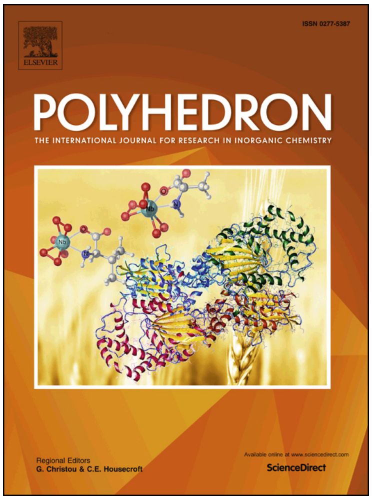

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Zinc complexes supported by N,O-bidentate amino-alkoxyl ligands: synthesis, characterization and catalytic property for the ring-opening polymerization of L-lactide

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Abstract

A series of new zinc complexes based on the amino-alkoxyl ligands [1-HOC(R^1R^2)-2-$NMe_2C_6H_4$ [R^1 = H, R^2 = Ph (**L**^{1}H), R^1 = Et, R^2 = Ph (**L**^{2}H), R^1 = H, R^2 = 2-FPh (**L**^{3}H), R^1 = H, R^2 = 2-BrPh (**L**^{4}H)] were synthesized. The zinc complexes were characterized by NMR spectroscopy and elemental analysis, as well as by an X-ray diffraction study. The solid-state structures of **2** and **3** reveal that the Zn centers adopt four-coordinated distorted tetrahedral geometries. These complexes show high activities in the ring-opening polymerization of L-lactide in the presence of benzyl alcohol in a living fashion. Complex **3** (R^1 = H, R^2 = 2-FPh) shows the highest activity among complexes **1**-**4**.

Keywords:

Catalyst

Zinc complex

Lactide

Ring-opening polymerization

Amino-alkoxyl ligands

1. Introduction

Over the past few decades, there has been a great increase in the development of polylactide (PLA) because of its biodegradability and biocompatibility. PLAs are being exploited for a wide range of applications, such as packaging materials, bio-absorbable implants, drug delivery and tissue engineering scaffolds [1]. The ring-opening polymerization (ROP) of lactide (LA) is the most efficient method to prepare PLA, owing to the advantage of achieving well controlled molecular weights and a narrow molecular weight distribution [2]. Metal complexes, such as lithium [3], aluminum [4], magnesium [5], titanium [6], zinc [7] and others [8] with ancillary ligands, have been proven to be powerful catalysts for the ROP of LA. Among the reported catalysts, zinc complexes have been intensively studied due to their excellent catalytic properties for the ROP of LA. Recently, zinc complexes bearing N,O-bidentate, N,N,O-tridentate or N,N,N,O-tetradentate ligands were efficient catalysts for the ROP of LA [7]. Carpentier's group reported an efficient system for the ROP of LA using fluorous alkoxide-imino zinc complexes [7a]. A series of N,N,O-chelate zinc complexes reported by Wang's group efficiently catalyzed the ROP of *rac*-LA in a controlled fashion [7b]. Ma's group reported that aminophenolate N,N,O-zinc complexes showed moderate catalytic activities for the ROP of LA [7c]. Recently, the same group found that N,N,N,O-Zn complexes are efficient initiators for the ROP of *rac*-LA at ambient temperature [7d].

In the search for new polymerization catalysts, amino-alkoxy zinc complexes have been prepared. In this paper, we report the synthesis and full characterization of these complexes, which, in the presence of benzyl alcohol (BnOH), catalyze the ROP of L-LA with high activities. It was found that the ligand architecture and the reaction conditions significantly influence the polymerization activity.

2. Experimental

2.1. General considerations

All reactions and manipulations which related to the preparation of the metal complexes were carried out under nitrogen with standard Schlenk-line or glovebox techniques. All solvents were refluxed over the appropriate drying agent and distilled prior to use. Ligand **1** (Scheme 1) was prepared according to a literature procedure [9]. ^{1}H and ^{13}C NMR spectra were measured using a Varian Mercury-300 NMR spectrometer, a Bruker AVANCE-400 NMR spectrometer or a Bruker AVANCE-600 NMR spectrometer. The elemental analyses were performed on a Perkin-Elmer 2400 analyzer. The molecular weight and molecular weight distribution of the polymers were measured on a TOSOH HLC 8220 GPC at 40 °C using THF as the eluent against polystyrene as a standard.

2.2. *Synthesis of* $\mathbf{L}^2H$

A dry 250 mL two-necked flask was filled with 5.00 g (41 mmol) of N,N-dimethylaniline, 50 mL of anhydrous diethyl ether and 5 mL of TMEDA, and the solution was stirred under a nitrogen atmosphere. *n*-BuLi (20.5 mL, 2.0 M in hexane) was added at –78 °C. The solution was allowed to warm to room temperature, stirred for 12 hrs, then propiophenone (5.50 mL, 41 mmol) in 30 mL of anhydrous diethyl ether was added dropwise to the reaction mixture. The resulting mixture was stirred for an additional 5 hrs. The precipitate was collected and washed with dry hexane (20 mL). The solid was poured into a water/diethyl ether solution (1/5, 30 mL). The organic extract was dried over anhydrous $MgSO_4$ and evaporated to yield a yellow solid product (0.73 g, 89%). *Anal. Calc*. for $C_{17}H_{21}NO$ (255.16): C, 79.96; H, 8.29; N, 5.49. Found: C, 79.90; H, 8.31; N, 5.40%. ^1H NMR (400 MHz, $CDCl_3$, 293 K) δ, ppm: 7.51 (d, J = 6.8 Hz, 1H, Ar–*H*), 7.40 (t, J = 6.6 Hz, 2H, Ar–*H*), 7.30 (d, J = 6.8 Hz, 2H, Ar–*H*), 7.27–7.21 (m, 3H, Ar–*H*), 7.15 (m, 1H, Ar–*H*), 2.74 (s, 6H, NCH_3), 2.27 (q, J = 7.3 Hz, 2H, CH_2CH_3), 0.95 (t, J = 7.3 Hz, 3H, CH_2CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 293 K) δ, ppm: 151.6, 149.2, 141.8, 128.0, 127.7, 127.7, 126.0, 125.9, 125.8, 123.3, 79.2, 46.5, 35.7, 8.2.

2.3. *Synthesis of* $\mathbf{L}^3H$

The reaction was carried out by a similar procedure as described for $\mathbf{L}^2$H, except that 4.40 mL (41 mmol) of 2-flurobenzaldehyde was used instead of propiophenone. The product, as yellow solid, was obtained in 75% yield. *Anal. Calc.* for $C_{15}H_{16}FNO$ (245.12): C, 73.45; H, 6.57; N, 5.71. Found: C, 73.51; H, 6.62; N, 5.78%. ^1H NMR (300 MHz, $CDCl_3$, 293 K) δ, ppm: 7.54 (t, J = 7.1 Hz, 1H, Ar–*H*), 7.33–7.29 (m, 3H, Ar–*H*), 7.18 (t, J = 6.9 Hz, 1H, Ar–*H*), 7.09 (m, 2H, Ar–*H*), 6.98 (d, J = 7.1 Hz, 1H, Ar–*H*), 6.39 (s, 1H, PhC*H*OH), 2.74 (s, 6H, NCH_3). ^{13}C NMR (75MHz, $CDCl_3$, 293 K) δ, ppm: 153.4, 146.7, 132.4, 132.6, 123.3, 123.2, 123.1, 120.2, 119.0, 116.5, 110.5, 109.8, 64.3, 40.5.

2.4. *Synthesis of* $\mathbf{L}^4H$

The reaction was carried out by a similar procedure as described for $\mathbf{L}^2$H, except that 4.90 mL (41 mmol) of 2-bromobenzaldehyde was used instead of propiophenone.

The product, as yellow solid, was obtained in 80% yield. *Anal. Calc.* for $C_{15}H_{16}BrNO$ (305.04): C, 58.84; H, 5.27; N, 4.57. Found: C, 58.76; H, 5.31; N, 4.625%. ^1H NMR (600 MHz, $CDCl_3$, 293 K) δ, ppm: 7.59 (dd, J = 12.8, 4.8 Hz, 2H, Ar–*H*), 7.38 (t, J = 7.5 Hz, 1H, Ar–*H*), 7.35–7.31 (m, 1H, Ar–*H*), 7.31–7.25 (m, 1H, Ar–*H*), 7.20 (td, J = 7.8, 1.7 Hz, 2H, Ar–*H*), 7.06–6.96 (m, 1H, Ar–*H*), 6.64 (s, 1H, PhC*H*OH), 2.81 (s, 6H, NC*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 293 K) δ, ppm: 152.0, 141.8, 137.3, 132.5, 129.4, 129.0, 128.6, 128.1, 127.8, 125.2, 123.6, 121.1, 73.3, 45.4.

*2.5. Synthesis of (**L^1**ZnEt)$_2$ (**1**)*

$ZnEt_2$ (0.8 mL, 0.8 mmol, 1.0 M in hexane) was added to a solution of **L**^{1}H (0.18 g, 0.8 mmol) in toluene (10 mL) at 0 °C with stirring. The reaction mixture was gently heated to 80 °C for 12 hrs. After removal of the solvent, the product was recrystallized using hexane to give the desired complex as a colorless solid (0.22 g, 88%). *Anal. Calc.* for $C_{34}H_{42}N_2O_2Zn_2$ (638.18): C, 63.66; H, 6.60; N, 4.37. Found: C, 63.61; H, 6.57; N, 4.32%. ^1H NMR (300 MHz, C_6D_6, 293 K) δ, ppm: 7.45 (m, 4H, Ar–*H*), 7.33–6.98 (m, 14H, Ar–*H*), 6.17 (s, 2H, PhC*H*O), 2.29 (s, 12H, NC*H*$_3$), 1.32 (q, J = 6.7 Hz, 6H, CH$_2$C*H*$_3$), 0.19 (t, J = 6.7 Hz, 4H, C*H*$_2$CH$_3$). ^{13}C NMR (75 MHz, $CDCl_3$, 293 K) δ, ppm: 149.8, 147.6, 140.7, 131.8, 127.9, 127.4, 126.5, 125.1, 120.6, 119.4, 80.2, 47.0, 13.0, –3.2.

*2.6. Synthesis of (**L^2**ZnEt)$_2$ (**2**)*

The reaction was carried out by a similar procedure as described for **1**, except that 0.23 g (0.9 mmol) of **L**^{2}H was used instead of **L**^{1}H. The product, as colorless solid, was obtained in 90% yield. *Anal. Calc.* for $C_{38}H_{50}N_2O_2Zn_2$ (694.25): C, 65.43; H, 7.22; N, 4.02. Found: C, 65.50; H, 7.25; N, 4.12%. ^1H NMR (400 MHz, $CDCl_3$, 293 K) δ, ppm: 7.52 (m, 4H, Ar–*H*), 7.47–7.27 (m, 10H, Ar–*H*), 7.10 (m, 4H, Ar–*H*), 2.85 (s, 12H, NC*H*$_3$), 2.23 (m, 6H, CH$_2$C*H*$_3$),1.37 (m, 4H, ZnC*H*$_2$C*H*$_3$), 1.04 (m, 6H, CH$_2$C*H*$_3$), 0.21 (m, 4H, ZnC*H*$_2$CH$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 293 K) δ, ppm: 150.2, 147.2, 142.8, 128.4, 127.9, 127.5, 126.3, 126.2, 126.1, 125.3, 125.0, 123.2, 77.3, 45.3, 33.4, 13.3, 8.2, –3.2.

*2.7. Synthesis of (**L^3**ZnEt)$_2$ (**3**)*

The reaction was carried out by a similar procedure as described for **1**, except that

0.24 g (1.0 mmol) of **L**^{3}H was used instead of **L**^{1}H. The product, as colorless solid, was obtained in 87% yield. *Anal. Calc.* for $C_{34}H_{40}F_2N_2O_2Zn_2$ (674.16): C, 60.28; H, 5.95; N, 4.13. Found: C, 60.31; H, 5.99; N, 4.08%. ^{1}H NMR (300 MHz, C_6D_6, 293 K) δ, ppm: 7.78 (m, 2H, Ar–*H*), 7.49 (m, 4H, Ar–*H*), 7.13–7.01 (m, 10H, Ar–*H*), 6.99 (s, 2H, PhC*H*O), 2.94 (s, 12H, NC*H*$_3$), 1.39 (t, J = 7.0 Hz, 6H, ZnCH$_2$C*H*$_3$), 0.22 (q, J = 7.0 Hz, 4H, ZnC*H*$_2$CH$_3$). ^{13}C NMR (75 MHz, CDCl$_3$, 293 K) δ, ppm: 149.5, 145.7, 138.7, 132.1, 130.0, 129.0, 128.3, 128.0, 127.3, 124.8, 123.4, 118.7, 76.1, 45.9, 13.0, –3.3.

*2.8. Synthesis of (**L^4**ZnEt)$_2$ (**4**)*

The reaction was carried out by a similar procedure as described for **1**, except that 0.34 g (1.0 mmol) of **L**^{4}H was used instead of **L**^{1}H. The product, as colorless solid, was obtained in 88% yield. *Anal. Calc.* for $C_{34}H_{40}Br_2N_2O_2Zn_2$ (794.00): C, 51.09; H, 5.04; N, 3.50. Found: C, 51.00; H, 5.07; N, 3.54%. ^{1}H NMR (400 MHz, CDCl$_3$, 293 K) δ, ppm: 7.63–7.51 (m, 4H, Ar–*H*), 7.39–7.36 (m, 4H, Ar–*H*), 7.20–7.13 (m, 4H, Ar–*H*), 6.49 (s, 2H, PhC*H*O), 2.83 (s, 6H, NC*H*$_3$), 2.81 (s, 6H, NC*H*$_3$), 1.36 (t, J = 8.1 Hz, 6H, ZnCH$_2$C*H*$_3$), 0.21 (q, J = 8.1 Hz, 4H, ZnC*H*$_2$CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$, 293 K) δ, ppm: 149.6, 145.8, 138.8, 132.2, 130.1, 129.1, 128.3, 128.1, 127.4, 123.5, 121.1, 118.8, 76.1, 45.3, 13.1, –3.3.

2.9. ROP of L-LA

In a typical polymerization experiment, the zinc complex, the required amount of *L*-LA and BnOH in toluene were loaded in a flame-dried vessel containing a magnetic bar. The vessel was placed in an oil bath. After a certain reaction time, the polymer was isolated by precipitation with cold methanol. The precipitate was collected and dried under vacuum at 40 °C for 24 hrs. For some polymerization reactions, samples were taken to determine the monomer conversion by ^{1}H NMR spectroscopy during the reaction.

2.10. X-ray crystallography

Diffraction data of **2** and **3** were collected at 120 K with a Xcalibur, Eos, Gemini diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ = 0.71073

Å). Using OLEX2 [10], the structures were solved with the SHELXS [11] structure solution program using direct methods and refined with the SHELXL [11] refinement package using least squares minimization. Further crystal data details for complexes **2** and **3** are found in Table S1.

3. Results and discussion

3.1. Synthesis and characterization of the zinc complexes

New ligands and Zn complexes **1**-**4** were synthesized as described in Scheme 1. The ligands [1-HOC(R^1R^2)-2-$NMe_2C_6H_4$ [R^1 = H, R^2 = Ph (**L**^{1}H), R^1 = Et, R^2 = Ph (**L**^{2}H), R^1 = H, R^2 = 2-FPh (**L**^{3}H), R^1 = H, R^2 = 2-BrPh (**L**^{4}H)] were synthesized by the reaction of 2-$NMe_2C_6H_4Li$ with the corresponding ketone or aldehyde in high yield (75-89%) [9].

Treatment of **L**^{1}H–**L**^{4}H with an equivalent of $ZnEt_2$ in toluene with the release of ethane gave the zinc complexes ((**L**^{1}ZnEt)$_2$ (**1**), (**L**^{2}ZnEt)$_2$ (**2**) (**L**^{3}ZnEt)$_2$ (**3**) and (**L**^{4}ZnEt)$_2$ (**4**)). When the ligand 1-HOC$(Ph)_2$-2-$NMe_2C_6H_4$, containing bulky substituents, was chosen to react with $ZnEt_2$, an unknown complex was obtained. The complex was insoluble in organic solvents, even in DMSO or DMF. Complexes **1**-**4** were characterized by ^{1}H and ^{13}C NMR spectra and elemental analysis.

The molecular structures of **2** and **3** were determined by single crystal X-ray diffraction studies. Crystals of **2** and **3** suitable for the X-ray diffraction studies were obtained from a solution of toluene and *n*-hexane at 4 °C overnight. The molecular structures of **2** and **3** are illustrated in Figs. 1 and 2, and the crystal data are given in Table S1. The solid-state structures of **2** and **3** reveal that the Zn centers adopt four-coordinated distorted tetrahedral geometries. Complexes **2** and **3** exist as dimers with coordination of the ethyl residue, nitrogen atoms of the ligands and the O atom, which bridges between the two Zn centers; All complexes are C2 symmetric, generating a Zn_2O_2 planar core in the center of each molecule, which have previously been observed in other zinc compounds that contain, for example, thiolate-oxo [12a], alkoxide-imino [12b], aryloxide [12c], aminoalcoholate [12d], aminophenoxide [12e] or pyrazolyl-alkoxide [12f] ligands. The Zn–O distances (1.996(1) and 2.034(1) Å in **2**, and 1.999(1) and 1.994(1) Å in **3**) are shorter than those of ethylzinc complexes bearing aminophenoxo ligands [2.055(2)-2.084(2) Å in ref. 12e], but longer than those of mononuclear zinc complex with two aminophenoxo ligands [1.911(1) and 1.918(1) Å in ref. 12e]. The Zn–N bonds (2.207(2) Å in **2**, and 2.174(1) Å in **3**) are comparable with those of dimeric zinc complexes with aminoalcoholate ligands [2.180(9) and 2.185(2) Å in ref. 12d]

3.2. Ring-opening polymerization of L-LA

Complexes **1**-**4** were examined for the ROP of L-LA under different conditions. As shown in Table 1, **1**-**4** showed moderate catalytic activities toward the polymerization, yielding PLA with broad molecular weight distributions in the absence of BnOH (Entries 1-4). By contrast, **1**-**4** were efficient catalysts in the presence of BnOH, yielding PLA with narrow molecular weight distributions (Entries 5-8). Their activities are higher than those of the fluorous alkoxide-imino zinc complexes [7a]. **1**, bearing a bulky substituted group bound to the alkoxyl function (R^1 = H, R^2 = Ph), has a high catalytic activity for L-LA polymerization. An increase in steric bulk results in a slight increase of the turnover frequency (TOF) from 1380 h^{-1} for **1** to 1500 h^{-1} for **2** (R^1 = Et, R^2 = Ph). The replacement of the aryl group at the *ortho*-position with a halogen atom causes an increase of activity for complexes **3** and **4**. The value of the TOF increases to 2000 and 1880 h^{-1}, respectively. For 1000 equiv. of L-LA ($[LA]_0$ = 0.25 M), in the presence of 1 equiv. of BnOH, the polymerization initiated by complex **3** proceeded fast to 95% within 5 mins (TOF = 11400 h^{-1}), yielding PLA with M_n =1.22×10^5 g mol^{-1} and a narrow PDI of 1.26 in a controlled fashion (entry 17). Fast polymerization could also be initiated by complexes **1**, **2** and **4**, when 1000 equiv. of L-LA were used. The different catalytic performances suggest that the change of substituents influences the polymerization activities, as reported in other metal catalyst systems [14].

The influences of the Zn/BnOH molar ratio and the reaction temperature on the polymerization were investigated in detail with complex **3** (Entries 7, 9-11). Variations of the Zn/BnOH molar ratio affected the polymerization activities, and the highest polymerization activity was observed at a Zn/BnOH molar ratio of 1. In general, complex **3** shows remarkably higher catalytic activity at higher temperature. Meanwhile, a decrease of the reaction temperature to 20 °C significantly reduces the activity.

To further investigate the performance of complex **3**, polymerization experiments for different times with a monomer/**3**/BnOH = 300/1/1 system were performed. A linear relationship between the number-averaged molecular weight (M_n) and the monomer conversion, as shown in Fig. 3, implies the “living” character of the polymerization process catalyzed by **3**/BnOH.

For studying the mechanism of the polymerization, the end group of a typical polymer sample was analyzed by its ^{1}H NMR spectrum (Fig. S1). The ^{1}H NMR spectrum shows prominent peaks of the PLA main chain at δ 1.48-1.60 and 5.00-5.25 ppm. Two peaks at δ 5.00-5.25 and 7.31-7.36 ppm were attributed to the benzyl protons on the benzyloxycarbonyl end. The peak at δ 4.35 ppm was attributed to the methenyl proton connected to the hydroxyl end. The results demonstrate that the PLA chain is capped by one benzyl and one hydroxyl end. The ROP of L-LA follows a coordination insertion mechanism [15].

4. Conclusion

In conclusion, four zinc complexes based on amino-alkoxy ligands are reported. All of complexes **1**-**4** are efficient catalysts for the ring-opening polymerization of L-LA in the presence of BnOH. The polymerization reactions of L-LA catalyzed by these catalyst systems take place in a living fashion with narrow molecular weight distributions. Overall, those performances compare well with those of related efficient N,O-bidentate zinc systems [7a].

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Appendix A. Supplementary data

CCDC 949036 and 949037 contain the supplementary crystallographic data for **2** and **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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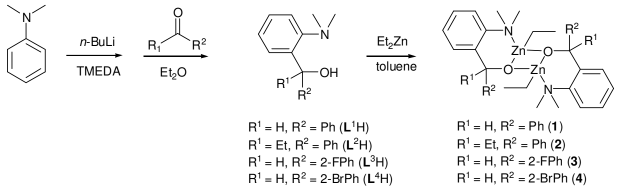


Scheme 1. Synthesis of complexes **1**-**4**.

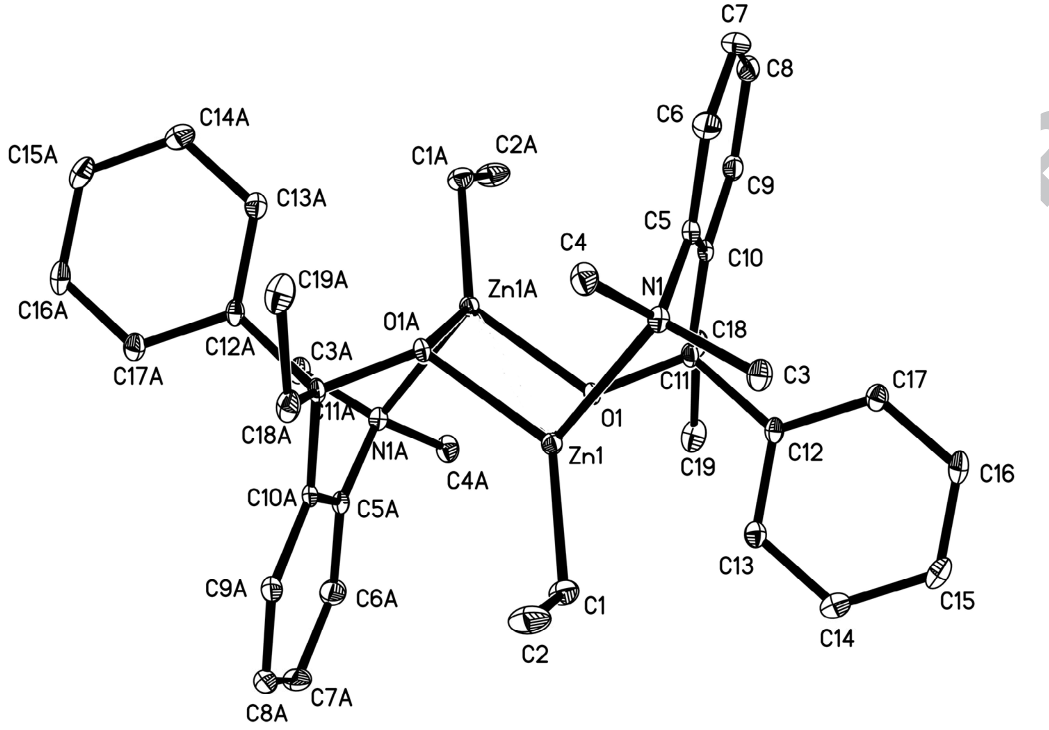


Fig. 1. The molecular structure of complex **2**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (^{o}): Zn(1)–N(1) 2.207(2), Zn(1)–O(1) 1.996(1), Zn(1)–C(1) 1.986(2), Zn(1)–O(1A) 2.034(1), N(1)–Zn(1)–O(1) 91.09(6), O(1)–Zn(1)–O(1A) 84.90(6), C(1)–Zn(1)–O(1) 130.97(7), C(1)–Zn(1)–O(1A) 129.51(8), C(1)–Zn(1)–N(1) 91.09(6), N(1)–Zn(1)–O(1A) 97.59(6).

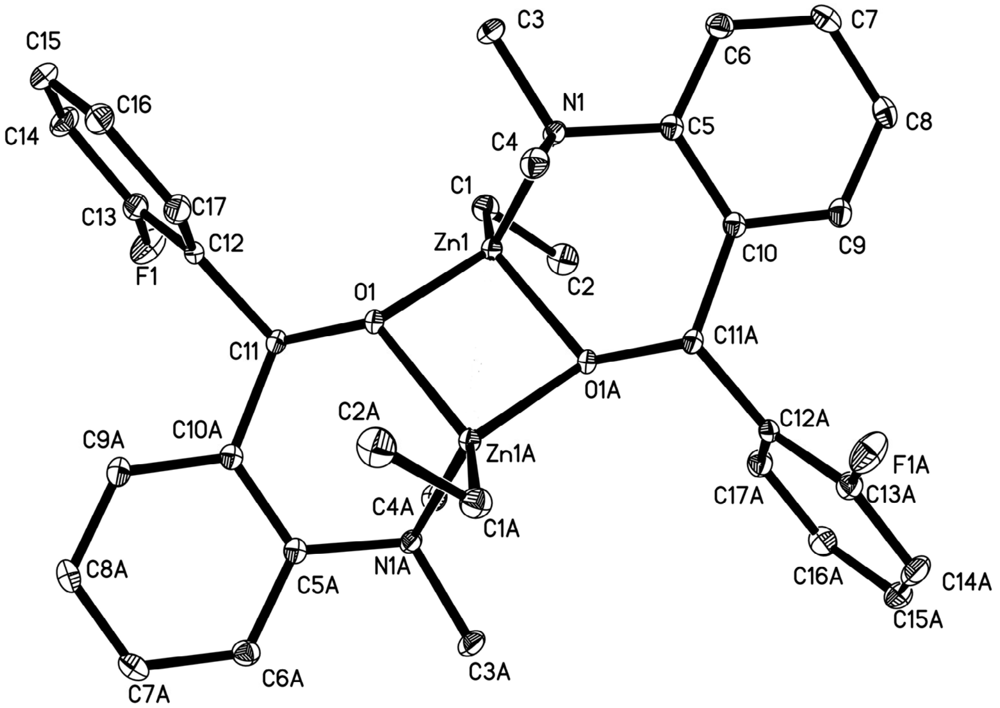


Fig. 2. The molecular structure of complex **3**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Zn(1)–N(1) 2.174(1), Zn(1)–O(1) 1.999(1), Zn(1)–C(1) 1.976(2), Zn(1)–O(1A) 1.994(1), N(1)–Zn(1)–O(1) 99.52(5), O(1)–Zn(1)–O(1A) 83.97(5), C(1)–Zn(1)–O(1) 127.27(6), C(1)–Zn(1)–O(1A) 127.62(6), C(1)–Zn(1)–N(1) 119.88(6), N(1)–Zn(1)–O(1A) 87.69(5).

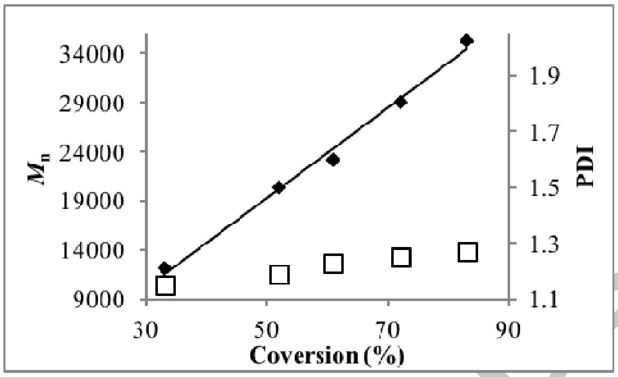


Fig. 3. Linear relationship between M_n and L-LA conversion initiated by **3** ([L-LA]$_0$/[**3**]$_0$/[BnOH]$_0$ = 300/1/1, T = 60 ^{o}C, toluene).

Table 1. ROP of L-LA catalyzed by **1**-**4**[a].

Entry	Cat.	$[LA]_0/[Zn]_0/[BnOH]_0$	T (°C)	Time (min)	Yield (%)[b]	TOF[c]	$M_{n,calcd}$[d] ($\times10^3$)	M_n[e] ($\times10^3$)	PDI[e]
1	**1**	100:1:0	60	30	88	176	12.9	12.3	1.24
2	**2**	100:1:0	60	30	90	180	13.2	12.7	1.20
3	**3**	100:1:0	60	30	93	186	13.6	13.1	1.25
4	**4**	100:1:0	60	30	90	180	13.3	13.1	1.27
5	**1**	100:1:1	60	4	92	1380	13.4	13.0	1.15
6	**2**	100:1:1	60	4	100	1500	14.5	13.1	1.14
7	**3**	100:1:1	60	3	100	2000	14.5	13.2	1.18
8	**4**	100:1:1	60	3	94	1880	13.6	12.4	1.17
9	**3**	100:1:1	40	10	97	1582	14.1	13.4	1.10
10	**3**	100:1:1	20	50	93	112	13.5	12.9	1.07
11	**3**	100:1:2	60	12	92	460	6.7	6.7	1.24
12	**3**	150:1:1	60	7	96	1234	21.7	20.7	1.15
13	**3**	200:1:1	60	12	95	950	27.6	26.1	1.24
14	**3**	250:1:1	60	17	96	847	34.7	34.0	1.20
15	**1**	1000:1:1	60	7	91	7800	131.0	114.2	1.18
16	**2**	1000:1:1	60	6	92	9200	132.5	118.7	1.22
17	**3**	1000:1:1	60	5	95	11400	136.8	122.4	1.26
18	**4**	1000:1:1	60	5	90	10800	129.6	111.2	1.24

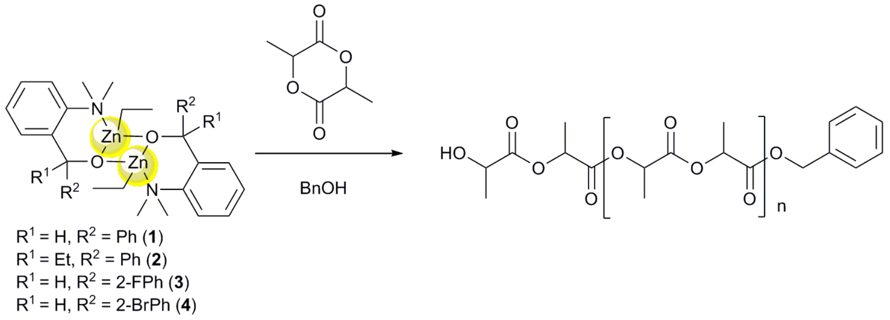
[a] Polymerization conditions: catalyst, 30 μmol, $[\text{L-LA}]_0 = 0.25$ M in toluene, N_2 atmosphere.

[b] Determined by ^1H NMR spectroscopy.

[c] Mole of LA consumed per mol of catalyst per hour.

[d] Calculated from $([\text{L-LA}]_0/[Zn]_0) \times \text{conversion} \times 144.13$ or $([\text{L-LA}]_0/[BnOH]_0) \times \text{conversion} \times 144.13 + 108$.

[e] Determined by GPC against polystyrene standards in THF, multiplied by 0.58 [13].



A series of new zinc complexes based on amino-alkoxyl ligands have been synthesized and fully characterized. These zinc complexes show high activities for the ring-opening polymerization of L-lactide in the presence of benzyl alcohol in a living fashion.