Dalton Transactions

Cite this: *Dalton Trans.*, 2011, **40**, 12886

www.rsc.org/dalton

PAPER

Structural and catalytic studies of zinc complexes containing amido-oxazolinate ligands†

Ming-Tsz Chen and Chi-Tien Chen*

Received 25th May 2011, Accepted 12th September 2011
DOI: 10.1039/c1dt10974j

Several zinc complexes bearing amido-oxazolinate ligands are described. Reactions of ligand precursors, HNC_2^EOxa (HNC_2^EOxa = $HNC_2^{Me}Oxa$, $HNC_2^{OMe}Oxa$, $HNC_2^{StBu}Oxa$ and $HNC_2^{NMe2}Oxa$) or $HNPh^{SMe}Oxa$, with half or one molar equivalent of $ZnEt_2$ afford bis(chelate) zinc complexes, $(NC_2^EOxa)_2Zn$ [C_2^E = propyl, (**1**); C_2^E = 2-methoxyethyl, (**2**); C_2^E = 2-*N*,*N*′-dimethylethyl, (**3**)] or zinc ethyl complexes, $(NC_2^{StBu}Oxa)ZnEt$(**4**) and $(NPh^{SMe}Oxa)ZnEt$(**5**), using tetrahydrofuran or hexane as solvents. The zinc benzyl oxide complexes, $[(NC_2^EOxa)Zn(\mu\text{-}OBn)]_2$ [C_2^E = propyl, (**6**); C_2^E = 2-methoxyethyl, (**7**); C_2^E = 2-*tert*-butylthioethyl, (**8**)], are obtained from the reactions of ligand precursors, HNC_2^EOxa, with one molar equivalent of ZnEt(OBn) (generated *in situ* on 1 : 1 ratio of $ZnEt_2$ and BnOH) in tetrahydrofuran. The molecular structures are reported for compounds **1**, **3**, **5**, **6** and **7**. All eight compounds were assessed as efficient catalyst precursors towards the ring-opening polymerization of L-lactide and ε-caprolactone.

Introduction

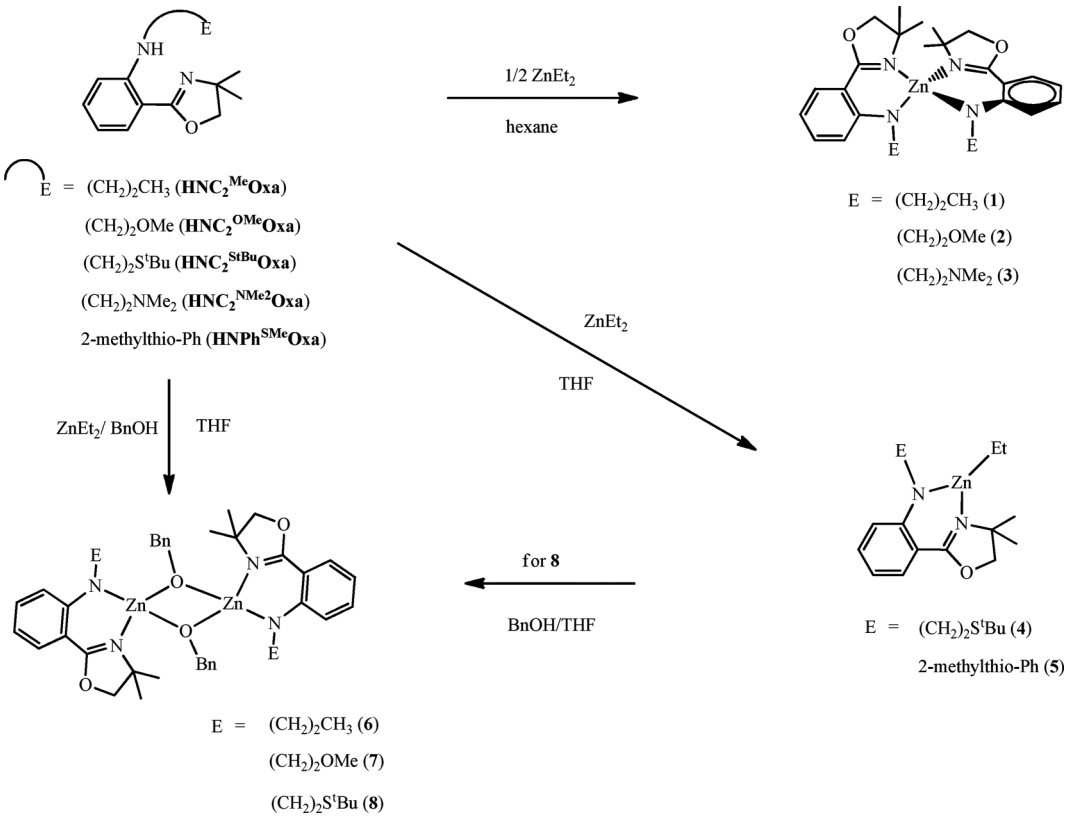
Biodegradable polymers such as poly(ε-caprolactone) (PCL) and poly(lactide) (PLA), as well as their copolymers, are useful for their application for tissue engineering, drug delivery, and environmentally friendly wrapping materials.[1] The major polymerization method for synthesizing biodegradable polymers using metal-based initiators/catalysts for ring opening polymerization has been proven to provide greater control over the molecular characteristics of the polymers.[2] Therefore metal complexes bearing auxiliary ligands for ring opening polymerization have attracted great interest, mainly because of their promising activities and great success in preparing the well-defined polyesters. Due to the promising catalytic application of metal β-diketiminate complexes in ring opening polymerization, metal centres including magnesium, calcium and zinc, with structurally-related ligands were synthesized and some of them have been examined for their catalytic activities in ring opening polymerisation.[3] The efficient performance of these metal complexes encourages us to investigate ligand precursors bearing similar chelating systems and isoelectronic feature related to β-diketiminate ligands. According to our previous catalytic studies on metal anilido-oxazolinate[3k,3o,3p] or anilido-pyrazolate[3q] complexes and the catalytic activities demonstrated by some zinc complexes bearing β-diketiminate ligands in ring opening polymerization,[4] zinc amido-oxazolinate complexes are expected to be useful initiators/catalysts in ring opening polymerization. In this paper, several zinc amido-oxazolinate complexes have been synthesized and their catalytic activities in ring opening polymerization of L-lactide or ε-caprolactone in the presence of benzyl alcohol are also investigated.

Department of Chemistry, National Chung Hsing University, Taichung 402, Taiwan, Republic of China. E-mail: ctchen@dragon.nchu.edu.tw

† CCDC reference numbers 827166–827170. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10974j

Results and discussion

The preparation of ligand precursor $HNPh^{SMe}Oxa$[3o] has been reported by us using palladium-catalyzed amination.[5] According to the previous established procedure, similar ligand precursors with aliphatic functionalities were prepared straightforward by using copper-catalyzed amination[6] of 2-(2-bromophenyl)-4,4-dimethyl-2-oxazoline[7] with suitable amine or hydrochloride salt of amine (propylamine for $HNC_2^{Me}Oxa$;[3p] 2-methoxyethylamine for $HNC_2^{OMe}Oxa$;[3p] 2-*tert*-butylthioethylamine hydrochloride[8] for $HNC_2^{StBu}Oxa$;[3p] unsym-dimethyl-ethylenediamine for $HNC_2^{NMe2}Oxa$) in the presence of CuI, L-proline and K_3PO_4 in DMSO at 110 °C for 14 h. All of these ligand precursors are characterized by NMR spectroscopy as well as elemental analyses. Syntheses and the proposed structures are summarized in Scheme 1. In view of the promising catalytic activities of zinc β-diketiminate complexes,[3,4] preparation of zinc amido-oxazolinate complexes was examined using one molar equivalent of ligand precursors with one molar equivalent of $ZnEt_2$ resulting in the isolation of zinc ethyl complexes, **4** or **5** as yellow solid. Repeated reactions using one molar equivalent of HNC_2^EOxa with half molar equivalent of $ZnEt_2$ in hexane yielded zinc bis(amido-oxazolinate) complexes **1–3**. Syntheses of zinc benzyl oxide complexes **6–8** can be achieved by the reactions of $HNC_2^{Me}Oxa$, $HNC_2^{OMe}Oxa$ or $HNC_2^{StBu}Oxa$ with one molar equivalent of ZnEt(OBn) (generated *in situ* on 1 : 1 ratio of $ZnEt_2$ and BnOH) in tetrahydrofuran solution. Alternative route for



Scheme 1 Structures of **1–8**.

the preparation of zinc benzyl oxide complex **8**, was achieved by the reaction of **4** with one equivalent of benzyl alcohol in tetrahydrofuran solution. The spectroscopic data of **1–8** are consistent with the structures proposed in Scheme 1.

Suitable crystals of **1**, **3**, **5**, **6** and **7** for structural determination are obtained from concentrated hexane or concentrated tetrahydrofuran solutions. The molecular structures are depicted in Fig. 1–5. The geometry at the zinc centre of **1** can be described as distorted tetrahedral geometry with two chelates coordinating with bite angles of 94.25(7)° and 94.67(7)°, which are smaller than those (94.8(2)–99.67(1)°) found in zinc β-diketiminate complexes with alkyl oxide bridge functionalities.[4a–c,4f,g] The Zn–N_{amido} bond lengths (1.9468(18) and 1.9448(17) Å) are shorter than Zn–$N_{oxazoline}$ bond lengths (2.0113(16) and 2.0077(16) Å), which might result from the π-donation ability of the anionic amido nitrogen.[9] For **3**, similar to those discussed above, two bite angles, 94.50(7) and 93.99(7)°, are similar to those discussed for **1**, and the Zn–N_{amido} bond lengths (1.9459(18) and 1.9491(18) Å) are also shorter than the Zn–$N_{oxazoline}$ bond lengths (2.0069(18) and 2.0110(19) Å). For **5**, a distorted trigonal planar geometry can be described with zinc metal center coordinated with two nitrogen atoms from ligand and one carbon atom from ethyl group. The bite angle (93.36(11)°) is smaller than those discussed above and the Zn–N_{amido} bond length (1.944(3) Å) is shorter than Zn–$N_{oxazoline}$ bond length (1.991(3) Å). The molecular structures of **6** and **7** exist as benzoxyl-bridged dimers with a core planar Zn–O–Zn–O ring in each case and their molecular structure diagrams can be described as distorted tetrahedron geometry for zinc centre. The dimers lie about inversion centres in the crystal structures.

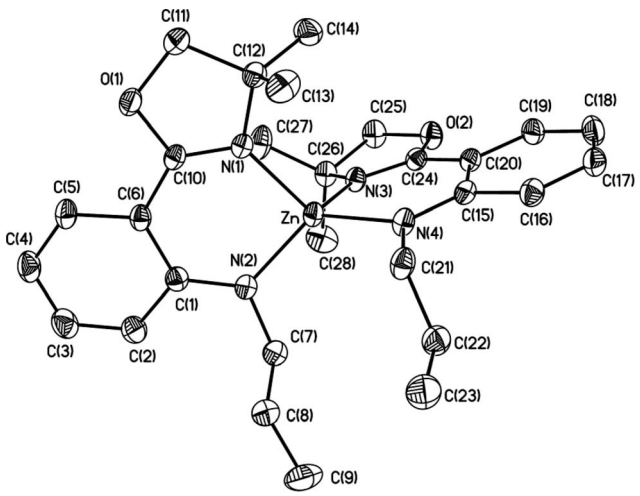


Fig. 1 Molecular structure of **1**. Selected bond lengths (Å) and bond angles (°): Zn–N(1), 2.0113(16); Zn–N(2), 1.9468(18); Zn–N(3), 2.0077(16); Zn–N(4), 1.9448(17); C(1)–N(2), 1.348(3); C(10)–N(1), 1.283(3); C(15)–N(4), 1.348(3); C(24)–N(3), 1.292(3); N(2)–Zn–N(4), 127.01(8); N(4)–Zn–N(3), 94.25(7); N(1)–Zn–N(4), 114.76(7); N(2)–Zn–N(3), 114.34(7); N(1)–Zn–N(3), 112.87(7); N(1)–Zn–N(2), 94.67(7). Hydrogen atoms on carbon atoms omitted for clarity. Perspective view of **1** with probability ellipsoids at 20% level.

For **6**, the planar core features two similar Zn–$O_{benzoxyl}$ distances (1.9793(13) and 1.9637(13) Å) with ZnOZn and OZnO angles of 99.00(16) and 81.00(6)°. Each zinc atom is four-coordinate, which is coordinated with one nitrogen atom of the oxazoline

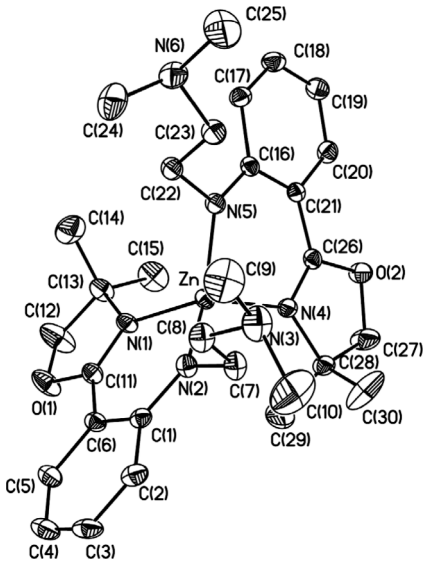


Fig. 2 Molecular structure of **3**. Selected bond lengths (Å) and bond angles (°): Zn–N(1), 2.0069(18); Zn–N(2), 1.9459(18); Zn–N(4), 2.0110(7); Zn–N(5), 1.9491(18); C(1)–N(2), 1.355(3); C(11)–N(1), 1.283(3); C(16)–N(5), 1.347(3); C(26)–N(4), 1.285(3); N(1)–Zn–N(2), 94.50(19); N(4)–Zn–N(5), 93.99(7); N(1)–Zn–N(5), 114.21(8); N(2)–Zn–N(4), 117.60(8); N(2)–Zn–N(5), 125.24(8); N(1)–Zn–N(4), 112.46(8). Hydrogen atoms on carbon atoms omitted for clarity. Perspective view of **3** with probability ellipsoids at 20% level.

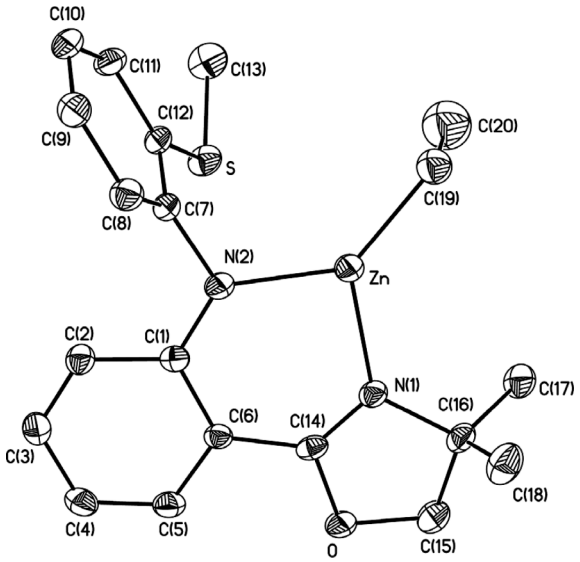


Fig. 3 Molecular structure of **5**. Selected bond lengths (Å) and bond angles (°): Zn–N(1), 1.991(3); Zn–N(2), 1.944(3); C(19)–C(20), 1.428(7); C(14)–N(1), 1.285(4); C(12)–S, 1.766(3); C(13)–S, 1.791(4); N(2)–Zn–N(1), 93.36(11); C(19)–Zn–N(1), 129.30(15); C(19)–Zn–N(2), 137.16(15). Hydrogen atoms on carbon atoms omitted for clarity. Perspective view of **5** with probability ellipsoids at 20% level.

group with Zn–N(1) bond length of 1.9795(16) Å, one nitrogen atom of the amido group with a Zn–N(2) bond length of 1.9414(17) Å and two oxygen atoms from two bridged benzyl oxide groups. These data are in the range of known distances and angles for zinc β-diketiminate complexes[4] and structurally-related zinc complexes.[3a–3c,3e,10] Basically, compound **7** is quite similar to compound **6** with 2-methoxyethyl substituent instead of propyl substituent on the amido group. Similar to **6**, two zinc metal centres are bridged *via* Zn–$O_{benzoxyl}$ bonds (1.9753(15) and 1.9637(16) Å) to form a planar core ring Zn–O(3)–ZnA–O(3A) with the angles subtended at the zinc atoms (81.01(6)°) narrower than those (98.99(6)°) at oxygen atoms. Bond lengths and bond angles are similar to those discussed above for **6**.

Polymerization studies

Several zinc β-diketiminate complexes[4] are known as efficient initiators/catalysts in the ring opening polymerization (ROP). Polymerization of L-lactide and ε-caprolactone employing **1–8** as catalysts has been systematically investigated under a dry nitrogen atmosphere. Representative results are collected in Table 1 and 2 for L-lactide and ε-caprolactone, respectively. Optimized conditions were found to be toluene at 50 °C in the presence of benzyl alcohol after several trials on running polymerization with dichloromethane, tetrahydrofuran and toluene for polymerization of L-lactide or ε-caprolactone. The same conditions were applied to examine the catalytic activities of the other seven catalysts. Typical polymerization reaction was carried out at 50 °C in 10 mL toluene solution for L-lactide, or in 15 mL toluene solution for ε-caprolactone. Experimental results show compound **7** demonstrates similar activities to **8** within the same period (entries 7–8), whereas **4** and **5** exhibit poor conversion with

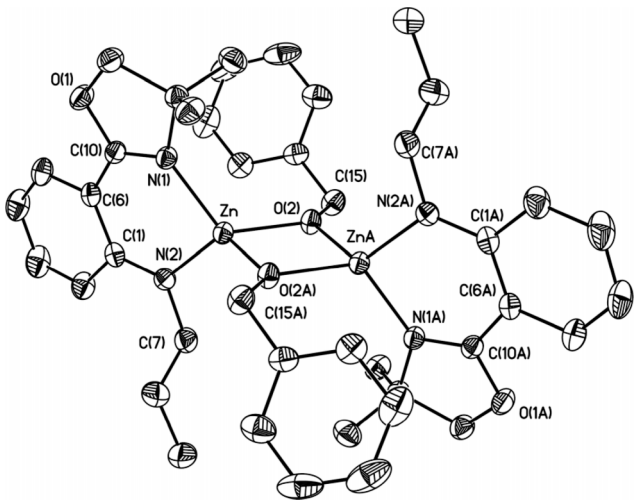


Fig. 4 Molecular structure of **6**. Selected bond lengths (Å) and bond angles (°): Zn–N(1), 1.9795(16); Zn–N(2), 1.9414(17); Zn–O(2), 1.9793(13); Zn–O(2A), 1.9637(13); O(2)–C(15), 1.404(2); N(1)–C(10), 1.300(2); N(2)–C(1), 1.354(3); N(1)–Zn–N(2), 96.52(7); N(2)–Zn–O(2A), 120.57(7); O(2A)–Zn–O(2), 81.00(6); O(2)–Zn–N(1), 120.93(7); N(2)–Zn–O(2), 120.82(7); N(1)–Zn–O(2A), 119.32(6). Zn–O(2)–Zn(A), 99.00(6). Hydrogen atoms on carbon atoms omitted for clarity. Perspective view of **6** with probability ellipsoids at 20% level. Symmetry code A = 2–x,–y, –z.

time up to 60 min (entries 4–5). Zinc benzyl oxide complexes **6–8** behave in a controlled manner and show better activities than our previous report with aromatic functionality.[3k] These good conversions demonstrated by **6–8** might result from the tuning of Lewis acidity of metal centre with pendant functionality or decrease of the rigidity by the alkyl group, which make coordination of monomer to the metal centre easily, leading to an increase in propagation. Due to the ease of preparation and better

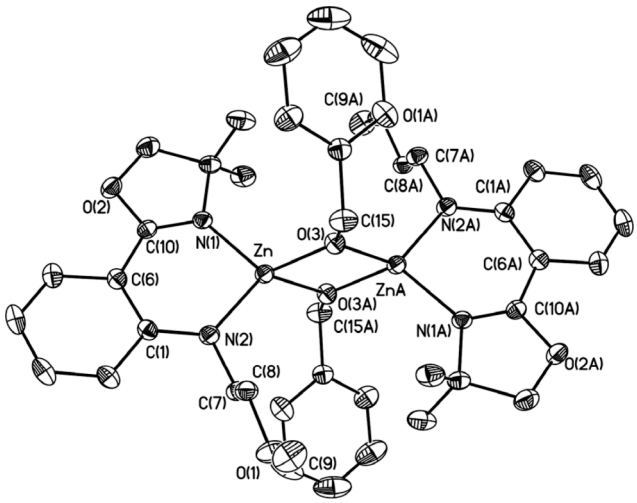


Fig. 5 Molecular structure of **7**. Selected bond lengths (Å) and bond angles (°): Zn–N(1), 1.9855(18); Zn–N(2), 1.396(18); Zn–O(3), 1.9753(15); Zn–O(3A), 1.9637(16); O(3)–C(15), 1.418(3); N(1)–C(10), 1.287(3); N(2)–C(1), 1.358(3); N(1)–Zn–N(2), 95.93(8); N(2)–Zn–O(3A), 121.66(7); O(3A)–Zn–O(3), 81.01(6); O(3)–Zn–N(1), 121.12(7); N(2)–Zn–O(3), 121.11(8); N(1)–Zn–O(3A), 117.44(7). Zn–O(3)–Zn(A), 98.99(6). Hydrogen atoms on carbon atoms omitted for clarity. Perspective view of **7** with probability ellipsoids at 20% level. Symmetry code A = 1−x,−y, −z.

controlled character, compound **6** was introduced to examine the living and immortal characters under optimized conditions. The linear relationship between the number-average molecular weight (Mn) and the monomer-to-initiator ratio ($[M]_0/[I]_0$) demonstrated in Fig. 6 (entries 6, 9–11) implies the "living" character of the polymerization process. The 'immortal' character was examined using one equiv. ratio (on $[M]_o/[Zn]_o$) of benzyl alcohol as the chain transfer agent (entry 12). The Mn of the polymers created from these polymerization reactions became half or one third of those found in the reactions without the addition of benzyl alcohol. The end group analysis is demonstrated by the ^{1}H NMR spectrum of the polymer produced from L-lactide and **6** ($[M]_o/[BnOH]$ = 50). Peaks are assignable to the corresponding protons in the proposed structure with capped benzyl alkoxyl group, as shown in Fig. 7. Complexes **1–8** were also investigated to explore their catalytic behavior in the ROP of ε-caprolactone. Representative results are collected in Table 2. Experimental results indicate that complexes have lower activity in catalyzing ROP of ε-caprolactone than that in catalyzing ROP of L-lactide. These reactions give PCLs with reasonable number-average molecular weight (Mn) and narrow PDI values (1.05–1.13). The plot of Mn *vs.* $([M]_0/[I]_0)$ demonstrated by those data initiated by **6** exhibits a linear relationship indicating the "living" character of the polymerization process, as shown in Fig. 8 (entries 6, 9–11). Based on the ^{1}H NMR spectroscopy, polymers are capped with benzyl alkoxyl group, as shown in Fig. 9.

In conclusion, eight zinc complexes have been prepared and fully characterized. Under optimized conditions, zinc benzyl oxide complexes bearing amido-oxazolinate ligands demonstrate efficient activities for the ring opening polymerization of both L-lactide and ε-caprolactone than other zinc ethyl or zinc bis(chelate) complexes in the presence of benzyl alcohol. Zinc benzyl oxide complexes bearing aliphatic functionalities show better catalytic activities than those bearing aromatic ones which have been reported by us previously. Those results demonstrate the Lewis acidity of metal centre could be tuned *via* the substitution of functionality on the amino group with aliphatic substituents resulting in the enhancement of catalytic activities. Furthermore the decrease of ligand's rigidity caused by the aliphatic group might make the coordination of monomer to the metal centre more easily, leading to an increase in propagation. Preliminary studies on fine-tuning of ligand precursors and further application of metal complexes to the catalytic reactions are currently underway.

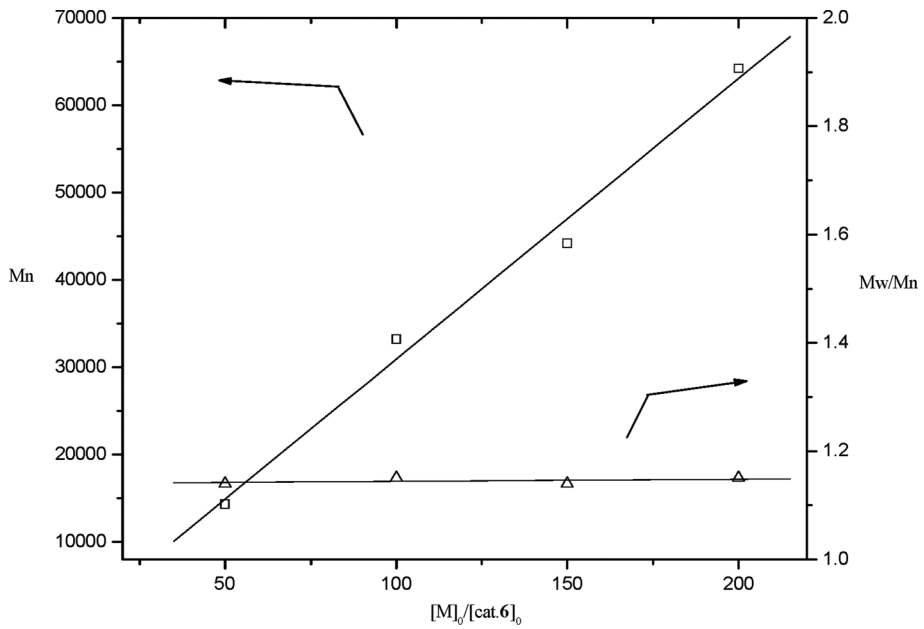


Fig. 6 Polymerization of L-lactide catalyzed by **6** in toluene at 50 °C.

Table 1 Polymerization of L-lactide using compounds **1–8** as catalysts at 50 °C[a]

Entry	Catalyst	{[M]$_0$:[Zn]$_0$}:[BnOH]	Time (min)	Mn (obsd)[b]	Mn (calcd)[c]	Conv. (%)[d]	Yield (%)[e]	Mw/Mn[b]
1	**1**	50 : 1	60	14600 (8500)	6600	90	81	1.09
2	**2**	50 : 1	60	13800 (8000)	6100	83	74	1.08
3	**3**	50 : 1	60	10400 (6000)	6000	97	85	1.71
4	**4**	50 : 1	60	—	—	54	—	—
5	**5**	50 : 1	60	—	—	76	—	—
6	**6**	50 : 0	10	14300 (8300)	6600	90	83	1.14
7	**7**	50 : 0	15	19800 (11500)	6500	88	77	1.12
8	**8**	50 : 0	15	12900 (7500)	6600	90	80	1.11
9	**6**	100 : 0	25	33200 (19300)	14000	96	85	1.15
10	**6**	150 : 0	40	44200 (25600)	21300	98	90	1.14
11	**6**	200 : 0	55	64200 (37200)	28400	98	89	1.15
12	**6**	100 : 1	10	16200 (9400)	7100	97	83	1.08

[a] In 10 ml toluene, [Zn]$_0$ = 0.05 M; [BnOH] = 0.05M. [b] Obtained from GPC analysis and calibrated by polystyrene standard. Values in parentheses are the values obtained from GPC times 0.58. [c] Calculated from [M(lactide) × [M]$_0$/[Zn]$_0$ × conversion yield/([BnOH]$_{eq}$)] + M(BnOH). [d] Obtained from ^{1}H NMR analysis. [e] Isolated yield.

Table 2 Polymerization of ε-caprolactone using compounds **1–8** as catalysts at 50 °C[a]

Entry	Catalyst	{[M]$_0$:[Zn]$_0$}:[BnOH]	Time (min)	Mn (obsd)[b]	Mn (calcd)[c]	Conv. (%)[d]	Yield (%)[e]	Mw/Mn[b]
1	**1**	50 : 1	90	11400 (6400)	6400	92	83	1.06
2	**2**	50 : 1	90	8100 (4500)	4600	77	63	1.05
3	**3**	50 : 1	90	11500 (6400)	6500	91	81	1.17
4	**4**	50 : 1	70	13200 (7400)	6200	90	82	1.17
5	**5**	50 : 1	70	12400 (6900)	5400	93	85	1.16
6	**6**	50 : 0	30	12400 (6900)	5800	99	85	1.13
7	**7**	50 : 0	30	14000 (7800)	5500	94	81	1.15
8	**8**	50 : 0	30	13000 (7300)	5700	98	84	1.16
9	**6**	100 : 0	30	23800 (13300)	11400	99	89	1.10
10	**6**	150 : 0	30	33200 (18600)	15700	91	85	1.13
11	**6**	200 : 0	40	47700 (26700)	22000	96	82	1.13
12	**6**	100 : 1	30	12700 (7100)	5800	99	87	1.13

[a] In 15 ml toluene. [Zn]$_0$ = 0.125 M; [BnOH] = 0.125M. [b] Obtained from GPC analysis and calibrated by polystyrene standard. Values in parentheses are the values obtained from GPC times 0.56. [c] Calculated from [M(ε-caprolactone) × [M]$_0$/[Zn]$_0$ × conversion yield/([BnOH]$_{eq}$)] + M(BnOH). [d] Obtained from ^{1}H NMR analysis. [e] Isolated yield.

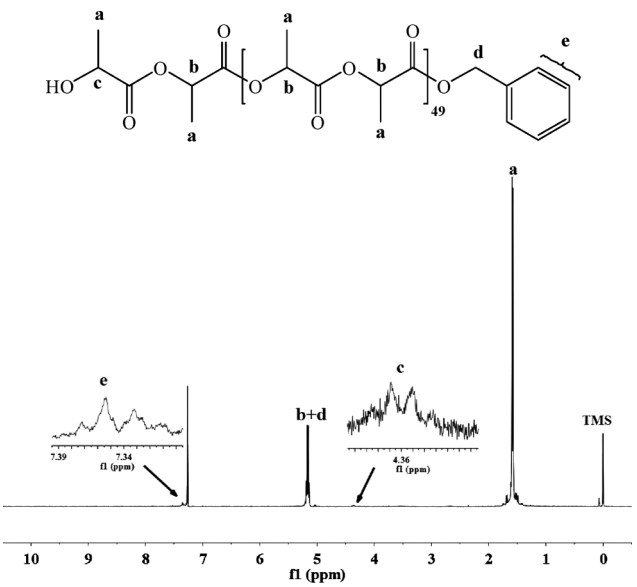


Fig. 7 ^{1}H NMR spectrum of PLA-50 catalyzed by **6** in toluene at 50 °C.

Experimental

All manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk-line or drybox techniques. Solvents were refluxed over the appropriate drying agent and distilled prior to use. DMSO (dimethyl sulfoxide, TEDIA) was used as supplied. Deuterated solvents were dried over molecular sieves.

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded either on Varian Mercury-400 (400 MHz) or Varian Inova-600 (600 MHz) spectrometers in chloroform-*d* at ambient temperature unless stated otherwise and referenced internally to the residual solvent peak and reported as parts per million relative to tetramethylsilane. Elemental analyses were performed by Elementar Vario ELIV instrument. The GPC measurements were performed in THF at 35 °C with a Waters 1515 isocratic HPLC pump, a Waters 2414 refractive index detector, and Waters Styragel column (HR4E). Molecular weights and molecular weight distributions were calculated using polystyrene as standard.

Diethylzinc (1 M in hexane, Aldrich), CuI (Strem), K_3PO_4 (Lancaster), L-proline (Alfa) and unsym-dimethyl-ethylenediamine (Acros) were used as supplied. Ligand precursors such as 2-(2-bromophenyl)-4,4-dimethyl-2-oxazoline,[11] $HNC_2^{Me}Oxa$,[3p] $HNC_2^{OMe}Oxa$,[3p] $HNC_2^{StBu}Oxa$,[3p] or $HNPh^{SMe}Oxa$[3o] were prepared

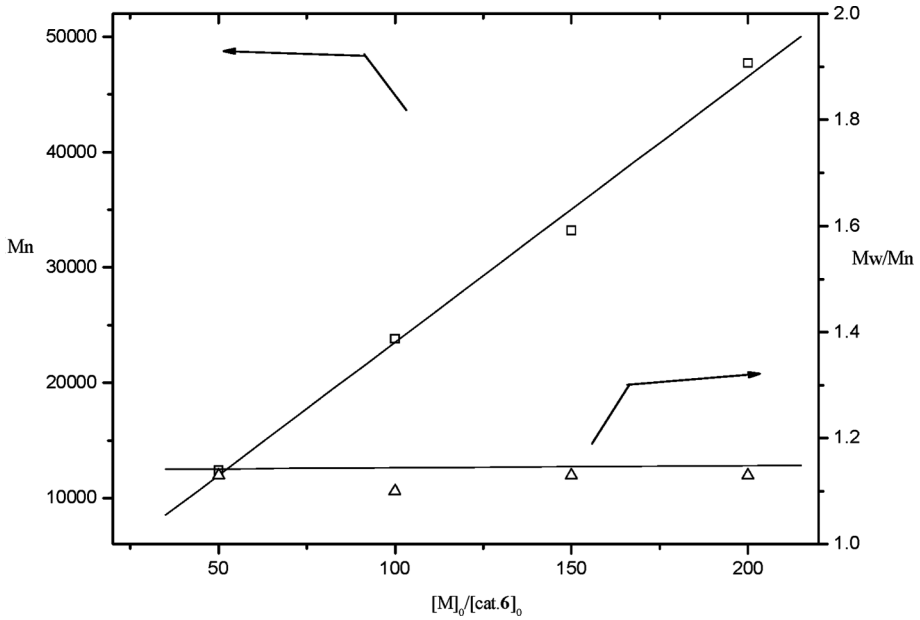


Fig. 8 Polymerization of ε-caprolactone catalyzed by **6** in toluene at 50 °C.

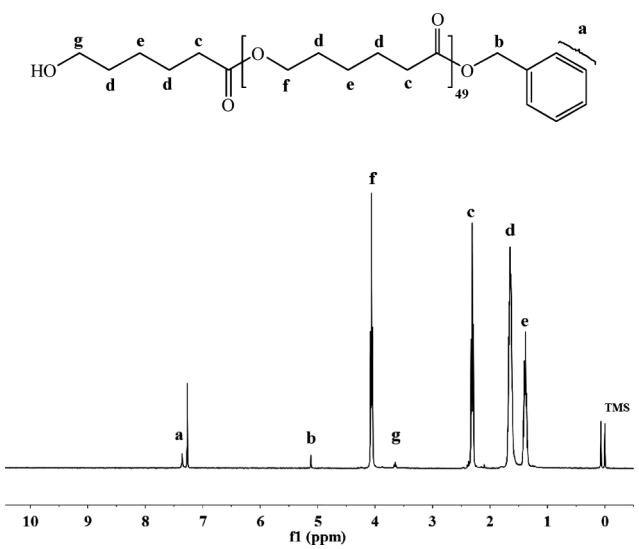


Fig. 9 ^{1}H NMR spectrum of PCL-50 catalyzed by **6** in toluene at 50 °C.

using the literature method. Benzyl alcohol (TEDIA) was dried over magnesium sulfate and distilled before use. ε-Caprolactone (Acros) was dried over magnesium sulfate and distilled under reduced pressure. L-lactide was recrystallized from toluene prior to use.

Preparations

HNC_2^{NMe2}Oxa. To a Schlenk flask containing 2-(2-Bromophenyl)-4,4-dimethyl-2-oxazoline (0.76 g, 3 mmol), unsym-dimethyl-ethylenediamine (0.98 mL, 9 mmol), CuI (0.06 g, 0.3 mmol), L-proline (0.07 g, 0.6 mmol), K_3PO_4 (1.27 g, 6 mmol) and DMSO (3.5 mL) was added at room temperature under nitrogen. The reaction mixture was heated to 110 °C for 14 h. The resulting dark-brown solution was extracted with EA/H_2O three times. The organic layer was dried over Na_2SO_4 and filtered. All volatiles were removed in vacuum to yield a yellow solid. The yellow solid was purified by flash column chromatography on silica gel (ethyl acetate/hexane 1 : 8 then methanol). The final band (pale yellow) was collected. Solvents were removed in vacuum to give a white solid; yield 0.61 g, 78%. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.35(s, oxazoline-CH_3, 6H), 2.32(s, N(CH_3)$_2$, 6H) 2.61(t, CH_2, 2H, J = 6.6 Hz), 3.33 (q, CH_2, 2H, J = 6.2 Hz), 3.97(s, oxazoline-CH_2, 2H), 6.59(t, CH-Ph, 1H, J = 7.5 Hz), 6.67(d, CH-Ph, 1H, J = 8.4 Hz), 7.27(d, CH-Ph, 1H, J = 7.8 Hz), 7.70(d, CH-Ph, 1H, J = 6.6 Hz), 8.54(s, NH, 1H). ^{13}C {^{1}H} NMR ($CDCl_3$, 150 MHz): δ 8.7(oxazoline-CH$_3$), 41.7(CH$_2$), 45.7(N(CH$_3$)$_2$), 58.2(CH$_2$), 67.7(C(CH$_3$)$_2$), 76.8(oxazoline-CH$_2$), 110.1, 114.1, 129.6, 132.0(CH-Ph), 108.7, 148.9, 162.2(one *tert*-*C*-oxazoline and two *tert*-*C*-Ph). Anal. Calc. for $C_{15}H_{23}N_3O$: C, 68.93; H, 8.87; N, 16.08. Found C, 68.88; H, 8.66; N, 16.28.

(NC$_2^{Me}$Oxa)$_2$Zn (1). To a flask containing HNC$_2^{Me}$Oxa (0.93 g, 4 mmol) and 15 mL hexane, 3.12 mL $ZnEt_2$ (1.0 M in hexane, 3.12 mmol) was added at 0 °C. The reaction mixture was allowed to warm to room temperature and reacted overnight. After 14 h of stirring, the yellow suspension was filtered and washed with hexane to afford a yellow solid. Yield 0.47 g, 49%. ^{1}H NMR (C_6D_6, 600 MHz): δ 0.79(s, CH$_2$CH_3, 3H), 0.93(t, oxazoline-CH_3, 6H, J = 9.3 Hz), 1.67(m, CH_2, 1H), 2.09(m, CH_2, 1H), 3.33(d, oxazoline-CH_2, 1H, J = 8.4 Hz), 3.38 (d, oxazoline-CH_2, 1H, J = 8.4 Hz), 3.48(m, CH_2, 1H), 3.57(m, CH_2, 1H), 6.43(t, CH-Ph, 1H, J = 7.2 Hz), 6.92(d, CH-Ph, 1H, J = 9 Hz), 7.26(t, CH-Ph, 1H, J = 9 Hz), 8.14(d, CH-Ph, 1H, J = 8.4 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 150 MHz): δ 11.9(CH$_2$CH_3), 22.9(CH$_2$), 27.7(oxazoline-CH$_3$), 27.8(oxazoline-CH$_3$), 53.7(CH$_2$), 77.0 (oxazoline-CH$_2$), 110.1, 113.9, 132.6, 134.4(CH-Ph), 66.4, 104.9, 159.7, 167.1 (two *tert*-*C*-oxazoline and two *tert*-*C*-Ph). Anal. Calc. for $C_{28}H_{38}N_4O_2Zn$: C, 63.69; H, 7.25; N, 10.61. Found: C, 64.04; H, 7.20; N, 10.64.

(NC$_2^{OMe}$Oxa)$_2$Zn (2). The procedure for the preparation of **2** was similar to that used for **1** but with HNC$_2^{OMe}$Oxa (0.99 g, 4 mmol), 2.8 mL $ZnEt_2$ (1.0 M in hexane, 2.8 mmol) and

15 mL hexane. A yellow solution was obtained. Yield 0.75 g, 67%. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.14(s, oxazoline-CH_3, 3H), 1.24(s, oxazoline-CH_3, 3H), 3.32(s, OCH_3, 3H), 3.50(m, CH_2, 1H), 3.58(m, CH_2, 1H), 3.67(m, CH_2, 2H), 3.97(d, oxazoline-CH_2, 1H, J = 8.4 Hz), 4.06 (d, oxazoline-CH_2, 1H, J = 7.8 Hz), 6.28(t, CH-Ph, 1H, J = 7.5 Hz), 6.83(d, CH-Ph, 1H, J = 9 Hz), 7.21(t, CH-Ph, 1H, J = 7.8 Hz), 7.75(d, CH-Ph, 1H, J = 8.4 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 28.0(oxazoline-CH$_3$), 28.1(oxazoline-CH$_3$), 49.9(CH$_2$), 58.8(OCH$_3$), 71.1(CH$_2$), 77.3(oxazoline-CH$_2$), 109.7, 113.2, 132.1, 133.9(CH-Ph), 66.7, 104.7, 159.3, 166.8(two *tert*-*C*-oxazoline and two *tert*-*C*-Ph). Anal. Calc. for $C_{28}H_{38}N_4O_4Zn$: C, 60.05; H, 6.84; N, 10.00. Found: C, 59.72; H, 6.86; N, 10.18.

(NC$_2^{NMe2}$Oxa)$_2$Zn (3). The procedure for the preparation of **3** was similar to that used for **1** but with HNC$_2^{NMe2}$Oxa (1.05 g, 4 mmol), 3.12 mL $ZnEt_2$ (1.0 M in hexane, 3.12 mmol) and 15 mL hexane. A yellow solution was obtained. Yield 0.58 g, 49%. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.14(s, oxazoline-CH_3, 3H), 1.25(s, oxazoline-CH_3, 3H), 2.29(s, N(CH_3)$_2$, 6H), 2.46(m, CH_2, 1H), 2.67(m, CH_2, 1H), 3.97(d, oxazoline-CH_2, 1H, J = 8.4 Hz), 4.07 (d, oxazoline-CH_2, 1H, J = 7.8 Hz), 6.27(t, CH-Ph, 1H, J = 7.2 Hz), 6.80(d, CH-Ph, 1H, J = 8.4 Hz), 7.23(t, CH-Ph, 1H, J = 6.9 Hz), 7.76(d, CH-Ph, 1H, J = 6 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 28.0(oxazoline-CH$_3$), 28.2(oxazoline-CH$_3$), 46.0(N(CH$_3$)$_2$), 46.4(CH$_2$), 57.8(CH$_2$), 77.3(oxazoline-CH$_2$), 109.5, 113.4, 132.1, 133.8(CH-Ph), 66.7, 104.6, 159.2, 166.9(two *tert*-*C*-oxazoline and two *tert*-*C*-Ph). Anal. Calc. for $C_{30}H_{44}N_6O_2Zn$: C, 61.48; H, 7.57; N, 14.34. Found: C, 61.43; H, 7.69; N, 13.97.

(NC$_2^{StBu}$Oxa)ZnEt (4). To a flask containing HNC$_2^{StBu}$Oxa (0.61 g, 2 mmol) and 15 mL THF, 2.2 mL $ZnEt_2$ (1 M in hexane, 2.2 mmol) was added at 0 °C under nitrogen. The reaction mixture was allowed to warm to room temperature and reacted for 12 h or overnight. Volatile materials were removed under vacuum to yield yellow powder. The powder was washed with hexane and the yellow powder was obtained after filtration. Yield 0.71 g, 89%. ^{1}H NMR (C_6D_6, 600 MHz): δ 0.72(q, 2H, J = 8 Hz, ZnCH_2CH$_3$), 0.91(s, 6H, oxazoline-CH_3), 1.21(s, S(CH_3)$_3$, 9H), 1.68(t, ZnCH$_2$CH_3, 3H, J = 7.8 Hz), 2.80(t, CH_2, 2H, J = 7.2 Hz), 3.32(s, oxazoline-CH_2, 2H), 3.84(t, CH_2, 2H, J = 7.2 Hz), 6.51(t, CH-Ph, 1H, J = 6.9 Hz), 6.91(d, CH-Ph, 1H, J = 9 Hz), 7.25(t, CH-Ph, 1H, J = 6.9 Hz), 8.13(d, CH-Ph, 1H, J = 6 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 150 MHz): δ –0.1(ZnCH$_2$CH$_3$), 13.5(ZnCH$_2$$CH_3$), 28.2(oxazoline-$CH_3$), 29.6($CH_2$), 31.1(C($CH_3$)$_3$), 42.1($C$(CH$_3$)$_3$), 50.8($CH_2$), 76.9(oxazoline-$CH_2$), 111.7, 113.4, 132.2, 134.6(CH-Ph), 65.9, 105.6, 158.2, 167.5(two *tert*-*C*-oxazoline and two *tert*-*C*-Ph). Anal. Calc. for $C_{19}H_{30}N_2OSZn$: C, 57.06; H, 7.56; N, 7.00. Found: C, 57.17; H, 7.07; N, 7.52.

(NPh^{SMe}Oxa)ZnEt (5). The procedure for the preparation of **5** was similar to that used for **4** but with HNPh^{SMe}Oxa (0.31 g, 1 mmol), 1.1 mL $ZnEt_2$ (1.0 M in hexane, 1.1 mmol) and 15 mL THF. A yellow solid was obtained. Yield 0.38 g, 82%. ^{1}H NMR (C_6D_6, 400 MHz): δ 0.57(q, ZnCH_2CH$_3$, 2H, J = 8.1 Hz), 0.88(s, oxazoline-CH_3, 6H), 1.34(t, ZnCH$_2$CH_3, 3H, J = 8.2 Hz), 1.92(s, SCH_3, 3H), 3.32(s, oxazoline-CH_2, 2H), 6.50(t, CH-Ph, 1H, J = 7.4 Hz), 6.86(m, CH-Ph, 1H), 6.99(m, CH-Ph, 2H), 7.70(t, CH-Ph, 1H), 7.11(m, CH-Ph, 2H), 7.24(d, CH-Ph, 1H, J = 7.6 Hz), 8.11(d, CH-Ph, 1H, J = 9.6 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 150 MHz): δ –0.4(ZnCH$_2$CH$_3$), 14.8(ZnCH$_2$$CH_3$), 28.1(oxazoline-$CH_3$), 77.1(oxazoline-$CH_2$), 113.2, 115.5, 124.5, 126.1, 127.0, 131.5, 134.4(CH-Ph), 66.0, 105.2, 135.8, 149.3, 157.2, 167.7(two *tert*-*C*-oxazoline and four *tert*-*C*-Ph). Anal. Calc. for $C_{20}H_{24}N_2OSZn$: C, 59.18; H, 5.96; N, 6.90. Found: C, 58.79; H, 5.49; N, 6.79.

[(NC$_2^{Me}$Oxa)Zn(μ-OBn)]$_2$ (6). To a flask containing 2.2 mL $ZnEt_2$ (1.0 M in hexane, 2.2 mmol), 20 mL THF, and BnOH (0.23 mL, 2.2 mmol) was added at 0 °C. The reaction mixture was allowed to warm to room temperature and reacted for 3h. The colorless solution was cooled down to 0 °C and NHC$_2^{Me}$Oxa (0.47 g, 2 mmol) was added. After additional 3 h of stirring, the yellow solution was pumped to dryness and the residue was washed with 10 mL hexane to afford a yellow solid. Yield 0.59 g, 73%. ^{1}H NMR (C_6D_6, 600 MHz): δ 0.95(s, CH_3, 12H, J = 7.5 Hz), 0.98(s, oxazoline-CH_3, 12H), 1.83(m, CH_2, 4H), 3.35(s, oxazoline-CH_2, 4H), 3.61(m, CH_2, 4H), 4.78 (d, OCH_2Ph, 2H, J = 5.7 Hz), 4.86(d, OCH_2Ph, 2H, J = 5.7 Hz), 6.53(t, CH-Ph, 2H, J = 7.5 Hz), 6.95(q, CH-Ph, 2H, J = 7.4 Hz), 6.99(m, CH-Ph, 4H), 7.26(m, CH-Ph, 4H), 7.34(m, CH-Ph, 2H), 8.19(m, CH-Ph, 2H). ^{13}C {^{1}H} NMR ($CDCl_3$, 150 MHz): δ 11.7(CH$_3$), 22.6(CH$_2$), 27.9(CH$_3$), 52.5(CH$_2$), 70.1(CH$_2$), 76.8(CH$_2$), 110.5, 113.7, 127.1, 128.4, 129.2, 132.7, 134.4(CH-Ph), 66.0, 104.7, 144.4, 159.7, 168.1(two *tert*-*C*-oxazoline and three *tert*-*C*-Ph). Anal. Calc. for $C_{42}H_{52}N_4O_4Zn_2$: C, 62.46; H, 6.49; N, 6.94. Found: C, 61.88; H, 6.86; N, 6.94.

[(NC$_2^{OMe}$Oxa)Zn(μ-OBn)]$_2$ (7). The procedure for the preparation of **7** was similar to that used for **6** but with HNC$_2^{OMe}$Oxa (0.5 g, 2 mmol), 2.2 mL $ZnEt_2$ (1.0 M in hexane, 2.2 mmol), BnOH (0.23 mL, 2.2 mmol) and 20 mL THF. A yellow solid was obtained. Yield 0.32 g, 38%. ^{1}H NMR (C_6D_6, 600 MHz): δ 0.83(s, oxazoline-CH_3, 4H), 1.00(s, oxazoline-CH_3, 8H), 3.07(s, OCH_3, 4H), 3.15(s, OCH_3, 2H), 3.29(d, oxazoline-CH_2, 2H, J = 11.4 Hz), 3.48(t, CH_2, 2H, J = 7.5 Hz), 3.66(t, CH_2, 2H, J = 6.6 Hz), 3.91(t, CH_2, 2H, J = 7.5 Hz), 4.03(t, CH_2, 2H, J = 6.6 Hz), 4.72(d, OCH_2Ph, 2H, J = 10.8 Hz), 4.78(d, OCH_2Ph, 2H, J = 10.8 Hz), 6.42(q, CH-Ph, 2H, J = 7.5 Hz), 6.84(t, CH-Ph, 4H, J = 7.4 Hz), 6.91(t, CH-Ph, 4H, J = 7.5 Hz), 7.03(m, CH-Ph, 4H), 7.20(t, CH-Ph, 4H, J = 8.4 Hz), 8.10(t, CH-Ph, 2H, J = 9.6 Hz). ^{13}C {^{1}H} NMR (C_6D_6, 150 MHz): δ 27.9(CH$_3$), 28.1(CH$_3$), 49.5(CH$_2$), 50.0(CH$_2$), 28.5(CH$_3$), 58.5(OCH$_3$), 59.0(OCH$_3$), 70.1(CH$_2$), 71.2(CH$_2$), 72.0(CH$_2$), 77.0(CH$_2$), 110.7, 113.5, 114.1, 127.1, 129.0, 129.43, 132.7, 134.6(CH-Ph), 58.5, 104.9, 144.5, 160.2, 168.0(two *tert*-*C*-oxazoline and three *tert*-*C*-Ph). Anal. Calc. for $C_{42}H_{52}N_4O_6Zn_2$: C, 60.08; H, 6.24; N, 6.67. Found: C, 59.48; H, 5.85; N, 6.55.

[(NC$_2^{StBu}$Oxa)Zn(μ-OBn)]$_2$ (8). The procedure for the preparation of **8** was similar to that used for **6** but with HNC$_2^{StBu}$Oxa (1.16 g, 3.79 mmol), 4.92 mL $ZnEt_2$ (1.0 M in hexane, 4.92 mmol) BnOH (0.51 mL, 4.92 mmol) and 20 mL THF. A yellow solid was obtained. Yield 1.3 g, 70%. ^{1}H NMR (C_6D_6, 600 MHz): δ 1.21(s, oxazoline-CH_3, 6H), 1.30(s, SC(CH_3)$_3$, 18H), 2.91(t, CH_2, 4H, J = 8.4 Hz), 3.38(s, oxazoline-CH_2, 4H), 3.94(t, CH_2, 4H, J = 8.4 Hz), 4.86 (d, OCH_2Ph, 2H, J = 5.4 Hz), 4.87(d, OCH_2Ph, 2H, J = 5.7 Hz), 6.51(t, CH-Ph, 2H, J = 7.5 Hz), 6.92(t, CH-Ph, 2H, J = 7.4 Hz), 6.99(t, CH-Ph, 4H, J = 7.5 Hz), 7.10(d, CH-Ph, 2H, J = 9 Hz), 7.32(m, CH-Ph, 6H), 8.17(d, CH-Ph, 2H, J = 7.8 Hz). ^{13}C {^{1}H} NMR (C_6D_6, 150 MHz): δ 27.5(CH$_2$),

Table 3 Summary of crystal data for compounds **1**, **3**, **5**, **6** and **7**

	1	**3**	**5**	**6**	**7**
Formula	$C_{34}H_{52}N_4O_2Zn$	$C_{30}H_{44}N_6O_2Zn$	$C_{20}H_{24}N_2OSZn$	$C_{42}H_{52}N_4O_4Zn_2$	$C_{42}H_{52}N_4O_6Zn_2$
Fw	614.17	586.08	405.84	807.62	839.62
T (K)	297(2)	297(2)	297(2)	297(2)	297(2)
Crystal system	Triclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$Pbca$	$P2_1/n$	$P2_1/c$
a (Å)	9.9372(8)	11.1690(11)	14.5692(11)	11.0773(7)	10.8346(9)
b (Å)	11.1773(9)	8.6171(8)	15.4862(12)	16.3723(10)	19.8535(17)
c (Å)	17.8036(14)	32.893(3)	17.1701(13)	11.3458(7)	9.8078(8)
α (°)	73.9740(10)	90	90	90	90
β (°)	87.5980(10)	94.650(2)	90	99.0590(10)	103.536(2)
γ (°)	66.0250(10)	90	90	90	90
V (Å)	1731.1(2)	3155.3(5)	3873.9(5)	2032.0(2)	2051.1(3)
Z	2	4	8	2	2
ρ_c (Mg m^{-3})	1.178	1.234	1.392	1.287	1.359
μ(Mo-Kα) (mm^{-1})	0.743	0.813	1.385	1.225	1.220
Reflections collected	9785	17161	20817	11282	11474
No. of parameters	370	352	226	235	244
Indep. reflns (R_{int})	6686 (0.0180)	6184 (0.0406)	3821 (0.0629)	3978 (0.0244)	4036 (0.0273)
Final R indices R_1[a], wR_2[a]	0.0395, 0.1126	0.0380, 0.1037	0.0411, 0.0987	0.0315, 0.0987	0.0340, 0.0959
R indices (all data)	0.0469, 0.1180	0.0507, 0.1104	0.0809, 0.1159	0.0461, 0.1077	0.0460, 0.1033
GoF[b]	1.022	1.005	0.933	1.031	1.014

[a] $R_1 = [\Sigma(|F_o| - |F_c|)/\Sigma |F_o|]$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = 0.10$. [b] $GoF = [\Sigma w(F_o^2 - F_c^2)^2/(N_{rflns} - N_{params})]^{1/2}$.

28.5(CH_3), 31.3(CH_3), 50.1(CH_2), 70.1(CH_2), 77.0(CH_2), 105.3, 110.0, 113.5, 127.2, 128.9, 132.8, 134.7(*C*H-Ph), 41.8, 50.1, 144.2, 159.5, 168.0, 187.1(two *tert*-*C*-oxazoline, one S*C*(CH_3)$_3$ and three *tert*-*C*-Ph). Anal. Calc. for $C_{42}H_{52}N_4O_4S_2Zn_2$: C, 60.31; H, 6.75; N, 5.86. Found: C, 59.73; H, 6.71; N, 5.56.

Polymerization procedure for L-lactide and ε-caprolactone

Typically, to a flask containing the prescribed amount of monomer (L-lactide or ε-caprolactone) and catalyst (0.05 mmol for L-lactide; 0.125 mmol for ε-caprolactone) were added 10 mL (for L-lactide) or 15 mL (for ε-caprolactone) of solvent. The reaction mixture was stirred at the prescribed temperature for the prescribed time. After the reaction was quenched by the addition of 10 mL acetic acid solution (0.35 N), the resulting mixture was poured into 50 mL *n*-heptane to precipitate polymers. Crude products were recrystallized from THF–hexane and dried *in vacuo* up to a constant weight.

Crystal structure data

Crystals were grown from concentrated hexane solutions (**1**, **3**, **5**) or tetrahydrofuran/hexane solution (**6**, **7**), and isolated by filtration. Suitable crystals of **1**, **3**, **5**, **6** or **7** were sealed in thin-walled glass capillaries under a nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. The absorption correction was based on the symmetry equivalent reflections using the SADABS program.[12] The space group determination was based on a check of the Laue symmetry and systematic absences and was confirmed using the structure solution. The structure was solved by direct methods using a SHELXTL package.[13] All non-H atoms were located from successive Fourier maps, and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms. Some details of the data collection and refinement are given in Table 3.

Acknowledgements

We would like to thank the National Science Council of the Republic of China for financial support (grant number NSC 98-2113-M-005-002-MY3).

References

1 O. Dechy-Cabaret, B. Martin-Vaca and D. Bourissou, *Chem. Rev.*, 2004, **104**, 6147.
2 (*a*) B. J. O'Keefe, M. A. Hillmyer and W. B. Tolman, *J. Chem. Soc., Dalton Trans.*, 2001, 2215; (*b*) G. W. Coates, *J. Chem. Soc., Dalton Trans.*, 2002, 467; (*c*) K. Nakano, N. Kosaka, T. Hiyama and K. Nozaki, *Dalton Trans.*, 2003, 4039; (*d*) M. H. Chisholm and Z. Zhou, *J. Mater. Chem.*, 2004, **14**, 3081; (*e*) G. W. Coates and D. R. Moore, *Angew. Chem., Int. Ed.*, 2004, **43**, 6618; (*f*) J. Wu, T.-L. Yu, C.-T. Chen and C.-C. Lin, *Coord. Chem. Rev.*, 2006, **250**, 602; (*g*) C. A. Wheaton, P. G. Hayes and B. J. Ireland, *Dalton Trans.*, 2009, 4832; (*h*) A. K. Sutar, T. Maharana, S. Dutta, C.-T. Chen and C.-C. Lin, *Chem. Soc. Rev.*, 2010, **39**, 1724.
3 (*a*) M. Cheng, N. A. Darling, E. B. Lobkovsky and G. W. Coates, *Chem. Commun.*, 2000, 2007; (*b*) M. S. Hill and P. B. Hitchcock, *J. Chem. Soc., Dalton Trans.*, 2002, 4694; (*c*) M. Kröger, C. Folli, O. Walter and M. Döring, *Adv. Synth. Catal.*, 2005, **347**, 1325; (*d*) D. V. Vitanova, F. Hampel and K. C. Hultzsch, *J. Organomet. Chem.*, 2005, **690**, 5182; (*e*) B. Y. Lee, H. Y. Kwon, S. Y. Lee, S. J. Na, S.-I. Han, H. Yun, H. Lee and Y.-W. Park, *J. Am. Chem. Soc.*, 2005, **127**, 3031; (*f*) M. T. Gamer, M. Rastätter, P. W. Roesky, A. Steffens and M. Glanz, *Chem.–Eur. J.*, 2005, **11**, 3165; (*g*) M. Kröger, C. Folli, O. Walter and M. Döring, *J. Organomet. Chem.*, 2006, **691**, 3397; (*h*) A. Alaaeddine, A. Amgoune, C. M. Thomas, S. Dagorne, S. Bellemin-Laponnaz and J.-F. Carpentier, *Eur. J. Inorg. Chem.*, 2006, 3652; (*i*) M. Wiecko, P. W. Roesky, V. V. Burlakov and A. Spannenberg, *Eur. J. Inorg. Chem.*, 2007, 876; (*j*) B. Liu, D. Cui, J. Ma, X. Chen and X. Jing, *Chem.–Eur. J.*, 2007, **13**, 834; (*k*) C.-T. Chen, C.-Y. Chan, C.-A. Huang, M.-T. Chen and K.-F. Peng, *Dalton Trans.*, 2007, 4073; (*l*) W. Yao, Y. Mu, A. Gao, Q. Su, Y. Liu and Y. Zhang, *Polymer*, 2008, **49**, 2486; (*m*) W. Yao, Y. Mu, A. Gao, W. Gao and L. Ye, *Dalton Trans.*, 2008, 3199; (*n*) S. Gong and H. Ma, *Dalton Trans.*, 2008, 3345; (*o*) C.-T. Chen, H.-J. Weng, M.-T. Chen, C.-A. Huang and K.-F. Peng, *Eur. J. Inorg. Chem.*, 2009, 2129; (*p*) M.-T. Chen, P.-J. Chang, C.-A. Huang, K.-F. Peng and C.-T. Chen, *Dalton Trans.*, 2009, 9068; (*q*) K.-F. Peng and C.-T. Chen, *Dalton Trans.*, 2009, 9800.

4 (*a*) M. Cheng, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 1998, **120**, 11018; (*b*) M. Cheng, A. B. Attygalle, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 1999, **121**, 11583; (*c*) B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2001, **123**, 3229; (*d*) M. Cheng, D. R. Moore, J. J. Reczek, B. M. Chamberlain, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2001, **123**, 8738; (*e*) H. Hao, C. Cui, H. W. Roesky, G. Bai, H.-G. Schmidt and M. Noltemeyer, *Chem. Commun.*, 2001, 1118; (*f*) J. Prust, A. Stasch, W. Zheng, H. W. Roesky, E. Alexopoulos, I. Usón, D. Böhler and T. Schuchardt, *Organometallics*, 2001, **20**, 3825; (*g*) M. H. Chisholm, J. Gallucci and K. Phomphrai, *Inorg. Chem.*, 2002, **41**, 2785; (*h*) L. R. Rieth, D. R. Moore, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2002, **124**, 15239; (*i*) D. R. Moore, M. Cheng, E. B. Lobkovsky and G. W. Coates, *Angew. Chem., Int. Ed.*, 2002, **41**, 2599; (*j*) J. Prust, H. Hohmeister, A. Stasch, H. W. Roesky, J. Magull, E. Alexopoulos, I. Usón, H.-G. Schmidt and M. Noltemeyer, *Eur. J. Inorg. Chem.*, 2002, 2156; (*k*) S. D. Allen, D. R. Moore, E. B. Lobkovsky and G. W. Coates, *J. Organomet. Chem.*, 2003, **683**, 137; (*l*) R. Eberhardt, M. Allmendinger, G. A. Luinstra and B. Rieger, *Organometallics*, 2003, **22**, 211; (*m*) D. R. Moore, M. Cheng, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2003, **125**, 11911; (*n*) A. P. Dove, V. C. Gibson, E. L. Marshall, A. J. P. White and D. J. Williams, *Dalton Trans.*, 2004, 570; (*o*) H.-Y. Chen, B.-H. Huang and C.-C. Lin, *Macromolecules*, 2005, **38**, 5400.

5 (*a*) J. P. Wolfe, S. Wagaw, J.-F. Marcoux and S. L. Buchwald, *Acc. Chem. Res.*, 1998, **31**, 805; (*b*) J. F. Hartwig, *Acc. Chem. Res.*, 1998, **31**, 852; (*c*) B. Schlummer and U. Scholz, *Adv. Synth. Catal.*, 2004, **346**, 1599.

6 H. Zhang, Q. Cai and D. Ma, *J. Org. Chem.*, 2005, **70**, 5164.

7 A. Marxer, H. R. Rodriguez, J. M. McKenna and H. M. Tsai, *J. Org. Chem.*, 1975, **40**, 1427.

8 M. Fujita, M. Otsuka and Y. Sugiura, *J. Med. Chem.*, 1996, **39**, 503.

9 X. Liu, W. Gao, Y. Mu, G. Li, L. Ye, H. Xia, Y. Ren and S. Feng, *Organometallics*, 2005, **24**, 1614.

10 (*a*) J. Castro, S. Cabaleiro, P. P'erez-Lourido, J. Romero, J. A. Garc'ıa-V'azquez and A. Sousa, *Z. Anorg. Allg. Chem.*, 2002, **628**, 1210; (*b*) A. G. M. Barrett, A. A. Gray, M. S. Hill, P. B. Hitchcock, P. A. Procopiou and A. J. P. White, *Inorg. Chem.*, 2006, **45**, 3352; (*c*) D. J. Doyle, V. C. Gibson and A. J. P. White, *Dalton Trans.*, 2007, 358.

11 A. Marxer, H. R. Rodriguez, J. M. McKenna and H. M. Tsai, *J. Org. Chem.*, 1975, **40**, 1427.

12 G. M. Sheldrick, *SADABS, Program for area detector absorption correction*, Institute for Inorganic Chemistry, University of Göttingen, Germany, 1996.

13 G. M. Sheldrick, *SHELXTL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.

