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Aluminum Chelates Supported by β -Quinolyl Enolate Ligands: Synthesis and ROP of ε-CL[†]

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Treatment of tautomers of β -quinolyl ketone-enaminones **1a-6a** with AIMe₃ afforded the aluminium β -quinolyl enolato dialkylaluminium complexes LAIMe₂ **1b-6b** (L = $[(2-C_3H_6N)-CH=C(R)-O_-]$ (R = CH₃ (**1b**), ^tBu (**2b**), Ph (**3b**), o-Tolyl (**4b**), p-Tolyl (5b), p-OMePh (6b)), respectively. 2b reacted with benzyl alcohol to generate the corresponding LAI(OBn)₂ complex 2c. Complexes 1b-6b and 2c were characterized by ¹H and ¹³C NMR spectroscopy, elemental analyses and single crystal X-ray diffraction analyses. All complexes were tested as catalyst precursers for ring-opening polymerization of ϵ -caprolactone (ϵ -CL). The results indicated that LAIMe₂ (1b-6b) were good activity towards the ROP of ε-CL in the presence of benzyl alcohol at 80 °C, and LAI(OBn)₂ 2c exhibited higher catalytic activity in the absence of alchol than 1b-6b for the ROP of ε-CL. However, both polymerizations were less controlled. Kinetic studies showed the polymerization reaction catalyzed by 1b-6b and 2c proceeded with first-order dependence on monomer and performanced through coordination-insertion.

Introduction

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Biodegradable polyesters such as polycaprolactone (PCL), polylactide (PLA) and their copolymers have attracted considerable interest from industrial and academic research groups.¹ Although they can be produced by condensation reactions, these polymers are effectively prepared by ringopening polymerization (ROP) via a coordination-insertion mechanism initiated by metal-based complexes due to the advantages of well-controlled molecular weight and regularity.² To date, a huge number of metal-based catalysts have been developed, e.g. zinc,³ magnesium,⁴ aluminium,⁵ stannous,⁶ calcium,⁷ iron⁸ and rare earth,⁹ and their catalytic performances have been widely investigated. Among these metal-based ROP initiators, aluminum alkoxides have attracted considerable attention due to the oxophilicity and Lewis acidity of the metal center.

In recent years, aluminum β -diketiminate,^{5c-e} Salen,^{5f-g} phenolate,^{5h-i} or amidinate^{5j-k} complexes have proved to be efficient and excellent initiators for the ROP of cyclic esters.^{5a,5b} Relevant to these aluminum initiators, the relationships between structure and activity have been discussed in the ROP process. The steric hindrance and electronic effect of ligand seems to be crucial in determining



the catalytic performances of ROP initiators.¹⁰ Among these metal complexes, steric bulky ligands usually play a crucial roles in chain-end controlled ROP processes, so that subtle modifications of ligand or metal may result in great effects on stereoselectivity.9k,10c Most of the current reports with alkoxide-based ligands are focused on ketiminate and Schiff base,¹¹ surprisingly, few studies have involved the aluminium complexes bearing quinolyl-enolate ligands where the imine donor is part of a heteroaromatic ring system (Chart 1).

Recently, Bildstein and his co-workers have synthesized pyridyl/chinolyl [N,O] β-ketiminato and [N,N] β-diketiminato ligands by modifying literature procedure, which utilizes the reaction of picolyl/quinolyl-lithium with acetonitrile or benzonitrile followed by acidic hydrolysis.¹² We have reported the insertion reaction of lithiated picoline with nitriles gave [N,N] β-diketiminato complexes¹³ and lithium guinolylamide with nitriles afford quinolylgunidinates.¹⁴

With this mind, we decided to explore the preparation of aluminum derivatives coordinated by bidentate quinolylenolate ligands and to mediate as a catalyst in the polymeriza-



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Scheme 1 Synthesis of aluminium β -quinolyl enolates 1b-6b



Fig. 1 X-ray structure of 1b with thermal ellipsoids represented at the 30% probability level. Hydrogen atoms are omitted for clarity.

tion of cyclic esters. In this contribution, we report the synthesis and characterization of some novel aluminum complexes containing differently substituted β -quinolyl enolate [N,O] ligands, and develop their application for the ROP of ϵ -CL.

Results and discussion

Synthesis and Characterization

Synthesis of ligand precursors 1a-6a. As depicted in Scheme 1, the proligands of quinolyl β-ketiminate were synthesized according to the improved literature procedures.¹² Firstly, the addition of quinolyl-lithium with aliphatic or aromatic nitriles yielded quinolyl azaazyl-lithiums. Then, the mixture followed by acid hydrolysis gave quinolyl-enolates **1a-6a** in good yields (68-88%). The proligands **1a-6a** were slightly air-sensitive or stable as yellow solids. Compounds **1a-6a** were characterized by NMR spectroscopy, which showed three different tautomers: quinolyl-ketone (I), -enol (II) and -enaminone (III). In genral, enaminones are favored over enols for 2-substituted quinolines probably due to stabilization by hydrogen bonding.¹⁵ The equilibria between these tautomers may be

changed according to the polarity of the solvent. For example, the proligand **3a** exists in $CDCl_3$ as a mixture of 80% enaminone (III) and 20% ketone (I) whereas in $(D_3C)_2SO$ only enaminone is present. In the solid state, both of **4a** and **6a** exist in their enaminone (III) tautomer, which is consistent with the previous report.¹²

Synthesis and characterization of aluminum complexes 1b-6b. Aluminum complexes **1b-6b** were obtained in good yields by the stoichiometric reactions of AIMe₃ with the corresponding ligands under mild conditions and isolated as yellow solid from toluene in 70-91% yield (Scheme 1). These complexes are air and moisture sensitive, they are soluble in aromatic hydrocarbons (benzene, toluene) except for complex 6b which is slightly soluble in toluene but readily soluble in THF. All aluminum complexes were characterized by ¹H and ¹³C NMR spectroscopy and elemental analysis. Compared to the ligands 1a-6a, the ¹H NMR spectra of 1b-6b show no proton signals appeared in low field regions (δ 14.95 to 15.70 ppm) and the resonances for the protons of Al-CH₃ appeared in the highfield regions (δ -0.60 to -0.48 ppm). The ¹H and ¹³C NMR spectra of all the complexes 1b-6b show one resonance for the methine CH resonances of ketiminate framework at ca. 5.44-6.19 and 93.89-100.44 ppm, which confirmed that the metal complexes are pure.

Complexes **1b**, **2b**, **5b** and **6b** were further characterized by single crystal X-ray diffraction. Their molecular structures are displayed in Fig. 1-4, and selected bond lengths and angles are showed in Table 1. Complexes **1b**, **2b**, **5b** and **6b** have a similar geometry. Each of complexes contains a six-membered metallacycle AINCCCO, where the six-membered ring is almost coplanar with the quinolyl group. For the structure of **1b**, **2b**, **5b** and **6b**, the aluminum atom is four-coordinated bearing bidentate ligands in a distorted-tetrahedral geometry.The biting angles of enolate ligands, N-Al-O, are in the range of 96.63(6)-97.57(5)°, smaller than regular tetrahedral bond angle of 109.28°. The bond lengths of Al-O and Al-N in these

	1b	2b	5b	6b
Al(1)-O(1)	1.7814(11)	1.7786(15)	1.769(2)	1.7809(12)
Al(1)-N(1)	1.9682(12)	1.9761(16)	1.967(3)	1.9699(13)
O(1)-C(11)	1.3086(18)	1.312(2)	1.309(4)	1.3154(18)
C(11)-C(10)	1.356(2)	1.358(3)	1.358(4)	1.365(2)
O(1)-AI(1)-N(1)	97.57(5)	96.63(6)	97.53(11)	97.44(5)



Fig. 2 X-ray structure of 2b with thermal ellipsoids represented at the 30% probability level. Hydrogen atoms are omitted for clarity.



Fig. 3 X-ray structure of 5b with thermal ellipsoids represented at the 30% probability level. Hydrogen atoms are omitted for clarity. Symmetry codes: (i): x, 0.5-y, z.



Fig. 4 X-ray structure of **6b** with thermal ellipsoids represented at the 30% probability level. Hydrogen atoms are omitted for clarity.

complexes are in the range of 1.769(2)-1.781(2) and 1.967(3)-1.976(2) Å, which are comparable to those in the phenoxyimine aluminum complexes [Al-O (1.772(2)-1.861(2), Al-N (1.970(2)-2.027(3) Å] reported by Carpentier^{5h} and ketiminates [1.788(2)-1.820(2), 1.954(6)-2.044(2)] described by Huang.^{5c} For the enolate backbone of complexes **1b**, **2b**, **5b** and **6b**, the C10-C11 and C11-O1 distances are all in the same ranges of



Scheme 2 Synthesis of aluminium benzyloxide 2c

1.356(2)-1.1.358(3) and 1.308(2)-1.315(2) Å, being indicative of enolate structure, which is consistent with those observed in enolates [Al(Me₂){OCR=CHP(Ph₂)=N(8-C₉H₆N)}] [C-C = 1.365(5) Å, C-O = 1.284(5) Å].¹⁶

Reactivity of aluminium β-quinolyl enolates toward alcohols

We attempted to prepare the aluminium benzyloxide complexes of β -quinolyl enolates **1b-6b**, because alkoxide derivatives are ideal catalysts for ROP of ϵ -CL, which are formed in situ by the reaction between an exogenous alcohol and an enolate. Treatment of **1b**, **3b-6b** with 2 equivalent of BnOH in THF solvent over room temperature, respectively, resulted in intractable mixtures due to the poor solubility in THF which were hardly purified, and no clear evidence of ¹H NMR spectra were obtained. However, conducting the same reaction of **2b** with BnOH, the product **2c** dissolved completely in THF (Scheme 2). **2c** was isolated in 73% yield as yellow crystals suitable for X-ray diffraction from a concentrated toluene solution at room temperature for 2 days.

The ¹H NMR spectrum of **2c** in $CDCl_3$ at room temperature shows two sets of resonance peaks with a ratio of 1:1, indicating the existence of dimeric species. It was mainly identified by the appearance of two doublet resonances of the quinolyl protons (8.98 and 9.29 ppm) and two singlet resonances of the tertbutyl protons (1.06 and 1.33 ppm). Other aluminium benzyloxides resulted in intractable mixtures due to the poor solubility and no clear evidences were gained.

The X-ray structure of **2c** (Fig. 5) illustrates a dimeric behaviour with two symmetrical pentacoordinated aluminium center bridging through the oxygen atom of the benzyl alkoxy group. The geometry around Al atoms are distorted triangular bipyramidal with an compressed axial O3-Al1-N1 169.22(6)° and the equatorial O2-Al1-O1, O2-Al1-O3 and O1-Al1-O3 are 115.49(7), 129.17(6) and 113.80(6)° (Table 2). The Al1-O3 distances of bridging benzyloxide groups ranging from

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Fig. 5 X-ray structure of **2c** with thermal ellipsoids represented at the 30% probability level. Hydrogen atoms are omitted for clarity. Symmetry codes: (i): 1-x, -y, 1-z.

1.8236(11) to 1.9141(11) Å are longer than Al1-O1 [1.7682(12) Å] and Al1-O2 [1.7362(12) Å], which are comparable to those in the dimeric aluminium ketiminate (from 1.8445(15) to 1.9091(16) Å) reported by Chen.⁵¹

Ring opening polymerization of ϵ -caprolactone

The ring-opening polymerization of ϵ -CL using Al complexes **1b-6b** and **2c** as the initiators was conducted in different conditions, and the results were listed in Table3. The monomer conversion was measured by ¹H NMR spectroscopy and the polymer was characterized by GPC. According to the results, **1b-6b** showed good activity within 60 min at 80 ° C with adding

Al(1)-O(1)	1.7682(12)
Al(1)-O(2)	1.7362(12)
Al(1)-O(3)	1.8236(11)
Al(1)-O(3)i	1.9141(11)
Al(1)-N(1)	2.0487(14)
O(1)-C(11)	1.304(2)
C(10)-C(11)	1.355(3)
O(1)-Al(1)-O(2)	115.49(7)
O(1)-Al(1)-O(3)	113.80(6)
O(3)-Al(1)-N(1)	169.22(6)
O(2)-Al(1)-O(3)	129.17(6)
Al(1)-O(3)-Al(1) ⁱ	104.23(5)

Table 2 Selected bond lengths (Å) and angles (°) for complexes 2c

1 equiv. benzyl alcohol (Table 3, entries 1-6) and their PDIs were in the range of 1.47-1.64. 5b was used as an example to study the influence of temperature and the amount of monomer and BnOH on polymerization reaction. The polymerization reaction proceeded by **5b** (in a ratio of [CL]₀: [Al]₀: [BnOH]₀ = 200 : 1 : 1) showed a high rate at 80 °C in 60 min giving 94% monomer conversion (Table 3, entry 7). Meanwhile, at lower reaction temperature the monomer conversion also decreased (Table 3, entries 8-10). For example, at 20 °C in 420 min the polymerization reaction was very slowly, and the monomer conversion only reached 20% (Table 3, entry 8). As many reported Al complexes, the presence of benzyl alcohol in the system can improve the catalytic activity and control PDI.¹⁸ In the absence of benzyl alcohol, 5b displayed poor activity with trace conversion after 60 min at 80 ° C (Table 3, entry 11). And in the presence of 2 equiv. or 4 equiv. benzyl alcohol, 5b exhibited good catalytic activity

Table 3 The ROP of ε-CL catalyzed by complexes 1b-6b and 2c								
Entry	Complex	CL:Al:BnOH	T/° C	Time/min	Conv. ^b (%)	$M_{n,calc}^{c}$ (10 ⁻⁴)	$M_{n,GPC}^{d}(10^{-4})$	PDI ^e
1	1b	100:1:1	80	60	96	1.11	0.93 (0.52)	1.52
2	2b	100:1:1	80	60	92	1.06	1.09 (0.61)	1.57
3	3b	100:1:1	80	60	91	1.04	0.92 (0.52)	1.51
4	4b	100:1:1	80	60	92	1.06	1.04 (0.58)	1.52
5	5b	100:1:1	80	60	95	1.10	1.05 (0.59)	1.47
6	6b	100:1:1	80	120	92	1.06	1.10 (0.62)	1.64
7	5b	200:1:1	80	60	94	2.16	2.04 (1.14)	1.38
8	5b	200:1:1	20	420	20	0.47	0.66 (0.37)	1.07
9	5b	200:1:1	40	300	61	1.41	1.64 (0.92)	1.40
10	5b	200:1:1	60	180	95	2.18	2.24 (1.25)	1.21
11	5b	100:1:0	80	60	Trace			
12	5b	100:1:2	80	60	94	0.55	0.69 (0.39)	1.52
13	5b	100:1:4	80	60	93	0.28	0.42 (0.24)	1.34
14	5b	200:1:4	80	60	99	0.58	1.10 (0.62)	1.66
15	5b	400:1:4	80	60	99	1.14	1.63 (0.91)	1.86
16	5b	800:1:4	80	60	99	2.27	2.45 (1.37)	2.75
17	5b	800:1:8	80	60	78	0.90	1.81 (1.01)	1.57
18	2c	100:1:0	80	16	98	1.13	0.91 (0.51)	1.59
19	2c	200:1:0	80	16	89	2.05	1.37 (0.77)	1.80
20	2c	400:1:0	80	16	62	2.84	2.10 (1.18)	2.12

^{*a*} Unless otherwise specified, the polymerizations were carried out in toluene. ^{*b*} Measured by ¹H NMR spectroscopy. ^{*c*} $M_{n,calc} = 114.14 \times ([CL]_0/([BnOH]_0) \times conv. (%) + 108.13 ($ **1b** $-6b) or <math>M_{n,calc} = 114.14 \times ([CL]_0/([Al]_0) \times conv. (%) + 108.13 ($ **2c**). ^{*d*} Obtained from GPC analysis in THF using polystyrene standard. Values in parentheses are the values obtained from GPC multiplied by 0.56. ^{*c*} Obtained from GPC analysis.

Table 4 Catalytic activity of $k_{(obs)}$ Determined for the ROP of ε -CL with Al complexes					
Complex	[CL] ₀ /[Al]/[BnOH]	k _{obs} (min⁻¹)			
1b	100/1/1	0.0555(1)			
2b	100/1/1	0.0423(5)			
3b	100/1/1	0.0357(6)			
4b	100/1/1	0.0425(6)			
5b	100/1/1	0.0503			
6b	100/1/1	0.0220(3)			
2c	100/1/0	0.2334(9)			
^a All reactions were performed at 80 °C with $[CL]_{a} = 1.0 \text{ M}$ in toluene.					

(Table 3, entries 12 and 13) with similar conversion to that in the presence of 1 equiv. benzyl alcohol. When 4 equiv. BnOH was used, with the monomer to Al ratio varying from 100 to 400, the polymerization performed smoothly to give PCL with an increasing molecular weight, close to theoretic values. Note that, when the ratio was over 800, the polymerization was rapid and the polymerization system became viscous, which resulted in the deviation of the molecular weight of the resultant PCL from the theoretic value and the broadened PDI (Table 3, entries 13-16). With an increase of BnOH to 8 equiv., the monomer conversion was slower (Table 3, entry 17). The molecular weight was proportional decreased with the increment of benzyl alcohol, while the molecular weight distribution remained in a controlled range. This was consistent with the immortal polymerization initiated by aluminum complexes based on pyridine substituted alcohols and phenoxy-thioether aluminum complexes.¹⁹

The results of methyl groups complexes **1b-6b** in Table 3, entries 1-16, revealed the $M_{n,GPC}$ of these polymers proportionally were smaller than $M_{n,calc.}$ and their polydispersity index (PDI) was larger (1.47-1.64), which indicated that the Al/BnOH system may contain multiple active species, such as LAI(Me)OBn and LAI(OBn)₂, or include side reactions such as transesterification.



Fig. 6 Relationship between $Ln([CL]_0/[CL])$ and time of the polymerization initiated by 1b-6b in the presence of BnOH in toluene at 80 °C with a ratio of $[CL]_0: [AI]_0: [BnOH]_0 = 100: 1: 1 ([CL]_0 = 1 M).$



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Fig.8 Relationship between M_n (\bullet , obtained from GPC analysis) or polydispersity (\blacksquare , M_w/M_n) with ϵ -CL conversion using **2c** in toluene at 80 °C with a ratio of [CL]₀ : [Al]₀ = 100 : 1.

Accordingly, once aluminium benzyloxide **2c** was thoroughly characterized, it was also explored for its catalytic activity toward ROP of ε -CL. Aluminum alkoxides are ideal initiators especially for the ROP of cyclic ester, because they can mimic the propagation species better than alkyls. The results of the polymerization reactions are listed in Table 3, entries 18-20. The reactions were conducted in toluene at 80 °C, without the addition of a cocatalyst. **2c** was found to be highly active and polymerized monomer ε -CL with 98% conversion within 16 minutes, when the [CL]/[AI] ratio was 100/1 (Table 3, entry 18). Even when the ratio of [CL]₀ : [AI]₀ was increased to 400 : 1, the polymerization can be completed up to 62% in 16 min at 80 °C (Table 3, entry 20).

In order to investigate the process of the polymerization catalyzed by these complexes, the kinetic studies of ε -CL polymerization initiated by **1b-6b** and were carried out in the presence of BnOH at 80 °C ([CL]₀ : [Al]₀ : [BnOH]₀ = 100 : 1 : 1) (Fig. 6). The catalytic activity of $k_{(obs)}$ determined for the ROP of ε -CL with Al complexes were listed in Table 4. From the results, we can obtain the activity order is **1b** > **5b** > **4b** > **2b** > **3b** > **6b**. The result demonstrated that the catalytic activity of $k_{(obs)}$ was influenced by electronic effect. The ligands with electron withdrawing groups, such as **6b**, can decrease the catalytic activity.

In addition, the kinetic study of ε -CL poly-merization initiated by **2c** was carried out in the presence of BnOH at 80 °C ([CL]₀ : [AI]₀ = 100 : 1). A good liner relationship between Ln([CL]₀/[CL]) and time were showed in Fig. 7, which proved that the polymerization was carried out with first-order dependency on the monomer concentration. The



Fig. 9 The ¹H NMR spectrum of PCL initiated by **5b**/BnOH in the ratio of $[CL]_0 : [Al]_0 : [BnOH]_0 = 40 : 1 : 1 ([CL]_0 = 1 M) in toluene at 60 °C for 60 min.$

corresponding observed rate constant was $k_{obs} = 0.2334(9)$ min¹ (Table 4). This value of k_{obs} is significantly larger than those of **1b-6b**. The molecular weights *versus* conversation also showed a good liner relationship, however, the PDIs became broad after certain monomer conversions [e.g. PDI = 1.12 (conversion 35%), 1.18 (conversion 58%), 1.33 (conversion 83%), 1.52 (conversion 93%), 1.59 (conversion 98%), Fig. 8, Table S2]. Similar results were observed in the ROPs of ϵ -CL using the Al complexes **1b-6b** (Figs. S15-17). The results suggested that a certain degree of transesterfication accompanied the propagation in the ROPs under these conditions.

To understand the polymerization mechanism of ϵ -CL by these aluminium complexes **1b-6b**, PCL-40 was produced from the polymerization reaction initiated by **5b**/BnOH ([CL]₀ : [Al]₀ : [BnOH]₀ = 40 : 1 : 1) at 60 °C for 60 min. And the end group analysis of the PCL was determined by ¹H NMR spectrum (Fig. 9). As shown in the result, the peak ratio of PhCH₂O (H_b) and CH₂OH (H_g) was close to 1. All the results implied benzyloxy group and hydroxymethyl group were located at the ends of PCL and as many literatures reported the polymerization reaction may initiate through coordination-insertion menchanism.^{16,18a,20}

In addition, we also used **1b** and **5b** to initiate the ROP of *rac*-lactide: the result showed no polymer was produced with or without adding BnOH after 24 h at 80 $^{\circ}$ C, less than 40% monomer conversions were achieved within 72 h at 80 $^{\circ}$ C. We did not make further studies.

Conclusions

A series of four coordinated Al quinolyl-enolate complexes were synthesized and characterized by NMR spectroscopy and element analysis. The structure of **1b**, **2b**, **5b**, **6b** and **2c** were confirmed by X-ray crystallography. All the complexes showed good activity towards the ROP of ε -CL in the presence of benzyl alcohol at high temperature. Higher polymerization activity was achieved by the complexes with weaker electrondonating substituents at the para-position of aryl ring. Furthermore, the kinetic studies of **1b-6b** and **2c** revealed that polymerization reactions initiated by these Al complexes

within benzyl alcohol followed first-order kinetics. End group analyses of the polymer indicated polymerization was performed in accordance with a classical coordinationinsertion mechanism. However, the methyl groups of aluminium complexes 1b-6b are not real initiators. The real catalytic species, LAI(Me)OBn and LAI(OBn)₂ were formed by the reaction of LAIMe₂ and BnOH. Dimeric benzyloxide LAI(OBn)₂ 2c was isolated, which has higher activity toward ROP of ϵ -CL than methyl Al complexes. All the polymerizations of ϵ -CL using 1b-6b system or 2c were accompanied by a certain degree of side reaction such as transesterification. Although we could not find an efficient catalyst in a living polymerization fashion, these results clearly indicated that the benzyloxyl group plays an essential role in the polymerization. Further studies are required to understand the dinuclear benzyloxide [LAI(OBn)₂]₂ complexes with bridging benzyloxide and terminal benzyloxide to Al, resulting in the ability to initiate ROP.

Experimental

General remarks

All the reactions were carried out under nitrogen, using standard Schlenk techniques. All the solvents (toluene and THF) were dried and distilled from sodium, stored with 4 Å molecular sieves. AlMe₃ (1.0 M solution in toluene) and ε -Caprolactone were purchased from Alfa Aesar . ε -Caprolactone was dried by CaH₂ for 48 h, and then distilled under reduced pressure. ¹H and ¹³C NMR spectra were recorded on Bruker DRX 300 and 600 instruments. Elemental analyses were performed with a Vario EL–III instrument. The molecular weight and PDI of the polymers were measured by a TOSOH HLC8220 GPC at 40 °C using THF as eluent (0.35 mL/min), calibrated by polystyrene standards. Ligands **1a-6a** were prepared according to the published methods.¹²

Synthesis of Complexes

Synthesis of LAIMe₂ (1b). To a stirred solution of AIMe₃ (2.1 mL of a 1.0 M solution in toluene, 2.1 mmol) was added **1a** (0.371 g, 2.0 mmol) in toluene (10 mL). The yellow solution was heated at 120 °C overnight. And after that the resulting solution was concentrated and gave pale yellow crystals (0.434 g, 90%). Anal. Calcd. for C₁₄H₁₆AINO: C, 69.70; H, 6.68; N, 5.81. Found: C, 69.74; H, 6.53; N, 5.74. ¹H NMR (CDCl₃, 300 MHz): *δ* 8.12 (d, *J* = 8.7 Hz, 1H, Ar*H*), 7.96 (d, *J* = 8.7 Hz, 1H, Ar*H*), 7.67 (t, *J* = 7.8 Hz, 2H, Ar*H*), 7.43 (t, *J* = 7.5 Hz, 1H, Ar*H*), 6.95 (d, *J* = 8.7 Hz, 1H, Ar*H*), 5.44 (s, 1H, -*CH*), 2.10 (s, 3H, -*CH*₃), -0.56 (s, 6H, AICH₃). ¹³C NMR (CDCl₃, 75 MHz): *δ* 175.58, 158.45, 143.03, 139.38, 130.94, 128.45, 125.80, 125.18, 123.22, 122.47, 98.38, 22.58, -8.46.

Synthesis of LAIMe₂ (2b). Complex **2b** was synthesized using the same procedure as for **1b**. Reaction of **2a** (0.455 g, 2 mmol) with AIMe₃ (2.1 mL of a 1.0 M solution in toluene, 2.1 mmol) in toluene (10 mL) yielded pale yellow crystals (0.482 g, 85%).

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Anal. Calcd. for $C_{17}H_{22}AINO$: C, 72.06; H, 7.83; N, 4.94. Found: C, 72.01; H, 7.93; N, 5.01. ¹H NMR (CDCl₃, 300 MHz): δ 8.10 (d, J = 8.4 Hz, 1H, Ar*H*), 7.95(d, J = 9.0 Hz, 1H, Ar*H*), 7.63-7.68 (m, 2H, Ar*H*), 7.41 (t, J = 7.5 Hz, 1H, Ar*H*), 7.02 (d, J = 8.7 Hz, 1H, Ar*H*), 5.54 (s, 1H, -*CH*), 1.23 (s, 9H, -(*CH*₃)₃), -0.60 (s, 6H, Al*CH*₃). ¹³C NMR (CDCl₃, 75 MHz): δ 185.61, 159.23, 140.08, 138.98, 130.80, 128.34, 125.79, 125.06, 124.04, 122.57, 93.89, 38.93, 28.26, -8.66.

Synthesis of LAIMe₂ (3b). Complex **3b** was synthesized using the same procedure as for **1b**. Reaction of **3a** (0.495 g, 2 mmol) with AlMe₃ (2.1 mL of a 1.0 M solution in toluene, 2.1 mmol) in toluene (10 mL) yielded yellow solid (0.516 g, 85%). Anal. Calcd. for C₁₉H₁₈AlNO: C, 75.23; H, 5.98; N, 4.62. Found: C, 75.11; H, 6.13; N, 4.71. ¹H NMR (CDCl₃, 300 MHz): δ 8.18 (d, J = 8.7 Hz, 1H, ArH), 8.04 (d, J = 8.7 Hz, 1H, ArH), 7.95-7.96 (m, 2H, ArH), 7.71 (t, J = 8.1 Hz, 2H, ArH), 7.44-7.49 (m, 4H, ArH), 7.18 (d, J = 9.0 Hz, 1H, ArH), 6.19 (s, 1H, -CH), -0.51 (s, 6H, AlCH₃). ¹³C NMR (CDCl₃, 75 MHz): δ 169.67, 158.61, 143.14, 139.37, 137.92, 131.11, 130.50, 128.46, 126.84, 126.06, 125.44, 124.17, 122.65, 96.49, -8.33.

Synthesis of LAIMe₂ (4b). Complex **4b** was synthesized using the same procedure as for **1b**. Reaction of **4a** (0.522 g, 2 mmol) with AIMe₃ (2.1 mL of a 1.0 M solution in toluene, 2.1 mmol) in toluene (10 mL) yielded yellow solid (0.539 g, 86%). Anal. Calcd. for C₂₀H₂₀AINO: C, 75.69; H, 6.35; N, 4.41. Found: C, 75.60; H, 6.53; N, 4.41. ¹H NMR (CDCl₃, 300 MHz): δ 8.22 (d, *J* = 7.2 Hz, 1H, ArH), 8.08 (d, *J* = 8.1 Hz, 1H, ArH), 7.72-7.77 (m, 2H, ArH), 7.48-7.53 (m, 2H, ArH), 7.24-7.30 (m, 3H, ArH)), 7.13 (d, *J* = 7.2 Hz, 1H, ArH), 5.79 (s, 1H, -CH), 2.55 (s, 3H, -CH₃Ph), -0.48 (s, 6H, AlCH₃). ¹³C NMR (CDCl₃, 75 MHz): *δ* 174.36, 158.57, 143.12, 139.54, 136.77, 131.15, 129.34, 128.52, 128.18, 126.13, 125.67, 125.51, 123.90, 122.72, 100.44, 20.62, -8.48.

Synthesis of LAIMe₂ (5b). Complex **5b** was synthesized using the same procedure as for **1b**. Reaction of **5a** (0.522 g, 2 mmol) with AIMe₃ (2.1 mL of a 1.0 M solution in toluene, 2.1 mmol) in toluene (10 mL) yielded yellow crystals (0.578 g, 91%). Anal. Calcd. for C₁₉H₁₈AINO: C, 75.69; H, 6.35; N, 4.41. Found: C, 75.68; H, 6.38; N, 4.53. ¹H NMR (CDCl₃, 300 MHz): δ 8.17 (d, *J* = 8.7 Hz, 1H, Ar*H*), 8.01 (d, *J* = 8.7 Hz, 1H, Ar*H*), 7.86 (d, *J* = 7.8 Hz, 2H, Ar*H*), 7.70 (t, *J* = 7.8 Hz, 2H, Ar*H*), 7.45 (t, *J* = 7.5 Hz, 1H, Ar*H*), 6.16 (s, 1H, -C*H*), 2.41 (s, 3H, -CH₃Ph), -0.52 (s, 6H, AlCH₃). ¹³C NMR (CDCl₃, 75 MHz): δ 169.95, 158.68, 143.21, 140.88, 139.18, 135.11, 131.02, 129.16, 128.44, 126.84, 125.95, 125.27, 124.20, 122.58, 95.95, 21.63, -8.35.

Synthesis of LAIMe₂ (6b). Complex 6b was synthesized using the same procedure as for 1b. Reaction of 6a (0.555 g, 2 mmol) with AIMe₃ (2.1 mL of a 1.0 M solution in toluene, 2.1 mmol) in toluene (10 mL) yielded yellow solid and recrystallized from THF (0.467 g, 70%). Anal. Calcd. for $C_{20}H_{20}AINO_2$: C, 72.06; H, 6.05; N, 4.20. Found: C, 71.98; H, 6.18; N, 4.23. ¹H NMR (CDCl₃, 300 MHz): δ 8.16 (d, J = 8.1 Hz, 1H, ArH), 7.91-7.98 (m, 3H, ArH), 7.67-7.70 (m, 2H, ArH), 7.42 (t, J = 7.2 Hz, 1H, ArH), 7.10 (d, J = 8.1 Hz, 1H, ArH), 6.94 (d, J = 8.4 Hz, 2H, ArH), 6.10 (s, 1H, -CH), 3.86 (s, 3H, -OCH₃Ph), -0.51 (s, 6H, AICH₃). ¹³C NMR

Synthesis of [LAI(µ-OBn)2]2 (2c). To a stirred solution of 2b (0.567 g, 2.0 mmol) in THF (10 mL) was added benzyl alcohol (0.42 mL, 4.0 mmol), and the mixture was stirred at room temperature for 24 h. Then the volatile materials were removed under vacuum and the residues were redissolved in hot toluene (10 mL). The solution was cooled to temperature affording a yellow crystalline solid after 2 d (0.683 g, 73%). Anal. Calcd. for C₅₈H₆₀Al₂N₂O₆: C, 74.50; H, 6.47; N, 3.00. Found: C, 74.59; H, 6.48; N, 2.95. ¹H NMR (CDCl₃, 600 MHz): δ 9.32 (d, J = 9.0 Hz, 1H, ArH), 9.01 (d, J = 8.4 Hz, 1H, ArH), 7.77-6.58 (m, 30H, ArH), 5.12-5.09 (m, 3H, CH₂ and -CH), 5.05 (s, 1H, -CH), 4.39 (d, J = 13.8, 1H, CH₂), 4.34 (d, J = 13.8, 1H, CH₂), 4.12-3.98 (m, 4H, CH₂), 1.36 (s, 9H, -(CH₃)₃), 1.08 (s, 9H, -(CH₃)₃). ¹³C NMR (CDCl₃, 150 MHz): δ 182.36, 182.10, 159.42, 159.18, 146.98, 146.02, 143.47, 143.34, 142.13, 142.02, 137.68, 137.30, 131.11, 130.27, 127.82, 127.74, 127.65, 127.57, 127.50, 127.32, 126.61, 126.48, 126.07, 125.93, 125.84, 125.71, 125.57, 125.46, 125.37, 125.22, 125.16, 124.92, 124.68, 124.61, 124.45, 124.13, 95.22, 94.84, 65.83, 65.60, 64.78, 64.46, 38.69, 38.57, 28.37, 28.24.

X-ray crystallography

Diffraction data of **1b**, **2b**, **5b**, **6b** and **2c** were collected on a Bruker Smart Apex CCD diffractometer with Mo K α radiation (λ =0.71073 Å). A total of N reflections were collected by using ω scan mode. The structures were solved by direct methods (SHELXS-97)²¹ and refined against F^2 by full-matrix least-squares using SHELXL-97.²² All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of all complexes were showed in Table 5.

Polymerization of ε-CL catalyzed by complexes 1b-6b

Complex **5b** was used as an example of typical polymerization procedure by in the presence of 1 equiv. BnOH (Table 2, entry 5). In a Schlenk tube, complex **5b** (0.016 g, 0.05 mmol) was dissolved in 4.5 mL toluene and an equiv. benzyl alcohol (0.5 mL, 0.1 M in toluene, 0.05 mmol) was added. The mixture was stirred for 30 min at 80 °C. Then ε -CL (0.571 g, 5 mmol) was added with stirring. After required time (60 min), several drops of glacial acetic were added to quench the polymerization reaction and the resulting solution was poured into MeOH (100 mL) with stirring 12 h. The PCL was procured through filtration and dried under vacuum.

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Complex	1b	2b	5b	6b	2c
Formula	C14H16AINO	C ₁₇ H ₂₂ AINO	C ₂₀ H ₂₀ AINO	$C_{20}H_{20}AINO_2$	$C_{58}H_{60}Al_2N_2O_6$
<i>M</i> _w (gmol ⁻¹)	241.26	283.34	317.35	333.35	935.04
<i>Т</i> (К)	200(2) K	200(2) K	200(2) K	200(2) K	299(2) K
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic,	Monoclinic
Space group	P21/n	P21/n	Pnma	P21/n	P21/n
<i>α</i> (Å)	7.0753(3)	8.4914(17)	19.546(4)	10.9124(4)	10.5275(4)
<i>b</i> (Å)	15.6291(6)	13.955(3)	7.1870(14)	11.7506(4)	18.9855(8)
c(Å)	11.8798(4)	14.174(3)	12.178(2)	13.8700(5)	13.0549(5)
α(°)	90	90	90	90	90
<i>θ</i> (°)	90.9470(10)	101.02(3)	90	99.8360(10)	103.3240(10)
γ(°)	90	90	90	90	90
∨(ų)	1313.50(9)	1648.6(6)	1710.8(6)	1752.37(11)	2539.05(17)
Ζ	4	4	4	4	2
$D_{\rm calcd}(\rm g cm^{-3})$	1.220	1.142	1.232	1.264	1.223
μ (mm ⁻¹)	0.138	0.119	0.122	0.127	0.110
F(000)	512	608	672	704	992
Reflections collected	9697	27725	9283	12522	18027
Independent(R _{int})reflections	2328	2915	1652	3089	4485
	(0.0275)	(0.0346)	(0.0342)	(0.0264)	(0.0292)
Goodness of fit on F^2	1.044	1.028	1.056	1.028	1.038
Final R indices $[I>2\sigma(I)]$					
<i>R</i> ₁	0.0357,	0.0418,	0.0563,	0.0392,	0.0417
wR ₂	0.0977	0.1338	0.1675	0.1249	0.1005
R indices (all data)					
<i>R</i> ₁	0.0385,	0.0559,	0.0614,	0.0428,	0.0543
wR ₂	0.1011	0.1576	0.1778	0.1344	0.1095
Largest diff. peak and hole [e $Å^{-3}$]	0.234 and	0.231 and	0.324 and	0.253 and	0.231 and
	-0.271	-0.330	-0.416	-0.353	-0.270

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Dalton Transactions Accepted Manuscript

Graphic abstract

The ROP towards ϵ -CL initiated by six aluminum β -quinolyl-enolates and their benzyloxids was reported.

