, ppm): 7.63, 7.06 (s, Ph*H*, 2H); 3.53 (s, PhCH_2N, 2H); 3.02 (br, OCH_2, 2H); 2.22 (br, CH_2NMe$_2$, 2H); 2.38–2.22, 2.11–2.08 (br, Ar*H*, NCH_3, 17H);1.85, 1.49 (s, C(CH_3)$_3$, 18H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 164.54, 135.84, 132.20, 125.70, 123.65, 120.30 (*Ph*); 62.86 (O*C*H$_2$CH$_2$N); 57.47 (OCH$_2$*C*H$_2$N); 52.29, 45.20 (*Ar*); 35.13 (N*C*H$_3$); 33.63 (ArN*C*H$_3$); 31.87, 29.92 (C(*C*H$_3$)$_3$); 31.61, 29.52 (*C*(CH$_3$)$_3$). Anal. Calc. For ($C_{24}H_{43}MgN_3O_2$): C, 67.05%; H, 10.08%; N, 9.77%. Found: C, 66.69%; H, 10.18%; N, 9.60%. Mp: 176–182 °C.

Synthesis of $L^5MgOC_2H_4NMe_2$ (5a). Using a method similar to that for **1a**. Yield: 1.16 g (43%). ^{1}H NMR (400 MHz, C_6D_6, ppm): 7.51–6.70 (m, Ar*H*, 8H); 3.73 (s, PhCH_2N, 2H); 1.76, 1.38 (s, C(CH_3)$_3$, 18H). ^{13}C NMR (100 MHz, C_6D_6, ppm): 154.87, 140.99, 136.29, 126.34, 123.35, 121.36 (*Ph*); 139.16, 126.84, 124.47 (*Ar*); 57.59 (Ph*C*H$_2$N); 50.14 (N*C*H$_2$Ar); 46.40 (O*C*H$_2$CH$_2$NMe$_2$); 35.39 (OCH$_2$*C*H$_2$NMe$_2$); 32.76 (N*C*H$_3$); 35.77, 34.35 (*C*CH$_3$); 31.94, 30.02 (C*C*H$_3$). Anal. Calc. For ($C_{29}H_{42}MgN_2O_2S_2$): C, 64.61%; H, 7.85%; N, 5.20%. Found: C, 62.03%; H, 8.25%; N, 6.31%. Mp: 182–184 °C.

Synthesis of L^2Mg^{n}Bu (2a′). Mg^{n}Bu$_2$ (5.5 mL, 1.0 M in hexane, 5.50 mmol) was added slowly to an ice cold (0 °C) solution of **L^2–H** (2.00 g, 5.00 mmol) in THF (15 mL). The mixture was stirred for 3 h, and then 2-(dimethylamino)ethanol (0.6 mL, 10.0 M, 6.0 mmol) was added to be stirred for 3 h at room temperature. Volatile materials were removed under vacuum to yield a yellow oil. The oil was washed with hexane (20 mL) and a white powder was obtained after filtration. Yield: 2.12 g (83.4%). ^{1}H NMR (400 MHz, C_6D_6, ppm): 7.55, 7.05 (s, Ph*H*, 2H); 4.40, 3.75 (dd, PhCH_2, *J* = 12.8 Hz, 2H); 2.73–1.78, 1.78–1.38, 1.38–0.026 (m, Cy-*H*, MgC$_4$H$_9$, 31H); 1.78, 1.38 (s, C(CH_3)$_3$, 18H). ^{13}C NMR (100 MHz, C_6D_6, ppm): 157.77, 140.80, 140.30, 127.37, 126.96, 125.57 (*Ph*); 59.96 (Ph*C*H$_2$N); 35.98, 34.16 (*C*CH$_3$); 31.72, 30.47 (C*C*H$_3$); 64.19, 31.89, 26.82, 27.81 (*Cy*); 30.46, 26.13, 14.35, 12.64 (Mg*C*$_4$H$_9$). Anal. Calc. For ($C_{31}H_{53}MgNO$): C, 77.56%; H, 11.13%; N, 2.92%.. Found: C, 77.45%; H, 11.59%; N, 2.99%. Mp: 212–214 °C.

Synthesis of L^2MgOBn (2c). Mg^{n}Bu$_2$ (5.5 mL, 1.0 M in hexane, 5.50 mmol) was added slowly to an ice cold (0 °C) solution of **L^2–H** (2.00 g, 5.00 mmol) in THF (15 mL). The mixture was stirred for 3 h, and then benzyl alcohol (0.6 mL, 10.0 M, 6.0 mmol) was added to be stirred for 3 h at room temperature. Volatile materials were removed under vacuum to yield a light yellow oil. The oil was washed with hexane (20 mL) and a white powder was obtained after filtration. Yield: 2.26 g (81%). ^{1}H NMR (400 MHz, C_6D_6, ppm):7.62–6.98 (m, Ph*H*, 7H); 5.10 (d, OCH_2Ph, *J* = 77.6 Hz, 2H); 3.55 (s, PhCH_2N, 2H); 2.52–2.10, 1.91–1.53, 1.38–0.73 (m, Cy-*H*, 22H); 1.96, 1.49 (s, 18H, C(CH_3)$_3$). ^{13}C NMR (100 MHz, C_6D_6, ppm): 164.16, 155.88, 144.57, 140.39, 136.93, 134.54, 126.84, 126.53, 123.47, 122.54 (*Ph*); 66.61 (O*C*H$_2$Ph); 57.43 (Ph*C*H$_2$N); 35.81, 34.15 (*C*CH$_3$); 30.87, 30.48 (C*C*H$_3$); 61.80, 32.35, 26.95, 26.34 (*Cy*). Anal. Calc. For ($C_{34}H_{51}MgNO_2$): C, 77.04%; H, 9.70%;

N, 2.64%. Found: C, 76.17%; H, 9.59%; N, 2.96%. Mp: 170–172 °C.

Synthesis of zinc complexes

Synthesis of L[1]ZnOBn (1b). $ZnEt_2$ (5.5 mL, 1.0 M in hexane, 5.50 mmol) was added slowly to an ice cold (0 °C) solution of **L^1–H_2** (2.91 g, 5.00 mmol) in THF (15 mL). The mixture was stirred for 3 h, and then benzyl alcohol (0.6 mL, 10.0 M, 6.0 mmol) was added to be stirred for 3 h at room temperature. Volatile materials were removed under vacuum to yield a light yellow oil. The oil was washed with hexane (20 mL) and a white powder was obtained after filtration. Yield: 1.89 g (81.6%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.37, 7.28, 7.16, 6.72 (s, Ph-*H*, 7H); 4.82 (s, OCH_2Ph, 2H); 3.42 (s, CH_2NEt$_2$, 2H); 2.39 (septet, N(CH_2CH$_3$)$_2$, J = 6.8 Hz, 4H); 1.58, 1.27 (s, C(CH_3)$_3$, 18H); 0.96 (t, N(CH$_2$CH_3)$_2$, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 163.64, 144.09, 137.38, 134.74, 128.28, 127.61, 127.02, 125.54, 124.00, 119.48 (*Ph*); 69.78 (O*C*H$_2$Ph); 59.54 (Ph*C*H$_2$NEt$_2$); 43.94 (N*C*H$_2$CH$_3$); 35.36, 33.81 (Ph*C*CH$_3$); 31.85, 29.61 (PhC*C*H$_3$); 7.87 (NCH$_2$*C*H$_3$). Anal. Calc. For ($C_{26}H_{39}NO_2Zn$): C, 67.45%; H, 8.49%; N, 3.03%. Found: C, 67.21%; H, 8.03%; N, 3.48%. Mp: 180–184 °C.

Synthesis of L[2]ZnOBn (2b). Using a method similar to that for **1b**. Yield: 2.19 g (77%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.43–6.77 (m, Ph*H*, 7H); 5.13, 4.87, 4.94 (s, OCH_2Ph, 2H);3.76(s, PhCH_2, 2H); 2.69–1.62, 1.56–1.27, 1.23–0.75(m, Cy-*H*, 22H); 1.59, 1.25 (s, 18H, C(CH_3)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 164.12, 144.29, 137.17, 134.34, 128.93, 127.91, 126.36, 126.18, 123.21, 121.36 (*Ph*); 68.12 (O*C*H$_2$Ph); 56.79 (Ph*C*H$_2$N); 35.37, 33.79 (*C*CH$_3$); 31.90, 29.92 (C*C*H$_3$); 63.41, 31.45, 30.73, 26.75, 25.74 (*Cy*). Anal. Calc. For ($C_{34}H_{51}NO_2Zn$): C, 71.50%; H, 9.00%; N, 2.45%. Found: C, 70.83%; H, 8.82%; N, 2.96%. Mp: 186–190 °C.

Synthesis of L[3]ZnOBn (3b). Using a method similar to that for **1b**. Yield: 2.00 g (84.4%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.36, 7.30, 7.14, 7.06, 6.68 (s, Ph-*H*, 7H); 4.87(br, OCH_2Ph, 2H); 3.63 (s, PhCH_2N, 2H); 2.68–1.65 (m, N(C$_5H_{10}$), 10H); 1.65, 1.29 (s, C(CH_3)$_3$, 18H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 164.58, 164.09, 137.81, 137.15, 134.84, 128.30, 127.04, 125.89, 124.24, 119.44 (*Ph*); 65.58 (O*C*H$_2$Ph); 55.86 (Ph*C*H$_2$); 56.37, 24.91, 23.58 (N(*C*$_5$H$_{10}$)); 35.36, 33.86 (*C*(CH$_3$)$_3$); 31.91, 29.73 (C(*C*H$_3$)$_3$). Anal. Calc. For ($C_{27}H_{39}NO_2Zn$): C, 68.27%; H, 8.28%; N, 2.95%. Found: C, 67.85%; H, 8.02%; N, 2.90%. Mp: 216–220 °C.

Synthesis of L[4]ZnOBn (4b). Using a method similar to that for **1b**. Yield: 1.57 g (64.1%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.41, 7.32, 7.11, 6.69 (s, Ph*H*, 7H); 4.88 (br, OCH_2Ph, 2H); 3.30 (s, PhCH_2N, 2H); 2.71–2.46, 2.32–2.09 (m, N(C$_5H_{10}$), 10H); 2.40 (s, NCH_3, 3H); 1.64, 1.29 (s, C(CH_3)$_3$, 18H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 163.68, 137.83, 137.17, 135.17, 129.02, 128.47, 128.21, 127.06, 125.96, 125.29, 124.43, 118.88 (*Ph*); 68.92 (O*C*H$_2$Ph); 64.92 (Ph*C*H$_2$); 54.94, 53.84 (N(*C*$_5$H$_{10}$)); 45.82 (N*C*H$_3$); 35.56, 33.86 (*C*CH$_3$); 31.88, 29.88 (C*C*H$_3$). Anal. Calc. For ($C_{27}H_{40}N_2O_2Zn$): C, 66.18%; H, 8.23%; N, 5.72%. Found: C, 66.54%; H, 8.35%; N, 5.46%. Mp: 228–230 °C.

Synthesis of L[5]ZnOBn (5b). Using a method similar to that for **1b**. Yield: 1.32 g (44.1%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.34–6.60 (m, 13H, Ar*H*); 4.43 (d, OCH_2Ph, J = 13.6 Hz, 2H); 3.86–3.66 (m, 6H, NCH_2); 1.61, 1.26 (s, C(CH_3)$_3$, 18H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 163.45, 144.26, 137.63, 134.74, 134.19, 133.96, 131.16, 131.00, 128.33, 127.33, 126.98, 126.66, 124.22, 118.31 (*Ar*); 68.80 (O*C*H$_2$Ph); 59.83 (Ph*C*H$_2$N); 49.10 (N*C*H$_2$); 35.52, 33.89 (*C*CH$_3$); 31.85, 29.82 (C*C*H$_3$). Anal. Calc. For ($C_{32}H_{39}NO_2S_2Zn$): C, 71.50%; H, 9.00%; N, 2.45%. Found: C, 70.83%; H, 8.82%; N, 2.96%. Mp: 176–178 °C.

Synthesis of L[2]ZnEt (2b′). $ZnEt_2$ (5.5 mL, 1.0 M in hexane, 5.50 mmol) was added slowly to an ice cold (0 °C) solution of **L^2–H** (2.00 g, 5.00 mmol) in THF (15 mL). The mixture was stirred for 3 h, and then 2-(dimethylamino)ethanol (0.6 mL, 10.0 M, 6.0 mmol) was added to be stirred for 3 h at room temperature. Volatile materials were removed under vacuum to yield a light yellow oil. The oil was washed with hexane (20 mL) and a white powder was obtained after filtration. Yield: 2.12 g (81%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.22, 6.87 (s, Ph*H*, 2H); 3.90 (s, PhCH_2N, 2H); 2.83–1.54, 1.40–1.31, 1.26–1.01 (m, Cy-*H*, ZnCH$_2$CH_3, 25H); 1.43, 1.28 (s, C(CH_3)$_3$, 18H); 0.36 (q, ZnCH_2CH$_3$, J = 5.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm):161.46, 138.02, 136.55, 125.43, 123.49, 123.03 (*Ph*); 51.93 (Ph*C*H$_2$N); 35.04, 33.89 (*C*CH$_3$); 29.65, 26.68 (C*C*H$_3$); 62.73, 31.79, 26.00, 25.70 (*Cy*); 12.04 (Zn*C*H$_2$CH$_3$); 1.05 (ZnCH$_2$*C*H$_3$). Anal. Calc. For ($C_{29}H_{49}NOZn$): C, 70.64%; H, 10.02%; N, 2.84%. Found: C, 69.59%; H, 9.58%; N, 2.70%. Mp: 202–204 °C.

X-ray crystallographic studies

A suitable crystal of complex **2b** was sealed in a thin-walled glass capillary under a dry nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. Intensity data were collected in 1350 frames with increasing w (width of 0.3° per frame). The absorption correction was based on the symmetry-equivalent reflections using 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 the direct method using the 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.

General procedures for the polymerization of L-lactides

A typical polymerization procedure was exemplified by the synthesis of entry 12 (Table 1) using complex **1b** as an initiator. The polymerization conversion was analyzed by ^{1}H NMR spectroscopic studies. Toluene (10.0 mL) was added to a mixture of complex **1b** (0.0291 g, 0.05 mmol) and L-lactide (0.36 g, 2.5 mmol) at 25 °C. After the solution was stirred for 70 min, the reaction was then quenched by adding to a drop of water, and the polymer was precipitated by pouring into n-hexane (100.0 mL) to give white solids. The white solid was dissolved in CH_2Cl_2 (10.0 mL) and then n-hexane (100.0 mL) was added to give a white crystalline solid. Yield: 0.54 g (75%).

GPC measurements

The GPC measurements were performed on a Waters 1515 Isocratic HPLC Pump system equipped with a difference Waters 2414 Refractive Index detector using THF (HPLC grade) as an eluent. The chromatographic column was a Waters Styragel Column (HR4E) and the calibration curve was made by polystyrene standards to calculate Mn(GPC). The solution (25 mL) was then injected into the GPC and the flow eluent rate was 1 mL min^{-1}. The results were calculated by SISC chromatography data solution 1.0 edition.

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