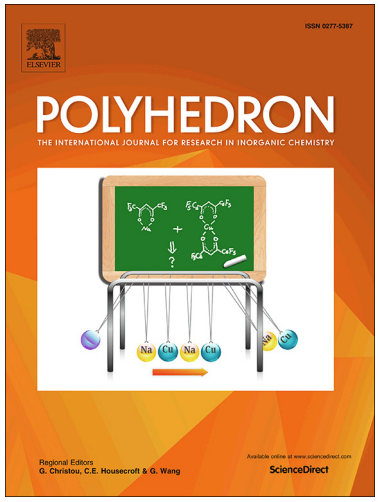

A series of aluminium complexes based on a β-diketiminate ligand: Synthesis, structures and their application to ring-opening polymerization of ε-caprolactone

Huifen Pan, Yafei Li, Yalan Wang, Yu Ge, Shengwang Xia, Yahong Li

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A series of aluminium complexes based on a β-diketiminate ligand: Synthesis, structures and their application to ring-opening polymerization of ε-caprolactone

Huifen Pan, Yafei Li, Yalan Wang, Yu Ge, Shengwang Xia, Yahong Li*

College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123

*Corresponding author. Tel: +86-512-65880323, Fax: +86-512-65880089, E-mail address: liyahong@suda.edu.cn (Y. H. Li)

Abstract: A series of aluminum complexes based on a β-diketiminate ligand HL (HL = N{-4-[(2,6-diisopropyl-phenylamino)pent-3-en-2-ylidene]-6-methyl}pyridin-2-amine) have been prepared and characterized spectroscopically and structurally. Reactions of the HL ligand with one equivalent of $AlMe_3$, $AlEt_3$ and $AlEt_2Cl$, respectively, in toluene, gave complexes [$LAlMe_2$] (**1**), [$LAlEt_2$] (**2**) and [LAlEtCl] (**3**) in high yields. Complexes **1** and **2** contain four-coordinated mononuclear aluminum center. The aluminum center of **3** is five-coordinated. Complexes **1**−**3** were used to catalyze the ring-opening polymerization of ε-caprolactone. Complexes **1**−**3** are very rare cases of aluminum alkyl compounds supported by β-diketiminate ligands, which show moderate activity toward the ring-opening polymerization (ROP) of ε-caprolactone (CL) in the absence of benzyl alcohol. However, in the presence of benzyl alcohol, the polymerization rate is remarkably accelerated and the conversions are greatly improved. The monomer conversion and number average molecular weight of poly(ε-caprolactone) (PCL) catalyzed by **1**−**3** shows a linear relationship. This result indicates that the polymerizations mediated by **1**−**3** exhibited controllable manner.

Keywords: β-Diketiminate ligand • Aluminum complexes • ε-Caprolactone • Ring-opening polymerization • Catalyze

1. Introduction

The desire to alleviate the environmental problem caused by the petrochemical plastics, which could not decompose naturally within a short time, has led to sustainable efforts to explore ecological friendly materials [1-2]. Biodegradable poly(ε-caprolactone) (PCL) and poly(lactide) (PLA) were developed to address this pollution challenge. Poly(ε-caprolactone) (PCL) and poly(lactide) (PLA) are very popular polyesters due to their bio-degradable, bio-compatible, and permeable properties and broad applications in various fields [3-10]. Ring-opening polymerization (ROP) of ε-caprolactone and lactide mediated by metal catalysts has proven to be a most promising approach to produce PCL and PLA. The key issue for designing catalysts for ring-opening polymerization (ROP) of ε-caprolactone depends on the choice of well-defined ligands and the employment of appropriate metal ions. A number of metal complexes, including K [11-12], Zn [13-16], Mg [17-20], Ca [21-23], Al [24-27], In [28-30], Sn [31-32], group IV metals [33-36], and rare earth metals [37-40] have been utilized as catalysts. Aluminum compounds have attracted intense attention over the past 20 years due to their strong Lewis acidity, easy availability and low toxicity. Ligand design is of vital importance for the catalysts because their catalytic activity is strongly affected by steric and electronic properties of the ligands. A plethora of organic moieties, *e.g.* O,O- [41,42], N,O- [43-46], N,N- [47-49], pyrrolide type-ligands [50-51], *etc.*, have been employed as the ligands for the polymerization catalysts. Among these ligand skeletons, β-diketiminates have proved to be appealing ligands which allow for adjusting the steric features by varying the amide moieties. Currently, the reported β-diketiminate ligands mainly focus on the symmetric N-substituent moieties with a C_2 symmetry [52-59], whereas the unsymmetrical ligand systems possessing adjustable steric and electronic features may coordinate with metal ions to generate the metal complexes with better catalytic activity [60-62]. Literature survey results indicate that aluminum complexes supported by unsymmetrical β-diketiminate ligands have rarely been reported [60-62].

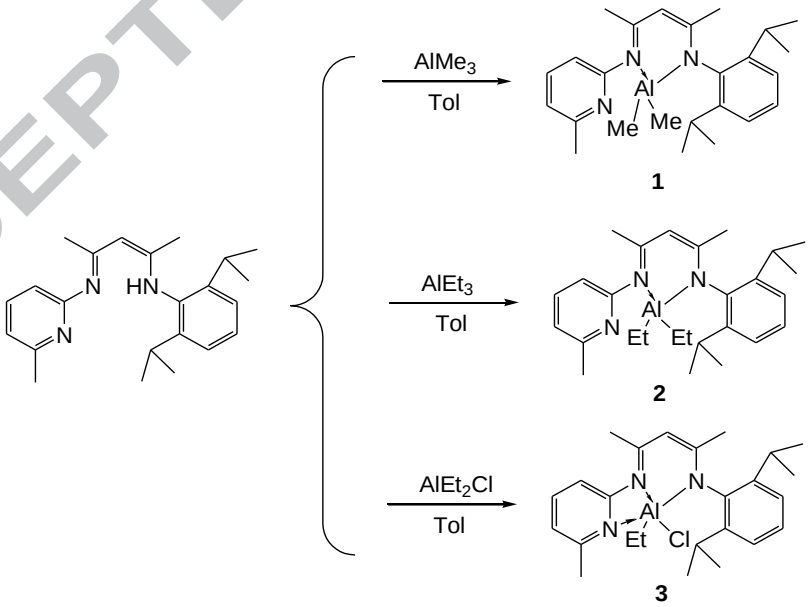
With these considerations in mind, we designed an unsymmetrical β-diketiminate ligand HL (HL = N{-4-[(2,6-diisopropyl-phenylamino)pent-3-en-2-ylidene]-6-methyl} pyridin-2-amine) and prepared three aluminum complexes [LAlMe_2] (**1**), [LAlEt_2] (**2**)

and [LAlEtCl] (**3**). Herein, we report the syntheses and structures of **1**−**3**. Their catalytic properties toward ring-opening polymerization of ε-caprolactone have also been presented.

2. Results and discussion

2.1. Synthesis and characterization

The ligand HL (HL = N{-4-[(2,6-diisopropylphenylamino)pent-3-en-2-ylidene] -6-methyl}pyridin-2-amine) was prepared by the condensation reaction of pentane-2,4-dione with 2,6-diisopropylaniline and 6-methyl-2-aminopyridine. Firstly, the condensation reaction between pentane-2,4-dione with 2,6-diisopropylaniline gave 4-((2,6-diisopropylphenyl)imino)pentan-2-one. Secondly, the reaction between 4-((2,6-diisopropylphenyl)imino)pentan-2-one and 6-methyl-2-aminopyridine generated the ligand N{-4-[(2,6-diisopropylphenylamino)pent-3-en-2-ylidene] -6-methyl}pyridin-2-amine (HL) as a yellow solid. Reactions of the ligand (HL) with one equivalent of $AlMe_3$, $AlEt_3$ and $AlEt_2Cl$, respectively, in toluene, gave complexes [$LAlMe_2$] (**1**), [$LAlEt_2$] (**2**) and [LAlEtCl] (**3**) in high yields (Scheme 1).



Scheme 1. Synthesis of aluminum complexes **1**−**3**.

The structures of the HL ligand and complexes **1**−**3** have been characterized by ^{1}H and ^{13}C NMR spectra with an Agilent-600 spectrometer. The crystals of the HL ligand

and **1**−**3** were grown in toluene for two weeks. The structures of the HL ligand and the aluminum complexes **1**−**3** were determined by X-ray diffraction analysis and are shown in Figs. 1−4. The crystallographic data of the HL ligand and complexes **1**−**3** are summarized in Table 1.

Table 1 Crystallographic data of the HL ligand and complexes **1**−**3**.

	HL	**1**	**2**	**3**
Empirical formula	$C_{23}H_{31}N_3$	$C_{25}H_{36}AlN_3$	$C_{27}H_{40}AlN_3$	$C_{25}H_{35}AlClN_3$
Formula weight [g mol^{-1}]	349.51	405.55	433.60	439.99
Temperature [K]	120.02	296.15	296.15	296.15
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/c$	P-1	$P2_1/c$	$P2_1/c$
a/Å	18.2426(8)	10.4738(11)	14.1775(9)	14.1635(16)
b/Å	10.7017(5)	10.4887(11)	9.2046(5)	10.9365(12)
c/Å	21.5388(8)	11.8208(12)	20.5039(12)	16.3706(19)
α/°	90	82.597(3)	90	90
β/°	95.264(1)	87.367(3)	100.330(2)	101.274(4)
γ/°	90	71.679(3)	90	90
Volume/Å^3	4187.2(3)	1222.5(2)	2632.4(3)	2486.9(5)
Z	4	2	4	4
ρ_{calc}g/cm^3	1.109	1.102	1.094	1.175
μ/mm^{-1}	0.065	0.098	0.095	0.205
F(000)	1520.0	440.0	944.0	944.0
Crystal size/mm^3	0.5 × 0.5 × 0.2	0.6 × 0.5 × 0.4	0.5 × 0.4 × 0.2	0.6 × 0.6 × 0.5
Radiation	Mo-K_α (λ = 0.71073)	Mo-K_α (λ = 0.71073)	Mo-K_α (λ = 0.71073)	Mo-K_α (λ = 0.71073)
2Θ range for data collection/°	4.23 to 55.014	4.822 to 55.186	4.54 to 55.114	4.74 to 55.122
Index ranges	$-23 \le h \le 23$, $-13 \le k \le 13$, $-26 \le l \le 27$	$-13 \le h \le 13$, $-13 \le k \le 13$, $-15 \le l \le 15$	$-18 \le h \le 18$, $-11 \le k \le 11$, $-25 \le l \le 26$	$-18 \le h \le 18$, $-14 \le k \le 14$, $-21 \le l \le 21$
Reflections collected	61198	46377	48090	59787
Independent reflections	9536 R_{int} = 0.0751	5615 R_{int} = 0.0297	6067 R_{int} = 0.0830	5727 R_{int} = 0.0607
Data/restraints/parameters	9536/0/483	5615/0/271	6067/0/289	5727/0/279
Goodness-of-fit on F^2	1.101	1.025	1.045	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0541, wR_2 = 0.1452	R_1 = 0.0414, wR_2 = 0.1184	R_1 = 0.0659, wR_2 = 0.1310	R_1 = 0.0512, wR_2 = 0.1439
Final R indexes [all data]	R_1 = 0.0848, wR_2 = 0.1795	R_1 = 0.0483, wR_2 = 0.1238	R_1 = 0.1094, wR_2 = 0.1465	R_1 = 0.0636, wR_2 = 0.1514
Largest diff. peak/hole / e Å^{-3}	0.53/-0.48	0.31/-0.24	0.28/-0.28	0.68/-0.43

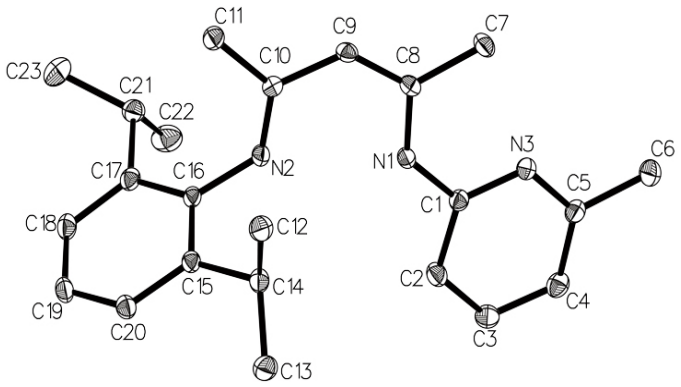
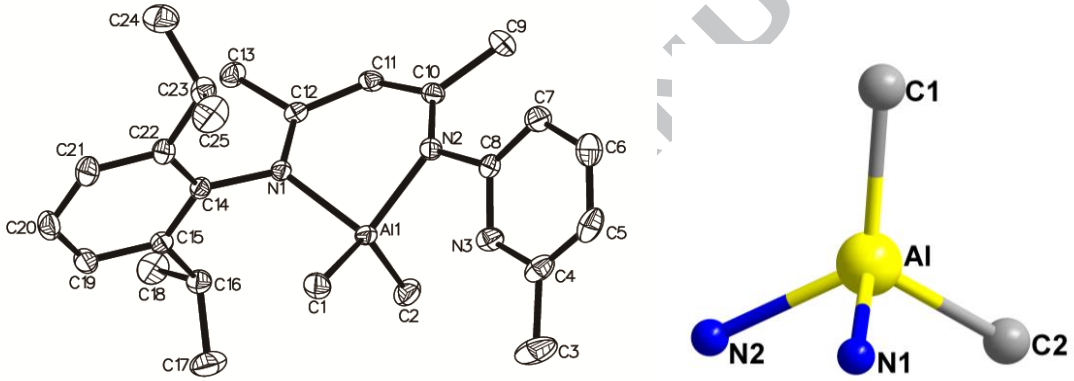
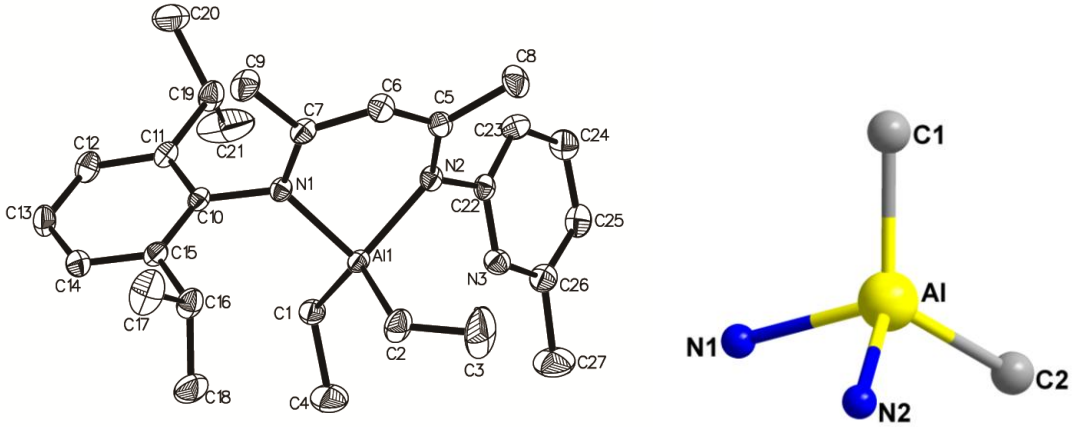


Fig. 1. ORTEP drawing of the ligand HL with thermal ellipsoids drawn at 30% probability level. Hydrogen atoms are omitted for clarity.



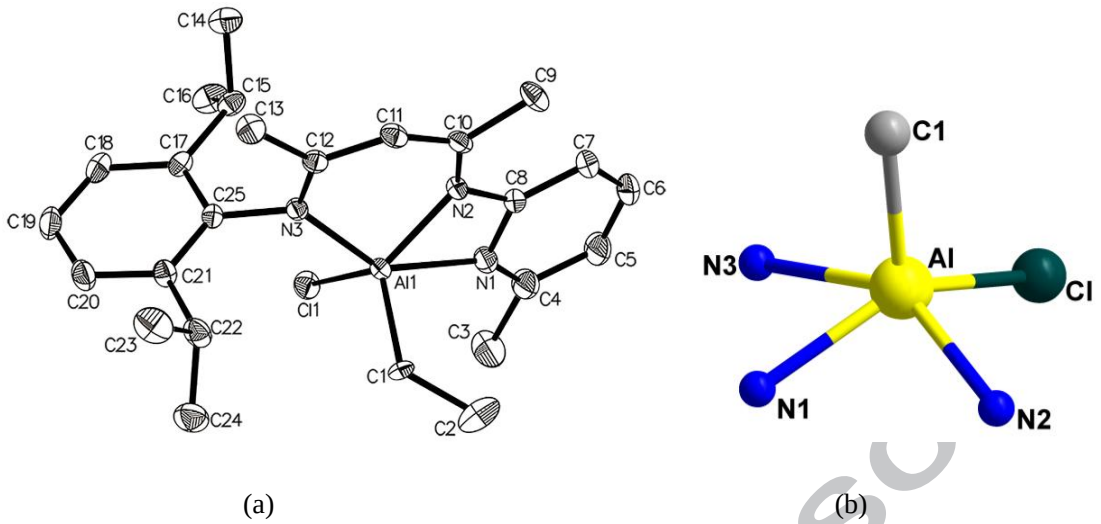
(a) (b)

Fig. 2. (a) ORTEP drawing of **1** with thermal ellipsoids drawn at 30% probability level. Hydrogen atoms are omitted for clarity. (b) Coordination polyhedron of Al^{III}.



(a) (b)

Fig. 3. (a) ORTEP drawing of **2** with thermal ellipsoids drawn at 30% probability level. Hydrogen atoms are omitted for clarity. (b) Coordination polyhedron of Al^{III}.



(a) (b)

Fig. 4. (a) ORTEP drawing of **3** with thermal ellipsoids drawn at 30% probability level. Hydrogen atoms are omitted for clarity. (b) Coordination polyhedron of Al^{III}.

The structure of **1** and the coordination polyhedron of Al^{III} ion are illustrated in Fig. 2. Complex **1** exists as twisted tetrahedral structure with the central Al^{III} ion being surrounded by two nitrogen atoms of chelating β-diketiminate and two methyl groups. The nitrogen atom of pyridine ring does not involve in the coordination. The angle of N1–Al–N2 (89.42(4)°) is smaller than the regular tetrahedral bond angle of 109.28°. The average Al–C and Al–N bond lengths are 1.966(5) and 1.963(7) Å, respectively, which are similar to those observed in the aluminum complexes stabilized by β-diketiminate ligands [63].

Complex **2** crystallizes in the monoclinic space $P2_1/c$ and the coordination polyhedron of Al^{III} (Fig. 3 (b)) ion is similar to that of **1**. Complex **2** displays twisted tetrahedral structure with the central Al^{III} ion being coordinated by two nitrogen atoms of chelating β-diketiminate and two ethyl groups. Wherein the nitrogen atom of pyridine doesn't participate in the coordination either. The angle of N1–Al–N2 of **2** is 91.81(8)° and it is larger than the angle of N1–Al–N2 of **1**. The average Al–C and Al–N bond lengths of **2** are 1.967(2) and 1.938(8) Å.

Complex **3** exhibits five-coordinated trigonal bipyramidal structure, with the central Al^{III} ion being surrounded by two nitrogen atoms of β-diketiminate motif, one pyridyl nitrogen atom, one carbon atom of ethyl group, and one chlorine atom. The angle of N3–Al–N2 of **3** (88.69(7)°) is smaller than those of **1** (89.42(4)°) and **2** (91.81(8)°).

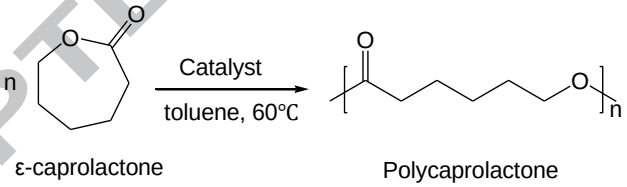
The average Al–C and Al–N bond lengths are 2.0022(18) and 1.969(8) Å, respectively, which are longer than those observed in complexes **1** and **2**. The Al–N_{pyridy} bond length is 2.1745(18) Å and the Al–Cl bond length is 2.1935(8) Å.

It is worth to mention that the structure of **3** is slightly different from those of **1** and **2**. While the Al^{III} centers of **1** and **2** are four-coordinated and display tetrahedral geometry, the Al^{III} ion of **3** is five-coordinated and shows trigonal bipyramidal geometry. We assume that the stereo hindrance of chloride ion is smaller than those of methyl- and ethyl-group, leading to the further coordination of the nitrogen atom of pyridine ring to the metal center.

Complexes **1–3** join a small family of aluminum complexes supported by β-diketiminate ligands [52-62]. However, the Al^{III} complexes supported by unsymmetrical β-diketiminate ligands are very rare [26, 62].

*2.2. ROP of ε-caprolactone initiated by **1**–**3***

The ring-opening polymerization of ε-caprolactone in toluene using complexes **1**–**3** as the catalysts under different conditions were investigated. The reaction of the ring-opening polymerization of ε-caprolactone was shown in Scheme 2.



Scheme 2. The ring-opening polymerization of ε-caprolactone initiated by **1**–**3**.

Initially, the catalytic activity of **1-3** in the absence of benzyl alcohol were tested. The polymerizations were conducted in toluene, and the molar ratio of ε-caprolactone to initiator was fixed to 200:1. The results were summarized in Table 2. As can be seen from Table 2, the complexes **1**, **2**, and **3** all can catalyze the ring-opening polymerization of ε-caprolactone and the polymerization product has a relatively high molecular weight. At the same temperature, the conversion rate of the monomer increases with the polymerization time (Table 2, entries 3−6, 8, 9). However, the polymers have broad molecular weight distribution (PDI = 1.62-2.12). The catalytic

activity of **2** is better than those of **1** and **3**, which are consistent with the literature reported results [63-65]. Complexes **1** and **3** exhibit moderate activity (Table 2, entries 1−4, 8-11) according to the evaluation standard established by Redshaw [66].

Table 2 ROP of ε-Caprolactone initiated by **1**, **2**, and **3**[a]

Entry	Initiator	CL:Al	Solvent	Temp. (℃)	Time (min)	Conv. (%)[b]	M_w[c]	M_n[c]	PDI[d]
1	**1**	200:1	Tol	60	60	17.4	26511	15185	1.746
2	**1**	200:1	Tol	80	60	24.5	47074	28706	1.640
3	**1**	200:1	Tol	100	60	23.1	31019	14667	2.115
4	**1**	200:1	Tol	100	80	54.2	40254	19708	2.043
5	**2**	200:1	Tol	60	60	87.3	79979	38268	2.090
6	**2**	200:1	Tol	60	180	99.9	52514	32295	1.626
7	**2**	200:1	Tol	80	120	99.8	95705	49526	1.932
8	**3**	200:1	Tol	60	60	43.8	18417	9827	1.874
9	**3**	200:1	Tol	60	120	76.3	45238	22275	2.031
10	**3**	200:1	Tol	80	60	45.2	11283	5726	1.971
11	**3**	200:1	Tol	100	60	51.3	18552	13202	1.405

[a] Reaction conditions: All polymerizations were carried out with toluene as solvent and under nitrogen atmosphere. [b] Measured by ^1H NMR spectroscopy. [c] Calibration was performed with standard polystyrene samples and measured by gel permeation chromatography (GPC) in THF. [d] PDI =Polydispersity index.

There are few examples of ring-opening polymerization of ε-caprolactone initiated by aluminum alkyl complexes in the absence of benzyl alcohol because the catalytic activity of aluminum alkyl compounds for ring-opening polymerization of ε-caprolactone is very low [63, 67]. Complexes **1**–**3** are special cases which exhibit catalytic properties for ring-opening polymerization of ε-caprolactone in the absence of benzyl alcohol.

It is reported that the reaction of aluminum alkyl compounds with benzyl alcohol can form aluminum oxide, which can better induce ROP of ε-caprolactone [26]. Therefore, the catalytic activity of **1**–**3** towards ROP in the presence of benzyl alcohol was examined. It is found that complexes **1**-**3** showed excellent activity when the molar ratios of ε-caprolactone, catalyst and benzyl alcohol (ε-CL/Al/OH) were set to 200:1:1 and 400:1:1 (Table S2 entries 1, 2 and 14) and the conversion of the monomer reached 99.6%. In order to compare the activities of **1**, **2** and **3** and also investigate the dynamic behavior of the catalytic reactions, the polymerizations initiated by **1**, **2** and

3, respectively, under the molar ratio of 600:1:1 (ε-CL/Al/OH) at 60°C were explored (Table 3). As can be seen from Table 3, even at the molar ratio of 600:1:1, complexes **1**-**3** still show very good activity. As the reaction time was extended, both conversions and molecular weights increased (Table 3, entries 1-12). Different from the results that complex **2** showed better activity in the absence of benzyl alcohol, complex **3** displayed high activity than those of **1** and **2**. For complex **1**, the conversions of the monomer increased from 42.9% to 73.5% (Table 3, entries 1-4). As complex **3** was employed as initiator, the conversions of the monomer increased from 66.5% to 92.0% (Table 3, entries 9-12). These results agree with the proposal that the polymerization mechanism in the presence of an alcohol is different from that of absent of the alcohol (Schemes S1 and S2) [26]. The catalytic activity of **1**-**3** are comparable to some reported symmetric β-diketiminate supported aluminum complexes [26, 61].

Table 3. ROP of ε-caprolactone initiated by **1**, **2**, and **3** in the presence of BnOH[a].

Entry	Initiator	CL:Al:BnOH	Solvent	Temp. (℃)	Time (min)	Conv. (%)[b]	M_w[c]	M_n[c]	PDI[d]
1	**1**	600:1:1	Tol	60	60	42.9	10828	8297	1.305
2	**1**	600:1:1	Tol	60	90	53.9	11494	8973	1.281
3	**1**	600:1:1	Tol	60	120	68.4	11777	9913	1.188
4	**1**	600:1:1	Tol	60	150	73.6	11706	10000	1.171
5	**2**	600:1:1	Tol	60	60	42.9	10606	9378	1.131
6	**2**	600:1:1	Tol	60	90	53.9	14323	12056	1.188
7	**2**	600:1:1	Tol	60	120	59.4	15161	13014	1.165
8	**2**	600:1:1	Tol	60	150	64.9	19057	14682	1.298
9	**3**	600:1:1	Tol	60	60	66.5	9413	8052	1.169
10	**3**	600:1:1	Tol	60	90	71.9	17523	13765	1.273
11	**3**	600:1:1	Tol	60	120	87.5	39709	30926	1.284
12	**3**	600:1:1	Tol	60	150	92.0	49279	38620	1.276

[a] Reaction conditions: All polymerizations were carried out with toluene as solvent and under nitrogen atmosphere. [b] Measured by ^1H NMR spectroscopy. [c] Calibration was performed with standard polystyrene samples and measured by gel permeation chromatography (GPC) in THF. [d] PDI =Polydispersity index.

To further study the dynamic behavior of the polymerization of ε-caprolactone initiated by **1**, **2** and **3**, respectively, the relationship between number average molecular weights (M_n) of the polymer and the monomer conversion, as well as the

correlation between PDI value and the monomer conversion, were investigated (600:1:1 at 60 °C). The results are depicted in Figures 5–7.

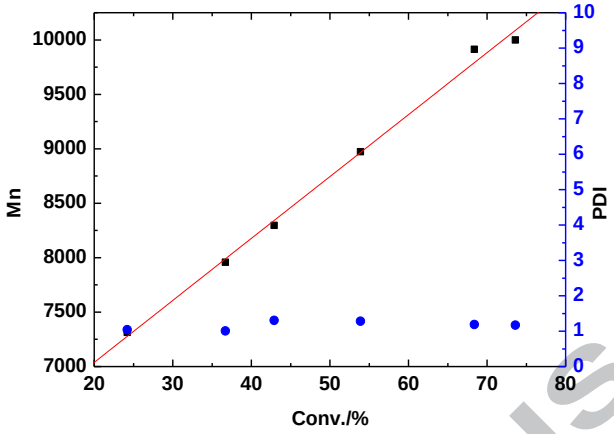


Fig. 5. Plot of Mn (■ obtained from GPC analysis) and PDI (●, M_w/M_n) in the ROP of ε-CL initiated by **1**/BnOH.

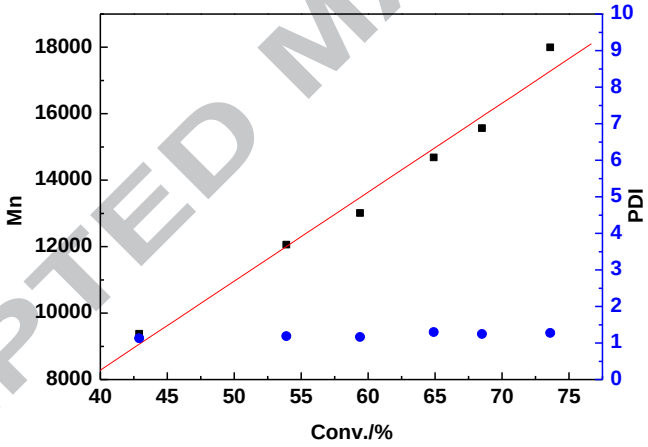


Fig. 6. Plot of M_n (■ obtained from GPC analysis) and PDI (●, M_w/M_n) in the ROP of ε-CL initiated by **2**/BnOH.

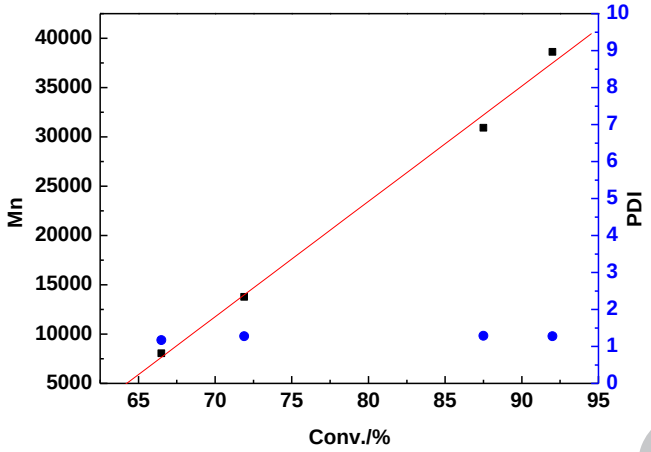


Fig. 7. Plot of M_n (■ obtained from GPC analysis) and PDI (●, M_w/M_n) in the ROP of ε-CL initiated by **3**/BnOH.

As illustrated in Figures 5-7, there is a linear relationship between monomer conversion and number average molecular weight (M_n), and the PDI values are about 1. These results indicate that the polymerization reactions initiated by complexes **1**–**3** are controllable in the presence of benzyl alcohol.

3. Conclusions

The synthesis, structures and reactivity of three aluminum complexes supported by a novel asymmetric β-diketiminate ligand containing pyridine group, namely, [LAlMe$_2$] (**1**), [Al(L)Et$_2$] (**2**), and [Al(L)EtCl] (**3**) are depicted. The structures of the ligand LH and complexes **1**–**3** were characterized by X-ray diffraction analysis, ^{1}H and ^{13}C NMR spectroscopy, and element analysis. The ROP of ε-caprolactone initiated by **1**–**3** were executed. Their catalytic activities for ε-caprolactone ROP with benzyl alcohol and without benzyl alcohol were compared. In the presence of BnOH, complexes **1**–**3** show higher activity toward the ring-opening polymerization, and the polymerization reactions exhibit controllable manner. The aim for synthesizing aluminum compounds with higher catalytic activity is achieved.

4. Experimental section

4.1. General details

All operations were carried out under dry nitrogen atmosphere using glove-box techniques and standard Schlenk-line. THF, n-hexane, toluene and dichloromethane were dried over sodium/benzophenone. $AlMe_3$, $AlEt_3$ and $AlEt_2Cl$ were used as received from commercial supplier. ε-Caprolactone (CL) was stirred over CaH_2 for 24h, and distilled. NMR spectra and elemental analysis were performed on Bruker Avance-III 600 MHz NMR spectrometer and Perkin-Elmer 2400 analyser, respectively. The GPC analysis was carried out at 40 ℃ in THF on PL-GPC50 gel permeation chromatograph. Single crystal X-ray diffraction data were collected at 293(2) K with a Bruker APEX II CCD diffractometer.

4.2. Synthesis of the ligand (HL)

Acetylacetone (10.00 g, 100.00 mmol) and 2,6-diisopropylaniline (DIPA, 18.02 g, 100.00 mmol) in toluene were reacted with a small amount of p-toluenesulfonic acid (0.20 g, 1.00 mmol) as catalysts, and the reaction was heated under reflux overnight. The solvent was evaporated to give a white solid. The resulting solid was reacted with triethyloxonium tetrafluoroborate (9.59 g, 50mmol) in CH_2Cl_2 and stirred at room temperature for one day, then one equivalent of 6-methyl-2-aminopyridine(10.81 g, 100.00 mmol) was added. The reaction mixture was further stirred for three days. The solvent was spun dry to give a yellow solid. Yield: 21.7 g (62%). ^{1}H NMR (600 MHz, Chloroform-*d*): δ = 13.21 (s, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 2H), 7.11 – 7.06 (m, 1H), 6.65 (d, *J* = 7.3 Hz, 1H), 6.42 (d, *J* = 8.1 Hz, 1H), 4.93 (s, 1H), 2.91 (h, *J* = 6.9 Hz, 2H), 2.49 (s, 3H), 2.43 (s, 3H), 1.70 (d, *J* = 1.1 Hz, 3H), 1.19 (d, *J* = 6.9 Hz, 6H), 1.12 (d, *J* = 6.8 Hz, 6H) ppm. ^{13}C NMR (151 MHz, Chloroform-*d*): δ = 165.79, 156.87, 155.07, 153.06, 144.80, 138.73, 137.57, 123.61, 122.87, 115.81, 110.84, 99.34, 28.23, 24.41, 23.93, 22.58, 22.46, 21.68 ppm. Elemental analysis calcd (%) for $C_{23}H_{31}N_3$ (349.51): C 79.10, H 8.76, N 12.24; found: C 79.04, H 8.94, N 12.02.

*4.3. Synthesis of $LAlMe_2$ (**1**)*

A solution of LH (0.349 g, 1.0 mmol) in Tol was added dropwise to $AlMe_3$ solution (1.00 mL, 1 M in hexane, 1.0 mmol) at -35 ℃. The mixture was stirred overnight at room temperature. Volatile materials were removed under vacuum to give a yellow

solid. Yield: 0.369 g (91%). Crystal were cultured in toluene at -35 ℃ for two weeks. ^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.50 (t, *J* = 7.8 Hz, 1H), 7.19 (dd, *J* = 8.4, 6.8 Hz, 1H), 7.14 – 7.12 (m, 2H), 6.81 (d, *J* = 7.5 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 5.15 (s, 1H), 3.03 (p, *J* = 6.8 Hz, 2H), 2.44 (s, 3H), 2.19 (s, 3H), 1.77 (s, 3H), 1.13 (t, *J* = 6.5 Hz, 12H), -1.00 (s, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*): δ = 170.71, 163.19, 157.62, 157.11, 143.18, 141.95, 137.69, 126.15, 123.75, 118.04, 113.96, 100.17, 27.81, 24.49, 23.72, 23.55, 23.12, -10.12. Elemental analysis calcd (%) for $C_{25}H_{36}AlN_3$ (405.55): C 74.72, H 8.33, N 10.39; found: C 74.04, H 8.31, N 10.36.

*4.4. Synthesis of LAlEt$_2$ (**2**)*

A solution of LH (0.349 g, 1.0 mmol) in Tol was added dropwise to $AlEt_3$ solution (1.00 mL, 1 M in hexane, 1.0 mmol) at -35 ℃. The mixture was stirred overnight at room temperature. Volatile materials were removed under vacuum to give a yellow solid. Yield: 0.412 g (95%). Crystal were cultured in toluene at -35 ℃ for two weeks. ^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.50 (t, *J* = 7.8 Hz, 1H), 7.19 (dd, *J* = 8.4, 6.9 Hz, 1H), 7.14 – 7.11 (m, 2H), 6.84 (d, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 5.15 (s, 1H), 3.01 (hept, *J* = 6.8 Hz, 2H), 2.48 (s, 3H), 2.15 (s, 3H), 1.76 (s, 3H), 1.13 (dd, *J* = 6.8, 2.2 Hz, 12H), 0.81 (t, *J* = 8.1 Hz, 6H), -0.28 (dq, *J* = 14.0, 8.1 Hz, 2H), -0.37 (dq, *J* = 14.0, 8.1 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*): δ = 170.75, 164.39, 157.87, 157.57, 143.32, 141.62, 137.28, 126.23, 123.74, 118.42, 114.85, 100.62, 27.80, 24.49, 24.35, 24.05, 23.42, 22.88, 9.89, -0.11. Elemental analysis calcd (%) for $C_{27}H_{40}AlN_3$ (433.60): C 74.54, H 8.93, N 9.43; found: C 74.79, H 9.30, N 9.69.

*4.5. Synthesis of LAlEtCl (**3**)*

A solution of LH (0.349 g, 1.0 mmol) in Tol was added dropwise to $AlEt_2Cl$ solution (1.00 mL, 1 M in hexane, 1.0 mmol) at -35 ℃. The mixture was stirred overnight at room temperature. Volatile materials were removed under vacuum to give a yellow solid. Yield: 0.409 g (93%). Crystal were cultured in toluene at -35 ℃ for two weeks. ^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.56 (t, *J* = 7.8 Hz, 1H), 7.23 – 7.11 (m, 3H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.85 (d, *J* = 7.5 Hz, 1H), 5.26 (s, 1H), 3.30 (hept, *J* = 6.8 Hz, 1H), 2.86 (hept, *J* = 7.0 Hz, 1H), 2.49 (s, 3H), 2.27 (s, 3H), 1.81 (s, 3H), 1.25 (d, *J* = 6.7 Hz, 3H), 1.15 (d, *J* = 6.8 Hz, 6H), 1.06 (d, *J* = 6.8 Hz, 3H), 0.60

(t, *J* = 8.1 Hz, 3H), -0.31 (qd, *J* = 8.1, 2.5 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*): δ = 172.53, 162.96, 157.30, 156.72, 143.93, 142.75, 141.42, 138.78, 126.76, 124.37, 123.68, 118.92, 112.90, 101.19, 28.20, 27.93, 25.40, 24.75, 24.62, 24.44, 23.87, 23.34, 23.05, 8.92, 0.44. Elemental analysis calcd (%) for $C_{25}H_{35}AlClN_3$ (439.99): C 67.89, H 8.30, N 9.72; found: C 68.24, H 8.02, N 9.55.

4.6. Ring-opening polymerization of ε-caprolactone

In the glove box, a solution of ε-caprolactone (0.228 g, 2 mmol) and complex **1** (0.01 mmol) in toluene (2 mL) was placed in a Schlenk flask equipped with a magnetic stirring bar. The reaction mixture was heated, out of glove-box, to the desired temperature and quenched with a mixture of HCl/MeOH (2 mL, 1:5 v/v) to give a white solid. The solid was dissolved in THF and washed with MeOH.

4.7. Ring-opening polymerization of ε-caprolactone in the presence of BnOH

In the glove box, a solution of ε-caprolactone (0.228 g, 2 mmol), complex **1** (0.01 mmol) in toluene (2 mL) and one equivalent of BnOH was placed in a Schlenk flask equipped with a magnetic stirring bar. The reaction mixture was heated, out of the glove box, to the desired temperature and quenched with a mixture of HCl/MeOH (2 mL, 1:5 v/v) to give a white solid. The solid was dissolved in THF and washed with MeOH.

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Appendix A. Supplementary data

CCDC <1890189, 1878871, 1878873 and 1878872> contains the supplementary crystallographic data for <LH, **1**, **2** and **3**>. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge

Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with NMR spectra of HL, complexes **1**–**3** and PCL, selected bond lengths and angles of ligand HL and complexes **1**−**3**, proposed mechanism for the ROP of ε-CL and MALDI-TOF mass spectrum of Poly(ε-caprolactone).

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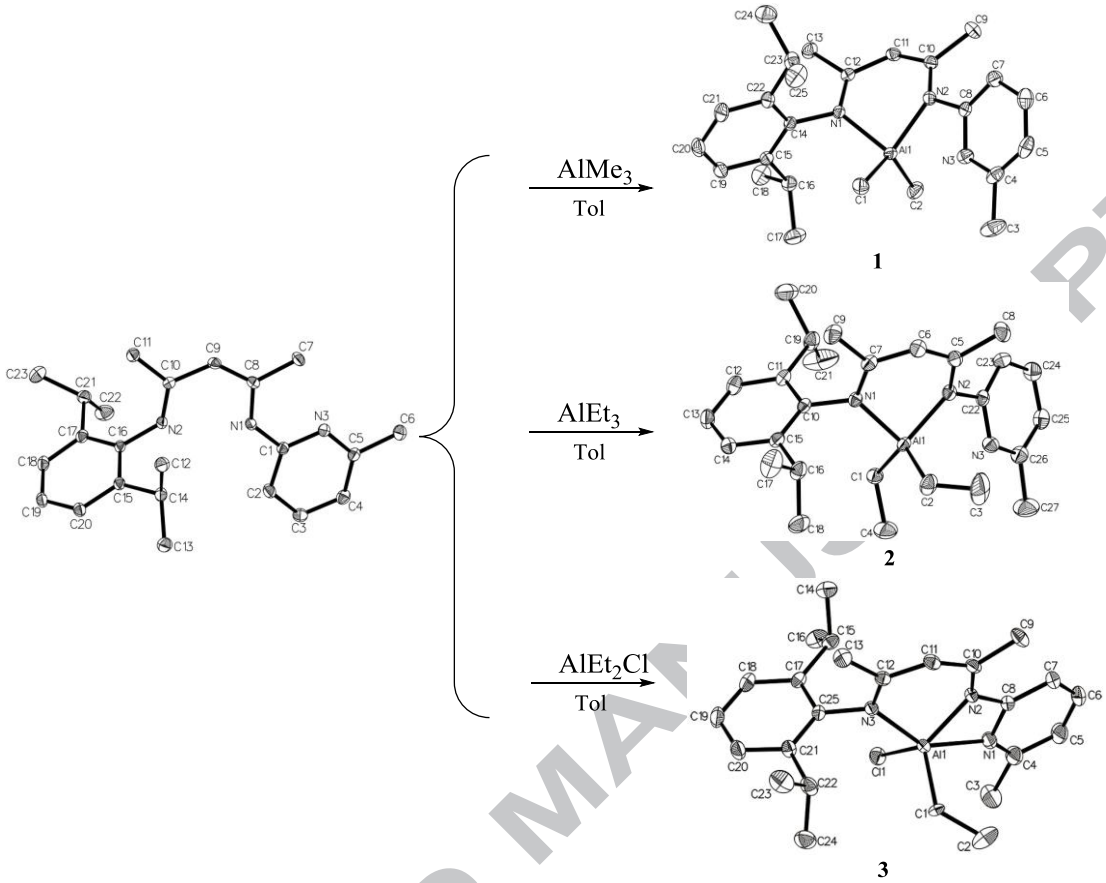

A series of aluminium complexes based on a β-diketiminate ligand: Synthesis, structures and their application to ring-opening polymerization of ε-caprolactone

Huifen Pan, Yafei Li, Yalan Wang, Yu Ge, Shengwang Xia, Yahong Li*

Three aluminum complexes based on a β-diketiminate ligand have been prepared and characterized. Complexes **1–3** showed moderate catalytic activity toward ring-opening polymerization (ROP) of ε-caprolactone in the absence of benzyl alcohol. The polymerization accelerated remarkably in the presence of benzyl alcohol (BnOH).