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Magnesium and Zinc Complexes Supported by *N,O*-Bidentate Pyridyl Functionalized Alkoxy Ligands: Synthesis and Immortal ROP of ε-CL and L-LA

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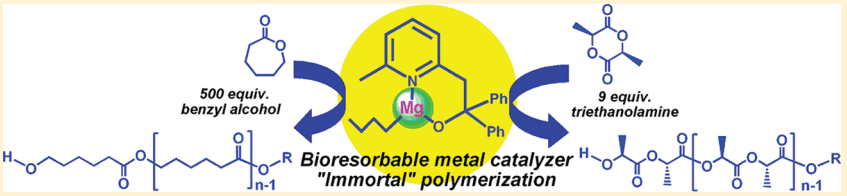
Supporting Information



ABSTRACT: The *N,O*-bidentate pyridyl functionalized alkoxy ligands 2-(6-methyl-2-pyridinyl)-1,1-dimethyl-1-ethanol (**L^1−H**) and 2-(6-methyl-2-pyridinyl)-1,1-diphenyl-1-ethanol (**L^2−H**) have been prepared by treatment of acetone and benzophenone with monolithiated 2,6-lutidine. Deprotonolysis of the ligands **L^1−H** and **L^2−H** with 1 equiv of Mg^{n}Bu$_2$ and ZnEt$_2$ in toluene by releasing butane and ethane, respectively, gave the corresponding dimeric metal-monoalkyl complexes [L^{1}Mg^{n}Bu]$_2$ (**1**), [L^{2}Mg^{n}Bu]$_2$ (**2**), [L^{1}ZnEt]$_2$ (**3**), and [L^{2}ZnEt]$_2$ (**4**). Complexes **1**−**4** were characterized by ^{1}H and ^{13}C NMR spectroscopy analysis, and the molecular structures of **1**, **3**, and **4** were further confirmed by X-ray diffraction analysis. The investigation of the catalytic behavior of these complexes toward ε-caprolactone (ε-CL) and L-lactide (L-LA) polymerizations showed that the Mg-based complexes gave higher activity than those attached to zinc metal, probably owing to the greater ionic character of the magnesium metal. Remarkably, the magnesium complex **2** exhibited a striking "immortal" nature in the presence of primary alcohols where up to 500 PCL chains grew from each Mg active center when benzyl alcohol was employed, while, in particular, in the presence of triethanolamine, complex **2** also displayed an immortal mode for the polymerization of L-LA.

INTRODUCTION

For the past decades, in view of their excellent biodegradable, biocompatible, and permeable properties both in the environment and in vivo, polyesters, in particular polycaprolactone (PCL), polylactide (PLA), and their copolymers, have found wide applications as packaging materials and devices in more sophisticated pharmaceutical and medical industries for controlled drug release and antibody and gene delivery and scaffolds in tissue engineering,[1] as well as the promising alternatives of synthetic petrochemical-based plastics.[2] Although polyesters can be produced by condensation polymerization or ring-opening polymerization (ROP) by anionic, cationic, and organic compounds, the ROP via a coordination−insertion mechanism initiated by metal-based complexes has been commonly accepted as a more efficient manner by providing polyesters with well-controlled molecular weight, composition, and regularity.[2d,3] To date, a huge number of metal-based complexes, including potassium,[4] lithium,[5] magnesium,[6] zinc,[6a,b,f,g,i,7] iron,[8] calcium,[9] aluminum,[10] stannous,[11] yttrium,[12] and lanthanide,[13] have been innovated, and their catalytic performances have been widely investigated. However, the amounts of catalysts in the obtained polymers are usually high, which may raise concerns regarding the potential health issues associated with the toxicity of some metal-based residues.[14] Moreover, the resulting single or linear PCL and PLA materials suffer the problems of brittleness and high process viscosity, which could be overcome by introducing flexible monomer units into these polymer backbones to prepare PCL-based and PLA-based block copolymers, or by forming such polymers with star-shaped or dendrimer, or hyperbranch topological architectures.[15−17] However, most of these metal-based coordination catalysts lack livingness, and the resultant polymer chain ends have no functionality; thus, the above target is difficult to reach.

Our interest has been concentrated on the biobenign calcium, magnesium, and zinc catalysts[18] because they participate in the human metabolism.[19] Herein, we wish to report the synthesis, characterization, and catalysis of novel magnesium and zinc derivatives coordinated by monovalent *N,O*-bidentate pyridyl alkoxy ligands. In the presence of excess benzyl alcohol, some complexes exhibit an interesting performance in immortal polymerization. Thus, each metal propagating species generates more than 1 and up to 500 PCL molecules

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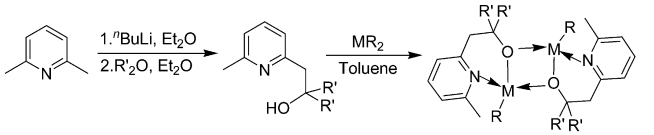
with an adjustable molecular weight and narrow polydispersity, and simultaneously, the PCL chain ends are capped with a hydroxyl functionality. The hydroxyl ends facilitate incorporation of flexible monomer units, in particular, of bioactive substituents, such as drugs or fluorescent tags, to construct novel PCL-based block copolymers or functionalized PCL, in one pot.[20,21]

RESULTS AND DISCUSSION

Synthesis and Structure Characterization. Treatment of 2,6-lutidine lithium salt with acetone and benzophenone afforded the corresponding ligands 2-(6-methyl-2-pyridinyl)-1,1-dimethyl-1-ethanol ($\mathbf{L^1}$–**H**) and 2-(6-methyl-2-pyridinyl)-1,1-diphenyl-1-ethanol ($\mathbf{L^2}$–**H**) as a yellow oil or white powder in 78% and 85% yields, respectively. Deprotonolysis of $\mathbf{L^1}$–**H** and $\mathbf{L^2}$–**H** by equimolar amounts of Mg^nBu_2 and $ZnEt_2$ in toluene with the releasing of butane and ethane, respectively, gave dimeric metal-monoalkyl complexes $[L^1Mg^nBu]_2$ (**1**), $[L^2Mg^nBu]_2$ (**2**), $[L^1ZnEt]_2$ (**3**), and $[L^2ZnEt]_2$ (**4**) in quantitative yields (Scheme 1). ^{1}H NMR spectrum analysis

Scheme 1. Preparation of Complexes 1–4



shows that the resonances of the methylene protons CH_2 from zinc complexes **3** and **4** give singlet peaks at 2.90 and 3.80 ppm, respectively, which shift downfield slightly compared with those in the corresponding neutral ligands (2.73 ppm for $\mathbf{L^1}$–**H**; 3.65 ppm for $\mathbf{L^2}$–**H**). The ^{1}H NMR spectra of the magnesium complexes **1** and **2** give different topologies from their zinc analogues, in which the methylene groups CH_2 show broad doublet resonances at 3.16 and 2.61 ppm for complex **1** and doublet–doublet resonances at 4.14 ppm ($^2J_{H-H}$ = 16 Hz) and 3.49 ppm ($^2J_{H-H}$ = 12 Hz) for complex **2**.

The structures of complexes **1**, **3**, and **4** were defined further by the X-ray diffraction technique, as shown in Figures 1–3. All of these complexes adopt dimeric structures, where two anionic lutidine functionalized alkoxy ligands bridge two metal alkyl moieties via oxygen atoms, generating a Mg_2O_2 or Zn_2O_2 planar core in the center of each molecule. All complexes are C_2 symmetric. The metal oxygen bond distances are odd, but comparable to the reported values:[22] Mg(1)–O(1A) 1.988(1) Å versus Mg(1)–O(1) 1.971(1) Å (**1**); Zn(1)–O(1) 2.030(1) Å versus Zn(1)–O(1A) 1.998(1) Å (**3**); Zn(1)–O(1) 2.025(5) Å versus Zn(1)–O(2) 2.009(6) Å (**4**). Meanwhile, all the metal carbon bonds (Mg(1)–C(8) 2.132(2) Å, Zn(1)–C(11) 1.984(2) Å, Zn(1)–C(21) 2.049(10) Å, Zn(2)–C(43) 1.988(10) Å) and the metal nitrogen bonds (Mg(1)–N(1) 2.186(2) Å, Zn(1)–N(1) 2.165(1) Å, Zn(1)–N(1) 2.137(7) Å, Zn(2)–N(2) 2.171(6) Å) fall in the reasonable ranges for those reported in the literature.[22]

Ring-Opening Polymerization of ε-Caprolactone. The ROP of ε-CL initiated by complex **1**, **2**, **3**, or **4** was carried out in THF at room temperature. All of these complexes **1**–**4** were active in the absence of alcohol, albeit in a less-controlled

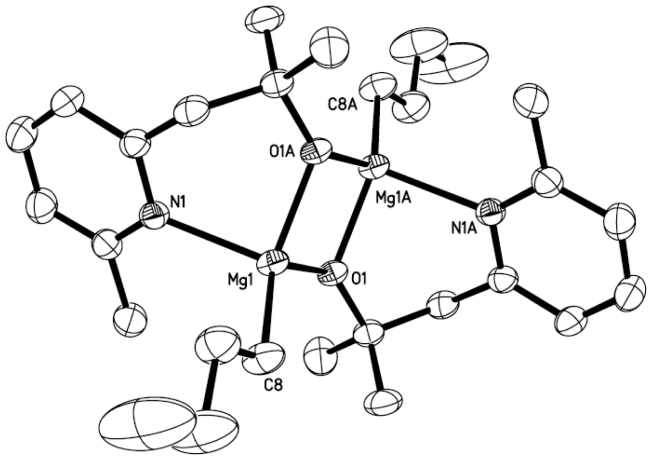


Figure 1. ORTEP diagram of the molecular structure of complex **1**. Thermal ellipsoids are drawn at the 35% probability level. All of the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mg(1)–O(1) 1.9712(14), Mg(1)–O(1A) 1.9880(14), Mg(1)–C(8) 2.132(2), Mg(1)–N(1) 2.1860(17); O(1)–Mg(1)–O(1A) 85.09(5), O(1)–Mg(1)–C(8) 124.14(8), O(1A)–Mg(1)–C(8) 132.14(8), C(8)–Mg(1)–N(1) 109.19(8), O(1)–Mg(1)–N(1) 110.89(6), O(1A)–Mg(1)–N(1) 89.68(6).

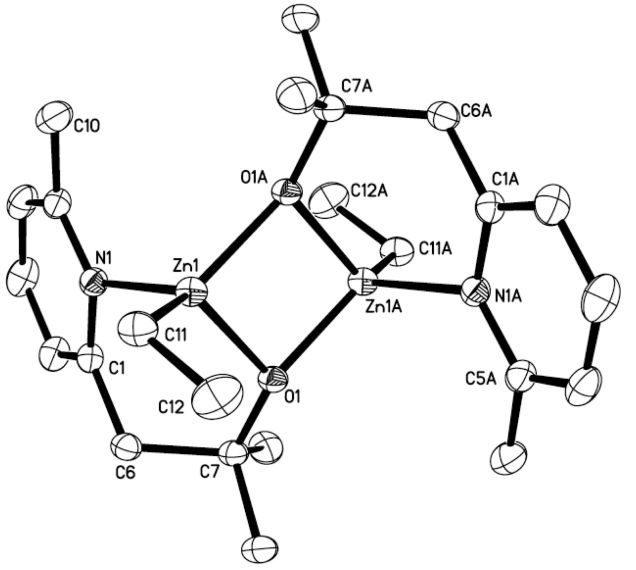


Figure 2. ORTEP diagram of the molecular structure of complex **3**. Thermal ellipsoids are drawn at the 35% probability level. All of the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zn(1)–O(1) 2.0300(12), Zn(1)–O(1A) 1.9976(12), Zn(1)–C(11) 1.9837(19), Zn(1)–N(1) 2.1648(15), O(1)–Zn(1)–O(1A) 83.78(5), O(1)–Zn(1)–C(11) 123.42(7), O(1A)–Zn(1)–C(11) 130.05(7), C(11)–Zn(1)–N(1) 119.03(7), O(1A)–Zn(1)–N(1) 100.06(5), O(1)–Zn(1)–N(1) 89.44(5).

mode, among which the magnesium complexes **1** and **2** displayed a similar high activity, independent of the ligand type, to transfer 100 equiv of ε-CL into PCL in less than 1 min, whereas their zinc counterparts **3** and **4** needed 4 h to reach 17% and 92% conversions, respectively (Table 1, entries 1–4). This could be attributed to the higher ionic character of the central Mg^{2+} ion than that of the Zn^{2+} ion,[6i,23] which facilitates coordination of ε-CL. Therefore, in the case of Mg-based precursors, the ligand type showed a minor effect on the catalytic activity, whereas in contrast, for zinc complexes,

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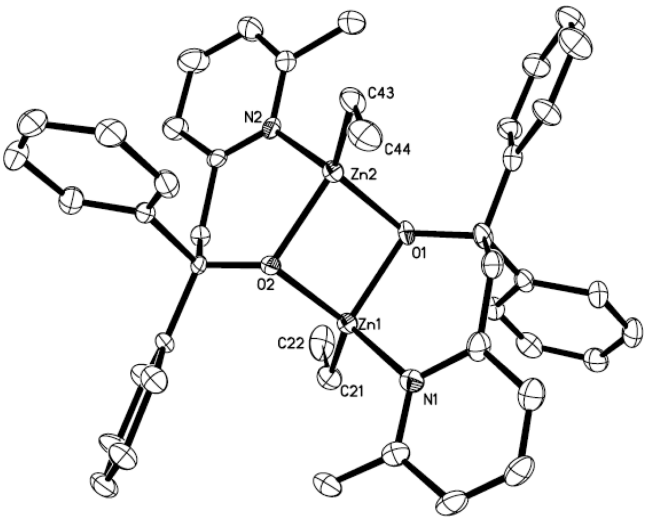
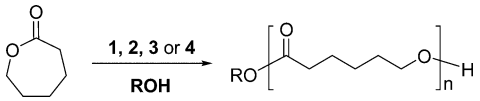


Figure 3. ORTEP diagram of the molecular structure of complex **4**. Thermal ellipsoids are drawn at the 35% probability level. All of the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zn(1)−O(2) 2.035(5), Zn(1)−C(21) 2.049(10), Zn(2)−C(43) 1.988(10), Zn(1)−O(1) 2.011(6), Zn(1)−N(1) 2.137(7), Zn(2)−N(2) 2.171(6), O(1)−Zn(1)−O(2) 85.8(2), O(2)−Zn(1)−C(21) 126.3(3), O(2)−Zn(1)−N(1) 95.5(2), C(21)−Zn(1)−N(1) 115.5(3).

ligands displayed more obvious influences on the activity electronically and sterically:[6a,e,24] complex **4** bearing the sterically bulky and electron-withdrawing $\mathbf{L}^2$ ligand (phenyl substituent) gave a much higher activity than complex **3** attached to the sterically less-hindered and electron-donating $\mathbf{L}^1$ ligand (methyl substituent). As metal alkoxide initiators that efficiently mimic the propagating groups of the presumed active species usually exhibit much more promising performances than their alkyl analogues, alcohols are always chosen to combine with *equivalent* metal alkyl precursors to generate in situ the metal alkoxide initiators via alcoholysis.[13b,d,25,26] Thus, we investigated the catalytic behaviors of the binary systems formed by complexes **1**−**4** in combination with isopropanol (^{i}PrOH), benzyl alcohol (BnOH), and triethanolamine (TEA), respectively. When BnOH was used to activate complexes **1** and **2**, the generated magnesium alkoxide initiators (Mg−OBn) behaved similarly to their metal alkyl precursors (Mg−^{n}Bu), but in a more controlled manner. The resultant PCL had molecular weights close to the theoretic values with a very narrow polydispersity. In contrast, activations of the zinc complexes **3** and **4** with BnOH did not perform smoothly to give complicated products that did not bring about obvious improvements in the catalytic performances than their congeners (Table 1, entries 5−8).[27] Fixing complex **2** as the precursor, switching the alcohol to ^{i}PrOH and a polyol $N(CH_2CH_2OH)_3$, respectively, the generated binary systems, unfortunately, were low active and even inert in the latter case (Table 1, entries 9 and 11). Thus, complex **2** and BnOH

Table 1. Ring-Opening Polymerization of ε-CL Initiated by Complexes 1−4



entry[a]	cat.	$[CL]_0/[I]_0$	ROH	$[OH]_0/[I]_0$	time (min)	conv. (%)[b]	$M_{n,calcd} \times 10^{-4}$[c]	$M_{n,SEC} \times 10^{-4}$[d]	M_w/M_n[d]
1	**1**	100		0	1	100	1.13	4.47	2.00
2	**2**	100		0	1	100	1.13	3.11	2.00
3	**3**	100		0	240	17	0.20	0.27	1.59
4	**4**	100		0	240	92	1.15	2.33	2.05
5	**1**	100	BnOH	1	1	100	1.14	1.09	1.21
6	**2**	100	BnOH	1	1	100	1.14	1.23	1.14
7	**3**	100	BnOH	1	240	21	0.25	0.23	1.94
8	**4**	100	BnOH	1	240	99	1.14	1.40	1.15
9	**2**	600	^{i}PrOH	1	5	67	4.59	3.07	1.07
10	**2**	600	BnOH	1	2	100	6.79	7.22	1.30
11	**2**	600	TEA	1	5	7	1.45	nd.	nd.
12	**2**	500	BnOH	1	2	100	5.66	6.55	1.20
13	**2**[e]	1000	BnOH	1	1	100	11.4	16.4	1.26
14	**2**[e]	1500	BnOH	1	5	100	17.0	20.8	1.63
15	**2**[e]	2000	BnOH	1	30	100	22.6	46.4	1.77
16	**2**	500	BnOH	2	30	100	2.84	3.15	1.14
17	**2**	500	BnOH	3	60	100	1.89	1.74	1.06
18	**2**	500	BnOH	4	120	100	1.42	1.60	1.08
19	**2**	500	BnOH	5	120	100	1.14	1.25	1.06
20	**2**	500	BnOH	8	120	100	0.72	0.91	1.07
21	**2**	500	BnOH	10	120	100	0.58	0.76	1.05
22	**2**[e]	1000	BnOH	100	60	100	0.12	0.18[b]	1.03
23	**2**[e]	2000	BnOH	200	120	100	0.12	0.18[b]	1.03
24	**2**[e]	5000	BnOH	500	300	100	0.12	0.14[b]	1.09

[a]Polymerizations were performed in THF, at 25 ± 2 °C, $[CL]_0$ = 0.88 M. [b]Obtained from ^{1}H NMR analysis. [c]Calculated by $([CL]_0/[I]_0) \times 114.14 \times$ conv. (%); with addition of alcohol, $([CL]_0/[OH]_0) \times 114.14 \times$ conv. (%) + M_{ROH}. [d]Determined by size exclusion chromatography (SEC) against a polystyrene standard. M_n values were obtained using a correcting factor for polycaprolactone (0.56).[30] [e]$[CL]_0$ = 2.63 M.

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established the best initiation system (Table 1, entry 10) and was studied in detail. With the monomer-to-Mg ratio varying from 100 to 1500, the polymerization performed smoothly to give PCL with a molecular weight increasing from M_n = 1.14 × 10^4 g/mol to M_n = 20.8 × 10^4 g/mol, well consistent with the theoretic values. Note that, when the ratio was over 2000, the polymerization was too rapid and the polymerization system became extremely viscous, which made the monomer diffusion difficult and aroused the deviation of the molecular weight of the resultant PCL from the theoretic value and the broadened PDI (Table 1, entries 6 and 12−15). Remarkably, complex **2** was so tolerant to the protic BnOH that, with an increase of BnOH loading from 2 to 10 equiv, the polymerization went rapidly; in addition, the molecular weight of the resultant PCL decreased reversibly with respect to the value calculated based on BnOH loading, while the molecular weight distribution remained constant (Table 1, entries 16−21; Figure 4). This

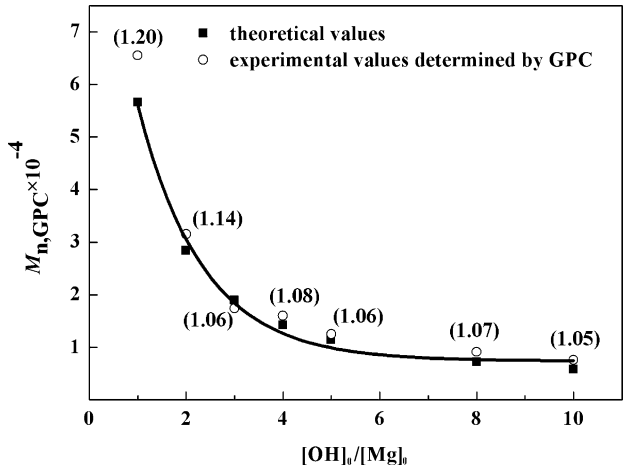

Figure 4. Dependence of the molar mass $M_{n,SEC}$ (PDI indicated in parentheses) on $[BnOH]_0$-to-$[Mg]_0$ ratio. Conditions: $[CL]_0$-to-$[Mg]_0$ ratio = 500; $[CL]_0$ = 0.88 M; solvent, THF; T_p = 25 °C.

result indicated that an excess amount of BnOH did not terminate the polymerization as usual but behaved as a chain transfer agent; in particular, it aroused a living chain-transfer polymerization. Strikingly, when the OH-to-Mg ratio varied from 100 to 500 while the CL-to-Mg ratio varied from 1000 to 5000, the polymerization still performed in obviously high activities so that 100% conversion could be achieved, albeit in a prolonged time (1−5 h), to provide PCL with narrow molecular weight distributions (PDI = 1.03−1.09) (Table 1, entries 22−24). This result indicated that the binary system **2**/BnOH possessed an immortal nature that up to 500 PCL chains grew from each Mg metal center. The molecular weight of the resultant PCL and its chain ends were defined by the ^{1}H NMR study. For example, the ^{1}H NMR spectrum (Figure 5) of PCL-40 (the number 40 indicates the designed $[CL]_0$/$[BnOH]_0$ value) gives a singlet resonance at 5.12 ppm assigned to H_f from the benzyloxide chain end −OCH_2Ph, a multiple resonance around 3.60 ppm attributed to H_a from methylene −CH_2 attaching to the hydroxyl end, and a triplet centered at 4.12 ppm arising from H_e ({−RCH_2OC(O)−}$_n$). The integral ratio of these resonances is 2:2:81, in precise accordance with the polymerization degree of 40. These results revealed that the PCL macromolecular chains are capped with benzylmethoxide at one end, probably attributed to the coordination−insertion

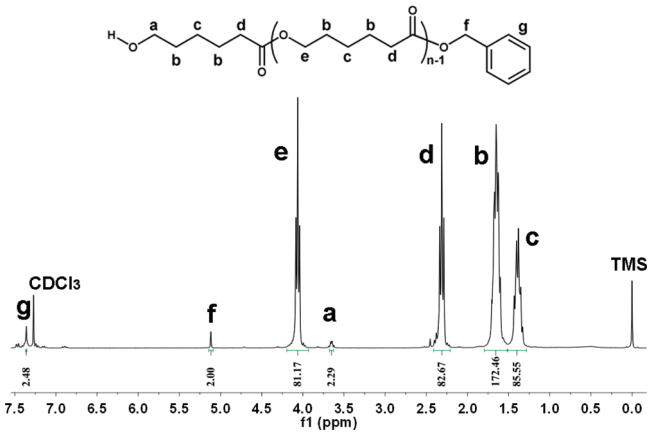

Figure 5. ^{1}H NMR spectrum of PCL-40 in $CDCl_3$.

mechanism, and with a hydroxyl functionality because of the immortal polymerization.[25,28] The alcoholysis reaction of magnesium complex **2** and excess benzyl alcohol was monitored by the ^{1}H NMR spectroscopy technique, which proved the formation of magnesium alkoxide active species Mg−OCH_2Ph (br 4.48 ppm) with the releasing of butane (1.34, 0.97 ppm) and the absence of ligand extrusion (Figure S1, Supporting Information). This further confirmed that the polymerization proceeded in the coordination−insertion mechanism, not via the activated monomer mechanism.[29] The hydroxyl ends provide a convenient approach to construct novel PCL-based block copolymers or functionalized PCL, in one pot.

Ring-Opening Polymerization of L-Lactide. The catalytic performances of complexes **1**−**4** toward the polymerization of L-lactide (L-LA) were also investigated. In the absence of alcohols, the magnesium complexes showed much higher activity for the ROP of L-LA at room temperature than the corresponding zinc analogues that initiated the polymerization at high temperature to reach quantitative yields (Table 2, entries 1−4). Nevertheless, the resultant PLLAs from both Mg-based and Zn-based systems had molecular weights slightly larger than the calculated values and medium polydispersity (PDI = 1.52−1.67). ^{1}H NMR spectroscopy analysis was employed to monitor the polymerization with complex **2** as the initiator under a very low monomer-to-Mg ratio, anticipated to obtain the end-group information of oligomeric PLA. The result showed that ^{n}Bu was found as one of the PLA chain ends (4.22, 1.50, 1.27, 0.90 ppm), and the signals from the $\mathbf{L^2}$**−H** ligand were not observed, suggesting that the Mg−^{n}Bu species initiated the polymerization, not the chelating ligand (Figure S3, Supporting Information). Addition of 1 equiv of benzyl alcohol, BnOH, to activate complexes **1** and **2**, respectively, seemed not to make any improvement in the catalytic performances. Increasing the BnOH loading (OH-to-Mg = 6) or using alcohol, ^{i}PrOH, aroused indeed a more controllable system without backbiting or transesterification (Table 2, entries 5−9 and 11); however, the catalytic activity dropped obviously (Table 2, entries 10 and 12). The resulting PLA macromolecular chain is capped with the hydroxyl group at one end, and with the PhCH_2O− group at the other end (PhCH_2O− is overlapped by methane in the polymer chain at about 5.12 ppm, Figure 6), suggesting probably a coordination insertion mechanism. To our delight, when TEA was employed to combine with complex **2**, the generated Mg−

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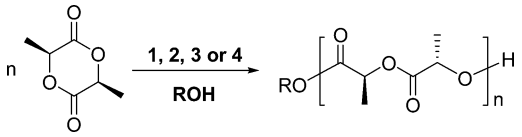
Table 2. Ring-Opening Polymerization of L-Lactide Catalyzed by Complexes 1−4



entry[a]	cat.	$[LA]_0/[I]_0$	ROH	$[OH]_0/[I]_0$	time (min)	conv. (%)[b]	$M_{n,calcd} \times 10^{-4}$[c]	$M_{n,SEC} \times 10^{-4}$[d]	M_w/M_n[d]
1	1	100		0	5	100	1.45	2.35	1.52
2	2	100		0	5	100	1.45	2.02	1.53
3	3[e]	100		0	1020	100	1.45	2.08	1.63
4	4[e]	100		0	1020	89	1.28	1.27	1.67
5	1	100	BnOH	1	15	75	1.09	1.23	1.32
6	1	100	BnOH	2	25	81	0.59	0.46	1.10
7	2	100	BnOH	1	5	100	1.45	1.44	1.48
8	2	100	BnOH	2	5	44	0.33	0.53	1.11
9	2[f]	600	^{i}PrOH	1	5	61	5.28	4.60	1.28
10	2[f]	600	^{i}PrOH	6	60	24	0.35	0.32	1.05
11	2[f]	600	BnOH	1	5	100	8.66	8.62	1.64
12	2[f]	600	BnOH	6	60	71	1.03	1.00	1.06
13	2[f]	600	TEA	1	5	100	25.9	18.9	1.95
14	2[f]	600	TEA	6	60	100	4.34	4.31	1.35
15	2[f]	900	TEA	3	5	100	13.0	13.7	1.09
16	2[f]	900	TEA	27	60	100	1.45	1.92	1.14

[a]In THF, at 25 ± 2 °C, $[LA]_0$ = 0.83 M. [b]Determined by ^{1}H NMR spectroscopy. [c]$M_{n,calcd} = ([LA]_0/[I]_0) \times 144.13 \times$ conv. (%); with addition of alcohol, $M_{n,calcd} = ([LA]_0/[OH]_0) \times 144.13 \times$ conv. (%) + M_{ROH}. [d]Determined by size exclusion chromatography against a polystyrene standard. M_n values were obtained using a correcting factor for polylactide (0.58).[30] [e]70 ± 2 °C. [f]$[LA]_0$ = 2.08 M.

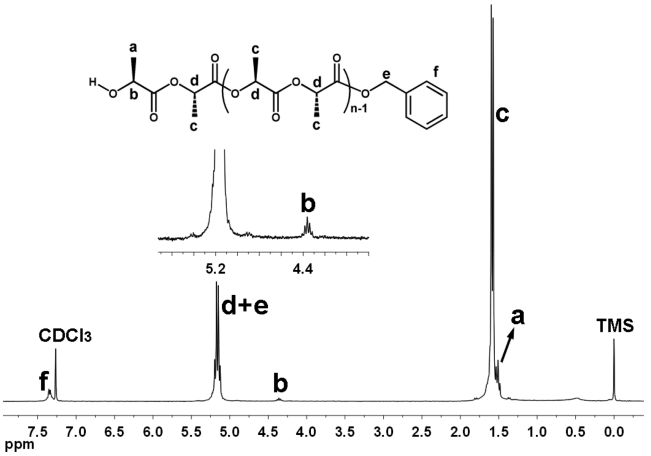


Figure 6. ^{1}H NMR spectrum of PLLA-20 in $CDCl_3$.

OCH_2CH_2N- active species initiated the polymerization in a livingness mode with high activity, which was dramatically different from its behavior toward ε-CL polymerization. Such a distinguished performance remained when both OH-to-Mg and LLA-to-Mg values were high (Table 2, entries 13−15), suggesting an immortal polymerization mode, and each magnesium active species grew up to 27 PLLA polymer chains (Table 2, entry 16). The ^{1}H NMR spectrum of the oligomeric polymer showed clearly the resonances from three HOCH-(CH_3)−CO end groups and a triethanolamine core for each macromolecule (Figure S4, Supporting Information). The completely opposite behavior of the binary systems **2**/BnOH and **2**/TEA toward the polymerizations of CL and LA is under investigation.

CONCLUSION

We have demonstrated that a new series of *N*,*O*-bidentate pyridyl functionalized alkoxyl ligated magnesium and zinc alkyl complexes have been synthesized selectively via a protonolysis reaction between the pyridyl alcohols and the corresponding dibutylmagnesium and diethylzinc. All of these complexes are well defined by NMR spectroscopy and X-ray diffraction analyses, adopting dimeric structures. The magnesium alkyl complexes show much higher activities toward both ε-CL and L-LA polymerizations than the corresponding zinc analogues, which might be attributed to the higher ionic properties of Mg^{2+} than that of Zn^{2+}. The bulkiness and the electron-withdrawing substituent lead to increasing of the catalytic activity to the attached zinc precursors but show no influence on that of Mg-based precursors. Strikingly, the binary system composed of magnesium complex **2** and benzyl alcohol, BnOH, displays excellent catalytic performances, which initiates the polymerization of ε-CL under a wide range of OH-to-Mg values (1−500) and high ε-CL loadings up to 5000, suggesting an immortal polymerization characteristic where up to 500 PCL molecules grew from each Mg active center, apparently. In contrast, the combination of complex **2** and triethanolamine, TEA, establishes an efficient catalytic system for the immortal polymerization of L-LA to provide PLLA with a predicted molecular weight and narrow molecular weight distribution. Both polymerizations are performed in a coordination−insertion mechanism, and the resultant PCL and PLLA chains are automatically end-capped by hydroxyl groups, which facilitate the preparation of PCL- and PLLA-based block functionalized copolymers in one pot.

EXPERIMENTAL SECTION

General Methods. All operations were carried out under an atmosphere of argon using standard Schlenk techniques. Solvents were reagent grade, dried by standard methods,[31] and distilled under

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nitrogen prior to use. Toluene, tetrahydrofuran, and *n*-hexane were dried over 4 Å molecular sieves for a week and distilled before use. C_6D_6 was purchased from Cambridge Isotopes, dried over Na, and stored in the glovebox. 2,6-Lutidine was purchased from Fluka and used after being carefully dried. 2-(6-Methyl-2-pyridinyl)-1,1-dimethyl-1-ethanol (**L^1−H**) and 2-(6-methyl-2-pyridinyl)-1,1-diphenyl-1-ethanol (**L^2−H**) were prepared as in the literature.[32] Mg^{n}Bu$_2$ and ZnEt$_2$ were purchased from Sigma-Aldrich. All reactions were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in an MBRAUN glovebox. ε-CL was dried over calcium hydride and distilled under nitrogen prior to its use. L-Lactide was recrystallized with dry toluene and then sublimed three times under vacuum at 80 °C. Benzyl alcohol, isopropanol, and triethanolamine were dried over calcium hydride prior to distillation. All other chemicals were commercially available and used after appropriate purification. Glassware and flasks used in the polymerization were dried in an oven at 115 °C overnight and exposed to a vacuum−argon cycle three times.

Measurements. Organometallic samples for NMR spectroscopic measurement were prepared in an Mbraun glovebox by use of NMR tubes sealed by paraffin film. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV300 and a Bruker AV400 (FT, 300 MHz for ^{1}H; 75 MHz for ^{13}C or 400 MHz for ^{1}H; 100 MHz for ^{13}C) spectrometer. NMR assignments were confirmed by the ^{1}H−^{1}H COSY and ^{1}H-^{13}C HMQC experiments when necessary. The number-average molar mass (M_n) and polydispersity index (PDI) of the polymer were measured by means of size exclusion chromatography on a TOSOH HLC-8220 SEC (column: Super HZM-H × 3) at 40 °C using THF as eluent (the flowing rate is 0.35 mL/min) against polystyrene standards.

Synthesis of Proligands and Complexes. *2-(6-Methyl-2-pyridinyl)-1,1-dimethyl-1-ethanol (**L^1−H**).* The compound was prepared using the modified method reported by Koning et al.[32] 2,6-Lutidine (10.0 g, 93.3 mmol) was dissolved in 200 mL of Et$_2$O and cooled to −40 °C, to which *n*-butyllithium (1.6 M in hexane, 59.4 mL, 95.0 mmol) was added under stirring. The mixture was warmed to 25 °C and reacted for 1 h. Acetone (7.00 mL, 95.0 mmol) in 25 mL of Et$_2$O was then added into the system, and the reaction was kept overnight. Adding 150 mL of water to the system and extracting the aqueous layer with dichloromethane twice gave an organic layer, which was dried over MgSO$_4$, filtered, and concentrated in vacuo to yield a yellow oil of **L^1−H** (12.5 g, 75.7 mmol, 81%). ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ = 7.52 (t, 1H, J_{H-H} = 9 Hz, *p*-Py−*H*), 7.03 (d, 1H, J_{H-H} = 9 Hz, *m*-Py−*H*), 6.92 (d, 1H, J_{H-H} = 9 Hz, *m*-Py−*H*), 6.29 (s, 1H, −O*H*), 2.86 (s, 2H, Py−C*H*$_2$−), 2.52 (s, 3H, Py−C*H*$_3$), 1.21 (s, 6H, Py−CH$_2$−C−(C*H*$_3$)$_2$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ = 158.89 (1C, *o*-Py−*C*), 156.76 (1C, *o*-Py−*C*), 136.65 (1C, *p*-Py−*C*), 120.90 (1C, *m*-Py−*C*), 120.60 (1C, *m*-Py−*C*), 70.19 (1C, Py−*C*−CH$_2$−), 48.07(1C, Py−*C*H$_2$−), 29.20 (2C, Py−CH$_2$*C*(OH)-(*C*H$_3$)$_2$), 23.94 (1C, Py−*C*H$_3$) ppm. Elemental analysis calcd (%) for C$_{10}$H$_{15}$NO: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.20; H, 9.00; N, 8.60.

*2-(6-Methyl-2-pyridinyl)-1,1-diphenyl-1-ethanol (**L^2−H**).* Following the similar procedure for the preparation of **L^1−H**, compound **L^2−H** was synthesized by using 2,6-lutidine (10.0 g, 93.3 mmol), *n*-butyllithium (1.6 M in hexane, 59.4 mL, 95.0 mmol), and benzophenone (17.3 g, 95.0 mmol). The mixture was allowed to reach ambient temperature overnight and was acidified to pH = 1 with 2 N HCl. After stirring for 1 h, the mixture was neutralized with 2 N NaOH. The aqueous layer was extracted with ethyl acetate twice. Combining of the organic layers, drying over MgSO$_4$, concentration in vacuo, and recrystallization from methanol yielded white solids (20.0 g, 69.1 mmol, 74%) with mp 124−125 °C. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ = 8.33 (s, 1H, −O*H*), 7. 89(s, 2H, *m*-Ar−*H*), 7.78 (s, 2H, *m*-Ar−*H*), 7.24 (m, 2H, *o*-Ar−*H*), 7.19 (m, 2H, *o*-Ar−*H*), 7.06 (t, 2H, J_{H-H} = 6 Hz, *p*-Ar−*H*), 6.87 (t, 1H, J_{H-H} = 6 Hz, *p*-Py−*H*), 6.50 (d, 1H, J_{H-H} = 6 Hz, *m*-Py−*H*), 6.32 (d, 1H, J_{H-H} = 9 Hz, *m*-Py−*H*), 3.62 (s, 2H, Py−C*H*$_2$−), 2.06 (s, 3H, Py−C*H*$_3$) ppm. ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C): δ = 158.48 (1C, *o*-Py−*C*), 156.82(1C, *o*-Py−*C*), 147.43 (2C, Ar−*C*), 137.04 (1C, *p*-Py−*C*), 127.82 (4C, *m*-Ar−*C*), 126.32 (2C, *p*-Ar−*C*), 126.16 (4C, *o*-Ar−*C*), 121.51 (1C, *m*-Py−*C*), 120.99 (1C, *m*-Py−*C*), 78.3 (1C, Py−*C*−CH$_2$−), 46.78 (1C, Py−*C*H$_2$−), 24.12 (1C, Py−*C*H$_3$) ppm. Elemental analysis calcd (%) for C$_{20}$H$_{19}$NO: C, 83.01; H, 6.62; N, 4.84. Found: C, 82.90; H, 6.55; N, 4.50.

*(L^{1}Mg^{n}Bu)$_2$ (**1**).* In an Mbraun glovebox, in a 25 mL flask, a toluene (10 mL) solution of **L^1−H** (165 mg, 1 mmol) was mixed with a toluene solution (5 mL) of Mg^{n}Bu$_2$ (1 mL, 1 M, 1 mmol). The reaction mixture was stirred at room temperature for 4 h and concentrated to approximately 2 mL, then cooled to −35 °C, to afford crystalline solids of **1** (211 mg, yield = 81.8%). Single crystals suitable for X-ray diffraction were obtained from a toluene−hexane solution. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 7.03 (t, 2H, J_{H-H} = 8 Hz, *p*-Py−*H*), 6.54 (d, 2H, J_{H-H} = 8 Hz, *m*-Py−*H*), 6.52(d, 2H, J_{H-H} = 12 Hz, *m*-Py−*H*), 3.17 (d, 2H, J_{H-H} = 12 Hz, Py−C*H*$_2$−), 2.63 (s, 6H, Py−C*H*$_3$), 2.61 (d, 2H, J_{H-H} = 16 Hz, Py−C*H*$_2$−), 1.95 (m, 4H, −CH$_2$*C*H$_2$CH$_2$CH$_3$), 1.63 (m, 4H, −CH$_2$CH$_2$*C*H$_2$CH$_3$), 1.54 (s, 6 H, −CH$_2$C(OH)(C*H*$_3$)$_2$), 1.33 (s, 6H, −CH$_2$C(OH)(C*H*$_3$)$_2$), 1.18 (t, 6H, −CH$_2$(CH$_2$)$_2$C*H*$_3$), 0.02 (t, 4H, −C*H*$_2$(CH$_2$)$_2$CH$_3$) ppm (Figure S5, Supporting Information). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 160.04 (2C, *o*-Py−*C*−CH$_2$−), 157.40 (2C, *o*-Py−*C*−CH$_3$), 138.92 (2C, *p*-Py−*C*), 123.66 (2C, *m*-Py−*C*), 122.27 (2C, *m*-Py−*C*), 69.95 (2 C, Py−*C*−CH$_2$−), 52.09 (2C, Py−*C*H$_2$−), 35.62 (4C, Py−CH$_2$(OH)-*C*−(CH$_3$)$_2$), 33.95 (2C, −*C*H$_2$CH$_2$CH$_2$CH$_3$), 32.49 (2C, −CH$_2$*C*H$_2$CH$_2$CH$_3$), 31.49 (2C, −CH$_2$CH$_2$*C*H$_2$CH$_3$), 24.55 (2C, Py−CH$_3$), 15.18 (2C, −CH$_2$(CH$_2$)$_2$CH$_3$), 9.82 (2C, −CH$_2$(CH$_2$)$_2$CH$_3$) ppm. Elemental analysis calcd (%) for C$_{28}$H$_{46}$Mg$_2$N$_2$O$_2$: C, 68.45; H, 9.44; N, 5.70. Found: C, 68.39; H, 9.33; N, 5.79.

*(L^{2}Mg^{n}Bu)$_2$ (**2**).* In an Mbraun glovebox, a toluene (10 mL) solution of **L^2−H** (289 mg, 1 mmol) and a toluene solution (5 mL) of Mg^{n}Bu$_2$ (1 mL, 1 M, 1 mmol) were added to a 25 mL flask. The reaction mixture was stirred at room temperature for 2 h and concentrated to approximately 2 mL, then cooled to −35 °C, to afford crystalline solids of **2** (288 mg, yield 78.0%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 7.89 (d, 4H, J_{H-H} = 8 Hz, *o*-Ar−*H*), 7.46 (t, 4H, J_{H-H} = 8 Hz, *m*-Ar−*H*), 7.39 (d, 4H, J_{H-H} = 8 Hz, *o*-Ar−*H*), 7.31 (t, 2H, J_{H-H} = 8 Hz, *p*-Ar−*H*), 7.25 (t, 4H, J_{H-H} = 8 Hz, *m*-Ar−*H*), 7.12 (t, 2H, J_{H-H} = 8 Hz, *p*-Ar−*H*), 6.78 (t, 2H, J_{H-H} = 8 Hz, *p*-Py−*H*), 6.35 (d, 2H, J_{H-H} = 8 Hz, *m*-Py−*H*), 6.20 (d, 2H, J_{H-H} = 8 Hz, *m*-Py−*H*), 4.15 (d, 2H, J_{H-H} = 16 Hz, Py−C*H*$_2$−), 3.50 (d, 2H, J_{H-H} = 12 Hz, Py−C*H*$_2$−), 1.88 (s, 6H, Py−C*H*$_3$), 1.70 (m, 4H, −CH$_2$*C*H$_2$CH$_2$CH$_3$), 1.56 (m, 4H, −CH$_2$CH$_2$*C*H$_2$CH$_3$), 1.15 (t, 6H, J_{H-H} = 8 Hz, −CH$_2$(CH$_2$)$_2$C*H*$_3$), −0.21 (t, 4H, J_{H-H} = 8 Hz, −C*H*$_2$(CH$_2$)$_2$CH$_3$) ppm (Figure S6, Supporting Information). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 160.99 (2C, *o*-Py−*C*−CH$_2$), 154.94 (2C, *o*-Py−*C*−CH$_3$), 137.96 (2C, *p*-Py−*C*), 135.79 (4C, Ar−*C*), 128.74, 128.50, 128.26, 127.84 (4C, *p*-Ar−*C*, 8C, *m*-Ar−*C*), 125.35 (8C, *o*-Ar−*C*), 122.75 (2C, *m*-Py−*C*), 121.81 (2C, *m*-Py−*C*), 79.43 (2C, Py−CH$_2$−*C*), 50.49 (2C, Py−*C*H$_2$−), 33.28 (2C, −CH$_2$CH$_2$CH$_2$CH$_3$), 32.39 (2C, −CH$_2$CH$_2$CH$_2$CH$_3$), 24.38 (2C, Py−CH$_3$), 15.20 (2C, −CH$_2$(CH$_2$)$_2$CH$_3$), 14.40 (2C, −CH$_2$(CH$_2$)$_2$CH$_3$) ppm. Elemental analysis calcd (%) for C$_{48}$H$_{54}$Mg$_2$N$_2$O$_2$: C, 77.95; H, 7.36; N, 3.79. Found: C, 77.55; H, 7.20; N, 3.89.

*(L^{1}ZnEt)$_2$ (**3**).* In a Mbraun glovebox, to a 25 mL flask, were added **L^1−H** (248 mg, 1.5 mmol, 10 mL toluene) and ZnEt$_2$ (1.54 mL, 1.5 mmol, 5 mL toluene). The reaction mixture was stirred at room temperature for 4 h. Removal of volatiles gave white solids that were washed with hexane to afford crystalline **3** (345 mg, yield 89.0%). Single crystals suitable for X-ray diffraction were obtained from a toluene−tetrahydrofuran−hexane solution cooled at −35 °C. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.01 (t, 2H, J_{H-H} = 9 Hz, *p*-Py−*H*), 6.56 (d, 4H, *m*-Py−*H*), 2.90 (s, 4H, Py−C*H*$_2$), 2.78 (s, 6H, Py−C*H*$_3$), 1.60 (t, 6H, J_{H-H} = 6 Hz, −CH$_2$C*H*$_3$), 1.51 (s, 12H, Py−CH$_2$−C(C*H*$_3$)$_2$), 0.52 (q, 4H, J_{H-H} = 9 Hz, −C*H*$_2$CH$_3$) ppm (Figure S7, Supporting Information). ^{13}C NMR (150 MHz, C_6D_6, 25 °C): δ = 158.59 (2C, *o*-Py−*C*−CH$_2$), 156.31 (2C, *o*-Py−*C*−CH$_3$), 136.38 (2C, *p*-Py−*C*−CH$_2$), 121.61 (2C, *m*-Py−*C*), 120.35 (2C, *m*-Py−*C*), 69.64 (2C, Py−CH$_2$−*C*), 51.30 (2C, Py−*C*H$_2$), 31.54 (4C, Py−CH$_2$−*C*−(*C*H$_3$)$_2$), 23.33 (2C, −*C*H$_2$CH$_3$), 12.59 (2C, Py−*C*H$_3$), 0.67 (2C,

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$-CH_2CH_3$) ppm. Elemental analysis calcd (%) for $C_{24}H_{38}N_2O_2Zn_2$: C, 68.45; H, 9.44; N, 5.70. Found: C, 68.40; H, 9.25; N, 5.77.

$(L^2ZnEt)_2$ (4). In a Mbraun glovebox, L^2–H (434 mg, 1.5 mmol, 10 mL of toluene) and $ZnEt_2$ (1.54 mL, 1.5 mmol, 5 mL of toluene) were added to a 25 mL flask. The reaction mixture was stirred at room temperature for 2 h. Removal of volatiles gave white solids that were washed with hexane to afford crystalline **4** (517 mg, yield 90%). Single crystals of **4** suitable for X-ray diffraction were obtained from a toluene–tetrahydrofuran–hexane solution cooled at −35 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 7.68 (br, 8H, *o*-Ar–*H*), 7.34 (br, 8H, *m*-Ar–*H*), 7.21 (br, 4H, *p*-Ar–*H*), 6.87 (t, 2H, J_{H-H} = 8 Hz, *o*-Py–*H*), 6.44 (d, 2H, J_{H-H} = 8 Hz, *m*-Py–*H*), 6.39 (d, 2H, J_{H-H} = 8 Hz, *m*-Py–*H*), 3.80 (br, 4H, Py–CH_2–), 2.00 (s, 6H, Py–CH_3), 1.30 (t, 6H, J_{H-H} = 8 Hz, $-CH_2CH_3$), 0.15 (t, 4H, $-CH_2CH_3$) ppm (Figure S8, Supporting Information). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 158.85 (2C, *o*-Py–*C*–CH_2), 157.54 (2C, *o*-Py–*C*–CH_3), 151.01 (4C, Ar–*C*), 137.29 (2C, *p*-Py–*C*), 127.95, 127.70 (8C, *o*-Ar–*C*, 8C, *m*-Ar–*C*), 126.08 (4C, *p*-Ar–C), 123.81 (2C, *m*-Py–*C*), 121.40 (2C, *m*-Py–*C*), 79.78 (2C, Py–CH_2–*C*), 50.81 (2C, Py–CH_2), 23.07 (2C, $-CH_2CH_3$), 13.19 (2C, Py–CH_3), 2.42 (2C, $-CH_2CH_3$) ppm. Elemental analysis calcd (%) for $C_{44}H_{46}N_2O_2Zn_2$: C, 69.02; H, 6.06; N, 3.66. Found: C, 68.95; H, 5.98; N, 3.76.

X-ray Crystallographic Studies. Suitable crystals of complex **1**, **3**, or **4**[33] were sealed in thin-walled glass capillaries. Data collection was performed at 20°C on a Bruker SMART diffractometer with graphite-monochromated Mo Kα radiation (l = 0.71073 Å). The SMART program package was used to determine the unit cell parameters. The absorption correction was applied using SADABS.[34] The structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were placed at calculated positions and were included in the structure calculation without further refinement of the parameters. All calculations were carried out using the SHELXS-97 program.[35] Molecular structures were generated using the ORTEP program.[36]

Polymerization of ε-CL Catalyzed by Complex 2. A typical polymerization procedure was exemplified by the synthesis of PCL-100 (the number 100 indicates the designed $[CL]_0/[BnOH]_0$). To a rapidly stirring THF solution (5 mL) of complex **2** (0.0163 g, 0.044 mmol) and benzyl alcohol (BnOH, 0.0048 g, 0.044 mmol) was added ε-CL (0.5 g, 4.4 mmol). The reaction mixture was stirred at 25 °C for 1 min. The yield (100%) of PCL-100 was analyzed by ^{1}H NMR spectroscopic studies. The acidic ethanol (0.5 mL of a 1.0 M HCl solution in EtOH) was added to the system to terminate the reaction. The resultant white precipitate was purified by redissolving the polymer in THF (10 mL), being precipitated in enthanol (60 mL). Finally, the white polymer solid was dried under vacuum to a constant weight (0.50 g, yielding 100%).

Polymerization of L-LA Catalyzed by Complex 2. A typical polymerization procedure was exemplified by the synthesis of PLLA-100 (the number 100 indicates the designed $[LA]_0/[BnOH]_0$). To a rapidly stirring solution of complex **2** (0.0129 g, 0.035 mmol) and benzyl alcohol (BnOH, 0.0038 g, 0.035 mmol) in THF (5 mL) was added L-lactide (0.5 g, 3.5 mmol). The reaction mixture was stirred at 25 °C for 5 min. The conversion yield (100%) of PLLA-100 was analyzed by ^{1}HNMR spectroscopic studies. The acidic ethanol (0.5 mL of a 1.0 M HCl solution in EtOH) was added to the system to terminate the reaction. The resultant white precipitate was purified by redissolving the polymer in THF (10 mL), being precipitated in enthanol (60 mL). Finally, the white polymer solid was dried under vacuum to a constant weight (0.50 g, yielding 100%).

Synthesis of Benzyl Ester End-Capped PCL. A typical polymerization procedure was exemplified by the synthesis of PCL-40 (the number 40 indicates the designed $[CL]_0/[BnOH]_0$). To a rapidly stirring solution of **2** (0.0370 g, 0.1 mmol) and ε-CL (0.23 g, 2.0 mmol) in THF (5 mL) was added a BnOH/toluene mixture solution (0.1 mmol, 1 mL). The reaction mixture was stirred at room temperature for 1 h. The acidic ethanol (0.5 mL of a 1.0 M HCl solution in EtOH) was added to the system to terminate the reaction. The white precipitate was resolved in dichloromethane and then precipitated into ethanol; it was then dried under vacuum to yield a white solid of the polymer (0.20 g, yielding 87%).

Synthesis of Benzyl Ester End-Capped PLLA. A typical polymerization procedure was exemplified by the synthesis of PLLA-20 (the number 20 indicates the designed $[M]_0/[LA]_0$). To a rapidly stirring solution of **2** (0.0370 g, 0.1 mmol) and L-lactide (0.29 g, 2.0 mmol) in THF (5 mL) was added a BnOH/toluene mixture solution (0.1 mmol, 1 mL). The reaction mixture was stirred at room temperature for 1 h. The acidic ethanol (0.5 mL of a 1.0 M HCl solution in EtOH) was added to the system to terminate the reaction. The white precipitate was resolved in dichloromethane and then precipitated into ethanol; it was then dried under vacuum to yield a white solid of the polymer (0.24 g, yielding 82%).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files for **1**, **3** and **4**; ^{1}H NMR spectra of complexes **1**–**4**; ^{1}H NMR spectra of complexes **2** and **3** in the presence of alcohol; and ^{1}H NMR spectra of PLA oligomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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