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Synthesis and characterization of aluminum and zinc complexes supported by pyrrole-based ligands and catalysis of the aluminum complexes toward the ring-opening polymerization of ε-caprolactone

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ABSTRACT

Reaction of quinolin-8-amine with 1*H*-pyrrole-2-carbaldehyde or 5-*tert*-butyl-1*H*-pyrrole-2-carbaldehyde catalyzed by HCO_2H forms *N*-((1*H*-pyrrol-2-yl)methylene)quinolin-8-amine (≡ HL, **3a**) or *N*-((5-*tert*-butyl-1*H*-pyrrol-2-yl)methylene)quinolin-8-amine (≡ HL′, **3b**). Treatment of **3a** and **3b** respectively with $AlMe_3$ or $AlEt_3$ in toluene affords corresponding aluminum complexes $LAlMe_2$ (**4a**), $L'AlMe_2$ (**4b**) and $LAlEt_2$ (**4c**). Reaction of **3a** and **3b** with an equivalent of $ZnEt_2$ in toluene generates L_2Zn and L'_2Zn, respectively. A related compound *N*-((1*H*-pyrrol-2-yl)methylene)-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)benzenamine (≡ HL″, **7**) was prepared by reaction of 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)benzenamine with 1*H*-pyrrole-2-carbaldehyde in the presence of HCO_2H. Reaction of **7** with $AlMe_3$ gives L''_2AlMe (**8**), and with $ZnEt_2$ yields L''_2Zn (**9**). All new compounds were characterized by NMR spectroscopy and elemental analysis. The structures of complexes **4b**, **5b** and **8** were additionally characterized by single crystal X-ray diffraction analyses. Complexes **4a**–**4c**, and **8** were proved to be active catalysts for the ring-opening polymerization (ROP) of ε-caprolactone (ε-CL) in the presence of BnOH. The kinetic study of the polymerization reactions catalyzed by **4a** and **8** was performed.

1. Introduction

Aliphatic polyesters such as poly(ε-caprolactone) (PCL), polylactide (PLA) and their copolymers are the most important synthetic biodegradable polymers. These polymers have attracted great interest for their applications in the medical field [1–11]. Among the polymers, PCL shows specific advantages in some applications [12–16]. For example, PCL is ideally suitable for long-term drug delivery due to its slow degradation in comparison to other polymers [16]. The major way to synthesize the polymers is the ring-opening polymerization of cyclic esters catalyzed by metal complexes [4–11,17–25]. A number of excellent catalysts have been reported for the polymerization. However, it is still of interest to find new catalysts for the synthesis of well-defined polyesters with precisely controlled end group functionalities. Recently, we synthesized some aluminum and zinc complexes supported by heterocyclic-containing multidentate ligands such as *N*,*N*-, *N*,O-, *N*,*N*,*N*- and *N*,*N*,O-ligands and found some of the complexes to have good catalytic activity for the ring-opening polymerization of ε-CL [26–31]. We wished to further investigate the catalysis of aluminum and zinc complexes supported by other heterocyclic-containing multidentate ligands. Hence, we designed two classes of pyrrole-based *N*,*N*,*N*-tridentate ligands. One involves 8-quinolyl moiety and the other contains pyrazolyl moiety. We synthesized Al or Zn complexes bearing these ligands and found the aluminum complexes to be efficient catalysts in the ROP of ε-CL. Herein we report the results.

2. Results and discussion

2.1. Synthesis of aluminum and zinc complexes

Reaction of quinolin-8-amine with 1*H*-pyrrole-2-carbaldehyde (**2a**) or 5-*tert*-butyl-1*H*-pyrrole-2-carbaldehyde (**2b**) in toluene in the presence of formic acid and 4 Å molecular sieves affords *N*-((1*H*-pyrrol-2-yl)methylene)quinolin-8-amine (≡ HL, **3a**) and *N*-((5-*tert*-butyl-1*H*-pyrrol-2-yl)methylene)quinolin-8-amine (≡ HL′, **3b**), respectively, in good yields (Scheme 1). Treatment of **3a** and **3b** with $AlMe_3$ or $AlEt_3$ in toluene at room temperature generates corresponding aluminum complexes $LAlMe_2$ (**4a**),

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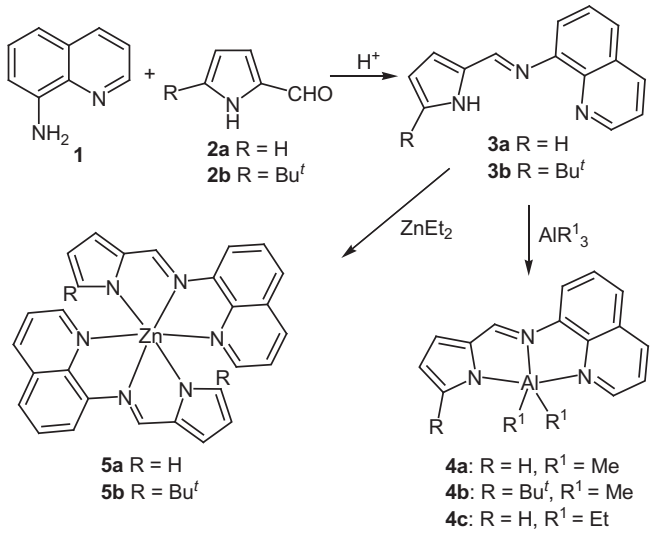


Scheme 1. Synthesis of complexes $LAlR_2$ (R = Me, Et), $L'AlMe_2$, L_2Zn and L'_2Zn.

$L'AlMe_2$ (**4b**) and $LAlEt_2$ (**4c**). Reaction between **3a** or **3b** and an equiv of $ZnEt_2$ always gives L_2Zn (**5a**) or L'_2Zn (**5b**) instead of expected LZnEt or L′ZnEt. Attempts to prepare LZnCl or L′ZnCl through reaction of lithiated **3a** or **3b** with $ZnCl_2$ were unsuccessful, yielding L_2Zn and L'_2Zn, respectively. Each of compounds **3a** and **3b** gave satisfactory elemental analysis. The NMR spectra are consistent with their respective molecular structure. The aluminum and zinc complexes were characterized by elemental analyses and NMR spectroscopy. The ^1H and ^{13}C NMR spectra of **4a**–**4c** display AlMe or $AlCH_2$ signals at low frequency regions. The other signals are consistent with the ligand structures. Each of the NMR spectra of **5a** and **5b** exhibits one set of ligand signals, implying that the two ligands have the same coordination mode.

The structures of complexes **4b** and **5b** were further characterized by single-crystal X-ray diffraction. Complex **4b** crystallizes with two molecules in the asymmetric unit (Fig. 1, one molecule was presented). The central aluminum atom is five-coordinated. The geometry of the aluminum coordination sphere can be best described as a distorted trigonal bipyramid with the imido nitrogen atom (N2) and two methyl carbon atoms (C19 and C20) occupying the equatorial positions and the quinolyl nitrogen atom (N1) and the pyrrolyl nitrogen atom (N3) occupying the axial positions. The N2, C19, C20 and Al atoms are approximately coplanar (the total angles of the trigonal plane are 358.01°). However, the N1, Al, and N3 atoms are not in a line due to strain of the ligand [N1–Al–N3 = 155.30(13)°]. The Al–N1 distance of 2.262(3) Å is longer than corresponding that in [Al(Me$_2$){OC(Me)=CHC(Me)=NC$_9$H$_6$N}] [2.1448(19) Å] [31]. The Al–N2 distance of 1.970(3) Å is a little shorter than the Al–N_{imine} distance in [Al(Me$_2$){OC(Me)=CHC(Me)=*N*-C$_9$H$_6$N}] [1.9956(19) Å]. The Al–N3 distance of 2.096(3) Å is longer than corresponding those found in [AlMe$_2${2 – (2′, 6′ – Pr$^i_2$C$_6$H$_3$N=CH) – 5 – Bu^{t}C$_4$H$_2$N}] [1.923(4) Å] [32] and [AlCl{2-(Me$_2$NCH$_2$C$_4$H$_3$N)$_2$] [1.896(3) and 1.906(3) Å, respectively] [33].

The molecular structure of complex **5b** is depicted in Fig. 2 along with selected bond lengths and bond angles. In the structure, the coordination geometry of the Zn atom is a distorted octahedron. The N2, N4, N5, and N6 atoms are approximately coplanar, the torsion angle of N6–N2–N4–N5 being 0.9°, while the Zn atom is out of the plane. The N(1)–Zn(1)–N(3) angle of 153.14(17)° shows that the arrangement of the atoms has a little derivation from a line. The Zn–$N_{quinoline}$ distances of 2.339(5) Å and 2.411(5) Å are longer than corresponding that in [Zn(Me){CH(8 – C$_9$H$_6$N)P(Pr$^i_2$)=NBu^t}] [2.1651(17) Å] [29]. The Zn-$N_{pyrrole}$ distances of 2.138(4) Å and 2.126(5) Å are also longer than corresponding that in [Zn(Bu^t){2-(Pr^{i}N=CHC$_4$H$_3$N)}] [1.996(2) Å] [34].

Synthesis of pyrazole-containing ligand and its aluminum and zinc complexes is shown in Scheme 2. Reaction of 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)benzenamine (**6**) with 1*H*-pyrrole-2-carbaldehyde (**2a**) in refluxed toluene in the presence of formic acid and 4 Å

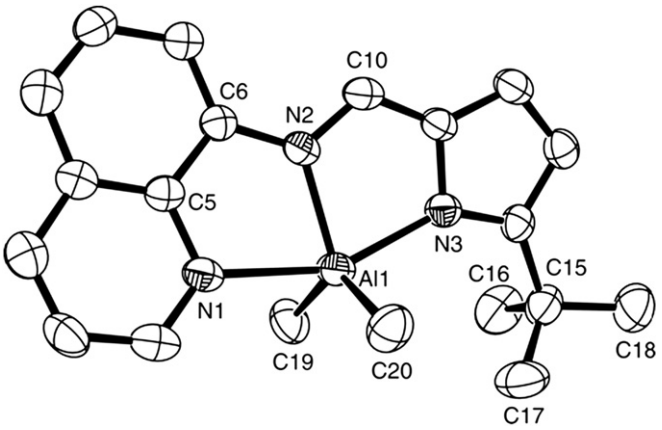


Fig. 1. ORTEP drawing of complex **4b** (30% probability thermal ellipsoids). C(16)′, C(17)′, and C(18)′, which represent alternative orientations of C(16), C(17), and C(18) in the disordered *t*-butyl group, have been omitted for the sake of clarity. Selected bond lengths (Å) and angles (°): Al(1)–C(19) 1.959(3), Al(1)–C(20) 1.961(4), Al(1)–N(1) 2.262(3), Al(1)–N(2) 1.970(3), Al(1)–N(3) 2.096(3), N(2)–C(10) 1.320(4), N(1)–Al(1)-N(2) 74.40(12), N(1)–Al(1)-N(3) 155.30(13), N(2)–Al(1)-N(3) 81.03(13), C(19)–Al(1)-C(20) 127.28(18), C(19)-Al(1)–N(1) 89.76(13), C(20)-Al(1)–N(1) 90.54(14), C(19)–Al(1)–N(2) 114.75(15), C(20)–Al(1)–N(2) 115.98(15), C(19)–Al(1)–N(3) 102.96(15), C(20)–Al(1)–N(3) 98.06(15), C(10)–N(2)–Al(1) 114.0(2), C(6)–N(2)–Al(1) 122.9(2), C(11)–N(3)–Al(1) 108.3(3).

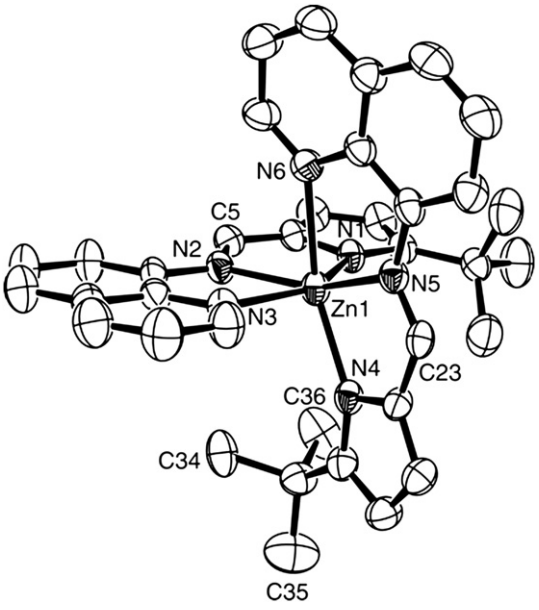
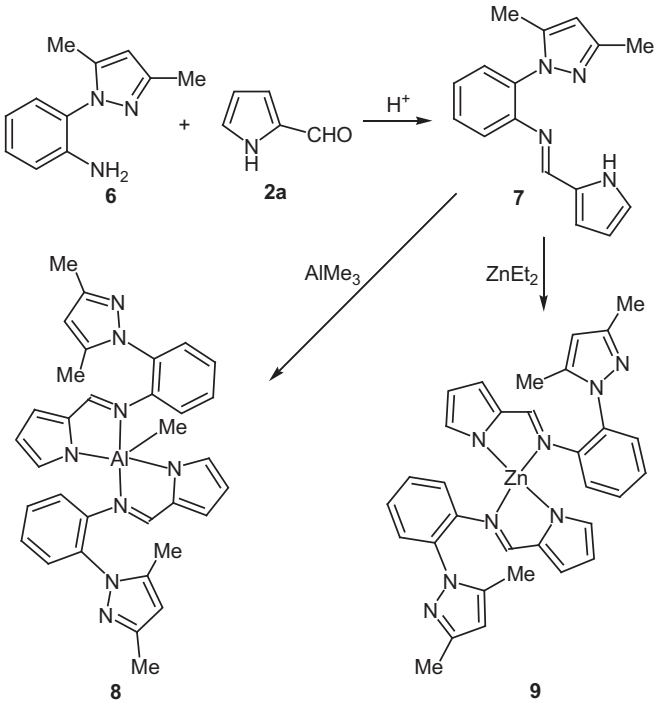


Fig. 2. ORTEP drawing of complex **5b** (30% probability thermal ellipsoids. Toluene molecules are omitted). C(34)′, C(35)′, and C(36)′, which represent alternative orientations of C(34), C(35), and C(36) in the disordered *t*-butyl group, have been omitted for the sake of clarity. Selected bond lengths (Å) and angles (°): Zn(1)–N(1) 2.138(4), Zn(1)–N(2) 2.057(4), Zn(1)–N(3) 2.339(5), Zn(1)–N(4) 2.126(5), Zn(1)–N(5) 2.062(4), Zn(1)–N(6) 2.411(5), N(1)–Zn(1)–N(2) 80.22(18), N(1)–Zn(1)–N(3) 153.14(17), N(1)–Zn(1)–N(4) 105.35(16), N(1)–Zn(1)–N(5) 113.76(16), N(1)–Zn(1)–N(6) 94.27(16), N(2)–Zn(1)–N(3) 73.11(19), N(2)–Zn(1)–N(4) 118.47(17), N(2)–Zn(1)–N(5) 153.68(17), N(2)–Zn(1)–N(6) 85.60(16), N(3)–Zn(1)-N(4) 90.39(16), N(3)–Zn(1)–N(5) 89.88(16), N(3)–Zn(1)-N(6) 80.75(15), N(4)–Zn(1)–N(5) 80.64(18), N(4)–Zn(1)–N(6) 150.82(17), N(5)–Zn(1)–N(6) 71.67(18).



Scheme 2. Synthesis of L''_2AlMe and L''_2Zn.

molecular sieves gives an imine **7** (≡ HL″) in 65% yield. Reaction of **7** with Me_3Al affords L''_2AlMe (**8**). We can not obtain $L''AlR_2$ through changing proportion of the reactants. Treatment of **7** with Et_2Zn produces L''_2Zn (**9**). Attempts to prepare L″ZnEt by changing reaction conditions such as the ratio of the reactants, reaction temperature and solvents were unsuccessful. Compounds **7**–**9** were characterized by ^1H and ^{13}C NMR spectroscopy and elemental analyses. Each of the ^1H NMR spectra gives appropriate ligand signals. In the ^1H NMR spectrum of complex **8** Al–Me signal was also observed at δ −0.21 ppm. The NMR spectra of complex **9** exhibit one set of ligand signals, implying that the two ligands adopt the same coordination mode in the solution. Single crystals of complex **9** suited for X-ray diffraction analysis can not be obtained. We guess the central zinc atom may be four-coordinated due to the steric hindrance. Complex **8** was additionally characterized by single-crystal X-ray diffraction. The ORTEP drawing is presented in Fig. 3, along with selected bond lengths and angles. Complex **8** is monomeric in the solid state and the aluminum atom is five-coordinated. The nitrogen atoms of the pyrazolyl groups do not coordinate to the central metal. The coordination geometry is a distorted trigonal bipyramid with two imido nitrogen atoms (N2 and N6) in axial positions and two pyrrolyl nitrogen atoms (N1 and

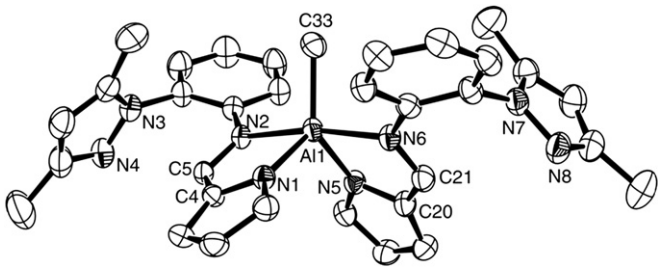


Fig. 3. ORTEP drawing of complex **8** (30% probability thermal ellipsoids. Benzene molecule is omitted). Selected bond lengths (Å) and angles (°): Al(1)–N(1) 1.899(4), Al(1)–N(5) 1.901(4), Al(1)–C(33) 1.949(5), Al(1)–N(2) 2.115(3), Al(1)–N(6) 2.112(4), N(1)–Al(1)–N(5) 104.89(16), N(1)–Al(1)–C(33) 124.78(18), N(5)–Al(1)–C(33) 130.32(19), N(1)–Al(1)–N(6) 94.86(15), N(5)–Al(1)–N(6) 81.00(15), C(33)–Al(1)–N(6) 94.46(18), N(1)–Al(1)–N(2) 81.01(15), N(5)–Al(1)–N(2) 91.70(15), C(33)–Al(1)-N(2) 94.96(17), N(2)–Al(1)–N(6) 170.45(16).

N5) and the carbon atom of methyl group in equatorial positions. The N1, N5, C33 and Al atoms are coplanar, the total angles of the trigonal plane being 359.99°. The N2, Al1, and N6 atoms are approximately in a line, the angle of N(2)–Al(1)–N(6) being 170.45(16)°. The Al–$N_{pyrrole}$ distances of 1.899(4) Å and 1.901(4) Å are shorter than corresponding Al–N distances in complex **4b** [2.096(3) Å] and in [$AlMe_2$\{2 − (2′, 6′ − $Pr^i_2C_6H_3N$=CH) − 5 − Bu^t C_4H_2N\}] [1.923(4) Å] [32], but are comparable to corresponding those in [AlCl\{2-($Me_2NCH_2C_4H_3N$\}$_2$] [1.896(3) and 1.906(3) Å, respectively] [33]. The Al–N_{imine} distances of 2.115(3) Å and 2.112(4) Å are longer than those found in complex **4b** [1.970(3) Å] and in [$AlMe_2$\{2 − (2′, 6′ − $Pr^i_2C_6H_3N$=CH) − 5 − $Bu^tC_4H_2N$\}] [1.9956(19) Å] [32], but are still in the normal range for Al-imine complexes.

2.2. Catalyzed ring-opening polymerization of ε-caprolactone

The ring-opening polymerization of ε-CL catalyzed by complexes **4a**–**4c** and **8** in the presence of benzyl alcohol was carried out and the results are listed in Table 1. Each of the complexes is an active catalyst toward the ROP of ε-CL at the elevated temperature. The polymerization catalyzed by **4a**/BnOH was performed at 70 °C. The monomer conversion reached 93% in 105 min. At the higher temperature the reaction went to completion in shorter time (entry 2 in Table 1). Complex **4c** exhibits a little higher catalytic activity than complex **4b**. The catalytic activity of each of **4a**–**4c** is comparable to those of *N*,*N*,O-chelate methylaluminium 8-quinolinolates [35]. It was also noted that complexes **4a**–**4c** lead to higher polymer molecular weights than calculated ones. This may be due to partial decomposition of the active catalysts during the reaction at the high reaction temperatures. Complex **8**/BnOH exhibits much higher activity than complexes **4a**–**4c**/BnOH systems. At 60 °C **8**/BnOH system leads to 90%

Table 1
Ring-opening polymerization of ε-CL catalyzed by complexes **4a**–**4c** and **8** in the presence of benzyl alcohol.[a]

Entry	Cat.	$[M]_0/[Al]_0/[BnOH]_0$	Temp. (°C)	Time (min.)	Conv. (%)[b]	M_n (GPC)[c]	M_n (Calcd)[d]	Yield (%)	PDI [e]
1	**4a**	200:1:1	70	105	93	54900	21300	90	1.17
2	**4a**	200:1:1	100	75	98	–	22500	94	–
3	**4b**	199:1:1	100	60	85	36900	19400	82	1.41
4	**4c**	200:1:1	100	60	94	48000	21600	90	1.30
5	**8**	204:1:1	60	2	90	25700	21100	87	1.20

[a] All polymerizations were carried out in toluene; $[CL]_0 = 2$ M.
[b] Measured by ^1H NMR spectra.
[c] Obtained from GPC analysis and calibrated against polystyrene standard, multiplied by 0.56 [37,38].
[d] Calculated from the molecular weight of ε-CL times the conversion of monomer and the ratio of $[CL]_0/[BnOH]_0$ plus the molecular weight of BnOH.
[e] Obtained from GPC analysis.

monomer conversion within 2 min, exhibiting comparable activity to that of *N*,*N*-dialkylaniline-arylamidoaluminum/BnOH [36]. The determined molecular weight by GPC closely matches the theoretical value, showing the catalytically active species to be stable at the reaction temperature. The higher catalytic activity of complex **8** than complexes **4a**–**4c** is attributed to difference of electronic effect of the auxiliary ligands. In complex **8** two anionic ligands coordinate to the aluminum center and this provides a proper electronic environment at the metal center for the catalysis.

In order to establish reaction order in monomer and metal concentration, kinetic studies of ε-CL polymerization catalyzed by complexes **4a** and **8** in the presence of BnOH were performed. Plots of $\ln([CL]_0/[CL])$ *versus* time using each catalyst exhibits a perfect linear relationship (Fig. 4), which indicates that the polymerization proceeds with first-order dependence on monomer concentration. The reaction rate remains constant with reaction time, indicating a constant number of active sites throughout the polymerization. This implies that the polymerizations catalyzed by **4a** and **8**, respectively, are controlled. A further indicator of controlled polymerization is the linear relationship of molecular weight with conversion in each catalytic reaction, along with relatively low PDI values (Figs. 5 and 6). In addition, it was noted the existence of CH_2 signals of BnO in the ^{1}H NMR spectra of the polymers. This shows that the polymerizations are initiated through the insertion of BnO group to ε-CL.

For the sake of comparison, we also investigated catalysis of complex **4a** toward the ROP of ε-CL in the absence of BnOH and in the presence of two equiv of BnOH. In the absence of BnOH complex **4a** showed a very poor catalytic activity. It leads to about 6% monomer conversion at 70 °C in 105 min when 200 equiv of ε-CL were used. In the presence of two equiv of BnOH complex **4a** exhibited a little higher catalytic activity than that using one equiv BnOH (Table 2). The monomer conversion reaches 95% in 60 min at 70 °C. However, the molecular weights of the polymers determined by ^{1}H NMR spectroscopy are about half of the theoretical values (Table 2, entries 1–5). This is attributed to that all the added alcohol molecules contribute to the immortal polymerization. Thus, one of the aluminum methyl groups in **4a** was replaced by OBn through reaction **4a** with one equiv of BnOH, and the resultant benzyloxyaluminum complex catalyzes the ring-opening polymerization. During the polymerization an exchange takes place between the growing polymer chains and the free alcohol, which generates PCL

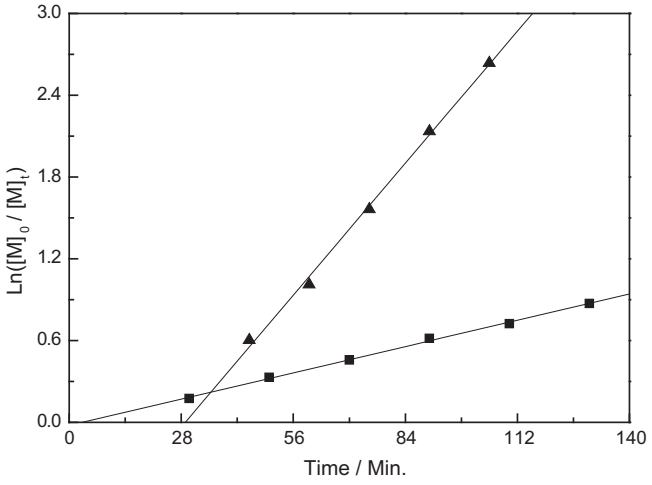


Fig. 4. Plots of $\ln([M]_0/[M])$ *versus* time for the polymerization of ε-CL catalyzed by **4a** (▲) and 8 (■). Conditions: Solvent: toluene; polymerization temperature: 70 °C for **4a** and 20 °C for 8; $[M]_0/[Al]/[BnOH]_0 = 200:1:1$, $M]_0 = 2$ M.

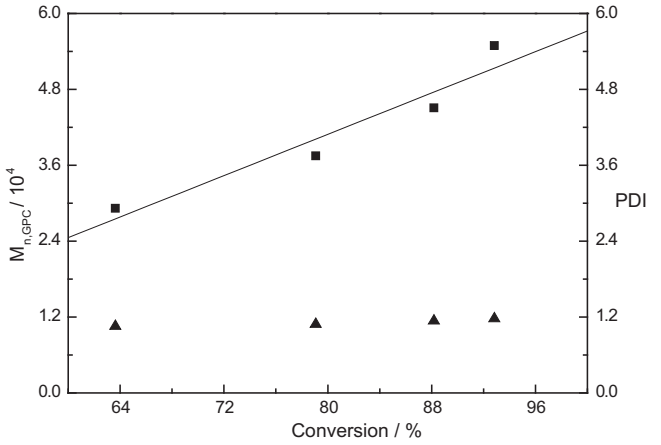


Fig. 5. Plots of PCL M_n (■ obtained from GPC analysis) and polydispersity (▲, M_w/M_n) as a function of ε-CL conversion using complex **4a** at 70 °C $[M]_0:[Al]_0:[BnOH]_0 = 200:1:1$, $[M]_0 = 2$ M.

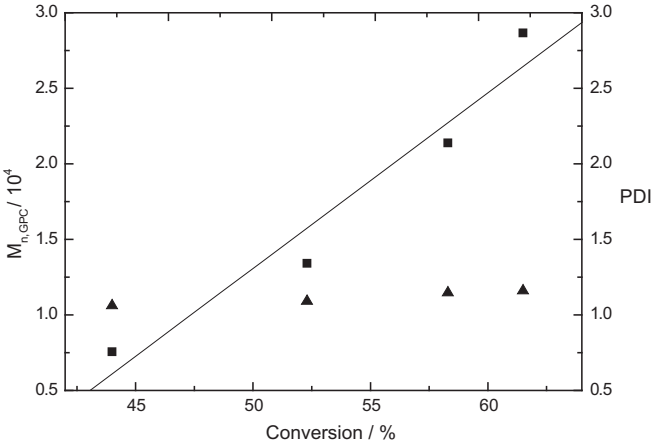


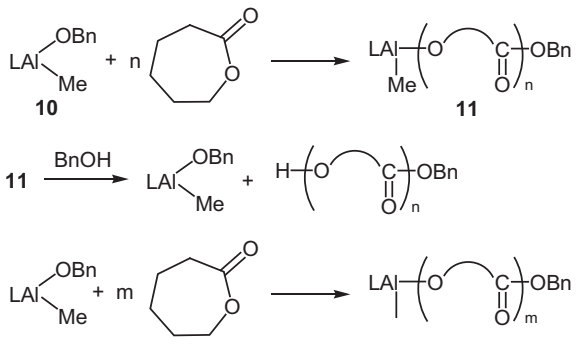
Fig. 6. Plots of PCL M_n (■ obtained from GPC analysis) and polydispersity (▲, M_w/M_n) as a function of ε-CL conversion using complex **8** at 20 °C $[M]_0:[Al]_0:[BnOH]_0 = 200:1:1$, $[M]_0 = 2$ M.

and a new benzyloxyaluminum molecule (Scheme 3) [39]. However, it is possible that the two methyl groups in **4a** were replaced by two OBn groups through reaction of **4a** with two equiv of BnOH and two polymer chains grow simultaneously at the metal center [36]. A well linear relationship of the concentration change of the monomer *versus* time supports the polymerization to be controlled (Fig. 7).

Table 2
Ring-opening polymerization of ε-CL catalyzed by complex **4a** in the presence of 2 equiv of benzyl alcohol.[a]

Entry	Time (min.)	Conv. (%)[b]	M_n (NMR)[b]	M_n (Calcd)[c]
1	30	57	6300	13100
2	45	84	10100	19050
3	60	95	12400	21800
4	75	98	13600	22600
5	90	99	14500	22700

[a] The polymerizations were carried out in toluene at 70 °C; $[CL]_0 = 2$ M, $[CL]_0/[Al]_0/[BnOH]_0 = 200:1:2$.
[b] Obtained from NMR analysis.
[c] Calculated from the molecular weight of ε-CL times the conversion of monomer and the ratio of $[CL]_0/[BnOH]_0$ plus the molecular weight of BnOH.



Scheme 3. [**4a**/BnOH]-mediated "immortal" ROP of ε-CL.

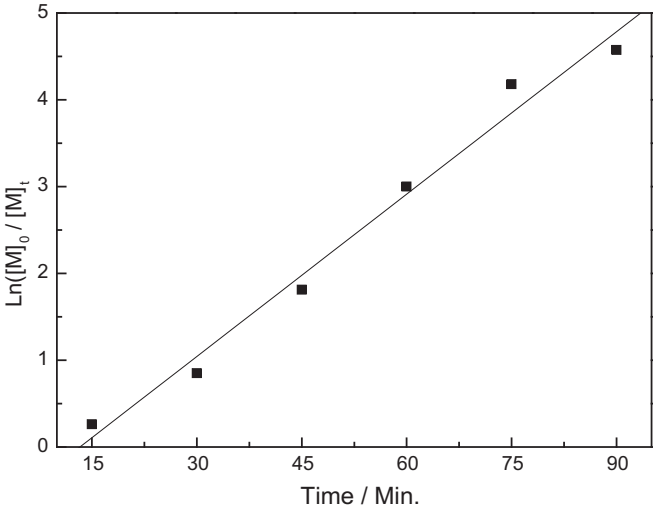


Fig. 7. Plots of $\ln([M]_0/[M])$ *versus* time for the polymerization of ε-CL catalyzed by **4a**. Conditions: Solvent: toluene; polymerization temperature: 70 °C; $[M]_0/[Al]/[BnOH]_0 = 200:1:2$, $[M]_0 = 2$ M.

3. Conclusions

We have synthesized and characterized aluminum and zinc complexes supported by two classes of pyrrole-based ligands. In the presence of BnOH the aluminum complexes **4a**–**4c** and **8** are active catalysts for the ROP of ε-CL. Complex **8** exhibits much higher catalytic activity than **4a**–**4c**. Kinetic studies reveal that each of the polymerization reactions catalyzed by complexes **4a** and **8** follows first-order kinetics in the concentration of monomer and gives polymers with relatively narrow molecular weight distributions, which indicate that the polymerizations proceed in a controlled manner.

4. Experimental

4.1. General remarks

All air- or moisture-sensitive manipulations were performed under nitrogen atmosphere using standard Schlenk and vacuum line techniques. Solvents were distilled under nitrogen over sodium (toluene), sodium/benzophenone (*n*-hexane, THF and Et_2O) or CaH_2 (CH_2Cl_2) and degassed prior to use. Compounds **2a** [40], **2b** [41] and **6** [42] were prepared according to the procedures described in literature. R_3Al (R = Me, Et) and Et_2Zn were purchased from Alfa-Aesar and used as received. $CDCl_3$ and C_6D_6, purchased from Cambridge Isotope Laboratories, were degassed and stored over 4 Å molecular sieves ($CDCl_3$) or Na/K alloy (C_6D_6). ε-Caprolactone, purchased from Acros Organics, was stirred over CaH_2 for 24 h and distilled under vacuum. All other chemicals were obtained from commercial vendors. NMR spectra were recorded on a Bruker av300 spectrometer at the ambient temperature. The chemical shifts of ^1H and ^{13}C NMR spectra were referenced to internal solvent resonances or TMS. Elemental analysis was performed on an Elementar Vario EL-III instrument. Gel permeation chromatograph (GPC) measurements were performed on a Waters 150C instrument equipped with UltraStyragel columns (103, 104, and 105 Å) and 410 refractive index detector, using monodispersed polystyrene as calibration standard. THF was used as eluent at a flow rate of 1 ml/min.

4.2. Synthesis of compounds

4.2.1. Synthesis of N-((1H-pyrrol-2-yl)methylene)quinolin-8-amine (*3a*)

A mixture of quinolin-8-amine (2.00 g 13.87 mmol), 1*H*-pyrrole-2-carbaldehyde (1.33 g, 13.99 mmol), 4 Å molecular sieves (10 g), toluene (15 ml) and five drops of HCOOH was stirred overnight at room temperature. Molecular sieves were filtered and washed with CH_2Cl_2. Solvents were removed from the filtrate by rotatory evaporation. The residue was dissolved in *n*-hexane. The solution was concentrated to yield white powder of **3a** (2.10 g, 68%), m.p. 179–180 °C. Anal. Calcd. for $C_{14}H_{11}N_3$: C, 76.00; H, 5.01; N, 18.99. Found: C, 75.83, H, 5.13; N, 18.88%. ^1H NMR ($CDCl_3$): δ 6.33 (t, J = 3.2 Hz, 1H, Ar), 6.72–6.75 (m, 1H, Ar), 7.04 (s, 1H, Ar), 7.29 (d, J = 7.2 Hz, 1H, Ar), 7.44 (dd, J = 4.2, 8.1 Hz, 1H, Ar), 7.53 (t, J = 7.5 Hz, 1H, Ar), 7.65 (d, J = 8.1 Hz, 1H, Ar), 8.18 (m, 1H, Ar), 8.42 (s, 1H, N=CH), 8.95 (m, 1H, Ar). ^{13}C NMR ($CDCl_3$): δ 1110.44, 116.92, 118.20, 121.54, 123.34, 124.67, 127.02, 136.20, 149.95, 151.71.

4.2.2. Synthesis of N-((5-tert-butyl-1H-pyrrol-2-yl)methylene) quinolin-8-amine (*3b*)

The same procedure as for **3a** was used to prepare **3b**. Thus, a mixture of quinolin-8-amine (2.00 g, 13.87 mmol), 5-*tert*-butyl-1*H*-pyrrole-2-carbaldehyde (2.11 g, 13.95 mmol), 4 Å molecular sieves (10 g), toluene (15 ml) and five drops of HCOOH was stirred overnight at room temperature. Molecular sieves were filtered and washed with CH_2Cl_2. Solvents were removed from the filtrate by rotatory evaporation. The residue was dissolved in *n*-hexane. The solution was concentrated to give a pale yellow solid of **3b** (2.78 g, 72%), m.p. 126–128 °C. Anal. Calcd. for $C_{18}H_{19}N_3$: C, 77.95; H, 6.90; N, 15.15. Found: C, 77.78; H, 7.02; N, 15.05. ^1H NMR ($CDCl_3$): δ 0.86 (s, 9H, Bu^t), 5.97 (dd, J = 4.5, 8.4 Hz, 1H, Ar), 6.30 (d, J = 3.9 Hz, 1H, Ar), 6.63 (d, J = 8.1 Hz, 1H, Ar), 6.81–6.86 (m, 1H, Ar), 6.91–6.98 (m, 2H, Ar), 7.15 (d, J = 6.9 Hz, 1H, Ar), 7.89 (dd, J = 1.8, 4.5 Hz, 1H, Ar), 8.37 (s, 1H, N=CH). ^{13}C NMR (C_6D_6): δ 31.23, 111.82, 114.17, 121.29, 122.33, 124.67, 128.03, 130.00, 136.48, 146.02, 146.87.

4.2.3. Synthesis of $LAlMe_2$ (*4a*)

To a stirred solution of **3a** (0.221 g, 1 mmol) in toluene (10 ml) was added dropwise $AlMe_3$ (0.5 ml, a 2.3 M solution in hexane, 1.15 mmol) at room temperature. The mixture was stirred overnight at that temperature. Solvent was removed under vacuum. The residue was dissolved in Et_2O and then filtered. The filtrate was concentrated under vacuum to yield colorless crystals of **4a** (0.22 g, 79%), m.p. 197–198 °C. Anal. Calcd. for $C_{16}H_{16}N_3Al$: C, 69.30; H, 5.82; N, 15.15. Found: C, 69.15; H, 5.88; N, 15.02. ^1H NMR (C_6D_6): δ −0.01 (s, 6H, Me), 6.66–6.71 (m, 1H, Ar), 6.87 (d, J = 7.5 Hz, 1H, Ar), 7.01 (d, J = 8.4 Hz, 1H, Ar), 7.09–7.14 (m, 2H, Ar), 7.40 (d, J = 8.4 Hz, 1H, Ar), 7.74 (s, 1H, Ar), 7.98 (s, 1H, N=CH), 8.51 (d, J = 8.4 Hz, 1H,

Ar). ^{13}C NMR (C_6D_6): δ −8.13, 106.71, 123.62, 126.34, 127.88, 127.94, 128.59, 129.36, 131.15, 134.38, 137.96, 140.05, 145.64, 145.68, 147.86.

4.2.4. Synthesis of L′AlMe$_2$ (**4b**)

Complex **4b** was synthesized using the same procedure as for **4a**. Thus, reaction of **3b** (0.277 g, 1 mmol) with $AlMe_3$ (0.5 ml, a 2.3 M solution in hexane, 1.15 mmol) in toluene (10 ml) at room temperature afforded, after recrystallizing from Et_2O, colorless crystals of complex **4b** (0.17 g, 51%), m.p. 225–226 °C. Anal. Calcd. for $C_{20}H_{24}N_3Al\cdot 0.2Et_2O$: C, 71.74; H, 7.53; N, 12.07. Found: C, 71.79; H, 7.35; N, 12.06. ^{1}H NMR (C_6D_6): δ −0.33 (s, 6H, Me), 1.35 (s, 9H, Bu^t), 6.30–6.35 (m, 2H, Ar), 6.50 (d, J = 7.8 Hz, 1H, Ar), 6.64 (d, J = 8.4 Hz, 1H, Ar), 6.73–6.79 (m, 2H, Ar), 7.03–7.06 (m, 1H, Ar), 7.54 (s, 1H, N=CH), 8.07–8.09 (m, 1H, Ar). ^{13}C NMR (C_6D_6): δ −3.07, 31.85, 35.17, 111.51, 117.10, 120.64, 122.67, 125.94, 129.18, 136.92, 138.17, 139.66, 141.20, 145.92, 146.14, 168.76.

4.2.5. Synthesis of LAlEt$_2$ (**4c**)

Complex **4c** was synthesized using the same procedure as for **4a**. Thus, reaction of **3a** (0.221 g, 1 mmol) with $AlEt_3$ (0.66 ml, a 1.82 M solution in hexane, 1.2 mmol) in toluene (10 ml) yielded colorless crystalline solid of **4c** (0.26 g, 85%), m.p. 145–146 °C. Anal. Calcd. for $C_{18}H_{20}N_3Al$: C, 70.80; H, 6.60; N, 13.76. Found: C, 70.52; H, 6.75; N, 13.59. ^{1}H NMR (C_6D_6): δ 0.47–0.71 (m, 4H, CH_2), 1.44 (t, J = 8.1 Hz, 6H, Me), 6.68–6.72 (m, 2H, Ar), 6.88 (d, J = 7.5 Hz, 1H, Ar), 7.02 (d, J = 8.1 Hz, 1H, Ar), 7.10–7.15 (m, 2H, Ar), 7.42 (d, J = 8.1 Hz, 1H, Ar), 7.79 (s, 1H, Ar), 8.00 (s, 1H, N=CH), 8.55 (d, J = 4.8 Hz, 1H, Ar). ^{13}C NMR (C_6D_6): δ −13.85, 11.00, 112.11, 118.43, 121.61, 122.61, 123.16, 129.27, 137.55, 142.58, 146.92, 148.54, 164.18.

4.2.6. Synthesis of L$_2$Zn (**5a**)

To a stirred solution of **3a** (0.221 g, 1 mmol) in toluene (15 ml) was added dropwise $ZnEt_2$ (1.24 ml, a 0.875 M solution in hexane, 1.09 mmol) at 0 °C. The resulting mixture was warmed to ambient temperature and stirred for 16 h. Solvent was removed and the residue was dissolved in Et_2O. The resultant solution was filtered and the filtrate was concentrated to generate yellow crystals of **5a** (0.21 g, 83%), m.p. 217–218 °C. Anal. Calcd. for $C_{28}H_{20}N_6Zn$: C, 66.48; H, 3.98; N, 16.61. Found: C, 66.71; H, 4.07; N, 16.42. ^{1}H NMR (C_6D_6): δ 5.90 (dd, J = 4.2, 8.1 Hz, 2H, Ar), 6.22 (d, J = 3.6 Hz, 2H, Ar), 6.67 (d, J = 8.1 Hz, 2H, Ar), 6.80–6.87 (m, 4H, Ar), 6.92–7.00 (m, 4H, Ar), 7.14 (d, J = 7.5 Hz, 2H, Ar), 7.76–7.80 (m, 2H, Ar), 8.45 (s, 2H, N=CH). ^{13}C NMR (C_6D_6): δ 111.99, 115.98, 121.74, 121.95, 121.16, 126.03, 129.67, 129.94, 136.58, 139.61, 141.33, 142.15, 146.90, 147.82.

4.2.7. Synthesis of L′$_2$Zn (**5b**)

The synthesis of complex **5b** was carried out using a similar procedure to that described for complex **5a**. Thus, a mixture of **3b** (0.277 g, 1 mmol), $ZnEt_2$ (1.25 ml, a 0.875 M solution in hexane, 1.09 mmol) and toluene (20 ml) was stirred at room temperature for 16 h. The resulting solution was filtered and the filtrate was concentrated to afford yellow crystals of **5b**·2PhCH$_3$ (0.19 g, 47%), m.p. 124–125 °C. Anal. Calcd. for $C_{36}H_{36}N_6Zn\cdot 2PhCH_3$: C, 74.84; H, 6.53; N, 10.47. Found: C, 75.02; H, 6.51; N, 10.47. ^{1}H NMR (C_6D_6): δ 1.19 (s, 18H, *t*Bu), 6.32 (dd, J = 4.2, 8.1 Hz, 2H, Ar), 6.64 (d, J = 3.9 Hz, 2H, Ar), 6.97 (d, J = 8.1 Hz, 2H, Ar), 7.16–7.21 (m, 2H, Ar), 7.27 (d, J = 8.1 Hz, 2H, Ar), 7.31 (d, J = 3.9 Hz, 2H, Ar), 7.49 (d, J = 7.8 Hz, 2H, Ar), 8.22–8.24 (m, 2H, Ar), 8.70 (s, 2H, N=CH). ^{13}C NMR (C_6D_6): δ 31.00, 34.14, 111.59, 113.94, 121.05, 122.10, 124.44, 126.03, 127.84, 128.90, 129.67, 136.25, 139.50, 145.83, 146.64, 166.41.

4.2.8. Synthesis of HL″ (**7**)

A mixture of 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)benzenamine (2.00 g, 10.68 mmol), 1*H*-pyrrole-2-carbaldehyde (1.10 g, 11.57 mmol), 4 Å molecular sieves (10 g), toluene (30 ml) and five drops of HCOOH was refluxed for 6 h. The resulting mixture was cooled to room temperature and then filtered. The molecular sieves were washed with CH_2Cl_2 and the combined organic phase was distilled to dryness by rotatory evaporation. The residue was dissolved in Et_2O. Concentration of the solution gave colorless crystals of **7** (2.08 g, 74%), m.p. 171–172 °C. Anal. Calcd. for $C_{16}H_{16}N_4$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.31; H, 6.23; N, 21.26. ^{1}H NMR ($CDCl_3$): δ 2.03 (s, 3H, Me), 2.28 (s, 3H, Me), 5.90 (s, 1H, Ar), 6.26 (s, 1H, Ar), 6.62 (s, 1H, Ar), 6.93 (s, 1H, Ar), 7.15 (d, J = 7.8 Hz, 1H, Ar), 7.23–7.28 (m, 1H, Ar), 7.40 (d, J = 7.5 Hz, 2H, Ar), 8.11 (s, 1H, N=CH). ^{13}C NMR ($CDCl_3$): δ 11.66, 13.65, 105.15, 110.54, 116.75, 119.83, 123.18, 125.72, 128.86, 129.66, 133.18, 140.87, 143.62, 148.30, 150.79.

4.2.9. Synthesis of [L″$_2$AlMe] (**8**)

To a stirred solution of **7** (0.264 g, 1 mmol) in toluene (10 ml) was added $AlMe_3$ (0.44 ml, a 2.3 M solution in hexane, 1.01 mmol) at room temperature and then stirred overnight. Solvent was removed under vacuum. The residue was dissolved in Et_2O and filtered. Concentration of the filtrate afforded colorless crystals of **8** (0.18 g, 63%), m.p. 248–249 °C. Anal. Calcd. for $C_{33}H_{33}N_8Al\cdot Et_2O$: C, 69.14; H, 6.74; N, 17.43. Found: C, 68.83; H, 6.86; N, 17.78. ^{1}H NMR (C_6D_6): δ −0.21 (s, 3H, AlMe), 1.11 (t, J = 6.9 Hz, Et_2O), 1.81 (s, 6H, Me), 2.31 (s, 6H, Me), 3.26 (q, J = 6.9 Hz, Et_2O), 5.72 (s, 2H, Ar), 6.17 (s, 2H, Ar), 6.63 (d, J = 2.7 Hz, 2H, Ar), 6.80 (t, J = 7.5 Hz, 2H, Ar), 6.92 (t, J = 8.1 Hz, 2H, Ar), 6.96 (s, 2H, Ar), 7.26 (d, J = 7.8 Hz, 2H, Ar), 7.48 (s, 2H, Ar), 7.74 (d, J = 8.1 Hz, 2H, Ar). ^{13}C NMR (C_6D_6): δ −9.63, 11.57, 14.06, 15.88, 66.21, 107.25, 116.01, 122.20, 126.14, 127.15, 130.10, 131.31, 132.85, 138.15, 141.02, 143.38, 150.34, 157.80.

Single crystals for X-ray diffraction were obtained by recrystallization the sample in benzene.

4.2.10. Synthesis of [ZnL″$_2$] (9)

To a stirred solution of **7** (0.264 g, 1 mmol) in toluene (10 ml) was added dropwise $ZnEt_2$ (1.2 ml, a 0.875 M solution in hexane, 1.05 mmol) at 0 °C. The mixture was warmed to room temperature and stirred overnight. Solvent was removed in vacuo and the residue was dissolved in Et_2O. The resulting solution was filtered and the filtrate was concentrated to form colorless crystals of **9** (0.22 g, 74%), m.p. 178–179 °C. Anal. Calcd. for $C_{32}H_{30}N_8Zn$: C, 64.92; H, 5.11; N, 18.93. Found: C, 64.75; H, 5.33; N, 18.73. ^{1}H NMR (C_6D_6): δ 1.59 (s, 6H, Me), 2.13 (s, 6H, Me), 5.59 (s, 2H, Ar), 6.49 (dd, J = 1.8, 3.6 Hz, 2H, Ar), 6.69 (t, J = 7.8 Hz, 2H, Ar), 6.77 (t, J = 7.5 Hz, 2H, Ar), 6.84 (d, J = 3.6 Hz, 2H, Ar), 6.95 (d, J = 8.1 Hz, 2H, Ar), 7.04 (d, J = 7.5 Hz, 2H, Ar), 7.09 (s, 2H, Ar), 7.56 (s, 2H, N=CH). ^{13}C NMR (C_6D_6): δ 11.85, 14.19, 107.12, 115.30, 121.51, 124.49, 125.33, 129.17, 129.55, 133.10, 138.56, 138.79, 141.23, 144.78, 150.56, 158.03.

4.3. X-ray crystallography

Single crystals of complexes **4b**, **5b** and **8** were respectively mounted in Lindemann capillaries under nitrogen. Diffraction data were collected at 298(2) K on a Bruker Smart CCD area-detector with graphite-monochromated Mo K_α radiation (λ = 0.71073 Å). Unit-cell dimensions were obtained with least-squares refinement. Data collection and reduction were performed using the SMART software [43]. Absorption corrections were applied using the SADABS program [44]. The structures were solved by direct methods using SHELXS-97 [45] and refined against F^2 by full-matrix least-squares using SHELXL-97 [46]. Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations are listed in Table 3.

Table 3
Details of the X-ray structure determinations of complexes **4b**, **5b** and **8**.

	4b	**5b**·2PhMe	**8**·C_6H_6
Formula	$C_{20}H_{24}N_3Al$	$C_{50}H_{52}N_6Zn$	$C_{39}H_{39}N_8Al$
fw	333.40	802.35	646.76
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	*P*2(1)2(1)2(1)	$P-1$	$P-1$
a (Å)	8.6567(9)	13.3250(14)	8.6826(12)
b (Å)	16.7879(16)	13.6230(16)	15.3608(16)
c (Å)	26.157(2)	14.468(2)	15.5650(18)
α (deg)	90	108.526(2)	69.6580(10)
β (deg)	90	106.686(2)	77.430(2)
γ (deg)	90	107.5660(10)	79.682(2)
V (Å^3)	3801.3(6)	2150.5(5)	1887.6(4)
Z	8	2	2
D_{calcd} (g/cm^3)	1.165	1.239	1.138
F (000)	1424	848	684
μ (mm^{-1})	0.112	0.612	0.091
θ range for data collecn (deg)	1.44–25.01	1.64–25.01	1.42–25.00
No. of reflns collected	19914	11493	10038
No. of indep reflns (R_{int})	6711(0.0587)	7488(0.0515)	6552(0.0373)
Restraints/params	0/489	0/618	0/438
Goodness of fit on F^2	1.000	1.032	1.056
Final *R* indices [$I > 2\sigma(I)$][a]	$R1 = 0.0481$	$R = 0.0679$	$R1 = 0.0757$
	$wR2 = 0.0751$	$wR2 = 0.1416$	$wR2 = 0.1966$
R indices (all data)	$R1 = 0.1110$	$R1 = 0.1551$	$R1 = 0.1539$
	$wR2 = 0.0879$	$wR2 = 0.1644$	$wR2 = 0.2305$
Largest diff peak and hole [e Å^{-3}]	0.133 and −0.237	0.524 and −0.379	0.928 and −0.423

[a] $R1 = \sum||Fo| - |Fc||/\sum|Fo|$, $wR2 = [\sum w(Fo^2 - Fc^2)^2/\sum w(Fo^4)]^{1/2}$.

4.4. Polymerization of ε-CL catalyzed by aluminum complexes *4a*–*4c* and *8*

A typical polymerization procedure is exemplified by the synthesis of PCL using complex **4a** as a catalyst in the presence of benzyl alcohol (Table 1, entry 2). Complex **4a** (0.042 g, 0.151 mmol) and toluene (15 ml) were added successively into a Schlenk tube. After the complex dissolved, benzyl alcohol (15.7 μl, 0.151 mmol) was added at room temperature. The mixture was stirred at room temperature for 1 h. The Schlenk tube was put into an oil bath which was preset at 100 °C. After 10 min ε-CL (3.447 g, 30.2 mmol) was added *via* a syringe. After the solution was stirred for 75 min the polymerization reaction was terminated by addition of several drops of glacial acetic acid. After stirring at room temperature for 0.5 h, the resulting solution was poured into cool methanol with stirring. The precipitate was collected by filtration under reduced pressure, washed with cool methanol and dried under vacuum to afford PCL as white solid (3.24 g, 94%).

For the GPC analysis, the sample was dissolved in dichloromethane, passed through a short neutral aluminum oxide column, precipitated in methanol and dried under vacuum.

For the kinetic studies, samples were taken from the reaction mixture using a syringe at a desired time interval.

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Appendix A. Supplementary data

CCDC 806572-806574 contain the supplementary crystallographic data for complexes **4b**, **5b** and **8**. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: t44-1223-336033; or e-mail: deposit@ccdc.cam.ac.uk.

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