

Enolic Schiff Base Zinc Amide Complexes: Highly Active Catalysts for Ring-Opening Polymerization of Lactide and ϵ -Caprolactone

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Abstract A series of zinc silylamido complexes based upon *NNO* tridentate enolic Schiff base framework have been synthesized and characterized. These complexes were tested for the ring opening polymerization of lactide and ϵ -caprolactone, exhibiting notably high activity at ambient temperature. The influence of imine bridge length and substituents of diketone over the course of polymerization was investigated in details. Remarkably, **4a** was confirmed to be a rare example of exceedingly active and robust zinc catalysts, achieving major transformation of lactide under extremely low loading (0.025 mol%) within 18 min. The influence of various monomers as well as the polymerization mechanism have also been discussed.

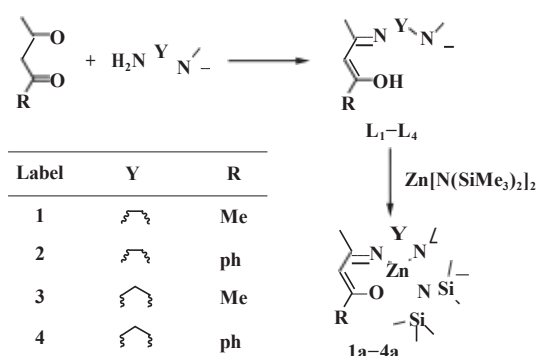
Keywords Zinc; β -Diketone; Ring-opening polymerization; Lactide; ϵ -Caprolactone

INTRODUCTION

In the last decade, the traditional non-recyclable plastic's surge has created enormous thorny waste stream and arisen great concerns on the environment. As promising alternatives to conventional petrochemical plastics, poly(lactic acid) (PLA) and poly(ϵ -caprolactone) (PCL) have been widely applied in the fields of tableware set, packaging materials, biomedical applications of surgical sutures, bone fixation parts, tissue engineering scaffolds, drug controlled delivery carriers and so on due to their renewability, biodegradability and biocompatibility^[1-5]. The most competent method for producing PLA and PCL is the ring opening polymerization (ROP) of lactide (LA) and ϵ -caprolactone (ϵ -CL), which possesses great efficiency and excellent control over the reaction^[6, 7]. For the catalysis of ROP, metal based complexes have been extensively studied during the last two decades^[6]. Numerous complexes were discovered with great control on the ROP of lactones. For instance, Xu and coworkers developed novel yttrium bis(phenolate) ether complexes for catalyzing ring opening polymerization of racemic LA with high activity and excellent isotactic

selectivity^[8]. However, the vast majority of reports still suffered from low activities and productivities, hindering the potential applicability^[9]. Accordingly, zinc species is particularly attractive, owing to not only the achievable high efficiency under elaborate design, but also its abundance, biocompatibility as well as resistance to impurities^[9]. Schiff base ligands are considered as "privileged ligands" with the ease of preparation and adjustment of flexibility/steric hindrance/electronic effect^[10]. Early organo-zinc catalysts based on Schiff base framework (with hydroxyl group) were investigated by Chisholm, who developed a series of bidentate ligands and achieved slow polymerization of LA^[11]. Zinc alkoxides of *NNO*-tridentate salicylaldiminato Schiff base ligands were utilized thereafter by Lin and coworkers^[12], exerting good reactivity toward the controlled polymerization of LA. Moreover, our preliminary trial, in which salicylaldehyde was replaced by β -diketone moiety in *NNO*-tridentate Schiff base system, effectively improved the catalytic efficiency under similar conditions^[13].

With the advantage of β -diketone segment, at the same time inspired by the critical role of amine bridge and substitutions in affecting catalytic activity^[9], a series of potentially-active enolic Schiff base zinc catalysts were designed and prepared (Scheme 1). Highly active silylamido axial group was chosen for the optimization of reactivity, and the applications in the LA and ϵ -CL polymerization were systematically explored.



Scheme 1 Synthetic pathway for the preparation of ligands and complexes

EXPERIMENTAL

General

All experiments were carried out under dry nitrogen using Schlenk techniques. Materials used to prepare ligands **L1–L4** were purchased from Aldrich and used without further purification. Toluene was distilled from Na-benzophenone. 2-Propanol and ethyl acetate were distilled from CaH₂. L-LA and *rac*-LA (Purac) were purified by recrystallization from ethyl acetate and dried under vacuum at room temperature (RT) before use. NMR spectra were recorded on Bruker AV 300 and 400 MHz in CDCl₃ at 25 °C. Chemical shifts were given in parts per million (ppm) from tetramethylsilane. Gel permeation chromatography (GPC) measurements were conducted with a Waters 515 GPC with CHCl₃ as the eluent (flow rate: 1 mL/min, at 35 °C). The molecular weights were calibrated against polystyrene (PS) standards. The true value of M_n could be calculated according to the formula $M_n = 0.58M_{n,GPC}$ for polylactide^[14] and $M_n = 0.56M_{n,GPC}$ for polycaprolactone^[15].

Synthesis of Ligands **L1–L4**

Ligands **L1–L4** were prepared by the condensation between β -diketone and diamine. Specifically, *N,N*-dimethylethylenediamine or *N,N*-dimethyl-1,3-propanediamine (0.02 mol) was dissolved in ethanol (10 mL) and slowly added into the ethanol solution (20 mL) of acetylacetone or benzoylacetone (0.02 mol). The reaction was carried out by refluxing for 10 h before cooling to RT. Removal of the solvent under vacuum produced white crystals, which were further purified by recrystallization in hexane.

Ligand **L1**

¹H-NMR (300 MHz, CDCl₃, δ , ppm): 10.74 (s, OH, 1H), 4.86 (s, CHCOH, 1H), 3.20 (q, $J = 9$ Hz, C=NCH₂, 2H), 2.37 (t, $J = 6$ Hz, C=NCH₂CH₂N(CH₃)₂, 2H), 2.16 (s, (CH₃)₂N, 6H), 1.88 (s, CH₃C=N, 3H), 1.82 (s, CHCOHCH₃, 3H). ¹³C-NMR (100 MHz, CDCl₃, δ , ppm): 194.3 (CH₃COH), 162.3 (CH₃C=N), 94.9 (CHCOH), 58.4 (C=NCH₂), 45.2 (C=NCH₂CH₂N(CH₃)₂), 40.8 ((CH₃)₂N), 28.4 (CHCOHCH₃), 18.6 (CH₃C=N). For further details, see reported literatures^[16, 17].

Ligand **L2**

See our previous report^[13].

Ligand **L3**

¹H-NMR (300 MHz, CDCl₃, δ , ppm): 10.68 (s, OH, 1H), 4.78

(s, CHCOH, 1H), 3.11 (q, $J = 9$ Hz, C=NCH₂, 2H), 2.16 (t, $J = 9$ Hz, C=NCH₂CH₂CH₂N(CH₃)₂, 2H), 2.04 (s, (CH₃)₂N, 6H), 1.81 (s, CH₃C=N, 3H), 1.76 (s, CHCOHCH₃, 3H), 1.56 (m, CH₂CH₂CH₂, 2H). ¹³C-NMR (100 MHz, CDCl₃, δ , ppm): 194.3 (CH₃COH), 162.9 (CH₃C=N), 94.9 (CHCOH), 56.3 (C=NCH₂), 45.2 (C=NCH₂CH₂CH₂N(CH₃)₂), 40.7 ((CH₃)₂N), 28.5 (CH₂CH₂CH₂), 27.9 (CHCOHCH₃), 18.5 (CH₃C=N). For further details, see reported literature^[18].

Ligand **L4**

¹H-NMR (300 MHz, CDCl₃, δ , ppm): 11.41 (s, OH, 1H), 7.83 (m, ArH, 2H), 7.37 (m, ArH, 2H), 5.63 (s, CHCOH, 1H), 3.33 (q, $J = 6$ Hz, C=NCH₂, 2H), 2.33 (t, $J = 9$ Hz, C=NCH₂CH₂CH₂N(CH₃)₂, 2H), 2.19 (s, (CH₃)₂N, 6H), 2.04 (s, CH₃C=N, 3H), 1.76 (m, CH₂CH₂CH₂, 2H). ¹³C-NMR (100 MHz, CDCl₃, δ , ppm): 187.3 (ArCOH), 164.8 (CH₃C=N), 140.3, 130.1, 127.9, 126.6 (ArC), 91.8 (CHCOH), 56.4 (C=NCH₂), 45.3 (C=NCH₂CH₂CH₂N(CH₃)₂), 41.1 ((CH₃)₂N), 28.0 (CH₂CH₂CH₂), 19.2 (CH₃C=N).

Synthesis of Zn[N(SiMe₃)₂]₂

Zn[N(SiMe₃)₂]₂ was synthesized by an adapted method from the literature^[19]. To the suspension of sodium amide (5.2 g, 0.133 mol) in toluene (100 mL), 1,1,1,3,3,3-hexamethyldisilazane (29 mL, 0.137 mol) was added dropwise. The suspension was stirred at ambient temperature for 40 min, refluxed for 6 h and subsequently cooled to room temperature. The solvent was then removed in vacuo for 2 h, giving Na[N(SiMe₃)₂]₂ as a white residue. 100 mL of diethyl ether was subsequently introduced to dissolve the compound. After cooling to -78 °C, anhydrous ZnCl₂ (7.62 g, 56 mmol) was added under continuous stir. The stirred mixture was then warmed up and refluxed for 1 h. After cooling and filtration, Zn[N(SiMe₃)₂]₂ was obtained as a colorless liquid by distillation. ¹H-NMR (300 MHz, CDCl₃, δ , ppm): 0.1 (s). ¹³C-NMR (100 MHz, CDCl₃, δ , ppm): 4.98 (s).

Synthesis of Complexes **1a–4a**

In a glove box filled with nitrogen, 0.1 mmol of ligand **L1** in toluene was charged into a vial, which had been pre-dried for 2 days in a drying oven under 120 °C. Equimolar Zn[N(SiMe₃)₂]₂, dissolved in toluene, was added into the vial, followed by stir for 10 h at room temperature. After the reaction was completed, toluene was removed under vacuum to give complex **1a**. Complexes **2a–4a** were prepared in a similar method by using ligands **L2–L4**, respectively.

Complex **1a**

¹H-NMR (300 MHz, CDCl₃, δ , ppm): 4.84 (s, CHCOZn, 1H), 3.38 (t, $J = 6$ Hz, C=NCH₂, 2H), 2.65 (t, $J = 6$ Hz, C=NCH₂CH₂N(CH₃)₂, 2H), 2.42 (s, (CH₃)₂N, 6H), 1.93 (s, CH₃C=N, 3H), 1.87 (s, CH₃CHCOZn, 3H), 0.01 (m, ZnN(SiCH₃)₂, 18H). ¹³C-NMR (100 MHz, CDCl₃, δ , ppm): 183.1 (CH₃COZn), 171.6 (CH₃C=N), 97.1 (CHCOZn), 58.7 (C=NCH₂), 45.4 (C=NCH₂CH₂N(CH₃)₂), 43.7 ((CH₃)₂N), 27.7 (CH₃CHCOZn), 21.1 (CH₃C=N), 5.1 (ZnN(SiCH₃)₂).

Complex **2a**

¹H-NMR (300 MHz, CDCl₃, δ , ppm): 7.87 (m, ArH, 2H), 7.34 (m, ArH, 2H), 5.59 (s, CHCOZn, 1H), 3.47 (t, $J = 6$ Hz, C=NCH₂, 2H), 2.71 (t, $J = 6$ Hz, C=NCH₂CH₂N(CH₃)₂,

2H), 2.46 (s, (CH₃)₂N, 6H), 2.04 (s, CH₃C=N, 3H), 0.04 (m, ZnN(SiCH₃)₂, 18H). ¹³C-NMR (100 MHz, CDCl₃, δ, ppm): 176.9 (ArCOZn), 173.0 (CH₃C=N), 141.2, 129.3, 127.8, 127.0 (ArC), 94.8 (CHCOZn), 58.5 (C=NCH₂), 45.4 (C=NCH₂CH₂N(CH₃)₂), 44.1 ((CH₃)₂N), 21.8 (CH₃C=N), 5.2 (ZnN(SiCH₃)₂).

Complex 3a

¹H-NMR (300 MHz, CDCl₃, δ, ppm): 4.76 (s, CHCOZn, 1H), 3.48 (t, *J* = 6 Hz, C=NCH₂, 2H), 2.63 (t, *J* = 6 Hz, C=NCH₂CH₂CH₂N(CH₃)₂, 2H), 2.44 (s, (CH₃)₂N, 6H), 1.90 (s, CH₃C=N, 3H), 1.86 (s, CH₃CHCOZn, 3H), 1.80 (m, CH₂CH₂CH₂, 2H), 0.02 (m, ZnN(SiCH₃)₂, 18H). ¹³C-NMR (100 MHz, CDCl₃, δ, ppm): 183.1 (CH₃COZn), 171.9 (CH₃C=N), 96.6 (CHCOZn), 61.3 (C=NCH₂), 49.5 (C=NCH₂CH₂CH₂N(CH₃)₂), 47.2 ((CH₃)₂N), 27.6 (CH₂CH₂CH₂), 26.3 (CH₃CHCOZn), 21.3 (CH₃C=N), 5.6 (ZnN(SiCH₃)₂).

Complex 4a

¹H-NMR (300 MHz, CDCl₃, δ, ppm): 7.87 (m, ArH, 2H), 7.33 (m, ArH, 2H), 5.51 (s, CHCOZn, 1H), 3.58 (t, *J* = 6 Hz, C=NCH₂, 2H), 2.62 (t, *J* = 3 Hz, C=NCH₂CH₂CH₂N(CH₃)₂, 2H), 2.47 (s, (CH₃)₂N, 6H), 2.02 (s, CH₃C=N, 3H), 1.86 (m, CH₂CH₂CH₂, 2H), 0.06 (m, ZnN(SiCH₃)₂, 18H). ¹³C-NMR (100 MHz, CDCl₃, δ, ppm): 176.6 (ArCOZn), 172.8 (CH₃C=N), 141.3, 129.1, 127.7, 126.9 (ArC), 94.6 (CHCOZn), 61.4 (C=NCH₂), 49.9 (C=NCH₂CH₂CH₂N(CH₃)₂), 47.3 ((CH₃)₂N), 26.4 (CH₂CH₂CH₂), 22.0 (CH₃C=N), 5.7 (ZnN(SiCH₃)₂).

The NMR spectra are presented in electronic supplementary information (Figs. S1–S15, in ESI).

General Procedure for Lactide and ε-Caprolactone Polymerization

In a glove box filled with nitrogen, 7 mmol of LA or ε-CL as well as 1.4 mL of toluene were added to a pre-dried phial. Then, a desired amount of complexes **1a–4a** as initiator was added to the phial. The mixtures were stirred at 25 °C or 50 °C in a thermostatic oil bath. After a certain reaction time, the polymerizations were quenched by addition of 5 mL of methanol acidified with HCl (5%). The quenched mixture was precipitated in cold methanol and centrifuged to yield isolated polymers, which were then dried under vacuum at 40 °C for 48 h.

RESULTS AND DISCUSSION

Ligands and Complexes Synthesis

As shown in Scheme 1, the tridentate enolic Schiff base ligands **L1–L4** with different amino bridges and diketone substituents were synthesized by the facile condensation between corresponding diamine and β-diketone. For a systematic tuning of catalytic activity, **L1–L4** were designed comparatively, in which **L1** and **L2** had the same C₂ amine bridge but electronically different diketone substituents, while **L3** and **L4** adopted a more flexible C₃ linkage and analogously diverse substituents on diketone. **L1–L4** were confirmed by ¹H and ¹³C-NMR spectra. Taking the case of **L4** for example, the signals at δ = 7.87 and 7.33 ppm were attributed to the ArH protons of benzoylacetone. The signals at δ = 5.63, 2.19 and 2.04 ppm of **L4** were attributed to the

CHCOH, (CH₃)₂N and CH₃C=N protons of tridentate backbones and the intensity ratio of these three signals was 1:6:3, respectively, therefore confirming the structure of **L4**.

The β-diketone moieties on ligands **L1–L4** underwent keto-enol tautomerism, in which the generated enol form further reacted with Zn[N(SiMe₃)₂] to produce tridentate enolic Schiff base complexes **1a–4a**. Meanwhile the intensity ratio of the signals at δ = 5.51 and 0.01 ppm (ZnN(SiCH₃)₂ protons) was 1:18 in the ¹H-NMR spectrum of complex **4a** (Fig. 1) while the signal at 5.63 ppm disappeared, which identified the successful deprotonation of enol hydroxyl group and further confirmed the structure of **4a** shown in Fig. 1. The ¹H-NMR spectra of complexes **1a–3a** were akin to complex **4a** and shown in Figs. S9, S11 and S13 (in ESI).

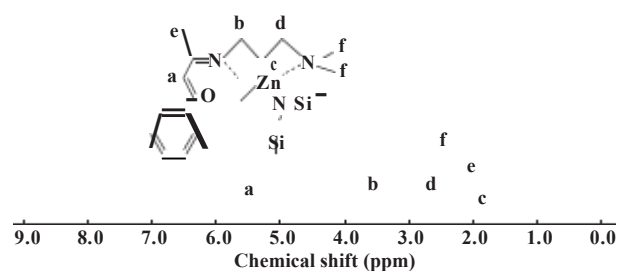


Fig. 1 ¹H-NMR spectrum of complex **4a**

Ring-Opening Polymerization of L-LA

Complexes **1a–4a** were firstly tested as initiators to polymerize L-LA in toluene. As depicted in Table 1, all zinc complexes exhibited rarely high activity and modest control over *M_w* and *D*, achieving fast polymerization even at ambient temperature under various [L-LA]/[Cat.] ratios. The activities of **1a** and **2a** were similar under low [L-LA]/[Cat.] ratios, whereas a clear distinction was observed when the ratio was raised to 600:1 (comparing runs 4 and 7, **2a** reached similar conversion within half of **1a**'s time under 600:1). This difference was tentatively attributed to the conjugation effect of benzene ring, which could further stabilize the central zinc species. Similar effect of improvement caused by phenyl substituent was also disclosed in our previous report of enolic Schiff base aluminum complexes^[20]. Complex **3a**, which had a longer C₃ aminebridge compared with **1a**, showed remarkably higher reactivity. Under the catalysis of **3a**, L-LA of up to 600 times higher than catalyst could be almost totally converted into polymer within only 7 min (runs 9–11). Thus, the structural clues were decided to seek for the elucidation of the significant activity difference between **1a** and **3a**. However, these complexes were too soluble in common solvents and therefore the X-ray study of corresponding single crystals was hampered. Fortunately, Schulz reported the solid-state structures of zinc alkyl and zinc chloride along with **L1** and **L3**^[21]. Interestingly, zinc complex with **L1** formed an oxygen-bridged dimer containing a central four-membered Zn₂O₂ ring, while that with **L3** adopted a monomeric structure in the solid state. Hence, it was

Table 1 Polymerization data of L-LA in toluene with complexes **1a–4a**^a

Run	Cat.	<i>T</i> (°C)	[L-LA]/[Cat.]	<i>t</i> (min)	Conv. ^b (%)	<i>M</i> _{n(c)} × 10 ⁻⁴	<i>M</i> _n ^d × 10 ⁻⁴	<i>D</i> ^d	TOF ^e (h ⁻¹)
1	1a	25	200	18	91	2.6	1.8	1.60	607
2	1a	25	400	31	75	4.3	2.8	1.91	581
3	1a	25	600	56	54	4.6	3.1	1.60	347
4	1a	50	600	23	62	5.3	4.1	1.68	970
5	2a	25	200	14	82	2.3	2.1	1.51	703
6	2a	25	400	21	68	3.9	2.8	1.63	777
7	2a	50	600	11	57	4.9	4.8	1.55	1865
8	2a	50	1000	46	53	7.6	6.7	1.39	691
9	3a	25	200	2	93	2.7	1.9	1.82	5580
10	3a	25	400	4	94	5.4	2.9	1.63	5640
11	3a	25	600	7	95	8.2	7.7	1.81	4886
12	4a	25	1000	5	91	13.1	9.8	1.68	10920
13	4a	25	2000	10	88	25.3	11.2	2.10	10560
14	4a	25	4000	18	71	40.9	12.6	1.88	9467

^a All polymerizations were carried out in toluene solution, [LA]₀ = 0.5 mol/L; ^b Measured by ¹H-NMR; ^c Calculated from the molecular weight of LA × [M]₀/[I] × conversion; ^d Obtained from GPC analysis and calibrated against polystyrene standard; ^e TOF = conversion × loading/time

hypothesized that the shorter amine linkage of **L1** made the central zinc atom more exposed, thereby inducing dimerization between heterogeneous metal centers, whereas the longer amine bridge of **L3** functioned as a better shield around active species and facilitated the mononuclear structure of catalyst remaining intact during polymerization. The reactivity of phenyl-substituted **4a** was further enhanced compared with **3a**. The reaction carried out with complex **4a** displayed remarkably high efficiency, proceeding to 71% conversion under extremely low loading ([M]:[I] = 4000:1) within only 18 min (run 14). And the turnover frequency (TOF) was as high as ~10000 h⁻¹, which rivals the most efficient zinc-based catalysts. To the best of our knowledge, this is the most active zinc catalyst for LA polymerization based upon Schiff base framework. Besides the metal-amide initiators, the metal alkoxides were reported to mediate a more-controllable ROP of cyclic esters with typically superior performances^[22]. For further improvement of the most efficient **4a**, equimolar 2-propanol was added to generate zinc alkoxides *via in situ* alcoholysis. According to the ¹H-NMR spectrum of **4a** and ⁱPrOH mixture (Fig. S16, in ESI), general shift to high magnetic fields of major signals

was observed, confirming the establishment of zinc-alkoxide bond. Representative data are summarized in Table 2, the results showed that ⁱPrOH exerted negligible influence on the activity of complex **4a** and gave rise to a minor decrease in *M*_w. This strongly contrasts the report of Ma's group, who discovered a significant activity enhancement by 2-propanol on zinc amide complexes of bidentate Schiff base^[23] as well as tridentate aminophenolate^[24], highlighting the particular feature of our tridentate system.

Polymerization of *rac*-LA and Stereoselectivity Investigation

Following preliminary studies on L-LA, the stereoselective polymerization on *rac*-LA was also investigated and the experimental data of complexes **1a–4a** are collected in Table 3. The activity towards *rac*-LA followed the same trend to that of L-LA, in which the order of reactivity was **1a** < **2a** < **3a** < **4a**. The microstructures of the obtained PLA were determined by the methine region on the homonuclear decoupled ¹H-NMR spectrum (Fig. 2). As listed in Table 3, complexes **1a–4a** displayed similarly modest isotacticity, furnishing PLA with *P*_m ranging from 0.56 to 0.6, regardless of considerably different activity.

Table 2 ROP of L-LA with ⁱPrOH initiated by complex **4a**^a

Run	Cat.	<i>T</i> (°C)	[L-LA]:[Cat.]:[ⁱ PrOH]	<i>t</i> (min)	Conv. ^b (%)	<i>M</i> _{n(c)} × 10 ⁻⁴	<i>M</i> _n ^d × 10 ⁻⁴	<i>D</i> ^d	TOF ^e (h ⁻¹)
1	4a	25	600:1:1	3	94	8.1	4.5	1.84	11280
2	4a	25	1000:1:1	4	97	13.9	3.6	2.16	14550
3	4a	25	2000:1:1	11	91	26.2	8.0	1.83	9927
4	4a	25	3000:1:1	24	90	38.9	8.1	2.03	6750

^a All polymerizations were carried out in toluene solution, [LA]₀ = 0.5 mol/L; ^b Measured by ¹H-NMR; ^c Calculated from the molecular weight of LA × [M]₀/[I] × conversion + *M*_w(ⁱPrOH); ^d Obtained from GPC analysis and calibrated against polystyrene standard; ^e TOF = conversion × loading/time

Table 3 Polymerization of *rac*-LA in toluene^a

Run	Cat.	<i>T</i> (°C)	[<i>rac</i> -LA]/[Cat.]	<i>t</i> (min)	Conv. ^b (%)	<i>M</i> _{n(c)} × 10 ⁻⁴	<i>M</i> _n ^d × 10 ⁻⁴	<i>D</i> ^d	<i>P</i> _m ^e	TOF ^f (h ⁻¹)
1	1a	50	400:1	18	60	3.4	2.8	2.01	0.57	800
2	1a	50	600:1	29	89	7.6	4.1	2.02	0.56	1105
3	2a	50	600:1	17	80	6.9	3.8	2.07	0.58	1694
4	3a	25	600:1	10	90	7.7	1.2	3.81	0.59	3240
5	4a	25	200:1	4	95	2.7	1.6	1.90	0.60	2850
6	4a	25	600:1	8	93	8.0	4.1	1.87	0.58	4185

^a All polymerizations were carried out in toluene solution, [LA]₀ = 0.5 mol/L; ^b Measured by ¹H-NMR; ^c Calculated from the molecular weight of LA × [M]₀/[I] × conversion; ^d Obtained from GPC analysis and calibrated against polystyrene standard; ^e Measured by homonuclear decoupled ¹H-NMR; ^f TOF = conversion × loading/time

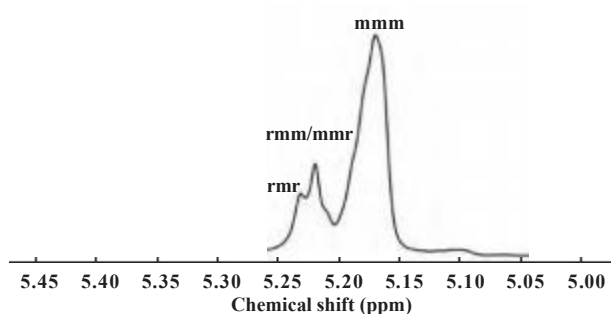


Fig. 2 Homonuclear decoupled ^1H -NMR spectrum by using complex **4a** ($[\text{M}]:[\text{I}] = 200:1$, 25°C)

Ring-Opening Polymerization of ϵ -CL

To study the applicability towards other lactone monomers, ϵ -CL was also utilized in the polymerization with complexes **1a–4a**. Representative polymerizations with monomer/catalyst ratios of 200:1 or 400:1 were carried out in toluene at room temperature. As shown in Table 4, distinctly different from the LA polymerization, the catalytic activity of ϵ -CL polymerization was generally much lower. Especially for C2 bridged **1a** and **2a**, which failed to reach half of the total conversion within several hours (runs 1–4), whereas the reactivity progressively increased from **1a** to **4a**, following an identical fashion to that of LA polymerization. However, as evidenced by the general broadening of \bar{D} from **1a** to **4a**, the boost of reactivity was deduced to be at the cost of control over polymerization.

In order to further investigate the initiation mechanism of the ROP catalyzed by above zinc complexes, end-group analysis by MALDI-TOF spectrum was carried out. PCL

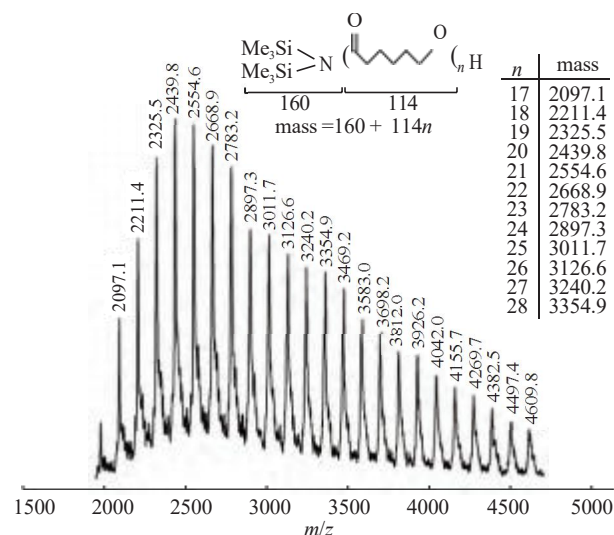


Fig. 3 MALDI-TOF mass spectrum of the oligomer of ϵ -CL obtained with **4a** ($[\epsilon\text{-CL}]_0:[\mathbf{4a}]_0 = 50:1$)

oligomer of **4a** was chosen as the representative sample due to the facilitation by moderate reactivity on ϵ -CL ROP for the preparation of low molecular weight polymer. As depicted in Fig. 3, the obtained PCL was interpreted to be a linear structure with end-cap of $\text{N}(\text{SiMe}_3)_2$ and hydroxyl group. A coordination-insertion mechanism was thus proposed, in which the polymerization starts from the insertion of coordinated monomer into metal-amide bond, and proceeds *via* the continuous approaching and ring-opening of subsequent monomers.

Table 4 Polymerization data of ϵ -CL in toluene with complexes **1a–4a**^a

Run	Cat.	T ($^\circ\text{C}$)	$[\epsilon\text{-CL}]/[\text{Cat.}]$	t (min)	Conv. ^b (%)	$M_{n(c)}^c \times 10^{-4}$	$M_n^d \times 10^4$	\bar{D}^d	TOF ^e (h^{-1})
1	1a	25	200	300	28	0.6	0.5	2.16	11
2	1a	25	400	420	34	1.5	0.7	1.87	19
3	2a	25	200	180	30	0.6	0.9	2.07	20
4	2a	25	400	420	43	1.9	0.8	1.95	25
5	3a	25	200	120	80	1.8	0.9	3.13	80
6	3a	25	400	150	85	3.8	1.5	3.39	136
7	4a	25	200	80	63	1.4	1.0	2.78	95
8	4a	25	400	120	88	4.0	1.3	3.89	176

^a All polymerizations were carried out in toluene solution, $[\text{CL}]_0 = 0.5 \text{ mol/L}$; ^b Measured by ^1H -NMR; ^c Calculated from the molecular weight of $\text{CL} \times [\text{M}]_0/[\text{I}] \times \text{conversion}$; ^d Obtained from GPC analysis and calibrated against polystyrene standard; ^e $\text{TOF} = \text{conversion} \times \text{loading}/\text{time}$

CONCLUSIONS

Four enolic Schiff-base zinc silylamido complexes derived from β -diketone and diamine were synthesized and applied in the ROP of LA and ϵ -CL. Significant improvements were achieved by tuning the length of amine bridge as well as substituents. A hyper-active catalyst **4a** was disclosed to mediate fast polymerization of LA under extremely low loading (4000:1). The stereoselective polymerization of *rac*-LA furnished modestly isotactic PLA. The polymerization was illuminated to proceed *via* a coordination-insertion mechanism.

REFERENCES

- Pang, X.; Zhuang, X.; Tang, Z.; Chen, X. Polylactic acid (PLA): research, development and industrialization. *Biotechnol. J.* 2010, 5, 1125–1136.
- Auras, R. A.; Lim, L. T.; Selke, S. E.; Tsuji, H. Poly(lactic

- acid): synthesis, structures, properties, processing, and applications. John Wiley & Sons (2011).
- Zhang, S. Y.; Chen, Z. F.; Wu, F.; Zhu, X. Y.; Liu, Z. Y.; Feng, J. M.; Yang, M. B. Studies on the effects of four-armed poly(L-lactide) on the crystallization behavior of four-armed poly(L-lactide)/linear poly(L-lactide) blends. *Acta Polymerica Sinica (in Chinese)* 2016, (5), 679–684.
 - Chen, Q.; Du, J.; Xie, H.; Zhao, Z.; Zheng, Q. Studies on preparation and properties of bio-based polymeric monomers and their bio-based polymers. *Acta Polymerica Sinica (in Chinese)* 2016, (10), 1330–1358.
 - Yang, J.; Sun, Z.; Duan, R.; Li, L.; Pang, X.; Chen, X. Copolymer of lactide and ϵ -caprolactone catalyzed by bimetallic Schiff base aluminum complexes. *Sci. China Chem.* 2016, 59, 1384–1389.
 - Thomas, C. M. Stereocontrolled ring-opening polymerization of cyclic esters: synthesis of new polyester microstructures. *Chem. Soc. Rev.* 2010, 39, 165–173.
 - Stanford, M. J.; Dove, A. P. Stereocontrolled ring-opening polymerisation of lactide. *Chem. Soc. Rev.* 2010, 39, 486–494.
 - Xu, T. Q.; Yang, G. W.; Liu, C.; Lu, X. B. Highly robust yttrium bis(phenolate) ether catalysts for excellent isoselective ring-opening polymerization of racemic lactide. *Macromolecules* 2017, 50, 515–522.
 - Guillaume, S. M.; Kirillov, E.; Sarazin, Y.; Carpentier, J. F. Beyond stereoselectivity, switchable catalysis: some of the last Frontier challenges in ring-opening polymerization of cyclic esters. *Chem. Eur. J.* 2015, 21, 7988–8003.
 - Cozzi, P. G. Metal-Salen Schiff base complexes in catalysis: practical aspects. *Chem. Soc. Rev.* 2004, 33, 410–421.
 - Chisholm, M. H.; Gallucci, J. C.; Zhen, H.; Huffman, J. C. Three-coordinate zinc amide and phenoxide complexes supported by a bulky Schiff base ligand. *Inorg. Chem.* 2001, 40, 5051–5054.
 - Chen, H. Y.; Tang, H. Y.; Lin, C. C. Ring-opening polymerization of lactides initiated by zinc alkoxides derived from NNO-tridentate ligands. *Macromolecules* 2006, 39, 3745–3752.
 - Pang, X.; Chen, X.; Zhuang, X.; Jing, X. Crown-like macrocycle zinc complex derived from β -diketone ligand for the polymerization of *rac*-lactide. *J. Polym. Sci., Part A: Polym. Chem.* 2008, 46, 643–649.
 - Baran, J.; Duda, A.; Kowalski, A.; Szymanski, R.; Penczek, S. Intermolecular chain transfer to polymer with chain scission: general treatment and determination of k_p/k_{tr} in L,L-lactide polymerization. *Macromol. Rapid Commun.* 1997, 18, 325–333.
 - Save, M.; Schappacher, M.; Soum, A. Controlled ring-opening polymerization of lactones and lactides initiated by lanthanum isopropoxide, 1. general aspects and kinetics. *Macromol. Chem. Phys.* 2002, 203, 889–899.
 - Gulli, S.; Daran, J. C.; Poli, R. Synthesis and structure of four-coordinate copper(II) complexes stabilized by β -Ketiminato ligands and application in the reverse atom-transfer radical polymerization of styrene. *Eur. J. Inorg. Chem.* 2011, 10, 1666–1672.
 - Tang, H. Y.; Chen, H. Y.; Huang, J. H.; Lin, C. C. Synthesis and structural characterization of magnesium ketiminato complexes: efficient initiators for the ring-opening polymerization of L-lactide. *Macromolecules* 2007, 40, 8855–8860.
 - Shit, S.; Sen, S.; Mitra, S.; Hughes, D. L. Syntheses, characterization and crystal structures of two square-planar Ni(II) complexes with unsymmetrical tridentate Schiff base ligands and monodentate pseudohalides. *Transition Met. Chem.* 2009, 34, 269–274.
 - Bochmann, M.; Bwembya, G.; Webb, K. J.; Malik, M. A.; Walsh, J. R.; O'Brien, P. Arene chalcogenolato complexes of zinc and cadmium, inorganic syntheses. John Wiley & Sons, Inc. 1997, 19–24.
 - Pang, X.; Du, H.; Chen, X.; Wang, X.; Jing, X. Enolic Schiff base aluminum complexes and their catalytic stereoselective polymerization of racemic lactide. *Chem. Eur. J.* 2008, 14, 3126–3136.
 - Scheiper, C.; Dittrich, D.; Wölper, C.; Bläser, D.; Roll, J.; Schulz, S. Synthesis, structure, and catalytic activity of tridentate, base-functionalized β -Ketiminato zinc complexes in ring-opening polymerization of lactide. *Eur. J. Inorg. Chem.* 2014, 2014, 2230–2240.
 - Hong, M.; Chen, E. Y. Completely recyclable biopolymers with linear and cyclic topologies *via* ring-opening polymerization of γ -butyrolactone. *Nat. Chem.* 2016, 8, 42–49.
 - Huang, M.; Pan, C.; Ma, H. Ring-opening polymerization of *rac*-lactide and α -methyltrimethylene carbonate catalyzed by magnesium and zinc complexes derived from binaphthyl-based iminophenolate ligands. *Dalton Trans.* 2015, 44, 12420–12431.
 - Wang, H.; Yang, Y.; Ma, H. Stereoselectivity Switch between zinc and magnesium initiators in the polymerization of *rac*-lactide: different coordination chemistry, different stereocontrol mechanisms. *Macromolecules* 2014, 47, 7750–7764.