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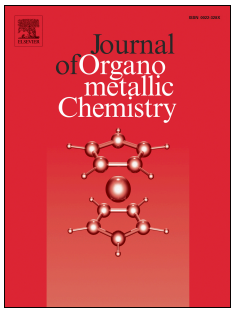

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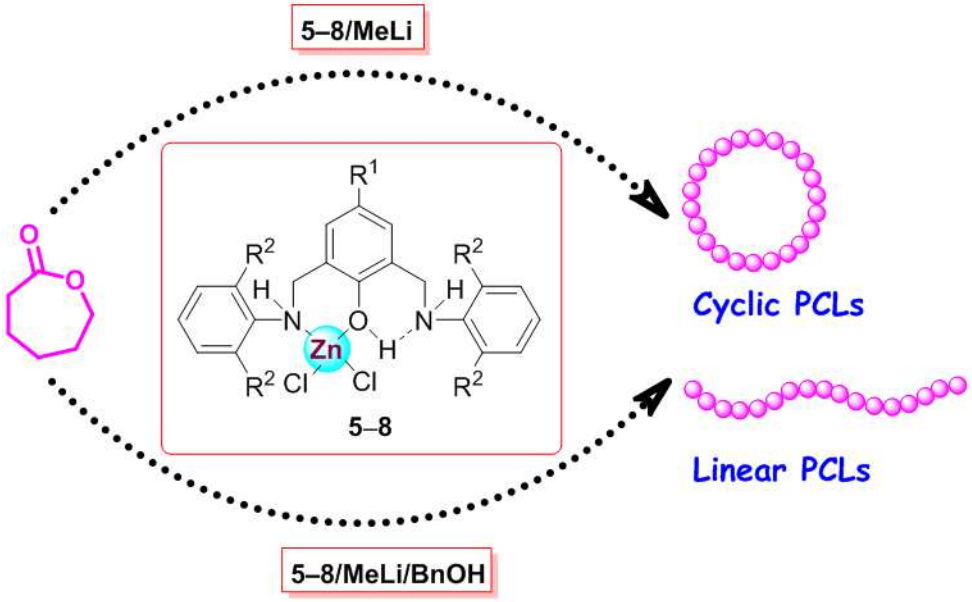

Highly active tridentate amino-phenol zinc complexes for the catalytic ring-opening polymerization of ε-caprolactone

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Abstract: Tridentate 2,6-bis(imino)phenol (**L1**−**L4**) and 2,6-bis(amino)phenol (**L5**−**L7**) ligands and their corresponding zinc chloride complexes (**1**−**7**) have been synthesized and well characterized by FT-IR, ^{1}H and ^{13}C NMR, elemental analysis and single-crystal X-ray diffraction analysis. It was found that zinc complexes (**1**−**4**) with 2,6-bis(imino)phenol ligands were inactive for the ring-opening polymerization (ROP) of ε-caprolactone (ε-CL) even if they were activated by methyllithium. Zinc complexes (**5**−**7**) with 2,6-bis(amino)phenol ligands were proved to be highly efficient initiators for the ROP of ε-CL in combination with 4 equiv. of methyllithium. The ROP of ε-CL in the absence or presence of benzyl alcohol, including the influence of monomer ratio, reaction temperature and the substituent in the ligand, were investigated. The structure and thermal properties of obtained polymers were analyzed by NMR and MALDI-TOF mass spectra, DSC and TGA, respectively.

Keywords: zinc, ring-opening polymerization, ε-caprolactone

1. Introduction

Aliphatic polyesters, such as poly(ε-caprolactone) (PCL) and polylactide (PLA), are important biodegradable materials, which have found wide applications in *i.a.* biomedical, packaging, and agricultural areas [1,2]. For the moment, the catalytic ring-opening polymerization (ROP) of cyclic esters is one of the most powerful and convenient methods for the preparation of aliphatic polyesters [3,4]. A challenge is to develop more efficient catalysts that also allow a better control of the ring-opening polymerization, the molecular weight and the molecular weight distribution of the resulting polymers. ROP is commonly catalyzed by metal coordination complexes [4,5] and improved activity, selectivity, and controllability, associated with a lower toxicity are highly desirable to provide these polyesters with good environmental

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and biological compatibility and a broader potential for biomedical application. Numerous metal complexes have been used to initiate the ROP of cyclic esters [4,5], mostly containing *e.g*. alkali metals [6-10], alkaline earth metals [11-15], Group IVB metals [16-21], rare earth metals [22-27], aluminum [28-34], copper [35,36], gallium [37,38]. However, traces of residual metal in the polymers formed are very hard to be completely removed, which is harmful to the environment or humans and consequently limits their applications of polymers. The use of harmless metal ions in the catalytic systems is one approach to solve this problem [39]. Zinc is one of the essential oligo-elements in the human bodies and has good biological activities. Therefore, zinc-based metal catalysts are attracting increasing attention as green catalysts for the ROP of cyclic esters. Zinc complexes bearing various organic ligands have been reported to be active for the ROP of cyclic esters to form biodegradable polyesters with high molecular weight and narrow molecular weight distribution [40-55].

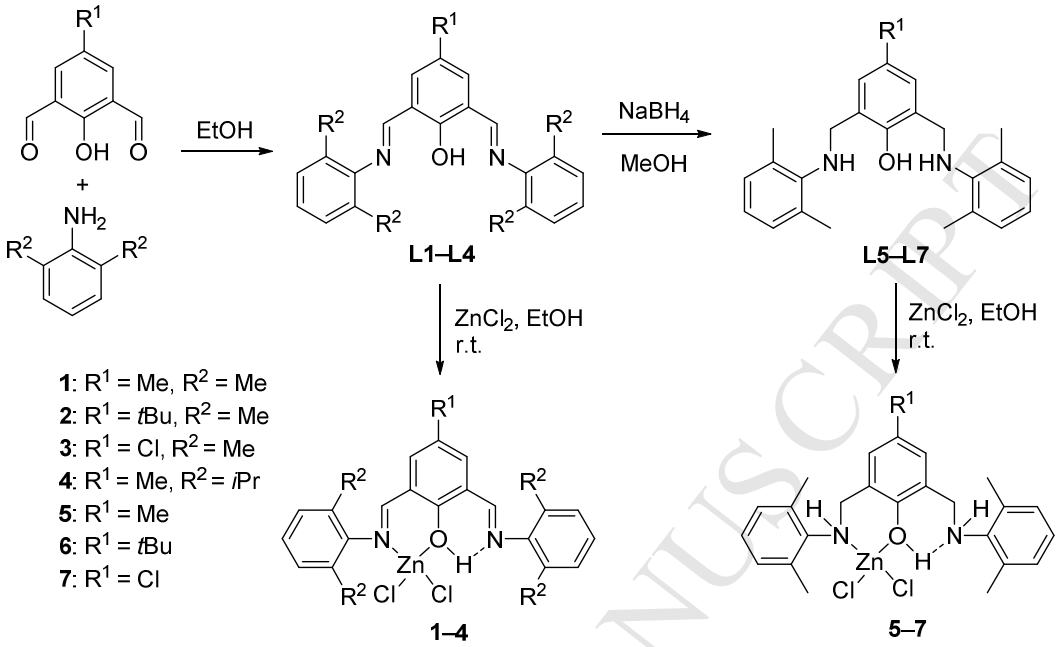
Most reported zinc-based catalysts for the ROP of cyclic esters were zinc alkyl complexes that are air-sensitive. There were only few examples of zinc chloride complexes used for the ROP of lactones. For instance, zinc dichloride or dichlorozinc complexes were reported to catalyze the ROP of ε-caprolactone or *rac*-lactide by a coordination-insertion mechanism [55,56]. Zinc chloride complexes with various ligands were also reported to be activated by methyllithium or $LiOCHMe_2$ to generate in situ zinc methyl species or zinc isopropoxide derivatives, respectively, which were active for the ROP of *rac*-LA [57-62]. We previously showed that zinc chloride complexes containing (benzimidazolyl)pyridine alcohol ligands were also activated by methyllithium and then used in the ROP of ε-CL with high efficiency, in the absence or presence of benzyl alcohol [63,64]. In this study, zinc complexes bearing tridentate bis(amino)phenol ligands were designed, synthesized and applied in combination with methyllithium, to the catalytic ROP of ε-CL, in the absence or presence of benzyl alcohol.

2. Results and discussion

2.1. Synthesis and characterization of the ligands and their zinc complexes

The 2,6-bis(imino)phenol ligands (**L1**–**L4**) were synthesized through the Schiff-base condensation reaction of 4-substituted 2,6-diformylphenols with 2,6-dimethylaniline or 2,6-diisopropylaniline in refluxing ethanol according to literature procedures and characterized by FT-IR and ^{1}H NMR spectroscopy (Scheme 1) [65–67]. The 2,6-bis(amino)phenol ligands (**L5**–**L7**) were prepared by reduction of the imine groups of ligands **L1**–**L3** with sodium borohydride and characterized by FT-IR, ^{1}H and ^{13}C NMR spectroscopy, and elemental analysis.

However, ligand **L4** was difficult to reduce using $NaBH_4$ because its imino groups are surrounded and protected by the bulky isopropyl groups.



Scheme 1. Synthesis of ligands **L1**–**L7** and Zn complexes **1**–**7**

The zinc complexes **1**–**7** were readily prepared by reaction of the corresponding ligand with anhydrous zinc chloride in absolute ethanol at room temperature and isolated as air-stable solids (Scheme 1). All the characterizing data for these complexes, including FT-IR, ^{1}H and ^{13}C NMR spectra as well as elemental analyses, were fully consistent with their structures. In the NMR spectra, the substituents on the two phenyl ring show slightly different chemical shifts, which is consistent with the asymmetrical structure of the zinc complexes. This was unambiguously established by single-crystal X-ray diffraction analysis of complex **4**.

Single crystals of complex **4** suitable for X-ray diffraction analysis were obtained by slow diffusion of *n*-hexane into an ethanol solution. As shown in Fig. 1, the coordination geometry around the zinc center is distorted tetrahedral, with bond angles in the range of 93.14(9) – 114.47(8)°. The structure is similar to that of the corresponding cobalt and nickel complexes [65–67]. The bond lengths C7–N1 (1.279(4) Å) and C14–N2 (1.286(4) Å) are consistent with the presence of C=N double bonds.

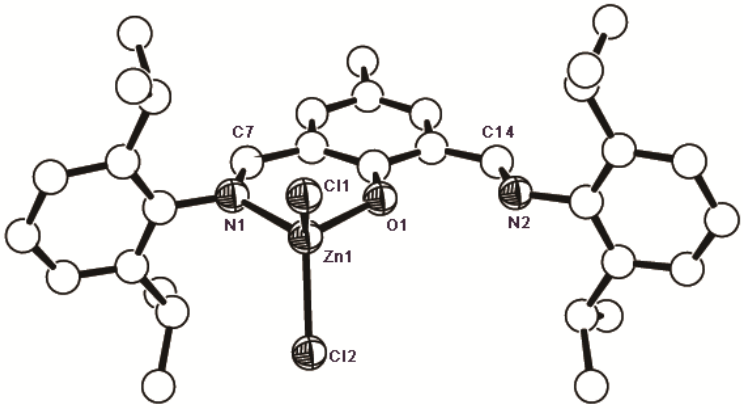


Fig. 1. Molecular structure of complex **4** with thermal ellipsoids at the 50% probability level. All the hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) as follows: Zn1–N1: 2.031(3), Zn1–O1: 1.973(2), Zn1–Cl1: 2.2164(11), Zn1–Cl2: 2.2260(11), C7–N1: 1.279(4), C14–N2: 1.286(4); Cl1–Zn1–Cl2: 110.36(5), O1–Zn1–Cl1: 113.54(7), O1–Zn1–Cl2: 110.44(7), O1–Zn1–N1: 93.14(9), N1–Zn1–Cl1: 113.94(8), N1–Zn1–Cl2: 114.47(8).

2.2. Ring-opening polymerization of ε-caprolactone

It is worth mentioning that the zinc dichloride complexes alone had no activity in the ring-opening polymerization (ROP) of ε-CL, whether benzyl alcohol (BnOH) was involved or not. However, addition of methyllithium activated the zinc dichloride complexes by generating zinc methyl species *in situ*. We [63,64] and others [57–59] have already used this approach.

Unexpectedly, even after the addition of 2 equiv. of MeLi, complexes **1**−**4** bearing 2,6-bis(imino)phenol ligands remained inactive for the ROP of ε-CL, in the presence or not of BnOH, owing to the influence of the imino groups. However, after these imino groups were reduced to amino groups, the corresponding zinc complexes **5**−**7**, associated with 4 equiv. of MeLi, showed excellent catalytic activity for the ROP of ε-CL, both in the presence or not of BnOH (Tables 1 and 2).

2.2.1. ROP of ε-CL in the absence of BnOH

In the absence of BnOH, the **5**−**7**/MeLi catalytic systems were highly active for the ROP of ε-CL in toluene and the monomers were completely converted into polymers within 3 min in most cases, giving a relatively broad molecular weight distribution (*Đ*) (Table1). The number-average molecular weight (M_n) of the polymers increased gradually with the $[CL]_0/[Zn]_0$ ratio, and the solution quickly became very sticky, preventing magnetic stirring.

The catalytic systems remained highly active over a broad temperature range (30−90 °C), but higher reaction temperatures resulted in slightly lower M_n of PCLs (entries 3−5 in Table 1).

Table 1 ROP of ε-CL catalyzed by zinc complexes **5**−**7**/MeLi[a]

Entry	Complex	T (°C)	time (min)	$[CL]_0/[Zn]_0$	Yield[b] (%)	$M_{n,cal}$[c] (kg/mol)	$M_{n,obs}$[d] (kg/mol)	$Đ$[d]
1	**5**	30	3	50	100	5.71	6.75	1.68
2	**5**	30	3	100	100	11.4	15.8	1.59
3	**5**	30	3	300	99.0	34.2	28.4	1.63
4	**5**	60	3	300	100	34.2	20.9	1.57
5	**5**	90	3	300	100	34.2	22.0	1.58
6	**5**	60	3	500	100	57.1	18.2	1.59
7	**5**	30	90	1000	100	114.1	42.7	1.31
8	**6**	30	15	100	91.4	11.4	6.89	1.34
9	**6**	30	3	200	100	22.8	21.0	1.47
10	**6**	30	3	300	100	34.2	23.4	1.27
11	**6**	30	3	500	100	57.1	26.8	1.65
12[e]	**6**	30	3+3	200+300	100	57.1	30.0	1.51
13	**7**	30	3	500	100	57.1	20.2	1.32

[a] Polymerization conditions: zinc complex: 0.02 mmol, [Zn] = 0.058 M, [MeLi]/[Zn] = 4:1, solvent: toluene.

[b] Determined by weight of isolated polymer.

[c] $M_{n,cal} = [CL]_0/[Zn]_0 \times 114.14 \times$ Yield%, assuming one propagation chain per zinc atom.

[d] Measured by GPC in THF, calibrated with polystyrene standards and corrected using a correction factor of 0.56 [68].

[e] 200 equiv. of CL was first added, and after 3 min, a second batch of 100 equiv. of CL was added and the polymerization reaction was continued for an additional 3 min.

The polymerization rate was so high that no influence of the substituent R^1 at the phenol ring on the activity could be detected, which is consistent with the substituent R^1 being far away from the metal center. Therefore, all the zinc complexes showed high activities for the ROP of ε-CL; however, they produced PCLs with different M_n and $Đ$.

The catalytic systems exhibited the "immortal" and controllable properties for ROP of ε-CL in the absence of BnOH although the $Đ$ was relatively broad. In one experiment (entry 12 in Table 1), the ROP of a first batch of monomer (200 equiv.) was initiated with complex **6**/MeLi and after 3 min, a second batch of monomer (300 equiv.) was added to the reaction mixture and the polymerization reaction was continued for an additional 3 min. This resulted in chain extension

and the *Đ* of polymers was narrower than when one batch of 500 equiv. of monomer was converted (entries 11 and 12 in Table 1, Fig.2).

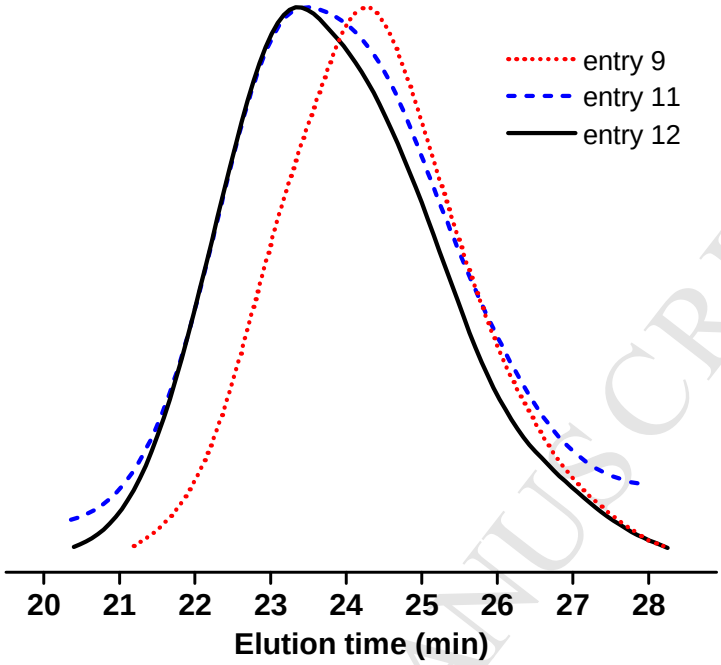


Fig. 2. GPC traces before and after the addition of a second batch of monomer (entries 9, 11 and 12 in Table 1)

2.2.2. ROP of ε-CL in the presence of BnOH

In the presence of BnOH, the current catalytic systems also showed high activity for the ROP of ε-CL and 100% yields of polymers were obtained in most cases (Table 2). It is worthy to note that the PCLs obtained in the presence of BnOH had much narrower molecular weight distributions than those obtained in the absence of BnOH, which suggested that the polymerization reactions under these conditions proceeded in a more controllable fashion. The BnOH not only served as an initiator but also as a chain transfer agent, leading to the decrease in the M_n of polymers. Increasing the amount of BnOH resulted in the decrease of yield and M_n of PCLs. For instance, the yields of PCLs with lower $[CL]_0/[BnOH]_0$ values could not reach 100% even though the polymerization reactions proceeded for a longer time and the M_n of PCLs were also much lower (entries 1 and 8 in Table 2). Varying the polymerization temperature had only a slight influence on the yields and M_n of the polymers; however, higher temperatures resulted in slightly broader molecular weight distributions (entries 3−5 in Table 2). With an increase of the $[CL]_0/[Zn]_0/[BnOH]_0$ ratio, the M_n of polymers increased gradually and the *Đ* of polymers changed slightly, in the range 1.08−1.58. A similar trend was observed for each complex.

Similarly, the catalytic activity and the M_n and $Đ$ of the polymers were only slightly affected by the substituent R^1 at the phenol ring and all the complexes (**5**−**7**) were highly active for the ROP of CL in the presence of BnOH. In order to verify the living character of the polymerization in the presence of BnOH, the ROP of a first batch of CL (200 equiv.) was initiated with complex **5**/MeLi/BnOH. After 3 min, a second batch of CL (100 equiv.) was added to the reaction mixture and the polymerization reaction was continued for an additional 3 min (entry 7 in Table 2). Extension of polymer chains was observed, but both M_n and $Đ$ of PCLs were lower than those of the PCLs obtained in a one-batch reaction involving 300 equiv. of monomer (entries 5−7 in Table 2 and Fig. 3).

Table 2 ROP of ε-CL catalyzed by zinc complexes **5**−**7**/MeLi in the presence of BnOH[a]

Entry	Complex	T (°C)	Time (min)	$[CL]_0/[Zn]_0/[BnOH]_0$	Yield[b] (%)	$M_{n,cal}$[c] (kg/mol)	$M_{n,obs}$[d] (kg/mol)	$Đ$[d]
1	**5**	30	90	50:1:1	31.3	1.89	1.58	1.24
2	**5**	30	3	100:1:1	100	5.82	6.77	1.08
3	**5**	30	3	200:1:1	100	22.9	9.86	1.18
4	**5**	60	3	200:1:1	100	22.9	10.4	1.51
5	**5**	90	3	200:1:1	100	22.9	9.22	1.45
6	**5**	30	3	300:1:1	100	34.4	21.6	1.44
7[e]	**5**	30	3+3	(200+100):1:1	100	34.4	15.6	1.31
8	**5**	30	30	300:1:5	65.7	4.61	3.17	1.07
9	**5**	30	3	500:1:1	99	56.6	21.7	1.27
10	**5**	30	3	1000:1:1	100	115.2	59.2	1.58
11	**6**	30	3	300:1:1	100	34.4	14.8	1.26
12	**6**	30	3	500:1:1	100	57.2	26.0	1.36
13	**7**	30	3	200:1:1	98.3	22.5	7.60	1.16
14	**7**	30	3	300:1:1	100	34.4	11.5	1.13
15	**7**	30	3	500:1:1	100	57.2	23.5	1.30

[a] Polymerization conditions: zinc complex: 0.02 mmol, [Zn] = 0.058 M, [MeLi]/[Zn] = 4:1, solvent: toluene.

[b] Determined by weight of isolated polymer.

[c] $M_{n,cal} = [CL]_0/[Zn]_0 \times 114.14 \times \text{Yield}\% + 108.14$, assuming one propagation chain per zinc atom.

[d] Measured by GPC in THF, calibrated with polystyrene standards and corrected using a correction factor of 0.56 [68].

[e] 200 equiv. of CL was added in the first stage, and after 3 min, the second batch of 100 equiv. of CL was added and the polymerization reaction was continued for an additional 3 min.

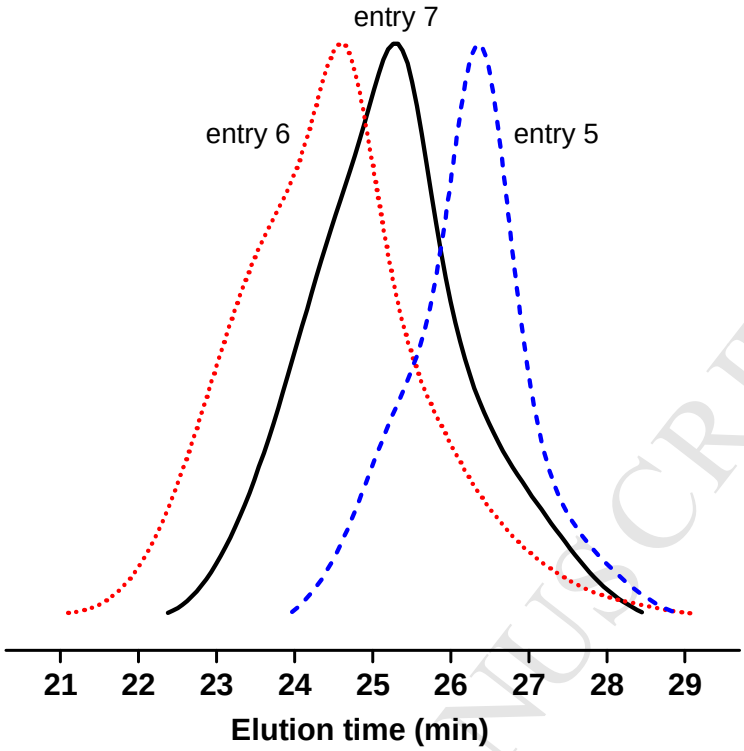


Fig. 3. GPC traces before and after the addition of a second batch of monomer in the presence of BnOH (entries 5−7 in Table 2)

2.3. Characterization of PCLs

2.3.1 NMR analysis

The PCLs produced by complex **5**/MeLi in the absence (entry 1 in Table 1) or presence (entry 8 in Table 2) of BnOH were analyzed by ^{1}H and ^{13}C NMR spectroscopy as representative samples to determine the terminal groups in the chain ends (Figs. 4 and 5). In the ^{1}H NMR spectra, the typical signals of characteristic methylene protons in the CL units around 1.36 (C***H***$_2$), 1.62 (C***H***$_2$), 2.28 (C***H***$_2$C=O), 4.03 (OC***H***$_2$) ppm were observed for both samples (Fig. 4). No signals corresponding to any end group could be found in the ^{1}H NMR spectra of PCLs obtained in the absence of BnOH. However, in the ^{1}H NMR spectra of PCLs obtained in the presence of BnOH, the triplet at 3.72 ppm was assigned to the protons of –C***H***$_2$OH groups in the chain ends and the resonances at 7.33 ppm and 5.09 ppm were assigned to the phenyl-***H*** and PhC***H***$_2$O– protons in the benzyl ester group, respectively.

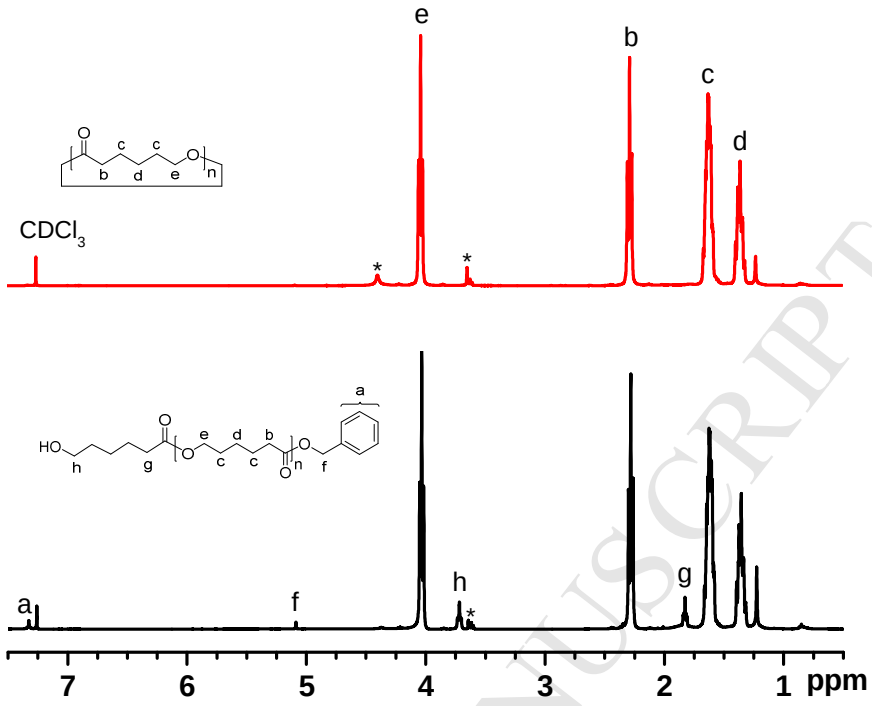


Fig. 4. ^{1}H NMR spectra of PCLs produced by complex **1**/MeLi in the absence (top, entry 1 in Table 1) or presence (bottom, entry 8 in Table 2) of BnOH. *, impurity.

The ^{13}C NMR spectra of both samples showed signals at 24.5 (***C***H_2), 25.5 (***C***H_2), 28.3 (***C***H_2), 34.1 (***C***H_2C=O), and 64.1 (O***C***H_2) ppm for the methylene-***C*** atoms and 173.5 ppm (***C***=O) for the carbonyl-***C*** atom in the CL repeating units (Fig. 5). There were no other signals in the ^{13}C NMR spectra of the PCLs obtained in the absence of BnOH. For the PCLs obtained in the presence of BnOH, the peaks at 128.5, 128.1 and 67.9 ppm were assigned to the phenyl-***C*** and methylene-***C*** (Ph***C***H_2O) atoms of the benzyl ester group, respectively. The resonances of the terminal ***C***H_2OH group in the chain ends appeared at 62.5 ppm. Compared with the main signals of repeating CL units, the signals of carbon atoms in the last CL unit were slightly shifted. In summary, both ^{1}H and ^{13}C NMR analyses indicated that the PCLs obtained in the absence of BnOH were mainly cyclic, whereas the polymers obtained in the presence of BnOH were linear PCLs with benzyl alcohol as an end group. This implies that the monomer inserted into the Zn−OBn bond formed after the addition of BnOH, thus initiating the polymerization. However, in the absence of BnOH, monomer insertion occurred into the Zn−L bond and was followed by repeated monomer insertion. The final intramolecular transesterification led to the formation of cyclic polymers.

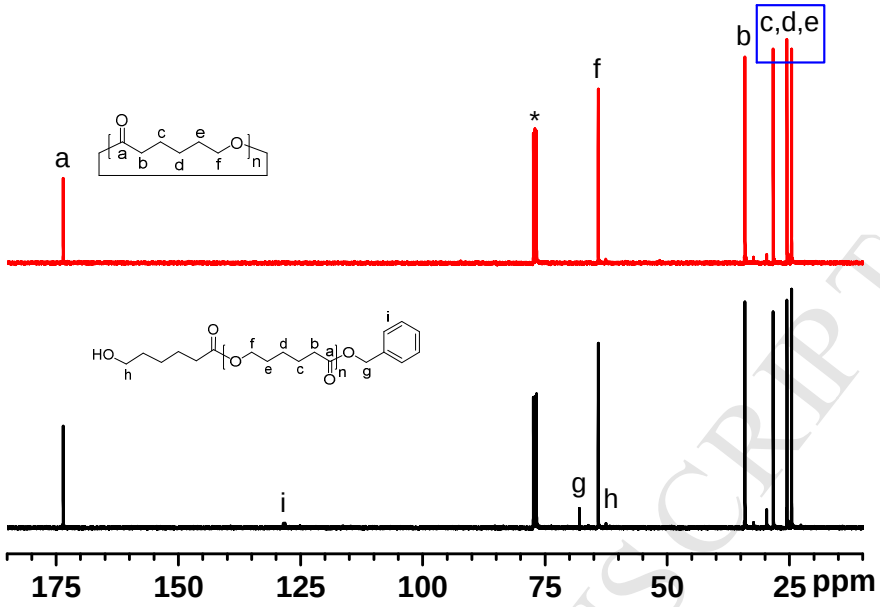


Fig. 5. ^{13}C NMR spectra of PCLs produced by complex **5**/MeLi in the absence (top, entry 1 in Table 1) or presence (bottom, entry 8 in Table 2) of BnOH

2.3.2 MALDI-TOF mass analysis

The MALDI-TOF mass spectra of PCLs obtained by complex **5**/MeLi in the absence (entry 1 in Table 1) or presence (entry 8 in Table 2) of BnOH are shown in Figs. 6 and 7. As shown in Fig. 6, the major signals at *m/z* 6200.8 (n = 54), 6314.8 (n = 55), 6428.7 (n = 56), *ect.* were attributed to the cyclic PCLs ($(CL)_n$) clustered with K^+ and the adjacent signals were separated by a CL repeating unit. There are two major series of signals in Fig. 7, located at *m*/*z* 2739.1 (n = 23), 2853.1 (n = 24), 2967.2 (n = 25), *etc.* and *m*/*z* 2755.0 (n = 23), 2869.1 (n = 24), 2983.2 (n = 25), *etc.*, which correspond to linear PCLs capped with BnO and hydroxyl end groups ($BnO(CL)_nOH$) clustered with Li^+ and Na^+, respectively. The successive series showed that there was a difference of 114 in *m*/*z* between every neighbor peaks, which corresponds to the molecular weight of the CL monomer. The other small peaks were probably produced by trace impurities generated during the polymerization process. Gratifyingly, the MALDI-TOF mass analysis was consistent with the results of NMR analysis.

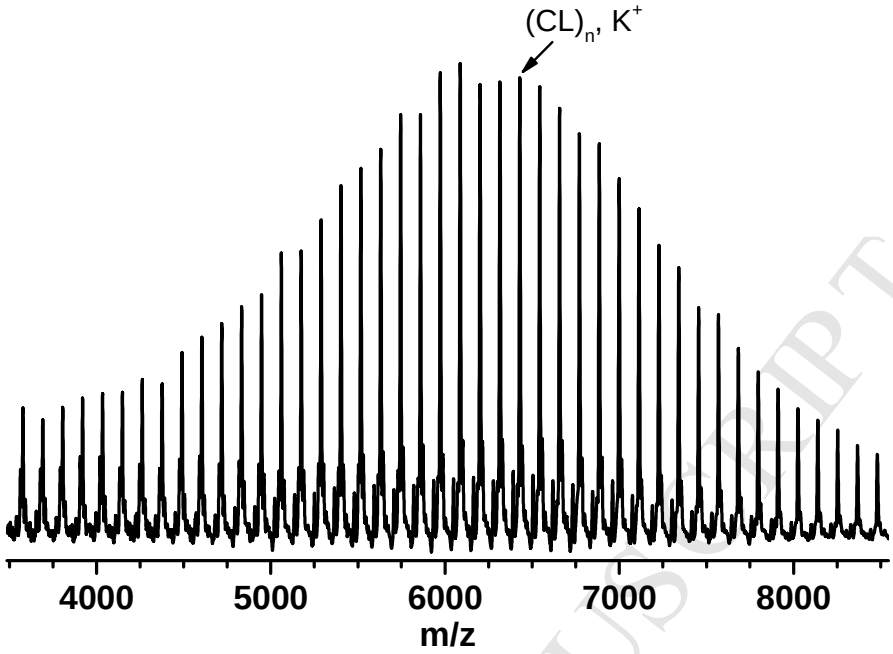


Fig. 6. MALDI-TOF mass spectrum of PCL samples prepared with complex **5**/MeLi (entry 1 in Table1)

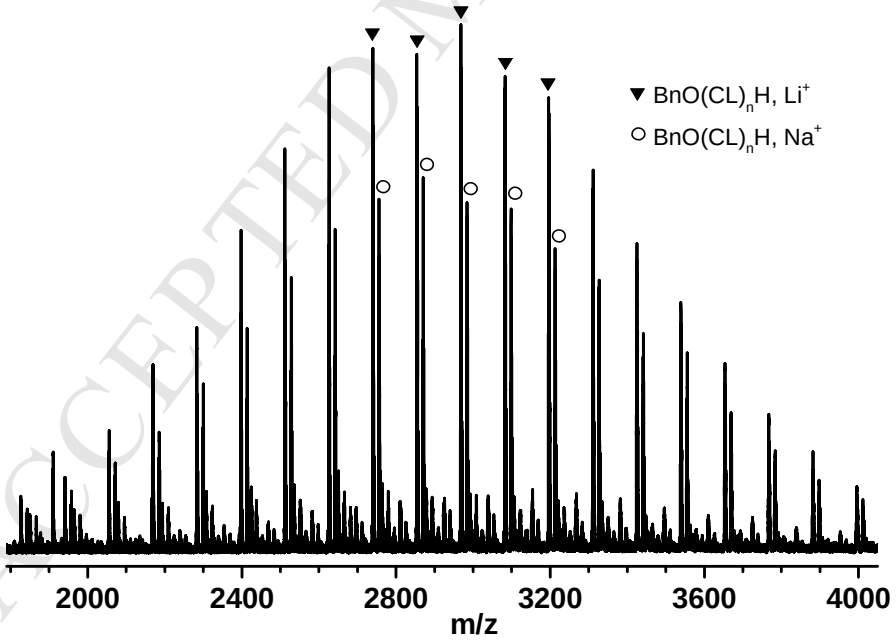


Fig. 7. MALDI-TOF mass spectrum of PCL samples prepared with complex **5**/MeLi in the presence of BnOH (entry 8 in Table 2)

2.3.3. Thermal properties

Differential scanning calorimetry (DSC) was applied to analyze the thermal properties of

cyclic and linear PCLs with similar molecular weight (entry 10 in Table 1 and entry 15 in Table 2). The DSC curves in Fig. 8 showed that the two samples had similar melting point around 55 °C (T_m, determined on the second heating scan). In order to determine the thermal stability of the polymers, a thermo-gravimetric analysis (TGA) of the cyclic and linear PCLs was carried out under a nitrogen atmosphere (Fig. 9). The results indicated that the cyclic PCLs exhibited better thermal stability than linear PCLs, with an initial degradation temperature of *ca.* 290 °C and 269 °C (5% weight loss), respectively. There were two thermal degradation stages observed for both samples and a similar complete degradation temperature was found at ca. 420 °C, with a fastest degradation rate at ca. 392 °C.

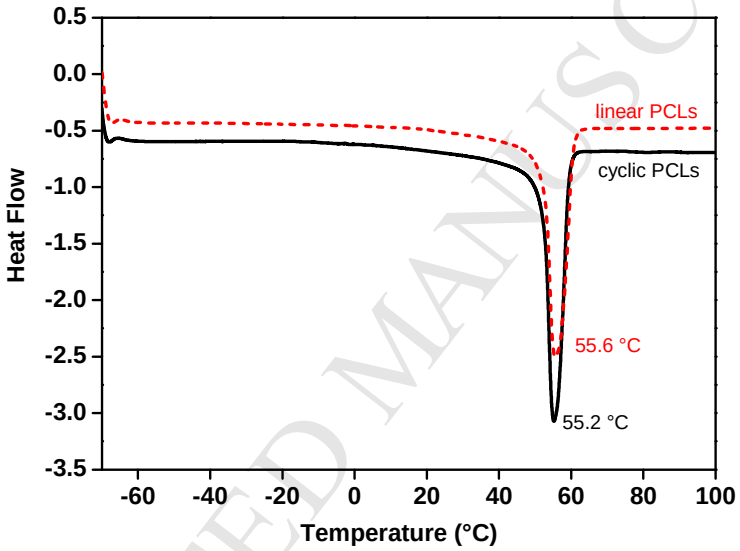


Fig. 8. DSC curves of PCLs obtained from entry 10 in Table 1 and entry 15 in Table 2

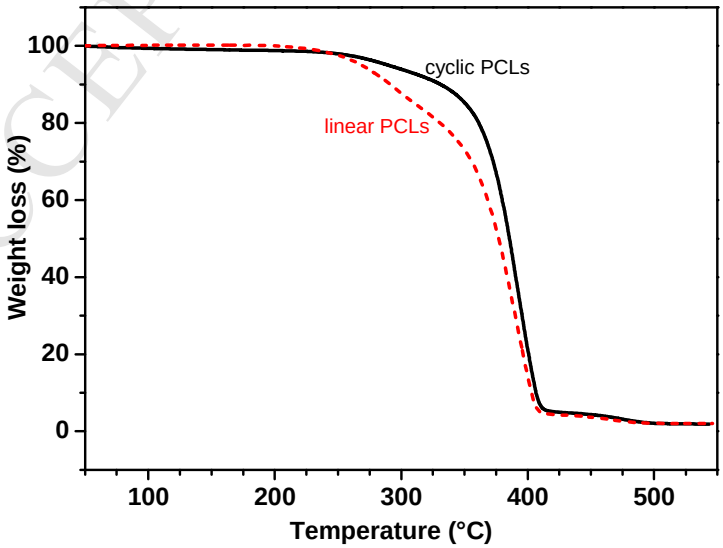


Fig. 9. TGA of polymers PCLs obtained from entry 10 in Table 1 and entry 15 in Table 2

3. Conclusions

Two series of tridentate ligands (imino-phenoxy ligands and amino-phenoxy ligands) and their corresponding zinc complexes **1**−**7** were synthesized and characterized. Complexes **1**−**4** bearing 2,6-bis(imino)phenol ligands were inactive for the ROP of ε-CL in the presence or absence of BnOH. However, in combination with 4 equiv. of methyllithium, complexes **5**−**7** with 2,6-bis(amino)phenol ligands were highly active for the ROP of ε-CL both in the presence and in the absence of BnOH. The "living" polymerization mode was observed in both situations and much narrower *Đ* of PCLs were obtained in the presence of BnOH. The structural analysis by NMR and MALDI-TOF mass spectra demonstrated that the PCLs obtained in the absence of BnOH were mainly cyclic, whereas the addition of BnOH led to the formation of linear PCLs. The cyclic and linear PCLs with similar molecular weight had a similar melting point, but the former had higher thermal stability.

4. Experimental section

4.1. General consideration and materials

All the manipulations of air- or moisture-sensitive compounds were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Hexamethylenetetramine, 4-methylphenol, 4-chlorophenol, 4-*tert*-butylphenol and sodium borohydride (from Sinopharm Chemical Reagent Co., Ltd.), and 2,6-dimethylaniline and 2,6-di-*iso*-propylaniline (from Aladdin) were directly used without further purification. Toluene from J&K Scientific Ltd. was purified by passing through solvent purification systems (MB-SPS, MBRAUN). Anhydrous zinc chloride ($ZnCl_2$) and methyllithium (MeLi, 1.6 M in diethylether) were purchased from J&K Scientific Ltd. Benzylalcohol (from J&K Scientific Ltd.) and ε-caprolactone (ε-CL, from Energy Chemical Ltd.) were dried over 5 Å molecular sieves and CaH_2, and further purified by vacuum distillation. All other chemicals were used directly without further purification unless otherwise stated. The starting materials, 4-methyl-2,6-diformylphenol, 4-chloro-2,6-diformylphenol and 4-*tert*-butyl-2,6-diformylphenol, were prepared from the corresponding 4-substituted phenols via the Dull reaction [69]. The 2,6-bis(imino)phenol ligands (**L1**–**L4**) were synthesized through the Schiff-base condensation reaction of 4-substituted 2,6-diformylphenols with 2,6-dimethylaniline or 2,6-diisopropylaniline according to the literatures [65-67].

^{1}H NMR and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker DMX-400 instrument in d_6-DMSO (for zinc complexes) or $CDCl_3$ (other compounds and PCLs) with TMS as the internal

standard. Splitting patterns are designated as follows: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet. FT-IR spectra were recorded on a Perkin-Elmer FT-IR 2000 spectrometer by using KBr disks in the range of 4000−400 cm^{-1}. Elemental analysis was performed on a Flash EA1112 microanalyzer and were the average of a minimum of two independent measurements. The molecular weight and molecular weight distribution of PCLs were determined by GPC using Waters 2414 series system in THF at 25 °C calibrated with polystyrene standards. MALDI-TOF mass spectra of PCLs were performed on a Bruker ultraflex TOF mass spectrometer equipped with a modified Nd:YAG laser (355 nm). The mass spectra were recorded in purified THF (2 mg ml^{-1}) at 25 °C in a linear mode using 2,5-dihydroxybenzoic acid (DHB) as the matrix. Thermogravimetric analysis (TGA) was carried out under nitrogen atmosphere on a PE TGA analyzer from 50 to 550 °C. The differential scanning calorimetry (DSC) analysis was recorded on a NETZSCH 214 Polyma DSC (NETZSCH, Germany) thermal analyzer under nitrogen atmosphere. The samples were first cooled from ambient temperature to –100 °C at 50 °C/min and then heated to 100 °C at 10°C/min to remove the thermal history, the samples were subsequently cooled to –100 °C at 10 °C/min and reheated to 100 °C at 10 °C/min.

*4.2. Synthesis of ligands **L5**–**L7***

*4.2.1. Synthesis of 2,6-bis(2,6-dimethylphenylaminomethyl)-4-methylphenol (**L5**)*

The compound **L1**, 2,6-bis(2,6-dimethylphenyliminomethyl)-4-methylphenol (1.52 g, 4.1 mmol) was dissolved in anhydrous methanol (25 ml). To the solution, 4.0 equiv. of sodium borohydride (0.62 g, 16.4 mmol) were slowly added at 0 °C in an ice-water bath. The reaction solution was slowly warmed to room temperature and stirred for 4 h. The color of solution changed from orange to light yellow and a pale yellow powder precipitated. A small amount of water was added slowly to quench the sodium borohydride in excess. Methanol was removed under reduced pressure and the residue was extracted with dichloromethane (30 ml × 4), and the combined organic extracts were washed with saturated brine (100 ml × 2) and then dried over anhydrous sodium sulfate and filtered. After all the volatiles were removed under reduced pressure, a pale yellow powder (**L5**) was obtained. Yield 1.45 g (94.7%). FT-IR (KBr, cm^{-1}): 3358, 3314, 2961, 2916, 2847, 1625, 1589, 1472, 1438, 1374, 1340, 1262, 1215, 1200, 1159, 1094, 1068, 1023, 990, 862, 839, 804, 774, 737. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.09 (d, 4 H, *J* = 7.6 Hz, Ar-***H***), 6.97 (s, 2 H, Ar-***H***), 6.96 (t, 2 H, *J* = 7.6 Hz, Ar-***H***), 4.17 (s, 4 H, C***H***$_2$NH), 2.43 (s, 12 H, C***H***$_3$), 2.30 (s, 3 H, C***H***$_3$). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 153.7, 144.9, 130.9,

129.0, 128.9, 128.4, 124.8, and 123.4 (Ar-***C***), 50.3 (***C***H_2NH), 20.34 and 18.3 (Ar-***C***H_3). Anal. Calcd. for $C_{25}H_{30}N_2O$ (374.53): C, 80.17; H, 8.07; N, 7.48; found: C, 79.66; H, 7.92; N, 7.30.

*4.2.2. Synthesis of 2,6-bis(2,6-dimethylphenylaminomethyl)-4-tert-butylphenol (**L6**)*

By using the similar procedure described for **L5**, ligand **L6** was obtained in the yield of 86.3% by the reduction reaction of compound **L2**. FT-IR (KBr, cm^{-1}): 3379, 3313, 2960, 2863, 1624, 1593, 1474, 1392, 1363, 1290, 1260, 1201, 1096, 1064, 1026, 984, 879, 820, 766. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.13 (s, 2 H, Ar-***H***), 7.05 (d, 4 H, *J* = 7.6 Hz, Ar-***H***), 6.96 (t, 2 H, *J* = 7.6 Hz, Ar-***H***), 4.19 (s, 4 H, C***H***$_2$NH), 2.41 (s, 12 H, C***H***$_3$), 1.30 (s, 9 H, C(C***H***$_3$)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 153.7, 144.9, 130.8, 129.0, 128.2, 125.4, 124.3, and 123.3 (Ar-***C***), 50.6 (***C***H_2NH), 33.9 (***C***(CH$_3$)$_3$), 31.5 (C(***C***H$_3$)$_3$), 18.4 (Ar-***C***H_3). Anal. Calcd. for $C_{28}H_{32}N_2O$ (416.61): C, 80.73; H, 8.71; N, 6.72; found: C, 80.81; H, 8.69; N, 6.75.

*4.2.3. Synthesis of 2,6-bis(2,6-dimethylphenylaminomethyl)-4-chlorophenol (**L7**)*

By using the similar procedure described for **L5**, ligand **L7** was obtained in the yield of 88.4% by the reduction reaction of compound **L3**. FT-IR (KBr, cm^{-1}): 3360, 3312, 2962, 2915, 2853, 1624, 1592, 1468, 1434, 1377, 1339, 1261, 1236, 1198, 1095, 1067, 1022, 913, 867, 839, 803, 775, 730. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.13 (s, 2 H, Ar-***H***), 7.07 (d, 4 H, *J* = 7.6 Hz, Ar-***H***), 6.95 (t, 2 H, *J* = 7.6 Hz, Ar-***H***), 4.14 (s, 4 H, C***H***$_2$NH), 3.68 (br, 2 H, CH$_2$N***H***), 2.40 (s, 12 H, C***H***$_3$). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 154.7, 144.4, 130.9, 129.0, 127.9, 126.5, 123.8, and 123.7 (Ar-***C***), 49.9 (***C***H_2NH), 18.3 (Ar-***C***H_3). Anal. Calcd. for $C_{24}H_{27}ClN_2O$ (394.94): C, 72.99; H, 6.89; N, 7.09; found: C, 72.79; H, 6.59; N, 7.06.

*4.3. Synthesis of Zinc Complexes (**1**–**7**)*

One equivalent of anhydrous Zinc chloride (0.25 g, 1.8 mmol) was added to a stirred solution of the corresponding ligand (1.8 mmol) in anhydrous ethanol (40 mL), and the reaction mixture was stirred at room temperature for 3 h. The resulting precipitate was collected by filtration, and the filtrate was washed three times with *n*-hexane then dried in vacuo to give the corresponding zinc complex. All the complexes were prepared in this manner.

Complex **1**: a yellow solid in 59.7% yield. FT-IR (KBr, cm^{-1}): 3448, 3041, 2969, 2921, 1634, 1605, 1588, 1543, 1498, 1471, 1386, 1351, 1324, 1277, 1232, 1184, 1093, 1070, 1047, 1000, 875, 810, 776. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.43 (s, 1 H, C***H***=N), 8.08 (s, 1H, C***H***=N), 7.56 (s, 1 H, phenol-***H***), 7.46 (s, 1 H, phenol-***H***), 7.25–7.06 (m, 6 H, Ar-***H***), 2.45 (s, 6 H, Ar-C***H***$_3$), 2.36

(s, 6 H, Ar-C***H***$_3$), 2.29 (s, 3 H, Ar-C***H***$_3$). ^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm): 172.4 (***C***H=N), 170.9 (***C***H=N), 165.7, 148.2, 147.6, 141.7, 135.1, 131.9, 130.1, 129.7, 129.5, 128.6, 126.7, 126.1, 121.9, and 116.8 (Ar-***C***), 19.7 (Ar-***C***H_3), 18.9 (Ar-***C***H_3), 18.8 (Ar-***C***H_3). Anal. Calcd. for $C_{25}H_{26}Cl_2N_2OZn$ (506.78): C, 59.25; H, 5.17; N, 5.53; found: C, 59.48; H, 5.66; N, 5.55.

Complex **2**: a yellow solid in 58.0% yield. FT-IR (KBr, cm^{-1}): 3443, 2961, 1635, 1540, 1465, 1370, 1329, 1296, 1234, 1185, 1091, 1058, 1029, 990, 885, 830, 781. ^{1}H NMR (400 MHz, DMSO): δ 10.43 (s, 1 H, Ar-O***H***), 8.74 (s, 1 H, C***H***=N), 8.68 (s, 1 H, C***H***=N), 8.09–7.85 (m, 2 H, Ar-***H***), 7.15–6.98 (m, 4 H, Ar-***H***), 6.79–6.39 (m, 2 H, Ar-***H***), 2.17–2.06 (m, 12 H, Ar-***C***H_3), 1.32 (d, *J* = 15.2 Hz, 9 H, C(C***H***$_3$)$_3$). ^{13}C NMR (101 MHz, DMSO), δ (ppm): 168.1 and 161.7 (***C***H=N), 146.8, 143.7, 141.3, 136.5, 128.14, 128.4, 128.05, 127.81, 127.76, 127.3, 125.3, 124.4, 123.0, 120.8, 119.7, and 116.1 (Ar-***C***), 34.0 (***C***$(CH_3)_3$), 31.1 and 30.9 (C(***C***H_3)$_3$), 18.12, 18.06, and 17.8 (***C***H_3). Anal. Calcd. for $C_{28}H_{32}Cl_2N_2OZn$ (548.86): C, 61.27; H, 5.88; N, 5.10; found: C, 61.04; H, 5.91; N, 5.00.

Complex **3**: a yellow solid in 46.4% yield. FT-IR (KBr, cm^{-1}): 3442, 3044, 2969, 1627, 1584, 1540, 1471, 1385, 1347, 1315, 1255, 1224, 1181, 1091, 1051, 885, 782. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.65 (s, 1 H, C***H***=N), 8.10 (s, 1 H, C***H***=N), 7.77 (d, *J* = 2.4 Hz, 1 H, Ar-***H***), 7.61 (d, *J* = 2.4 Hz, 1 H, Ar-***H***), 7.28 (t, *J* = 8.0 Hz, 1 H, Ar-***H***), 7.17–7.12 (m, 5 H, Ar-***H***), 2.43 (s, 6 H, Ar-C***H***$_3$), 2.40 (s, 6 H, Ar-C***H***$_3$). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 172.2, 169.8, 164.5, 147.3, 145.7, 139.8, 134.6, 131.9, 130.1, 129.9, 128.8, 127.1, 123.4, 120.9, and 117.8 (***C***H=N and Ar-***C***), 19.0, and 18.9 (Ar-***C***H_3). Anal. Calcd. for $C_{24}H_{23}Cl_3N_2OZn$ (527.19): C, 54.68; H, 4.40; N, 5.31; found: C, 54.25; H, 4.58; N, 4.73.

Complex **4**: an orange powder in 43.3% yield. FT-IR (KBr, cm^{-1}): 3462, 2964, 2922, 2866, 1628, 1579, 1537, 1456, 1361, 1325, 1293, 1257, 1182, 1104, 1055, 1009, 931, 856, 791, 758, 726. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.23 (s, 1 H, C***H***=N), 8.16 (s, 1 H, C***H***=N), 7.70, (s, 1 H, Ar-***H***), 7.55 (s, 1 H, C***H***=N), 7.40 (d, *J* = 8.0 Hz, 1 H, Ar-***H***), 7.35–7.27 (m, 5 H, Ar-***H***), 3.39 (sept, 1 H, *J* = 6.8 Hz, C***H***$(CH_3)_2$), 3.18 (sept, 1 H, *J* = 6.8 Hz, C***H***$(CH_3)_2$), 3.06 (sept, 2 H, *J* = 6.8 Hz, C***H***$(CH_3)_2$), 1.43 (d, 3 H, *J* = 6.8 Hz, CH(C***H***$_3$)$_2$), 1.40 (d, 3 H, *J* = 6.8 Hz, CH(C***H***$_3$)$_2$), 1.35 (d, 3 H, *J* = 6.8 Hz, CH(C***H***$_3$)$_2$), 1.28 (d, 12 H, *J* = 6.8 Hz, CH(C***H***$_3$)$_2$), 1.18 (d, 3 H, *J* = 6.8 Hz, CH(C***H***$_3$)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm): 172.8, 168.6, 166.7, 160.0, 146.0, 144.5, 143.0, 140.8, 139.7, 132.40, 130.8, 127.7, 124.7, 124.4, 124.1, 123.8, 123.4, 123.2, 122.7, 120.9, 118.5, and 117.6 (***C***H=N and Ar-***C***), 28.9, 28.3, 28.0, 27.9 (Ar-***C***H), 25.9 (Ar-***C***H_3), 24.0, 23.6, 23.5, 23.0, and 22.4 (***C***H_3). Anal. Calcd. for $C_{33}H_{42}Cl_2N_2OZn$ (618.99): C, 64.03; H, 6.84; N, 4.53; found: C, 64.16; H, 6.99; N, 4.53.

Complex **5**: a beige powder in 45.4% yield. FT-IR (KBr, cm^{-1}): 3443, 2918, 1633, 1483, 1378, 1260, 1186, 1155, 1099, 1025, 864, 769. ^{1}H NMR (400 MHz, DMSO), δ (ppm): 7.07–6.90 (m, 8 H, Ar-***H***), 4.31 (s, 4 H, C***H***$_2$NH), 2.45 (s, 12 H, Ar-C***H***$_3$), 2.24 (s, 3 H, Ar-C***H***$_3$). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 139.6, 131.8, 131.7, 131.1, 130.6, 130.1, 129.6, 129.3, 129.1, 128.7, 128.5, 128.4, 126.7, 124.6, and 121.1 (Ar-***C***), 52.3 (***C***H_2NH), 20.4, 18.6, 17.9. Anal. Calcd. for $C_{25}H_{30}Cl_2N_2OZn$ (510.81): C, 58.78; H, 5.92; N, 5.48; found: C, 58.74; H, 6.00; N,5.43.

Complex **6**: a light brown powder in 53.8% yield. FT-IR (KBr, cm^{-1}): 3444, 2960, 2864, 1637, 1486, 1441, 1363, 1299, 1213, 1181, 1103, 1027, 883, 821, 766. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.19 (s, 2 H, Ar-***H***), 6.92 (d, 4 H, *J* = 7.6 Hz, Ar-***H***), 6.74 (t, 2 H, *J* = 7.6 Hz, Ar-***H***), 4.40 (s, 4 H, C***H***$_2$NH), 2.46 (s, 12 H, Ar-C***H***$_3$), 1.26 (s, 9 H, C(C***H***$_3$)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 142.5, 138.9, 131.8, 129.6, 128.4, 127.2, 125.1, and 121.6 (Ar-***C***), 52.5 (***C***H_2NH), 34.0 (***C***$(CH_3)_3$), 31.4 (Ar-***C***H_3), 18.4 (C(***C***H_3)$_3$). Anal. Calcd. for $C_{28}H_{36}Cl_2N_2OZn$ (552.89): C, 60.83; H, 6.56; N, 5.07; found: C, 61.00; H, 6.07; N, 4.92.

Complex **7**: a beige solid in 40.9% yield. FT-IR (KBr, cm^{-1}): 3422, 3297, 3248, 2961, 2919, 1637, 1618, 1584, 1473, 1437, 1380, 1260, 1234, 1176, 1093, 1073, 1028, 871, 800, 768. ^{1}H NMR (400 MHz, DMSO), δ (ppm): 6.96–6.77 (m, 6 H, Ar-***H***), 6.39 (t, *J* = 7.6 Hz, 2 H, Ar-***H***), 4.48 (s, 4 H, C***H***$_2$NH), 2.06 (s, 12 H, Ar-C***H***$_3$). ^{13}C NMR (100 MHz, DMSO), δ (ppm): 144.1, 127.7, 120.4, 115.7 (Ar-***C***), 17.8 (Ar-***C***H_3). Anal. Calcd. for $C_{24}H_{27}Cl_3N_2OZn$ (531.22): C, 54.26; H, 5.12; N, 5.27; found: C, 54.52; H,5.84; N, 5.51.

4.4. Typical procedure for ring-opening polymerization of ε-CL

In a typical polymerization experiment, a suspension of zinc complex (0.02 mmol) in purified toluene was charged in a 100 mL sealed Schlenk flask with a magnetic stir bar under nitrogen. To this solution, a certain amount of methyllithium solution (MeLi, 0.04 mol/L in toluene, $[MeLi]_0/[\mathbf{1–4}]_0$ = 2 or $[MeLi]_0/[\mathbf{5–7}]_0$ = 4) was added dropwise at a temperature of –10 °C controlled with a thermostat. The mixture was slowly warmed to room temperature and stirred for 2 h; it consisted of a yellow solution and white precipitate. After that, BnOH (if needed) and ε-caprolactone were added to the above suspension in sequence at a certain temperature and the polymerization time was measured from that point. After polymerization, the reaction was quenched with deionized water (0.5 mL) and then poured into *n*-hexane to precipitate the polymer. The white precipitate was collected by filtration under reduced pressure, dissolved by a few drops of CH_2Cl_2 and then n-hexane (3ml) was added to precipitate the polymer; this process was repeated three times. The polymer was finally dried under vacuum.

Cyclic PCLs: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 4.04 (t, J = 6.8 Hz, 2n H, –OC***H***$_2$–), 2.28 (t, J = 7.6 Hz, 2n H, –C***H***$_2$C=O), 1.66–1.58 (m, 4n H, –C***H***$_2$–), 1.40–1.32 (m, 2n H, –C***H***$_2$–). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 173.5 (***C***=O), 64.1 (O***C***H$_2$), 34.1, 28.3, 25.5, and 24.5 (–***C***H$_2$–).

Linear PCLs: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.34–7.29 (m, 5 H, Ph-***H***), 5.09 (s, 2 H, PhC***H***$_2$O–), 4.03 (t, J = 6.8 Hz, 2n H, –OC***H***$_2$–), 3.72 (t, J = 6.4 Hz, 2 H, terminal –C***H***$_2$OH), 2.28 (t, J = 7.6 Hz, 2n H, –C***H***$_2$C=O), 1.67–1.58 (m, 4n H, –C***H***$_2$–), 1.39–1.32 (m, 2n H, –C***H***$_2$–). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 173.5 (***C***=O), 136.2, 128.5, 128.14, and 128.11 (Ph-***C***), 67.9 (Ph***C***H$_2$O), 64.1 (O***C***H$_2$), 34.0, 28.3, 25.5, and 24.5 (–***C***H$_2$–).

4.5. X-ray crystallographic analysis

Brown crystals of the zinc complex **4** suitable for single X-ray diffraction analysis were obtained by slow diffusion of *n*-hexane into their ethanol solution. The crystallographic data for **4** were collected at 296 K on a Bruker Smart Apex II CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structure was solved by direct methods and refined by full-matrix least-squares on F2. All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were placed in calculated positions. The crystallographic data have been deposited within the Cambridge Crystallographic Data Center (CCDC number 1868711) and are accessible free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for complex 4. $C_{33}H_{42}Cl_2N_2OZn$, M_w = 618.95 g mol^{-1}, T = 293(2) K, monoclinic crystal system, space group P21/n, a = 15.0619(12) Å, b = 16.7063(13) Å, c = 18.6514(12) Å, $\alpha = \gamma$ = 90 º, β = 92.587(7) º, V = 4688.4(6) Å^3, Z = 4, D_{calc} = 0.877 Mg m^{-3}, μ = 0.656 mm^{-1}, F(000) = 1304, 8543 reflections collected, 4983 unique which were used in all calculations. GOF = 1.033, Final R indices [I>2σ(I)] R_1 = 0.0523, wR_2 = 0.1350, R indices (all data) R_1 = 0.0933, wR_2 = 0.1609. Largest diff. peak and hole 0.452 and –0.267 e Å^{-3}.

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Highlights

- 2,6-Bis(amino)phenol ligands and their zinc complexes were synthesized.
- In combination with MeLi, zinc complexes were highly efficient for the ROP of ε-CL.
- The PCLs obtained in the absence of BnOH were mainly cyclic.
- The linear PCLs were produced in the presence of BnOH.