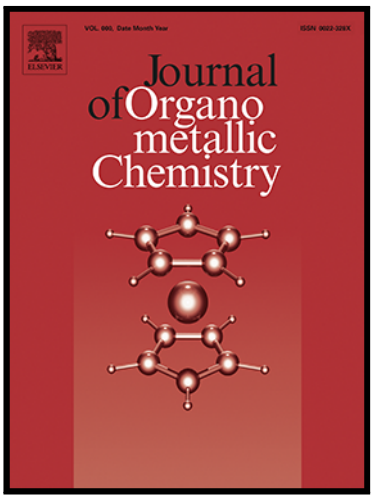


# The Homoleptic Bis($\beta$-quinolylenolate) Zinc Catalysts for the Ring-opening Polymerization of $\varepsilon$-Caprolactone: Kinetics and Mechanism

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Highlight:

- Five homoleptic bis(β-quinolylenolate) zinc complexes were synthesised and characterized.
- All bis(β-quinolylenolate) zinc complexes exhibited good activity toward the ROP of ε-CL, where their catalytic activity was significantly affected by different substituents of ligand.
- The resultant polymers contain three linear structures which are linear PCL capped with BnO- or MeO- as the major component and capped with ligand as the minor component.
- The kinetic studies revealed that polymerization reactions initiated by [Zn]/BnOH system followed first-order and the probable mechanisms have been proposed.



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# The Homoleptic Bis(β-quinolylenolate) Zinc Catalysts for the Ring-opening Polymerization of ε-Caprolactone: Kinetics and Mechanism

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**ABSTRACT** A series of bis(β-quinolylenolate) zinc complexes ($L_2Zn$) **1-5** (L = [(2-$C_9H_6N$)–CH=C(R)–O–], R = $^t$Bu (**1**), Ph (**2**), *o*-tolyl (**3**), *p*-tolyl (**4**), *p*-OMePh (**5**)), have been structurally characterized and used as initiators in the ring-opening polymerization (ROP) of ε-caprolactone (ε-CL). The molecular structures of **3** and **4** were defined by X-ray diffriaction analyses, showing a distorted-tetrahedral geometry around the zinc center. All complexes are stable in air and high temperature, and they efficiently catalyzed the ROP of ε-CL high conversions in a controlled manner. Kinetic studies showed that polymerization reaction catalyzed by **1-5** proceeded with first-order dependence on the monomer and their catalytic activity is correlated with the substituents on the Ar moieties of the ligand. Complex **3** displayed the higher activity than others, might be due to its stronger electron-donating nature of the *ortho*-Me group on the aryl ring (Ar) of the enamino framework than that of orther sites, however, complex **2** without substituent on the Ar group exhibited poor activity in the polymerization reaction. The resultant PCL was a mixture of linear BnO- and MeO-capped structures.

**Key words** Bis(β-quinolylenolate) zinc complexes; Catalysis; Ring-opening polymerization; ε-Caprolactone

## 1. Introduction

Today, Biodegradable materials are widely used in medical, biological and architectural fields due to their degradability and reproducibility [1-5]. It has been found that metal-catalyzed ring-opening polymerization (ROP) is the most effective method for the synthesis of biodegradable materials, especially polycaprolactone (PCL) [6-15]. Although many metal-based catalyst systems have been developed for the ROP of cyclic esters, zinc complexes have been widely preferable due to their low toxicity, highstability, biocompatibility, and easy of synthesis [16-22]. A number of effective zinc based complexes containing a variety of ligands with different steric and electronic properties have been established in the ROP of cyclic esters. The ligand structure and its coordination mode to the metal play a very crucial role in the polymerization, such as affecting the molecular weight and molecular weight distribution in the polymerization process.

Zn complexes coordinated with [N,O] ligands are known to effectively catalyze the ROP of cyclic esters. Many reports have focused on heteroleptic Zn alkoxides of $[LZn(\mu\text{-}OR)]_2$-type structure due to their high catalytic activity for ROP of cyclic esters [23-28]. Notably, homoleptic Zn complexes of $L_2Zn$-type commonly showed poor activity toward the ROP of cyclic esters, however, they could better control the process of polymerization to obtain polymer with narrow molecular weight distributions [29-31]. Gendre et al. prepared a family of di-nuclear phenoxyamidine Zn complexes as initiators for the ROP of rac-lactide, where the corresponding structure is $[LZnEt]_2$-type (L = phenol-amidine), and experimental $M_n$ of obtained PLA was in good accordance with theoretical $M_n$ (Chart 1) [32]. Lin et al. investigated the homo- and heteroleptic pyrazolonate zinc analogues (Chart 1) toward the ROP of cyclic esters, where the homoleptic complexes of $L_2Zn$-type were inactive for *rac*-lactide polymerization (Chart 1) [33]. Jones et al. investigated the mono- and dimeric Zn(II)-Schiff-base complexes for the ROP of cyclic esters and polymer degradation (Chart 1), where all of the complexes could catalyze LA polymerization in bulk at high temperatures and obtained PLAs showed broad dispersities (PDI = 1.83–2.04) [34]. Ejfler et al. reported a family of homo- and heteroleptic zinc complexes supported by aminonaphtholate ligands for the ROP of lactides (Chart 1); they confirmed that the catalytic activity of heteroleptic $[LZn(\mu\text{-}OR)]_2$ in the ring-opening polymerization (ROP) of lactides was lower than those of an in situ alcoholysis systems of $(LZnEt)_2$/ROH or $L_2Zn$/ROH based on the experimental and theoretical study, and the homoleptic complexes of $L_2Zn$ type generally exhibit better control over ROP reaction than those of heteroleptic zinc complexes $[LZn(\mu\text{-}OR)]_2$ (L = aminonaphtholate ligands) [35].

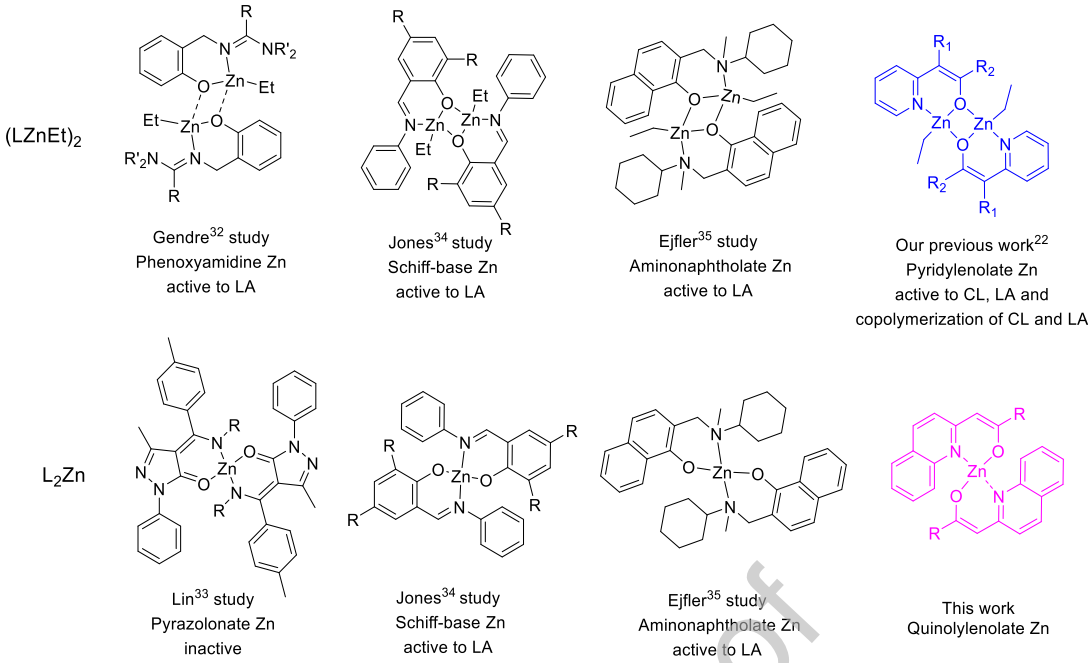



**Chart 1**. Different types of heteroleptic $(LZnEt)_2$ and homoleptic zinc $L_2Zn$ complexes

Besides, ligand structure is key component for metal initiators. In recent years, several groups reported on zinc complexes supported by secondary amine [36], imine [31], and tertiary amine ligands [37], respectively. Many report have focus on the complexes containing a central secondary amine or imine ligand due to their more reactive and better control over ROP reaction than tertiary amines based complexes [38]. However, few studies have involved the zinc complexes bearing quinolyl-enolate ligands where the imine donor is part of a heteroaromatic ring system.

Recently, we have demonstrated that the β-pyridylenolate zinc complexes with $[LZnEt]_2$-type structure as catalysts exhibit high activities toward the ROP of both ε-caprolactone (ε-CL) and lactides (LA) (Chart 1, our previous work), and their catalytic behavior could be able to tailor by varying the substituents on the β-pyridylenolate ligand to obtain homo- and copolymers with different thermal properties [22]. As part of our studies on β-pyridylenolate zinc complexes, herein we reported the synthesis and characterization of bis(β-quinolylenolate) zinc complexes with $[L_2Zn]$-type structure as catalysts for the ROP of ε-CL and LA, to investigate the substituents effects of the complexes on the propagation rate of the ROP. In the ROP of ε-CL, complex **3** having an *ortho*-methyl group in aryl ring (Ar) of enamino framework exhibited the higher activity than other analogue. This work elucidates the influence of substituents on the catalytic properties based on kinetic studies and insights into the mechanism for the ROP of ε-CL. However, those Zn complexes are almost inactive to LA.

## 2. Experimental

### *2.1. General considerations*

All experimental operations and reactions were performed under nitrogen protection, and standard Schlenk technology was used. The solvents used in the reactions (toluene and THF, n-hexane) were dried and distilled with sodium wires, and water was further removed in the storage bottles of solvent containing activated molecular sieves (4 Å). Both $CDCl_3$ purchased from Energy Chemical and ε-caprolactone purchased from Alfa Aesar were dried with $CaH_2$ for 24 h, then distilled under vacuum, and finally stored over activated molecular sieves(4 Å). Both n-Butyllithium (2.5 M solution in hexane) and $ZnEt_2$ (1.0 M solution in hexane) were purchased from Energy Chemical.

### *2.2. Measurements*

$^1H$ and $^{13}C$ NMR spectra of all compounds were determined using DRX-600 instruments. The crystal structure and data of complexes were collected using the D8 Venture -Single Crystal X-ray Diffraction instruments. Elemental analyses were performed on a Vario EL III instrument. The molecular weight and PDI of the polymer were measured with TOSOH-HLC-8220 GPC and Waters 2410 at 40 °C using THF as the eluent (1 mL·min$^{-1}$), and calibrated with polystyrene standards. Ligands **HL$^1$–HL$^5$** were prepared according to the published methods [39].

### *2.3. Synthesis of Bis(β-quinolylenolate) Zinc complexes*

#### *2.3.1. Synthesis of **1***

$ZnEt_2$ (1.1 mL of a 1.0 M solution in hexane, 1.1 mmol) was added to the solution of **HL$^1$** (0.454 g, 2 mmol) in THF (10 mL). The yellow solution was stirred at room temperature for 2 h. After that, the solvent was removed by vacuum and the solids washed with hexane to give a yellow solid. Yield: 0.46 g, 89%. Anal. calcd for $C_{30}H_{32}N_2O_2Zn$: C, 69.59; H,

6.19; N, 5.39. Found: C, 69.56; H, 6.23; N, 5.41. $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.76 (d, $J$ = 8.9 Hz, 1H, quinolone-*H*), 7.47 (d, $J$ = 7.4 Hz, 1H, quinolone-*H*), 7.36 (dd, $J$ = 18.8, 7.8 Hz, 2H, quinolone-*H*), 7.16 (d, $J$ = 7.0 Hz, 1H, quinolone-*H*), 7.00 (d, $J$ = 8.9 Hz, 1H, quinolone-H), 5.67 (s, 1H, -C*H*), 1.27 (s, 9H, -(C$H_3$)$_3$). $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ 191.12, 160.68, 145.31, 136.90, 130.06, 127.60, 125.05, 124.76, 123.98, 123.68, 91.60, 40.70, 29.15.

*2.3.2. Synthesis of **2***

Complex **2** was synthesized using the same procedure as for complex **1**. The reaction of **HL$^2$** (0.492 g, 2 mmol) with $ZnEt_2$ (1.1 mL of a 1.0 M solution in hexane, 1.1 mmol) in THF (10 mL) yielded a pale yellow solid. Yield: 0.47 g, 85%. Anal. calcd for $C_{34}H_{24}N_2O_2Zn$: C, 73.14; H, 4.41; N, 5.01. Found: C, 73.19; H, 4.34; N, 5.02. $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.97 (dd, $J$ = 7.2, 2.8 Hz, 1H, quinolone-*H*), 7.92 – 7.83 (m, 1H, quinolone-*H*), 7.62 – 7.48 (m, 1H, quinolone-*H*), 7.41 – 7.36 (m, 1H, Ar*H*), 7.19 – 7.17 (m, 1H, Ar*H*), 6.22 (s, 1H, -C*H*). $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ 176.32, 160.44, 145.36, 141.80, 137.52, 130.79, 129.52, 128.21, 127.88, 127.06, 125.37, 124.80, 124.22, 123.67, 94.93.

*2.3.3. Synthesis of **3***

Complex **3** was synthesized using the same procedure as for complex **1**. The reaction of **HL$^3$** (0.520 g, 2 mmol) with $ZnEt_2$ (1.1 mL of a 1.0 M solution in hexane, 1.1 mmol) in THF (10 mL) yielded a pale yellow crystals. Yield: 0.53 g, 91%. Anal. calcd for $C_{36}H_{28}N_2O_2Zn$: C, 73.82; H, 4.86; N, 4.71. Found: C, 73.79; H, 4.82; N, 4.78. $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.89 (d, $J$ = 8.8 Hz, 1H, quinolone-*H*), 7.72 (d, $J$ = 8.5 Hz, 1H, quinolone-*H*), 7.58 (d, $J$ = 7.8 Hz, 1H, quinolone-*H*), 7.49 (d, $J$ = 7.3 Hz, 1H, quinolone-*H*), 7.45 (s, 1H, Ar*H*), 7.17 (t, $J$ = 7.5 Hz, 2H, Ar*H*), 7.07 (d, $J$ = 8.9 Hz, 1H, Ar*H*), 5.72 (s, 1H, -C*H*), 2.49 (s, 3H, -C$H_3$Ph). $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ 180.34, 160.17, 145.10, 142.93, 137.59, 135.42, 130.50 (d, $J$ = 3.7 Hz), 128.15, 127.86, 127.68, 125.38, 125.30, 124.38, 124.25, 123.79, 98.21, 20.30.

*2.3.4. Synthesis of **4***

Complex **4** was synthesized using the same procedure as for complex **1**. The reaction of **HL$^4$** (0.520 g, 2 mmol) with $ZnEt_2$ (1.1 mL of a 1.0 M solution in hexane, 1.1 mmol) in THF (10 mL) yielded a pale yellow crystals. Yield: 0.52 g, 89%. Anal. calcd for $C_{36}H_{28}N_2O_2Zn$: C, 73.83; H, 4.82; N, 4.74. Found: C, 73.79; H, 4.82; N, 4.78. $^1$H NMR (600 MHz, $CDCl_3$): δ 7.86 (dd, $J$ = 17.6, 8.5 Hz, 1H, quinolone-*H*), 7.53 (dd, $J$ = 14.9, 8.1 Hz, 1H, quinolone-*H*), 7.34 – 7.29 (m, 1H, quinolone-*H*), 7.17 (dd, $J$ = 18.3, 8.2 Hz, 1H, Ar*H*), 6.20 (s, 1H, -C*H*), 2.37 (s, 3H, -C$H_3$Ph). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 176.25, 160.30, 145.28, 139.51, 138.81, 137.20, 130.58, 128.77, 127.68, 126.92, 125.15, 124.69, 123.91, 123.51, 94.34, 21.39.

*2.3.5. Synthesis of **5***

Complex **5** was synthesized using the same procedure as for complex **1**. The reaction of **HL$^5$** (0.552 g, 2 mmol) with $ZnEt_2$ (1.1 mL of a 1.0 M solution in hexane, 1.1 mmol) in THF (10 mL) yielded a pale yellow crystals. Yield: 0.57 g, 93%. Anal. calcd for $C_{36}H_{28}N_2O_4Zn$: C, 69.99; H, 4.56; N, 4.49. Found: C, 69.97; H, 4.57; N, 4.53. $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.95 (d, $J$ = 8.8 Hz, 2H, quinolone-*H*), 7.85 (d, $J$ = 9.0 Hz, 1H, quinolone-*H*), 7.52 (d, $J$ = 9.0 Hz, 2H, quinolone-*H*), 7.34 (dd, $J$ = 9.6, 5.6 Hz, 1H, quinolone-*H*), 7.15 (s, 2H, quinolone -*H*), 6.89 (d, $J$ = 8.8 Hz, 4H, Ar*H*), 6.17 (s, 1H, -C*H*), 3.83 (s, 3H, -OC$H_3$Ph). $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ 175.90, 160.80, 160.28, 145.32, 137.09, 134.12, 130.56, 128.55, 127.67, 125.08, 124.71, 123.79, 123.44, 113.30, 93.78, 55.35.

*2.4. ε-CL polymerization catalyzed by complexes **1-5***

Complex **3** was used as an example of a typical polymerization procedure in the presence of 1 equiv. BnOH (Table 3, entry 3). In a 50 mL Schlenk bottle, complex **3** (29 mg, 0.05 mmol) was completely dissolved in 4.5 mL toluene, and 1 equivalent of benzyl alcohol (0.5 mL, 0.1 M in toluene, 0.05 mmol) was added. The solution was stirred for 30 min at 100 ℃. Then ε-CL (5 mmol, 0.5 mL) was added for stir. After the required time (2 hours), 3 mL of quencher (95% MeOH and 5% HCI) was dropwise added to quench the polymerization. Pour the resulting solution of the schlenk bottle into cold methanol (100 mL) and stir 12h. The liquid was filtered and washed multiple times with methanol, and finally a white polymer was obtained after dried under vacuum at 35 ℃ for 24 h.

*2.5. X-ray crystallography*

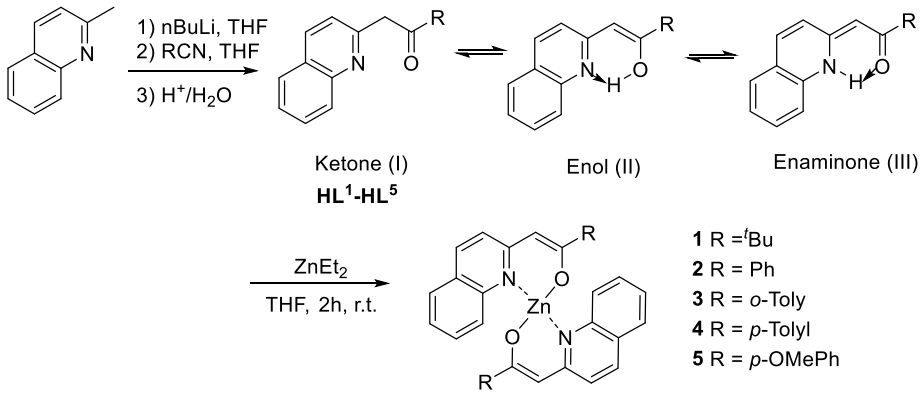
Diffraction data of complexes **3** and **4** were collected on a D8 Venture -Single Crystal X-ray Diffraction instruments with Mo Kα radiation($\lambda$ = 0.71073 Å). A total of $N$ reflections were collected by using the $\omega$ scan mode. The structures were solved by direct methods and refined against $F^2$ by full matrix least squares using SHELXL [40]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in the calculated positions. Crystal data and experimental details of all complexes are shown in Table S1. CCDC reference numbers 2012511 for **3**, and 2012510 for **4**.

## 3. Results and discussion

*3.1. Synthesis and characterization of zinc complexes **1–5**.*

The synthetic route of the bis(β-quinolylenolate) zinc complexes ($L_2Zn$) **1-5** is shown in scheme 1. The proligands β-quinolylenol **HL$^1$-HL$^5$** were obtained by the reaction of quinolyl lithium with nitriles followed by acidic hydrolysis [39]. Under mild conditions, the zinc complexes **1**–**5** was obtained by stoichiometric reaction of $ZnEt_2$ with 2 equivalents of ligands **HL$^1$-HL$^5$** in THF for an appropriate time with high yields (85%-93%), respectively. All zinc complexes were characterized by $^1$H and $^{13}$C NMR spectroscopy and elemental analysis.

Compared to ligands **HL$^1$–HL$^5$**, the $^1$H NMR spectra of **1**–**5** showed the absence of a singlet resonance appearing in low




**Scheme 1.** Synthesis of homoleptic bis(β-quinolylenolate) zinc catalysts **1**-**5**

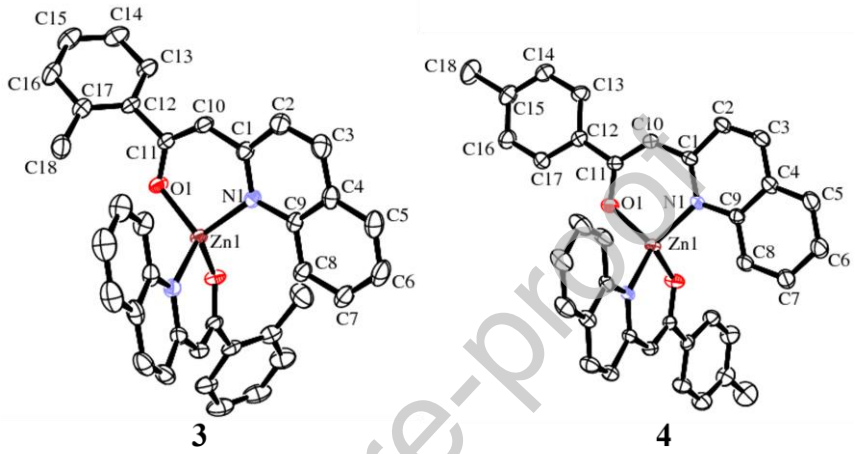



**Fig. 1.** X-ray structures of **3** and **4** with thermal ellipsoids represented at the 30% probability level. Hydrogen atoms are omitted for clarity

field regions ($\delta$ 14.95 to 15.70 ppm), confirmed the loss of OH functionality on coordination to the Zn center. The $^{1}$H and $^{13}$C NMR spectra of the zinc complexes **1**–**5** show one set of resonance for the methine C*H* resonances of the ketiminate framework at *ca*. 5.67-6.22 and 91.60–98.21 ppm, respectively, which confirmed that these zinc complexes are very pure. All complexes have a good solubility in THF and relatively low solubility in toluene at room temperature, however, their solubility increases obviously with rising temperature in toluene. In addition, these complexes are quite stable in the air and heating [41]. For example, when complex **3** was left in the air for three days, and then heated to 200-300 °C under a vacuum for about one hour, its $^{1}$H NMR spectrum was almost the same with that of untreated compound except for the solvent residual (Figure S11).

**Table 1**
Selected bond lengths (Å) and angles (°) for complexes **3** and **4**

| | **3** | **4** |
|---|---|---|
| Zn(1)-O(1) | 1.9225(13) | 1.9140(15) |
| Zn(1)-N(1) | 2.0120(15) | 1.9989(17) |
| O(1)-C(11) | 1.368(3) | 1.301(2) |
| C(10)-C(11) | 1.431(3) | 1.371(3) |
| O(1)-Zn(1)-N(10) | 98.82(6) | 99.37(7) |

X-ray quality crystals of complexes **3** and **4** were obtained from a concentrated THF solution at room temperature. Their molecular structures are displayed in Fig. 1, and the selected bond lengths and angles are listed in Table 1. For the complexes of **3** and **4**, the Zn atom is coordinated by two nitrogen atoms and two oxygen atoms to form a distorted-tetrahedral geometry. The bond angles of N–Zn–O for these complexes are in the range of 98.82(6)–99.37(7)°, narrower than the regular tetrahedral bond angle of 109.28°. The bond lengths of Zn–N and Zn–O in these compounds are in the range of 1.9989(17)–2.012(15) and 1.9140(15)–1.9225(13) Å, which are within the range expected [42].

We tried to prepare the LZnEt-type complexes and inhibit the formation of the $L_2$Zn-type complexes. But we failed to isolate the LZnEt-type products whether by changing the solvent or by controlling the reaction time and temperature. It is different from our previous research, in which the LZnEt-type complexes were easy obtained in high yields when using the β-pyridylenol ligands as the substrates instead of the β-quinolylenols [22]. It might be owing to the β-quinolylenols framework has stronger conjugation effect than β-pyridylenol.

### *3.2. Ring opening polymerization of ε-CL*

We firstly examined the effects of temperature and solvent in the ROP of ε-CL by using **2-4** with the $[CL]_0$:$[Zn]_0$:$[BnOH]_0$

**Table 2**
Effects of temperature and solvents on the ROP of ε-CL catalyzed by complexes **2-4**

| Entry | Complex | [ε-CL]:[Zn]:[BnOH] | Solvent | Time/h | T/°C | Conv.[a] (%) | Mn,calc[b] | Mn,GPC[c] | PDI[d] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | **2** | 100:1:1 | Tol | 12 | 80 | 71 | 8212 | 2135 | 1.20 |
| 2 | **3** | 100:1:1 | Tol | 5 | 80 | 98 | 11294 | 3075 | 1.24 |
| 3 | **3** | 100:1:1 | Tol | 10 | 50 | 38 | 4445 | 3487 | 1.04 |
| 4 | **4** | 100:1:1 | DCM | 8 | 25 | trace | | | |
| 5 | **4** | 100:1:1 | THF | 8 | 40 | trace | | | |
| 6 | **4** | 100:1:1 | Tol | 8 | 40 | 15 | - | - | - |
| 7 | **4** | 100:1:1 | Tol | 8 | 80 | 84 | 9595 | 3358 | 1.20 |
| 8 | **4** | 100:1:1 | Tol | 12 | 80 | 89 | 10267 | 3445 | 1.18 |

[a] Determined by $^1$H NMR spectroscopy. [b] $M_{n,calc}$ = 114.14 × ($[CL]_0$/ $[BnOH]_0$) × conv. (%) + 108.13. [c] Obtained from GPC analysis in THF using polystyrene standards and multiplied by 0.56. [d] Obtained from GPC analysis

**Table 3**
Effects of concentration of ε-CL and exogenous alcohol on the polymerization catalyzed by complexes **1-5** at 100 °C[a]

| Entry | Complex | [ε-CL]:[Zn]:[ROH] | Time/h | Conv.[b] (%) | Mn,calc[c] | Mn,GPC[d] | PDI[e] |
|---|---|---|---|---|---|---|---|
| 1 | **1** | 100:1:1 | 12 | 96 | 11100 | 3240 | 1.22 |
| 2 | **2** | 100:1:1 | 12 | 85 | 9810 | 3290 | 1.20 |
| 3 | **3** | 100:1:1 | 2 | 91 | 10495 | 3168 | 1.17 |
| 4 | **4** | 100:1:1 | 12 | 95 | 10951 | 3489 | 1.15 |
| 5 | **5** | 100:1:1 | 12 | 96 | 11066 | 3175 | 1.16 |
| 6 | **3** | 100:1:0 | 2 | 58 | 6620 | 1386 | 1.76 |
| 7[f] | **3** | 100:1:1 | 2 | 61 | 7022 | 3151 | 1.11 |
| 8 | **3** | 50:1:1 | 1 | 99 | 5758 | 3791 | 1.15 |
| 9 | **3** | 200:1:1 | 7 | 80 | 18370 | 3754 | 1.17 |
| 10 | **3** | 200:1:2 | 7 | 97 | 11180 | 4183 | 1.14 |
| 11 | **3** | 400:1:1 | 14 | 32 | 14718 | 3916 | 1.20 |
| 12 | **3** | 400:1:4 | 14 | 65 | 7527 | 4748 | 1.17 |

[a] Unless otherwise specified, the polymerizations were carried out in toluene and ROH used in the polymerization are BnOH. [b] Determined by $^1$H NMR spectroscopy. [c] $M_{n,calc}$ = 114.14 × ($[CL]_0$/ $[OH]_0$) × conv. (%) + $M_{ROH}$ or Mn,calcd= 114.14 × ($[\varepsilon\text{-CL}]_0$/$[Zn]_0$) × conv. (%)(Entry 6). [d] Obtained from GPC analysis in THF using polystyrene standards and multiplied by 0.56. [e] Obtained from GPC analysis. [f] ROH is $^i$PrOH.

= 100:1:1 system (Table 2). At the same temperature, the complex **2** exhibits lower catalytic activity than that of complex **3** and **4** under the same conditions (Table 2, entries 1-2 and 8). A comparison between **2** and **3** showed that the substituent of the ligand backbone had great influence on catalytic activity. At the different temperatures, using **3** as an initiator, when polymerization was performed at 50 °C, the monomer conversion of 38% in 10 h was significantly lower than that of 98% at 80 °C in 5 h (Table 2, entry 3). It showed the temperature highly affected the catalytic efficiency in the polymerization.

Complex **4** was used as an example to investigate the influence of the solvent and temperature on the polymerization of ε-caprolactone (Table 2, entries 4-8). The results showed that the polymerization reaction did not proceed in DCM and THF when the temperature was lower than 40 °C in 12 h (Table 2, entries 4-5). When polymerization was performed at 80 °C in toluene within 8 or 12 h, respectively, the monomer conversion was not improved greatly with the extension of time (Table 2, entries 6-8). Therefore, the conversion significantly increased with the raising temperature in the same time. PCLs were produced by **2-4** in Table 2 with a narrow polydispersity (ranging from 1.04 to 1.24) and lower $M_{n,GPC}$ values than theoretically expected, which indicated that the Zn/BnOH system may contain multiple active species or includes transesterification reactions.

To obtain PCL in a short time, we conducted the polymerization of ε-caprolactone at 100 °C. All Zn complexes could catalyze the ring-opening polymerization of ε-caprolactone in the presence of 1 equiv. BnOH (Table 3 entries 1–5), giving 85-96% monomer conversion within 2 to 12 h. In particular, **3** has a higher catalytic activity than other complexes, and the conversion in 2 h can reach to 91%. This may be due to the presence of alkyl substituents in aryl ring (Ar) ortho-methyl group on the enamino framework, which demonstrated an electro-donating group can increase the catalytic activity.[10-13]

As shown in Table 3, complex **3** exhibited the best catalytic activity for the ROP of ε-CL among the investigated binary Zn/BnOH systems (Table 3, entries 1-5), so complex **3** as an initiator was selected to examine the role of BnOH and the

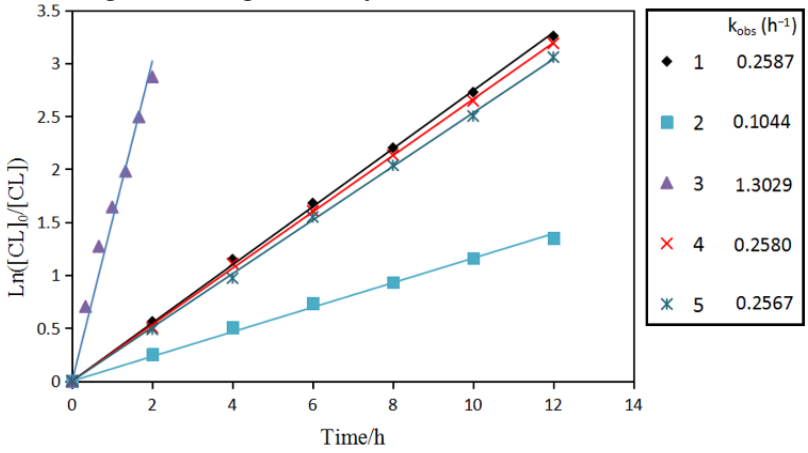



**Fig.2.** Relationship between Ln([CL]$_0$/[CL]) and time of the polymerization initiated by **1**–**5** in the presence of BnOH in toluene at 100 °C with a ratio of [CL]$_0$: [M]$_0$: [BnOH]$_0$ = 100:1:1 ([CL]$_0$ = 1 M)

effect of concentration of ε-CL in the polymerization. In the absent of BnOH, the monomer conversion was 58% in 2 hours, and PCL with a broad PDI (PDI = 1.76) and lower $M_{n,GPC}$ values than $M_{n,calc}$ was obtained (Table 3, entry 6), indicating that the catalyst was not well controlled in the polymerization reaction without co-catalyst. Using iPrOH as a cocatalyst, the conversion of 61% was slower than that of binary Zn/BnOH systems (Table 3, entry 7). Raising the monomer equivalent to 200 and 400, the polymerization rate decreased markedly (Table 3, entries 9 and 11). However, increasing the quantity of BnOH, the polymerization rate enhanced and the control efficiency improved (Table 3, entries 10 and 12). The $M_{n,GPC}$ values of these PCLs produced by Zn/BnOH systems appeared smaller than $M_{n,Calc}$ and their PDIs were narrow (1.11-1.22, Fig. S12), which may be the presence of variouse active species or intra-transeterification. We noticed that with addition of 2 or 4 equiv. of BnOH, the gap of $M_{n,GPC}$ with $M_{n,Calc}$ values went down, which suggested the more BnO- active species were generated with the increasing alcohol.

In order to further explore the catalytic properties of these complexes, the kinetic studies of ε-CL polymerization initiated by complex **1-5** are shown in Fig. 2 in the ratio of [CL]$_0$:[Zn]$_0$:[BnOH]$_0$ = 100:1:1. It can be seen from the

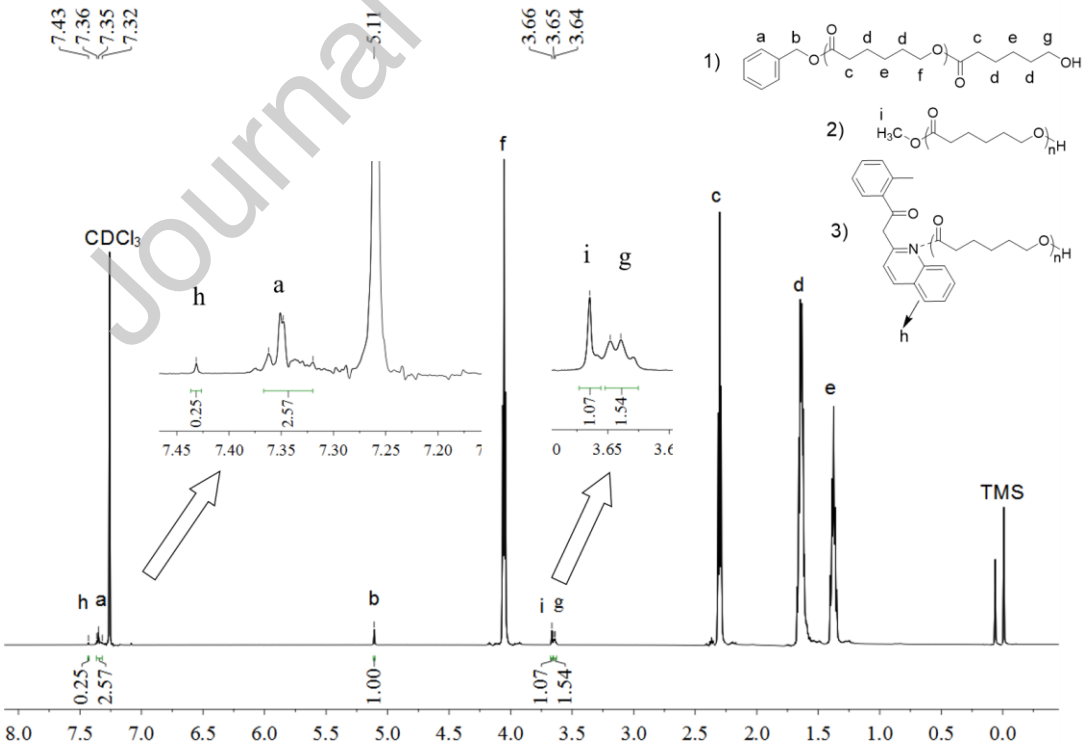


**Figure. 3.** The $^1$H NMR spectrum of PCL initiated by **3**/BnOH in the ratio of $[CL]_0$:$[Zn]_0$:$[BnOH]_0$ = 50:1:1 ($CDCl_3$, 25℃, 600 MHz) (Table 3, entry 8)

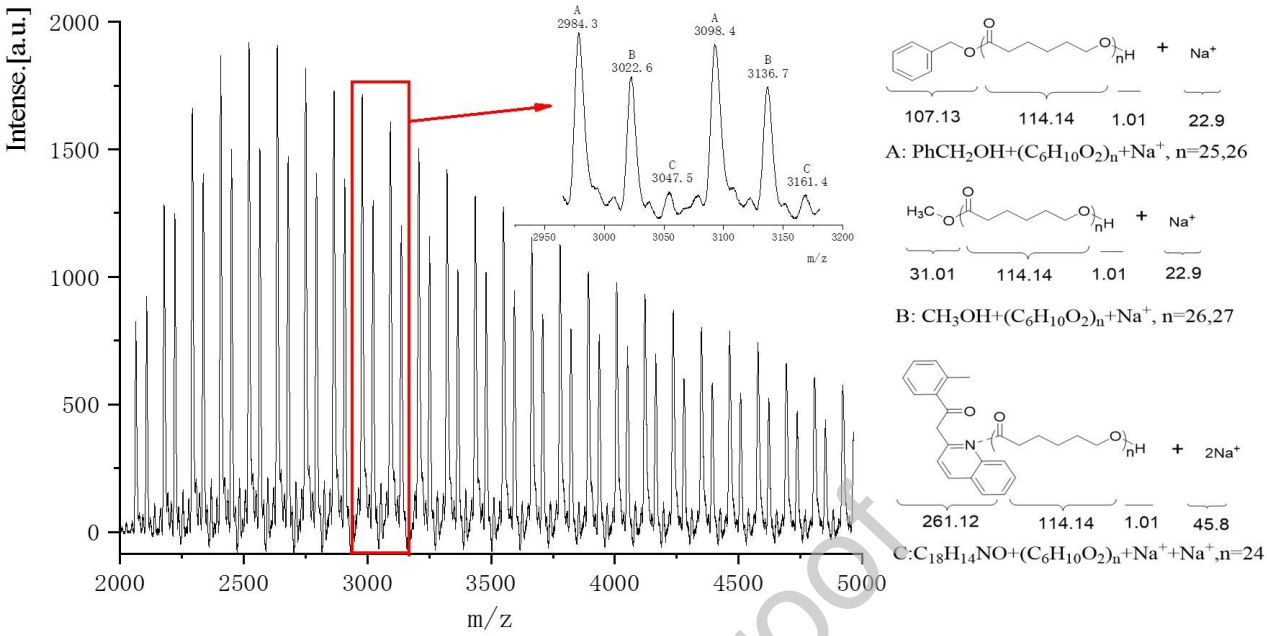
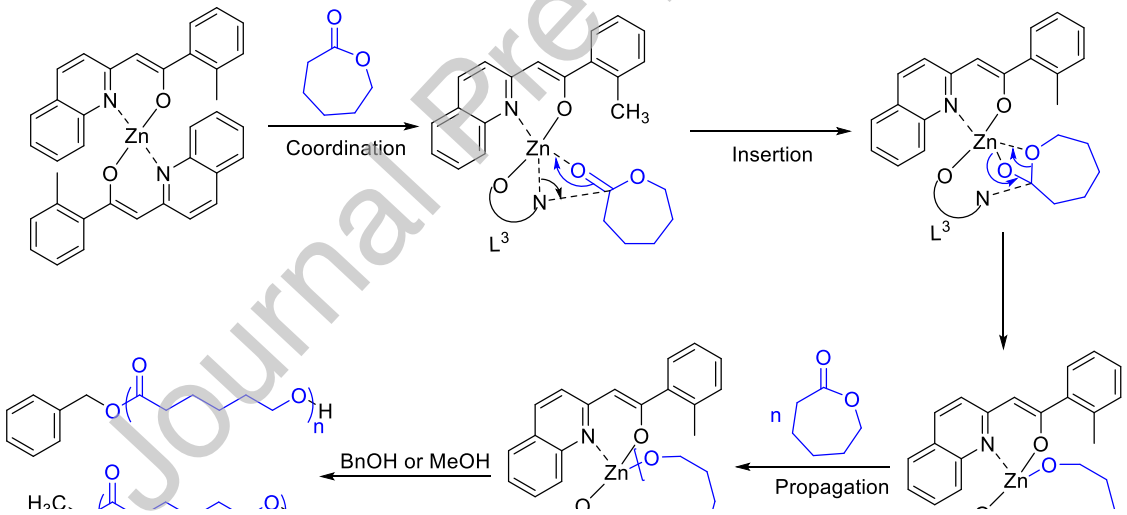



**Fig. 4.** MALDI-TOF MS analysis for the PCL produced by complex **3** ($[\varepsilon\text{-CL}]_0$:$[Znl]_0$:$[BnOH]_0$= 100:1:1, 100 °C)




**Scheme 2.** Proposed mechanism of the ROP of ε-caprolactone initiated by complex **3**

curve that Ln($[CL]_0$/[CL]) shows a good linear relationship with the reaction time, indicating that the monomer concentration follows the first-order propagation during the polymerization of these complexes. The results showed that the catalytic activity of complexes for ε-CL decreased in the order of **3** (*o*-tolyl) > **1** ($^t$Bu) ≈ **4** (*p*-tolyl) ≈ **5** (*p*-OMePh) > **2** (Ph). Although the structures of complexes **3** and **4** are similar, the difference between the two $k_{obs}$ is remarkable (1.3029 $h^{-1}$, 0.2580 $h^{-1}$), indicating that the position of the methyl group has a greater effect on the catalytic activity of ε-CL. The $k_{obs}$ value of complex **2** is 0.1044 $h^{-1}$ which is smaller than others due to its structure without substituent on the aryl ring (Ar) in the ligand backbone. It is suggested that the ligands with electronic donating groups, such as **3**, can increase the catalytic activity, which is in agreement with β-quinolyl/pyridyl enolato alkylaluminum.[10-13]

To further understand the polymerization mechanism, the end-group analysis was carried out by $^1$H NMR and MALDI-TOF spectra (Fig 3 and 4). The $^1$H NMR spectrum of final PCL-50 produced by [CL]/[**3**]/BnOH = 50:1:1 (Table 3, entry 8) showed the presence of *PhCH*$_2$OC(=O)- (δ 7.35, 5.11

ppm), C*H*$_3$OC(=O)- (δ 3.66 ppm) termini and a ligand moiety as one of the end groups (δ 7.43, 7.36 ppm) (Fig. 3).

In addition, the MALDI-TOF analysis of PCL obtained by [CL]/[**3**]/BnOH = 100:1:1 (Table 3, entry 3) demonstrated that there are two sets of signals ascribed to the polymers end-capped with benzyl alcohol and methyl alcohol (Fig 4, A and B), respectively, and the resulting polymers are linear structure. These two main series peaks are 107.13+114n+1.01+22.9 attributed to BnOH+$(C_6H_{10}O_2)_n$+ $Na^+$ (A) and 31.01+114n+1.01+22.9 attributed to $CH_3OH$ +$[C_6H_{10}O_2]_n$+$Na^+$ (B). Moreover, the low intensity peaks C series present in the spectrum are identified as peaks corresponding to the polymers end-capped with ligand moiety (Fig 4, C). From the intensity of the peaks in $^1$H NMR and MALDI-TOF spectrometry, it is distinct that the fraction of L-capped linear PCL is a minor product.

The $^1$H NMR and MALDI-TOF spectral analysis implies that the polymerization proceeds *via* the coordination-insertion mechanism, where the monomer coordinates to the metal followed by the acyl oxygen bond cleavage of the monomer and chain propagation (Scheme 2). We speculate that these observation result from (i) the monomer coordinates to the Zn center and forms hydroinitial nucleophilic attack of the coordinated monomer by one of the O atoms in **3**, where the ligand would act as a reactive nucleophile, (ii) followed by transesterification of the initial chain-end in the presence of $CH_3OH$ during quenching of the reaction and washing the polymer [43-46]. Our attempts to isolate or identify a putative ligand-capped PCL before quenching were unsuccessful. However, The $^1$H NMR spectrum of PCL-50 (Table 3, entry 8) clearly showed the signal of quinolyl group around δ 7.4 ppm, suggesting the possible existence of ligand-capped PCL.

## 4. Conclusion

In summary, a series of bis(β-quinolylenolate) zinc complexes **1-5** was prepared exhibited good activity toward the ROP of ε-caprolactone in the presence of BnOH at a CL/Zn molar ratio of 100:1. Higher polymerization activity was achieved by the complex **3** with methyl substituent at the *ortho*-position of the aryl ring, suggesting that the electron-donating nature of this site on the aryl ring is somewhat stronger than that of other sites. The kinetic studies revealed that polymerization reactions initiated by complexes **1-5** within benzyl alcohol followed first-order kinetics. End group analyses by $^1$H NMR spectroscopy and MALDI-TOF spectrometry indicated that the polymerizations of ε-CL using **1-5** systems were accompanied by a certain degree of transesterification to give the linear PCL capped with BnO- or MeO- as the major component and capped with ligand as the minor component. The probable reaction's mechanisms have been proposed, which will be useful in the area of ligand design for the ROP of cyclic esters.

## Declaration of competing interest

The authors declare that they have no known competing fifinancial interests or personal relationships that could have appeared to inflfluence the work reported in this paper.

## Acknowledgments

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at

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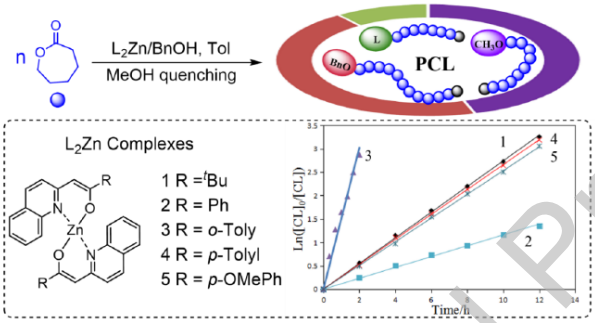
GRAPHICAL ABSTRACT




**Bis(β-quinolylenolate) zinc complexes were used to prepare PCL and substituents had a greater effect on the catalytic activity. $^1$H NMR and MALDI-TOF spectra demonstrated that the polymer is composed of two major polymers end-capped with benzyl alcohol and methyl alcohol and a few of polymers end-capped with ligands.**

**Declaration of interests**

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: