DOI: 10.1002/cjoc.201200613

Synthesis, Structure of Zinc Complexes Containing Sulfonylated Binaphtholate Ligands and Their Catalytic Activities towards Ring-Opening Polymerization of Lactide and ε-Caprolactone†

Zhou, Shuangliu*,[a](周双六) Jiang, Yongyao[a](姜永要) Xie, Tao[a](谢陶)
Wu, Zhanshuan[a](吴章栓) Zhou, Linmin[a](周凌敏) Xu, Wenjing[a](许文静)
Zhang, Lijun[a](张丽军) Wang, Shaowu*,[a,b](王绍武)

[a] *Laboratory of Functionalized Molecular Solids*, *Ministry of Education*, *Anhui Laboratory of Molecule-Based Materials*, *Institute of Organic Chemistry*, *College of Chemistry and Materials Science*, *Anhui Normal University*, *Wuhu*, *Anhui 241000*, *China*
[b] *State Key Laboratory of Organometallic Chemistry*, *Shanghai Institute of Organic Chemistry*, *Shanghai 200032*, *China*

Reaction of sulfonylated binaphthol [2-hydroxy-2'-tosyloxy-1,1-binaphthyl (**1a**, Ts-Binol) or 2-hydroxy-2'-(phenylsulfonyloxy)-1,1-binaphthyl (**1b**, Ps-Binol)] with 1 equiv. of $ZnEt_2$ afforded zinc complexes $[(Ts\text{-}Binol)ZnEt]_2$ (**2a**) and $[(Ps\text{-}Binol)ZnEt]_2$ (**2b**). Further reaction of zinc complexes **2a** and **2b** with benzyl alcohol (BnOH) gave the zinc benzyloxide $[(Ts\text{-}Binol)_2Zn_2(OBn)_2]_2$ (**3a**) and $[(Ps\text{-}Binol)_2Zn_2(OBn)2]_2$ (**3b**). Alternatively, the zinc benzyloxides **3a** and **3b** could also be obtained by reaction of compound **1a** or **1b** with $Zn(OBn)_2$ (*in situ* reaction of $ZnEt_2$ and BnOH). The complexes were fully characterized by elemental analyses and spectroscopic analyses, and complexes **2a**, **2b** and **3a** were further characterized by single-crystal X-ray analyses. The catalytic activities of these zinc complexes towards ring-opening polymerization of ε-caprolactone and *D*,*L*-lactide were studied.

Keywords zinc complex, ring-opening polymerization, binaphthol, ε-caprolactone, *D*,*L*-lactide

Introduction

The ring-opening polymerization (ROP) of cyclic esters[1] provides a convenient method for the synthesis of biodegradable polyesters such as polylactide (PLA) and poly(ε-caprolactone) (PCL), which have been attracting a considerable attention due to their biocompatibility, biodegradability, and good drug penetrability.[2] Many metal complexes including alkali metals,[3] alkaline earth metals,[4] aluminum,[5] zinc,[6] tin,[7] early transition metals,[8] and lanthanides [9] have been used as initiators for the ROP of lactide and ε-caprolactone.

Recently, a diversity of structurally well-defined zinc complexes as catalysts for living polymerization of lactide and ε-caprolactone were developed. The β-diketiiminate supported zinc complexes have been demonstrated to be efficient catalysts for the ring-opening polymerization of lactide with an excellent stereoselective character.[10] The zinc amide and phenoxide complexes supported by bulky Schiff base ligands were synthesized and used as catalysts for the ring-opening polymerization of *L*-lactide to produce isotactic PLA at room temperature.[11] The zinc complexes containing bisphenolate ligands also showed good catalytic activities for ROP of *L*-lactide and ε-caprolactone in a controlled fashion with a low polydispersity.[12] Diphenolate zinc complex as an initiator for lactide polymerization proceeds to a 96% conversion within 40 h at room temperature (PDI＝1.41).[13] We herein report the synthesis and characterization of sulfonylated binaphtholate supported zinc alkyl and benzylalkoxy complexes. The catalytic activities of new zinc complexes toward ROP of ε-caprolactone and lactide are also studied.

Experimental

General remarks

All syntheses and manipulations of air- and mois-

* E-mail: swwang@mail.ahnu.edu.cn; slzhou@mail.ahnu.edu.cn; Tel.: 0086-0553-3869310; Fax: 0086-0553-3883517
Received June 23, 2012; accepted July 30, 2012.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cjoc.201200613 or from the author.
† Dedicated to the 80th Anniversary of Chinese Chemical Society.

ture-sensitive materials were performed under dry argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents were refluxed and distilled over sodium benzophenone ketyl (THF, *n*-hexane or toluene) or P_2O_5 (dichloromethane) under argon prior to use. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-300 NMR spectrometer with chemical shifts relative to the internal TMS. The GPC analyses of polymer were performed on a Waters-2414 instrument using THF as an eluent running at 1 mL/min. Molecular weights and molecular weight distributions were calculated using polystyrene as standard.

Synthesis of 2-hydroxy-2'-tosyloxy-1,1-binaphthyl (1a)[14]

Binaphthol (1.43 g, 5.0 mmol), tolylsulfonyl chloride (1.09 g, 5.0 mmol) and DMAP (0.031 g, 0.25 mmol) were dissolved in 20 mL of freshly distilled CH_2Cl_2 and the resulting solution cooled to 0 ℃. To the solution was added dry NEt_3 (3.47 mL, 25.0 mmol) dropwisely, which was then stirred at ambient temperature for 12 h. The reaction mixture was neutralized in 1 mol/L HCl solution, extracted with CH_2Cl_2 (10 mL×3), dried over anhydrous $MgSO_4$, and filtered. The resulting filtrate was then dried under vacuum, and the colorless crystals were obtained by recrystallization from a mixed solution of CH_2Cl_2 and hexane in 87% yield. ^{1}H NMR ($CDCl_3$) δ: 8.08 (d, J=8.8 Hz, 1H), 7.98 (d, J=8.4 Hz, 1H), 7.86 (d, J=9.2 Hz, 1H), 7.79 (d, J=8.0 Hz, 1H), 7.74 (d, J=9.2 Hz, 1H), 7.54—7.50 (m, 1H), 7.36—7.24 (m, 7H), 7.19—7.11 (m, 3H), 6.92 (d, J=8.0 Hz, 1H), 6.84 (d, J=8.4 Hz, 1H), 5.02 (br, 1H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$) δ: 151.6, 146.4, 144.7, 133.4, 132.8, 132.5, 131.0, 130.4, 129.3, 128.9, 128.3, 127.8, 127.6, 127.5, 126.7, 126.6, 126.2, 124.7, 123.9, 123.3, 121.7, 118.1, 113.8, 21.6.

Synthesis of 2-hydroxy-2'-phenylsulfonyloxy-1,1-binaphthyl (1b)[14]

This compound was prepared as white solid in a quantitative yield from binaphthol and benzenesulfonyl chloride by using procedures similar to those used for the preparation of **1**. ^{1}H NMR ($CDCl_3$) δ: 8.09 (d, J=8.8 Hz, 1H), 7.99 (d, J=8.0 Hz, 1H), 7.85 (d, J=8.8 Hz, 1H), 7.79 (d, J=7.6 Hz, 1H), 7.73 (d, J=8.8 Hz, 1H), 7.55—7.51 (m, 1H), 7.42—7.25 (m, 7H), 7.18—7.14 (m, 3H), 6.89 (d, J=8.4 Hz, 1H), 4.99 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 151.6, 146.3, 135.8, 133.7, 133.4, 133.3, 132.5, 131.0, 130.5, 128.9, 128.6, 128.3, 127.9, 127.7, 127.4, 126.8, 126.7, 126.2, 124.6, 124.0, 123.5, 121.6, 118.0, 113.7.

Synthesis of zinc alkyl complex 2a•2C$_7$H$_8$

To a solution of $ZnEt_2$ (2.0 mL, 1.0 mol/L in hexane, 2.0 mmol) was added a THF solution (20 mL) of compound **1a** (0.88 g, 1.0 mmol) at 0 ℃. After stirring at room temperature for 12 h, volatile materials were removed *in vacuo*. The resulting solid was extracted with 20.0 mL toluene. The extracts were concentrated to about 10.0 mL. The colorless crystals were obtained by cooling the concentrated solution at 0 ℃ (0.92 g, 87% yield). ^{1}H NMR ($CDCl_3$) δ: 7.88 (d, J=8.4 Hz, 2H), 7.73—7.66 (m, 4H), 7.43—7.08 (m, 25H), 6.99—6.92 (m, 2H), 6.76 (d, J=8.0 Hz, 2H), 6.51 (d, J=8.4 Hz, 2H), 2.36 (s, 6H), 2.19 (s, 3H), 0.49 (t, J=8.0 Hz, 6H), −0.23 (br, 4H); IR (KBr) ν: 3055 (m), 1749 (m), 1620 (m), 1508 (m), 1458 (m), 1361 (s), 1271 (m), 1172 (m), 1091 (m), 948 (m), 864 (m), 819 (w) cm^{-1}. Anal. calcd for $C_{79}H_{72}O_8S_2Zn_2$: C 70.58, H 5.40; found C 70.90, H 6.05.

Synthesis of zinc alkyl complex 2b•2C$_7$H$_8$

This complex was prepared as white crystals in 84% yield from the reaction of **1b** with a solution of $ZnEt_2$ in hexane by using procedures similar to those used for the preparation of **2a**. ^{1}H NMR ($CDCl_3$) δ: 7.66—6.29 (m, 36H), 2.06 (s, 6H), 0.50—0.47 (m, 6H), −0.02——0.04 (m, 4H); IR (KBr) ν: 3055 (m), 2958 (m), 1595 (m), 1508 (m), 1458 (s), 1354 (m), 1273 (m), 1203 (m), 1172 (m), 1093 (m), 1018 (s), 958 (m), 819 (m) cm^{-1}. Anal. calcd for $C_{70}H_{60}O_8S_2Zn_2$: C 68.68, H 4.94; found C 68.51, H 4.73.

Synthesis of zinc benzyloxy complex 3a•C$_6$H$_{14}$

The zinc complex **2a** (1.06 g, 1.0 mmol) was redissolved in toluene (30 mL). To the mixture was added BnOH (0.11 mL, 1.0 mmol) at 0 ℃. The mixture was stirred at room temperature for another 3 h, and the volatile materials were removed *in vacuo*. The resulting solid was extracted with 20.0 mL toluene. The extracts were concentrated to about 10.0 mL. The colorless crystals were obtained by cooling the concentrated solution at 0 ℃ (1.11 g, 85% yield). ^{1}H NMR ($CDCl_3$) δ: 7.89—6.50 (m, 84H), 4.98 (s, 4H), 4.70 (s, 4H), 2.36 (s, 12H) 4.98 (s, 4H), 4.70 (s, 4H), 2.36 (s, 12H); IR (KBr) ν: 3061 (m), 3030 (m), 2926 (m), 2873 (m), 1909 (m), 1625 (m), 1593 (m), 1454 (m), 1429 (m), 1344 (s), 1300 (m), 1203 (m), 1166 (m), 1068 (m), 1018 (m), 956 (m), 860 (m), 819 (w) cm^{-1}. Anal. calcd for $C_{148}H_{132}O_{20}S_4Zn_4$: C 67.84, H 5.08; found C 67.44, H 5.28.

The complex **3a** can also be prepared through the reaction of compound **1a** with $Zn(OBn)_2$ (*in situ* reaction of $ZnEt_2$ and BnOH). A solution of $ZnEt_2$ (1.0 mL, 1.0 mol/L in hexane, 1.0 mmol) and BnOH (0.21 mL, 2.0 mmol) in THF (20 mL) was stirred over 3 h. To the mixture was added a THF solution (20 mL) of compound **1a** (0.44 g, 1.0 mmol) at 0 ℃. The mixture was stirred at room temperature for another 3 h, and the volatile materials were removed *in vacuo*. The resulting solid was extracted with 20.0 mL toluene. The extracts were concentrated to about 10.0 mL. The colorless crystals **3a** were obtained by cooling the concentrated solution at 0 ℃.

Synthesis of zinc benzyloxy complex 3b

This complex was prepared as colorless crystal sol-

ids in 84% yield from the reaction of **2b** with BnOH by using procedures similar to those used for the preparation of **3a**. ^{1}H NMR ($CDCl_3$) *v*: 8.09—6.86 (m, 88H), 4.97 (s, 4H), 4.70 (s, 4H); IR (KBr) *v*: 3061 (m), 3057 (m), 2958 (m), 2872 (m), 1602 (m), 1595 (m), 1506 (m), 1456 (m), 1433 (m), 1354 (s), 1273 (m), 1203 (m), 1172 (s), 1143 (m), 1091 (m), 1018 (m), 958 (m), 862 (m), 817 (m) cm^{-1}. Anal. calcd for $C_{144}H_{124}O_{20}S_4Zn_4$: C 67.45, H 4.87; found C 67.91, H 4.67.

The complex **3b** can also be prepared through the reaction of compound **1b** with $Zn(OBn)_2$ (*in situ* reaction of $ZnEt_2$ and BnOH).

X-ray structure determinations

Suitable crystal of complexes **2a**, **2b** and **3a** was each mounted in a sealed capillary. Diffraction was performed on a Burker SMART CCD area detector diffractometer using graphite-monochromated Mo Kα radiation (λ=0.71073 Å); An empirical absorption correction was applied using the *SADABS* program. All structures were solved by direct methods, completed by subsequent difference Fourier syntheses, refined anisotropically for all nonhydrogen atoms by full-matrix least-squares calculations on F^2 using the *SHELXTL* program package. All hydrogen atoms were refined using a riding model. See Table 1 for crystallographic data. CCDC-886299 (**2a**), -886300 (**2b**) and -886301 (**3a**) contain the supplementary crystallographic data of this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Polymerization of ε-caprolactone

In a typical polymerization procedure, the catalyst (20—50 mg) was loaded into the Schlenk flask and the solvent was added. ε-CL was added through a gastight syringe after the external bath temperature was stabilized. The reaction was quenched by the addition of an aqueous acetic acid solution (0.1 mol/L, 2.0 mL). The polymer was precipitated out as white crystalline solid on pouring the mixture into methanol (50.0 mL), and then dried to a constant weight under vacuum. The molecular weights of the polymers were analyzed by GPC techniques.

D,*L*-Lactide polymerization

A typical polymerization procedure was exemplified by the synthesis of entry 3 (Table 3) using complex **3a** as an initiator at 50 ℃. *D*,*L*-lactide (0.360 g, 2.5 mmol) was added to an toluene (5 mL) solution of complex **3a** (0.0180 g, 0.0125 mmol). The reaction was quenched by the addition of an aqueous acetic acid solution (0.1 mol/L, 2.0 mL). The polymer was precipitated out as white crystalline solid on pouring the mixture into methanol (50.0 mL), and then dried to a constant weight under vacuum. The molecular weights of the polymers were analyzed by GPC techniques.

Table 1 Crystallographic data for complexes **2a**, **2b** and **3a**

	2a•2C_7H_8	**2b**•2C_7H_8	**3a**•C_6H_{14}
Formula	$C_{43}H_{32}O_4SZn$	$C_{84}H_{76}O_8S_2Zn_2$	$C_{74}H_{52}O_{10}S_2Zn_2$
Formula weight	710.12	1408.31	1296.02
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	*P*-1	$P2_1/c$	*P*-1
a/Å	10.7461(6)	10.6817(16)	12.864(2)
b/Å	13.0700(7)	23.721(4)	14.732(2)
c/Å	14.4450(8)	14.610(2)	18.414(3)
α/(°)	98.0650(10)		67.501(2)
β/(°)	103.9160(10)	104.521(3)	85.480(2)
γ/(°)	106.8560(10)		78.524(2)
V/Å^3	1835.86(17)	3583.6(10)	3159.6(9)
T/K	293(2)	293(2)	293(2)
Z	2	2	2
D_{calcd}/(g•cm^{-3})	1.285	1.305	1.362
μ/mm^{-1}	0.767	0.785	0.886
F(000)	736	1472	1336
θ range/(°)	1.97 to 26.00	2.15 to 26.05	1.52 to 26.00
reflns collected	10416	20165	23887
unique reflns	7100 (R_{int}=0.0172)	7047 (R_{int}=0.0402)	12135 (R_{int}=0.0856)
Parameters	507	435	747
Goodness of fit	1.095	1.038	1.067
R_1 [$I>2\sigma(I)$]	0.0424	0.0503	0.0779
wR_2 [$I>2\sigma(I)$]	0.1225	0.1374	0.2004
Largest diff. peak and hole/(e•Å^{-3})	0.805 and −0.292	0.756 and −0.536	1.084 and −0.492

Results and Discussion

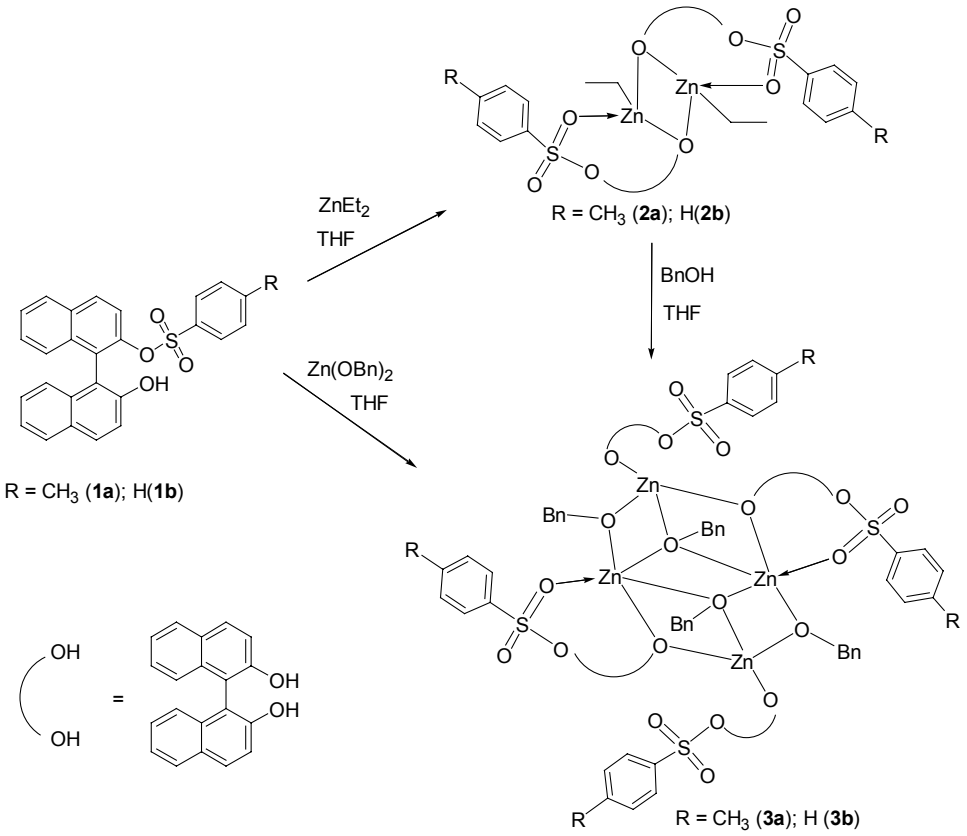
Synthesis and structure of zinc complexes containing sulfonylated binaphtholate ligands

Reaction of sulfonylated binaphthol with 1 equiv. of $ZnEt_2$ was performed in THF, affording the dinuclear zinc complexes [(Ts-Binol)ZnEt]$_2$ (**2a**) and [(Ps-Binol)-ZnEt]$_2$ (**2b**). Further reaction of zinc complexes **2a** and **2b** with BnOH gave the tetranuclear zinc benzyloxide [(Ts-Binol)$_2$Zn$_2$(OBn)$_2$]$_2$ (**3a**) and [(Ps-Binol)$_2$Zn$_2$-(OBn)$_2$]$_2$ (**3b**). Alternatively, the zinc benzyloxides **3a** and **3b** could also be obtained by reaction of compound **1a** or **1b** and $Zn(OBn)_2$ (*in situ* reaction of $ZnEt_2$ and BnOH) (Scheme 1). The complexes were fully characterized by elemental analyses and spectroscopic analyses, and complexes **2a**, **2b** and **3a** were further characterized by single-crystal X-ray analyses.

X-ray diffraction revealed that complexes **2a** (Figure 1) and **2b** (Figure 2) were an isostructural centrosymmetric dimeric geometry with a Zn_2O_2 core bridging through the oxygen atom of substituted binaphthol. The zinc metal centers in complexes **2a** and **2b** adopt a four coordinate distorted tetrahedral environment with

CHINESE JOURNAL OF CHEMISTRY

Scheme 1 Synthesis of zinc complexes



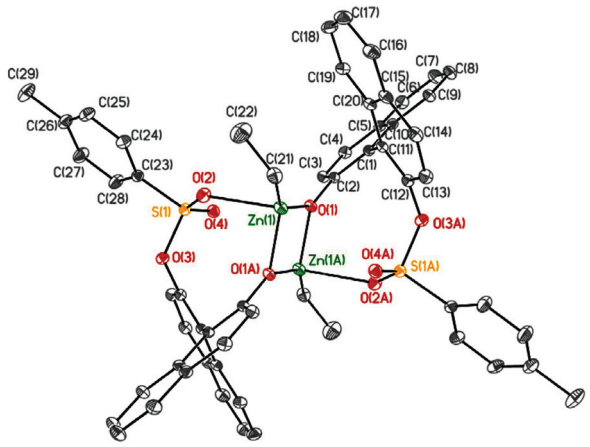


Figure 1 Molecular structure of zinc complex **2a**•2C_7H_8. Hydrogen atoms and solvents are omitted for clarity. Select bond lengths (Å): Zn—O(1) 1.964(2); Zn—O(2) 2.395(2); Zn—O(1A) 2.027(2); Zn—C(21) 1.950(2).

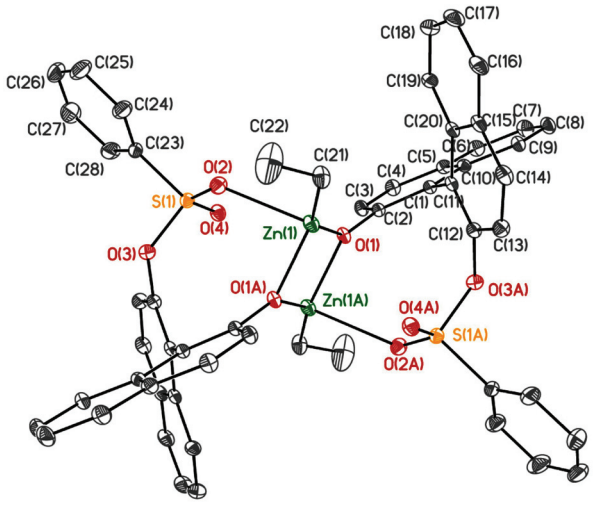


Figure 2 Molecular structure of zinc complex **2b**•2C_7H_8. Hydrogen atoms and solvents are omitted for clarity. Select bond lengths (Å): Zn—O(1) 1.969(2); Zn—O(2) 2.406(2); Zn—O(1A) 2.024(2); Zn—C(21) 1.952(4).

coordination to two bridging binaphtholate oxygen atoms, one oxygen atom of the sulfonyl group, and a methylene carbon atom of the ethyl group. The bridging oxygen atoms bond to the two metal centers asymmetrically with the Zn(1)—O(1) bond distance of 1.964(2) Å in complex **2a**, being shorter than the Zn(1)—O(1A) distance of 2.027(2) Å. Similarly, the Zn(1)—O(1) distance of 1.969(2) Å in **2b** is shorter than the Zn(1)—O(1A) distance of 2.024(2) Å. The Zn(1)—O(2) bond lengths in complex **2a** [2.395(2) Å] and complex **2b** [2.406(2) Å] are much longer than the distances of the bridging Zn—O bonds. The Zn—C(21) distances of 1.950(2) Å in complex **2a** and1.952(4) Å in complex **2b** are compared with those of 1.947(2) and 2.008(3) Å in the biphenolate zinc complex [(μ,μ-biphenolate)Zn(μ-OCH(^{i}Pr)$_2$)$_2$Zn$_2$Et$_2$][13] and zinc alkyl complex contain-

ing NNO-tridentate Schiff base ligand.[11b]

The zinc complexes **3a** (Figure 3) was a centrosymmetric tetranuclear complex. The two zinc metal centers in complexes **3a** adopt a five coordinate distorted trigonal bipyramidal environment, and other two zinc metal centers adopt a four coordinate distorted tetrahedral environment. The another feacture of the complex **3a** is that the Zn(1), O(9), Zn(2), and O(10) atoms are coplanar with the torsional angle of 2.3(2)° in Zn(1)-O(9)-Zn(2)-O(10).

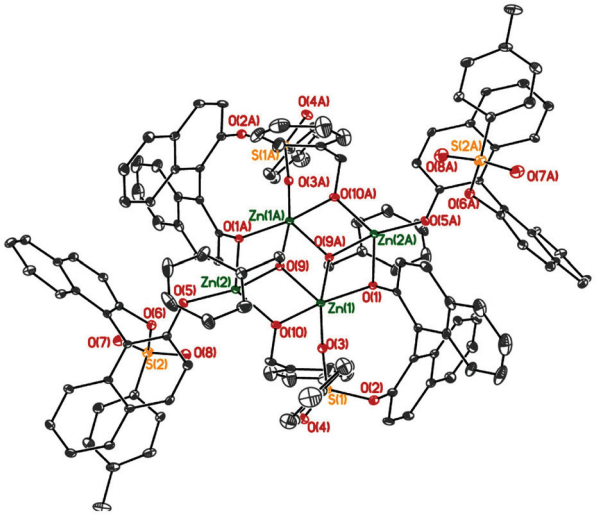


Figure 3 Molecular structure of zinc complex **3a**•C_6H_{14}. Hydrogen atoms and solvents are omitted for clarity. Select bond lengths (Å): Zn(1)—O(1) 1.929(5); Zn(1)—O(3) 2.223(5); Zn(1)—O(9) 2.033(5); Zn(1)—O(10) 1.943(5); Zn(1)—O(9A) 2.194(4); Zn(2)—O(5) 1.826(5); Zn(2)—O(9) 2.007(4); Zn(2)—O(10) 1.973(5); Zn(2)—O(1A) 2.019(5). Select torsional angles (°): Zn(1)-O(9)-Zn(2)-O(10) 2.3(2); Zn(1)-O(1)-Zn(2A)-O(9A) 15.67(18).

Ring-opening polymerization of ε-caprolactone

The catalytic activities of zinc benzyloxides **3a** and **3b** towards ROP of ε-caprolactone were firstly examined, and results are listed in Table 2. It was found that the zinc complexes showed a good catalytic activities at 20 ℃ (Table 2, Entries 1—4). Furthermore, zinc complex **3a** as an initator for ROP of ε-caprolactone was examined within 10 h at 20 ℃ in the monomer-to-initiator ratio ($[M]_0/[Zn]_0$) range of 100—600. Results revealed that the linear relationship was associated with the M_n and $[M]_0/[Zn]_0$ ratio and the narrow polydispersity index (PDI) ranging from 1.04 to 1.09 of the polymers ($[M]_0/[Zn]_0$ ratio of 100—500, Figure 4), implying the highly controlled and ''living'' character of the polymerization process. The $[M]_0/[Zn]_0$ ratio of 600 deviated from the linear relationship, maybe owing to the lower conversion of monomer (Table 2, Entry 9). In fact, the ε-caprolactone polymerization reaction proceeds in a living fashion, and M_n of poly(CL) increases linearly in proportion to the reaction time, while M_w/M_n values remain almost intact in respect to the reaction time (Figure 5).

Ring-opening polymerization of *D*,*L*-lactide

The catalytic activities of zinc complexes towards ROP of *D*,*L*-lactide were examined, and results are listed in Table 3. From the table, we can see that the catalytic activities of zinc complexes increase with increasing temperature (Table 3, Entries 1—3). Furthermore, zinc complex **3a** as an initator for ROP of *D*,*L*-lactide was examined at 50 ℃ in the monomer-to-initiator ratio ($[M]_0/[Zn]_0$) range of 100—500. Results revealed that the molecular weight of polymers increased as the monomer to initiator ratio increased. The molecular weights distribution of polymers

Table 2 Ring-opening polymerization of ε-caprolactone initiated by zinc complexes **3a**—**3b**[a]

Entry	$[Zn]_0$	$[M]_0/[Zn]_0$	Solvent	Temp./℃	M_n[b]	M_n (NMR)[c]	PDI[b]	Conv./%
1	**3a**	100∶1	toluene	0	13190 (7386)	—	1.08	49
2	**3a**	100∶1	toluene	20	12411 (6950)	—	1.06	91
3	**3a**	100∶1	toluene	50	13565 (4254)	—	1.13	79
4	**3b**	100∶1	toluene	20	11214 (6279)	7500	1.12	81
5	**3a**	200∶1	toluene	20	26386 (14776)	12500	1.07	84
6	**3a**	300∶1	toluene	20	40702 (22793)	21600	1.09	86
7	**3a**	400∶1	toluene	20	64151 (35925)	32300	1.04	83
8	**3a**	500∶1	toluene	20	95151 (53285)	53900	1.05	81
9	**3a**	600∶1	toluene	20	94460 (52898)	51500	1.03	69
10[d]	**3a**	400∶1	toluene	20	—	—	—	＜10%
11[e]	**3a**	400∶1	toluene	20	13269 (7430)	9000	1.09	29
12[f]	**3a**	400∶1	toluene	20	28476 (15946)	14800	1.06	51
13[g]	**3a**	400∶1	toluene	20	48562 (27194)	27500	1.07	70

[a] Solvent: toluene (5 mL); reaction time: 10 h. [b] Obtained from GPC analysis and calibrated by polystyrene standard. Values in parentheses are the values obtained from GPC times 0.56. [c] Obtained from ^{1}H NMR analysis. [d] Reaction time: 2 h. [e] Reaction time: 4 h. [f] Reaction time: 6 h. [g] Reaction time: 8 h.

CHINESE JOURNAL OF CHEMISTRY

Table 3 Ring-opening polymerization of *D*,*L*-lactide initiated by zinc complexes **3a**—**3b**[a]

Entry	$[Zn]_0$	$[M]_0/[Zn]_0$	Temp./℃	M_n[b]	M_n (NMR)[c]	PDI[b]	Conv./%
1	**3a**	100∶1	0	N.D.[d]	—	N.D.[d]	＜10%
2	**3a**	100∶1	20	9136 (5299)	4500	1.12	45
3	**3a**	100∶1	50	17422 (10105)	9800	1.09	96
4	**3b**	100∶1	50	18572 (10772)	10200	1.16	63
5	**3a**	200∶1	50	24851 (14414)	13600	1.02	92
6	**3a**	300∶1	50	28674 (16683)	15400	1.02	88
7	**3a**	400∶1	50	29811 (17290)	18200	1.02	91
8	**3a**	500∶1	50	30151 (17488)	20700	1.04	71

[a] Solvent: toluene (5 mL); reaction time: 10 h. [b] Obtained from GPC analysis and calibrated by polystyrene standard. Values in parentheses are the values obtained from GPC times 0.58. [c] Obtained from ^{1}H NMR analysis. [d] N.D.: not determined.

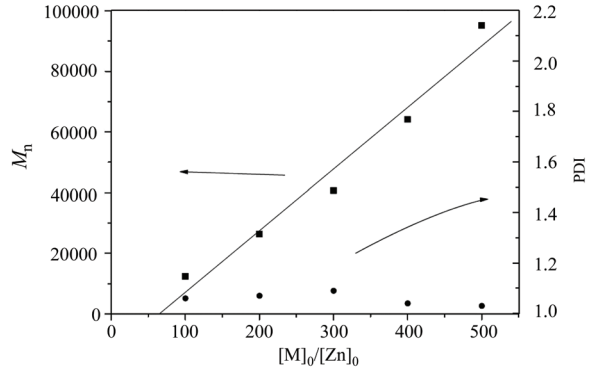


Figure 4 Polymerization of ε-caprolactone initiated by **3a** in toluene at 20 ℃. The relationship between M_n (■) [PDI (●)] of the polymer and the initial mole ratio $[M]_0/[Zn]_0$ is shown.

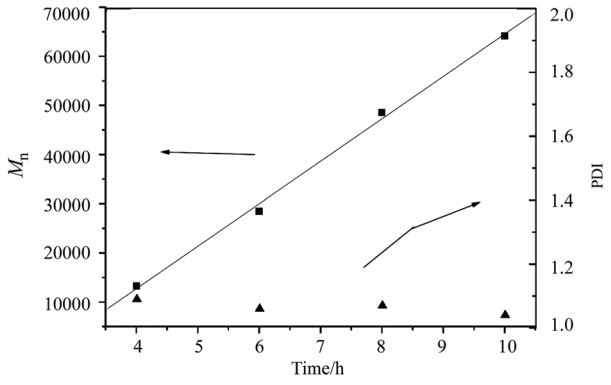


Figure 5 Polymerization of ε-caprolactone initiated by **3a** in toluene at the mole ratio $[M]_0/[Zn]_0$ of 400∶1. The relationship between M_n (■) [PDI (▲)] of the polymer and date at various time points is shown.

obtainted ranging from 1.02 to 1.09. However, the molecular weights are lower than the theoretical values when the ratio of *D*,*L*-lactide to catalyst is high due to transesterification.

Conclusions

A series of zinc alkyl and benzylalkoxy complexes containing sulfonylated binaphtholate ligands were synthesized and used as initiators for the ring opening polymerization of ε-caprolactone and *D*,*L*-lactide. The results of the study on the catalytic activity showed that the new zinc benzyloxides exhibited a high controllability for the ring opening polymerization of ε-caprolactone with a high molecular weight and narrow molecular weight distribution in a living fashion.

Acknowledgement

This work is supported by the National Natural Science Foundation of China (21172003, 21172004, 20832001), and grants from the Ministry of Education (20103424110001) and Anhui province (TD200707, 11040606M36).

References

[1] For reviews, see: (a) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. *Chem. Rev.* **2004**, *104*, 6147; (b) Wu, J. C.; Yu, T.-L.; Chen, C.-T.; Lin, C.-C. *Coord. Chem. Rev.* **2006**, *250*, 602; (c) Maharana, T.; Mohanty, B.; Negi, Y. S. *Prog. Polym. Sci.* **2009**, *34*, 99; (d) Sutar, A. K.; Maharana, T.; Dutta, S.; Chen, C.-T.; Lin, C.-C. *Chem. Soc. Rev.* **2010**, *39*, 1724.

[2] (a) Iannace, S.; De Luca, N.; Nicolais, L.; Carfagna, C.; Huang, S. J. *J. Appl. Polym. Sci.* **1990**, *41*, 2691; (b) Doi, Y.; Kumagai, Y.; Tanahashi, N.; Mukai, K. In *Biodegradable Polymers and Plastics*, Eds.: Vert, M.; Feijen, J.; Albertsson, A.; Scott, G.; Chiellini, E., The Royal Society of Chemistry, Cambridge, U. K., **1992**, p. 139; (c) Müller, H. M.; Seebach, D. *Angew. Chem., Int. Ed.* **1993**, *32*, 477; (d) Ni, Q.; Yu, L. *J. Am. Chem. Soc.* **1998**, *120*, 1645; (e) Okada, M. *Prog. Polym. Sci.* **2002**, *27*, 87; (f) Wiegand, T.; Karr, J.; Steinkruger, J. D.; Hiebner, K.; Simetich, B.; Beatty, M.; Redepenning, J. *Chem. Mater.* **2008**, *20*, 5016.

[3] (a) Morton, M.; Wu, M. Y. In *Ring-Opening Polymerization*, ACS Symposium Series, **1985**, Volume 286, Chapter 13, p. 175; (b) Wang, Z.; Qi, C. *Organometallics* **2007**, *26*, 2243; (c) Chen, L.; Jia, L.; Cheng, F.; Wang, L.; Lin, C.-C.; Wu, J.; Tang, N. *Inorg. Chem. Commun.* **2011**, *14*, 26; (d) Ko, B.-T.; Lin, C.-C. *J. Am. Chem. Soc.* **2001**, *123*, 7973; (e) Hsueh, M.-L.; Huang, B.-H.; Wu, J.; Lin, C.-C. *Macromolecules* **2005**, *38*, 9482.

[4] (a) Shueh, M.-L.; Wang, Y.-S.; Huang, B.-H.; Kuo, C.-Y.; Lin, C.-C. *Macromolecules* **2004**, *37*, 5155; (b) Sarazin, Y.; Schormann, M.; Bochmann, M. *Organometallics* **2004**, *23*, 3296; (c) Chisholm, M. H.; Gallucci, J. C.; Phomphrai, K. *Inorg. Chem.* **2004**, *43*, 6717; (d) Yu, T.-L.; Wu, C.-C.; Chen, C.-C.; Huang, B.-H.; Wu, J.; Lin, C.-C. *Polymer* **2005**, *46*, 5909; (e) Xu, X.; Chen, Y.; Zou, G.; Ma, Z.; Li,

G. *J. Organomet. Chem.* **2010**, *695*, 1155.

[5] (a) Duda, A.; Penczek, S. *Macromolecules* **1995**, *28*, 5981; (b) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **1999**, *121*, 4072; (c) Radano, C. P.; Baker, G. L.; Smith, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 1552; (d) Liu, Y.-C.; Ko, B.-T.; Lin, C.-C. *Macromolecules* **2001**, *34*, 6196; (e) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 1316; (f) Chen, C.-T.; Huang, C.-A.; Huang, B.-H. *Macromolecules* **2004**, *37*, 7968; (g) Iwasa, N.; Katao, S.; Liu, J.; Fujiki, M.; Furukawa, Y.; Nomura, K. *Organometallics* **2009**, *28*, 2179; (h) Gao, A.; Mu, Y.; Zhang, J.; Yao, W. *Eur. J. Inorg. Chem.* **2009**, 3613; (i) Li, W.; Yao, Y.; Zhang, Y.; Shen, Q. *Chin. J. Chem.* **2012**, *30*, 609.

[6] (a) Hannant, M. D.; Schormann, M.; Bochmann, M. *Dalton Trans.* **2002**, 4071; (b) Williams, C. K.; Breyfogle, L. E.; Choi, S. K.; Nam, W.; Young, V. G.; Hillmyer, M. A.; Tolman, W. B. *J. Am. Chem. Soc.* **2003**, *125*, 11350; (c) Chakraborty, D.; Chen, E. Y.-X. *Organometallics* **2003**, *22*, 769; (d) Walker, D. A.; Woodman, T. J.; Schormann, M.; Hughes, D. L.; Bochmann, M. *Organometallics* **2003**, *22*, 797; (e) Chen, H.-Y.; Huang, B.-H.; Lin, C.-C. *Macromolecules* **2005**, *38*, 5400; (f) Chai, Z.-Y.; Zhang, C.; Wang, Z.-X. *Organometallics* **2008**, *27*, 1626.

[7] (a) Deshayes, G.; Mercier, F. A. G.; Degée, P.; Verbruggen, I. I.; Biesemans, M.; Willem, R.; Dubois, P. *Chem. Eur. J.* **2003**, *9*, 4346; (b) Bratton, D.; Brown, M.; Howdle, S. M. *Macromolecules* **2005**, *38*, 1190; (c) Kowalski, A.; Libiszowski, J.; Biela, T.; Cypryk, M.; Duda, A.; Penczek, S. *Macromolecules* **2005**, *38*, 8170; (d) Dove, A. P.; Gibson, V. C.; Marshall, E. L.; Rzepa, H. S.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **2006**, *128*, 9834; (e) Chagneux, N.; Trimaille, T.; Rollet, M.; Beaudoin, E.; Gérard, P.; Bertin, D.; Gigmes, D. *Macromolecules* **2009**, *42*, 9435.

[8] (a) Thomas, D.; Arndt, P.; Peulecke, N.; Spannenberg, A.; Kempe, R.; Rosenthal, U. *Eur. J. Inorg. Chem.* **1998**, 1351; (b) Takeuchi, D.; Nakamura, T.; Aida, T. *Macromolecules* **2000**, *33*, 725; (c) Cayuela, J.; Bounor-Legaré, V.; Cassagnau, P.; Michel, A. *Macromolecules* **2006**, *39*, 1338; (d) Gowda, R. R.; Chakraborty, D.; Ramkumar, V. *Eur. J. Inorg. Chem.* **2009**, 2981.

[9] (a) Nishiura, M.; Hou, Z.; Koizumi, T.; Imamoto, T.; Wakatsuki, Y. *Macromolecules* **1999**, *32*, 8245; (b) Gamer, M. T.; Rastätter, M.; Roesky, P. W.; Steffens, A.; Glanz, M. *Chem. Eur. J.* **2005**, *11*, 3165; (c) Yang, Y.; Li, S.; Cui, D.; Chen, X.; Jing, X. *Organometallics* **2007**, *26*, 671; (d) Clark, L.; Deacon, G. B.; Forsyth, C. M.; Junk, P. C.; Mountford, P.; Townley, J. P. *Dalton Trans.* **2010**, *39*, 6693; (e) Schwarz, A. D.; Chu, Z.; Mountford, P. *Organometallics* **2010**, *29*, 1246; (f) Wang, J. F.; Yao, Y. M.; Zhang, Y.; Shen, Q. *Inorg. Chem.* **2009**, *48*, 744; (g) Zhang, Z. J.; Xu, X. P.; Li, W. Y.; Yao, Y. M.; Zhang, Y.; Shen, Q.; Luo, Y. J. *Inorg. Chem.* **2009**, *48*, 5715; (h) Schwarz, A. D.; Herbert, K. R.; Paniagua, C.; Mountford, P. *Organometallics* **2010**, *29*, 4171; (i) Zhang, L.; Wang, Y.; Shen, L.; Zhang, T. *Chin. J. Chem.* **2010**, *28*, 1019; (j) Yang, J.; Xu, P.; Luo, Y. *Chin. J. Chem.* **2010**, *28*, 457; (k) Peckermann, I.; Kapelski, A.; Spaniol, T. P.; Okuda, J. *Inorg. Chem.* **2009**, *48*, 5526; (l) Zhou, S.; Wu, S.; Zhu, H.; Wang, S.; Zhu, X.; Zhang, L.; Yang, G.; Cui, D.; Wang, H. *Dalton Trans.* **2011**, *40*, 9447; (m) Wang, L.; Liang, Z.; Ni, X.; Shen, Z. *Chin. Chem. Lett.* **2011**, *22*, 249; (n) Huang, J.; Yu, J.; Wu, G.; Sun, W.; Shen, Z. *Chin. Chem. Lett.* **2009**, *20*, 1357; (o) Zhou, S.; Yin, C.; Wang, H.; Zhu, X.; Yang, G.; Wang, S. *Inorg. Chem. Commun.* **2011**, *14*, 1194.

[10] (a) Cheng, M.; Attygalle, A. B.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **1999**, *121*, 11583; (b) Chamberlain, B. M.; Cheng, M.; Moore, D. R.; Ovitt, T. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 3229; (c) Chisholm, M. H.; Gallucci, J. C.; Phomphrai, K. *Inorg. Chem.* **2005**, *44*, 8004.

[11] Chisholm, M. H.; Gallucci, J.; Zhen, H.; Huffman, J. C. *Inorg. Chem.* **2001**, *40*, 5051; (b) Chen, H.-Y.; Tang, H.-Y.; Lin, C.-C. *Macromolecules* **2006**, *39*, 3745; (c) Wu, J.-C.; Huang, B.-H.; Hsueh, M.-L.; Lai, S.-L.; Lin, C.-C. *Polymer* **2005**, *46*, 9784.

[12] Huang, B.-H.; Lin, C.-N.; Hsueh, M.-L.; Athar, T.; Lin, C.-C. *Polymer* **2006**, *47*, 6622.

[13] Chisholm, M. H.; Lin, C.-C.; Gallucci, J. C.; Ko, B.-T. *Dalton Trans.* **2003**, 406.

[14] Solinas, M.; Meadows, R. E.; Wilson, C.; Blake, A. J.; Woodward, S, *Eur. J. Org. Chem.* **2007**, 1613.

(Zhao, X.)

