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Well-controlled ring-opening polymerization of cyclic esters initiated by dialkylaluminum β-diketiminates†

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A series of aluminum alkyl complexes *nacnac*^{R}AlMe$_2$ (**2a–2h**) bearing aliphatic *N*-substituted β-diketiminate ligands (*nacnac*^{R}H = *N*,*N*′-dialkyl-2-amino-4-iminopent-2-enes), were prepared from the reaction of trialkyl aluminum and the corresponding β-diketimines. All these aluminum complexes were characterized by NMR, elemental analysis and HRMS spectroscopy. The molecular structures of complexes **2a**, **2c** and **2h** were confirmed by single-crystal X-ray diffraction. These aluminum alkyl complexes show notable activity towards the ring-opening polymerization of ε-caprolactone in the absence and presence of alcohol, and the resulting polymers have narrow molecular weight distributions.

Introduction

Polycaprolactone (PCL) and polylactide (PLA) are important polymers in biomedical and pharmaceutical applications due to their biodegradable, biocompatible and permeable properties. They are widely applied in different fields such as fibers, plastics and coatings.[1] An efficient method to synthesize the polymers is ring-opening polymerization (ROP) of cyclic esters initiated by metal complexes.[2,3] Among the metal-based initiators, aluminum complexes have attracted much attention because they have a good control over the polymerization reaction and low toxicity.[4–7] However, in the absence of alcohol, very few aluminum alkyl complexes can act as efficient initiators for the ROP of ε-caprolactone (ε-CL), because most of the aluminum alkyls showed no or very low activity towards the polymerization and the processes were poorly controlled.[8–10]

The catalytic performances are greatly affected by the steric and electronic properties of the ligands in metal complexes, therefore, the choice of suitable ligands is of vital importance. Although some types of ligands have already been employed in the aluminum alkyl initiators,[8,11,12] aluminum complexes bearing *N*,*N*′-substituted β-diketiminate ("nacnac") ligands and their application in ROP of cyclic esters are still scarcely investigated.[11c] The β-diketiminates have proved to be attractive ligands to stabilize coordinatively unsaturated metal centers and unusual oxidation states, and their complexes can function as catalysts in olefin polymerization, ring-opening polymerization of lactide or related monomers, and copolymerization of expoxides and carbon dioxide.[13] Most of the current work with β-diketiminate ligands is focused on those containing aromatic *N*-substituents,[11c,13,14] and metal complexes with aliphatic *N*-substituents have been reported to a lesser extent. The aliphatic *N*-substituted "nacnac" ligands cannot only allow for adjusting the steric environment around the metal centers, but also allow for easily introducing chirality into the diketiminate ligands. Recently, Schaper *et al.* synthesized several complexes of transition metals (copper, zinc, chromium and zirconium) and one main group metal (magnesium) bearing chiral aliphatic *N*-substituted "nacnac" ligands as well as one achiral ligand *nacnac*^{Bn}, and investigated their application in the polymerization of lactide.[15] To the best of our knowledge, no examples bearing such kinds of *N*-alkyl "nacnac" ligands are known for aluminum alkyl complexes, neither for the application in the ROP of ε-CL and lactide except our latest work.[9]

In our recent communication,[9] we reported two dimethylaluminum complexes, *R*,*R*-*nacnac*$^{CH(Me)Ph}$AlMe$_2$ and *S*,*S*-*nacnac*$^{CH(iPr)Ph}$AlMe$_2$, with chiral *N*-alkyl "nacnac" ligands, and found that they could initiate the ROP of ε-CL in the absence of alcohol. In addition, the former complex showed a higher activity for the polymerization than the latter one, affording over 99% monomer conversion within 3 h at 80 °C and moreover in a well-controlled manner with narrow molecular weight distribution (PDI = 1.22) of the polymers. Comparably, the diethylaluminum complexes[11c] bearing *N*-aryl β-diketiminate ligands led to 96% conversion after 17 h and the polymerization products were poorly controlled with broader distributions (PDI = 1.66–3.74) under the same conditions. To explore more efficient catalysts for the ROP of ε-CL, and considering the chiral "nacnac" ligands are more expensive than

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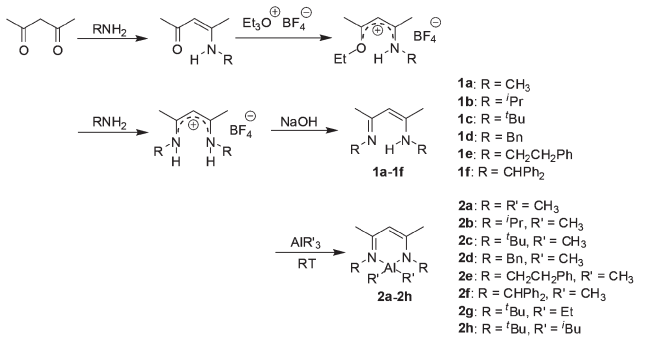


1a: R = CH_3
1b: R = ^{i}Pr
1c: R = ^{t}Bu
1d: R = Bn
1e: R = CH_2CH_2Ph
1f: R = $CHPh_2$

2a: R = R' = CH_3
2b: R = ^{i}Pr, R' = CH_3
2c: R = ^{t}Bu, R' = CH_3
2d: R = Bn, R' = CH_3
2e: R = CH_2CH_2Ph, R' = CH_3
2f: R = $CHPh_2$, R' = CH_3
2g: R = ^{t}Bu, R' = Et
2h: R = ^{t}Bu, R' = ^{t}Bu

Scheme 1 Synthesis of β-diketiminate aluminum complexes.

the achiral *N*-alkyl substituted diketiminate ligands, we attempted to synthesize aluminum alkyl complexes bearing achiral *N*-alkyl substituted diketiminate ligands (Scheme 1), and investigate the effects of the aliphatic *N*-substituents in the ligands on the catalytic activity for the ROP of ε-CL.

Results and discussion

Synthesis and characterization of β-diketiminate aluminum complexes 2a–2h

As depicted in Scheme 1, the β-diketimines **1a–1f** were synthesized according to the literature procedures.[16] Firstly, simple condensation of acetyl acetone with a primary amine yielded the monosubstituted product 4-ketiminpropan-2-one, which was normally obtained in its enamine form. The following step was condensation with a second amine, which required activation of the ketone, most commonly by alkylation with Meerwein salt. The aluminum alkyl complexes **2a–2h** were synthesized in good yields by the stoichiometric reactions of AlR'_3 (R′ = Me, Et, ^{i}Bu) with the corresponding ligands **1a–1f** (Scheme 1) according to the previous procedure,[9] and fully characterized by ^{1}H NMR, ^{13}C NMR, elemental analysis and HRMS spectroscopy. The ^{1}H NMR spectra indicate that, the chemical environments of the two backbone methyl groups are identical for aluminum complexes **2a–2h**. The disappearance of the N–H signals of the ligands, and the appearance of the resonances for the protons of Al–CH_3 or Al–CH_2 groups in the high-field region (δ −1.48 to 0.01 ppm), indicate the formation of the desired aluminum alkyl complexes. Complexes **2a–2e** are soluble in common organic solvents, such as toluene, benzene, hexane and pentane, and are not very sensitive to air and moisture.

Single crystals of aluminum complexes **2a**, **2c** and **2h** suitable for X-ray diffraction measurement, were obtained by slowly cooling a saturated *n*-hexane solution to −7 °C, 0 °C and −7 °C, respectively. Their molecular structures are shown in Fig. 1–3. Selected bond lengths and angles are summarized in Table 1. As shown by X-ray analysis, being surrounded by two nitrogen atoms of the chelating β-diketiminate ligand and two alkyl groups, the aluminum center in complexes **2a**, **2c** and **2h** possesses a distorted tetrahedral geometry.

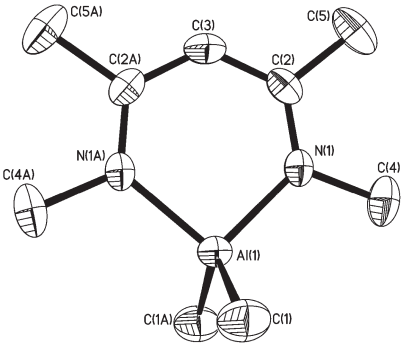


Fig. 1 ORTEP drawing of complex **2a**. Thermal ellipsoids are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity.

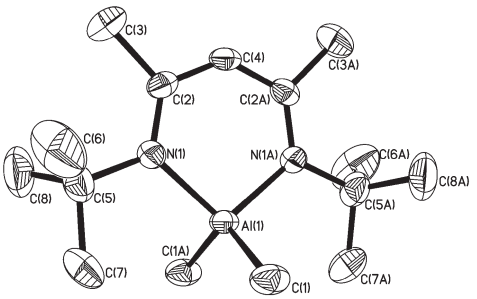


Fig. 2 ORTEP drawing of complex **2c**. Thermal ellipsoids are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity.

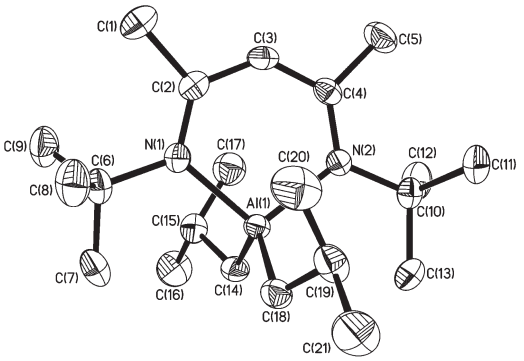


Fig. 3 ORTEP drawing of complex **2h**. Thermal ellipsoids are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity.

The N–Al–N angle of 95.76(14)° in **2a**, is comparable to those in our previously reported chiral complex *R*,*R*-*nacnac*$^{CH(Me)Ph}$$AlMe_2$ (94.96(6)°) and aluminum alkyl complexes with *N*-aryl "nacnac" ligands,[9] while apparently smaller than those in complexes **2c** (101.84(13)°) and **2h** (102.59(7)°), due to the smaller steric bulkiness of the methyl group compared to the *tert*-butyl group on the nitrogen atom of the ligands. The average Al–N bond length in complex **2a** (1.894 Å) is shorter than those in **2c** (1.933 Å) and **2h** (1.950 Å), which means a more crowded environment at the aluminum center in the latter two complexes. The same trends were also observed for the Al–C bond lengths in complexes **2a**, **2c** and

Table 1 Selected bond lengths (Å) and angles (°)

Complex **2a**			
Al(l)–N(1)	1.893(2)	Al(l)–N(1A)	1.893(2)
Al(1)–C(1)	1.964(3)	Al(1)–C(1A)	1.964(3)
N(1)–C(2)	1.318(3)	C(2)–C(3)	1.388(3)
N(1)–Al(1)–N(1A)	95.76(14)	N(1)–Al(1)–C(1)	111.49(6)
N(1A)–Al(1)–C(1)	111.49(6)	N(1)–Al(1)–C(1A)	111.49(6)
C(1)–Al(1)–C(1A)	113.79(19)	N(1A)–Al(1)–C(1A)	111.49(6)
Complex 2c			
Al(1)–N(1)	1.933(2)	Al(1)–N(1A)	1.933(2)
Al(1)–C(1)	1.984(3)	Al(1)–C(1A)	1.984(3)
N(1)–C(2)	1.324(3)	N(1)–C(5)	1.508(4)
C(2)–C(4)	1.408(3)	C(2)–C(3)	1.511(4)
N(1)–Al(1)–N(1A)	101.84(13)	N(1)–Al(1)–C(1A)	107.95(12)
N(1A)–Al(1)–C(1A)	109.53(12)	N(1A)–Al(1)–C(1)	107.95(12)
C(1A)–Al(1)–C(1)	118.7(2)	N(1)–Al(1)–C(1)	109.53(12)
Complex 2h			
Al(1)–N(1)	1.9499(17)	Al(1)–N(2)	1.9508(17)
Al(1)–C(14)	1.998(2)	Al(1)–C(18)	2.000(2)
N(1)–C(2)	1.328(3)	N(2)–C(4)	1.327(3)
C(2)–C(3)	1.404(3)	C(4)–C(3)	1.399(3)
C(14)–C(15)	1.540(3)	C(18)–C(19)	1.537(3)
N(2)–Al(1)–N(1)	102.59(7)	N(2)–Al(1)–C(14)	107.13(9)
N(1)–Al(1)–C(14)	108.38(8)	N(2)–Al(1)–C(18)	109.43(8)
N(1)–Al(1)–C(18)	107.31(9)	C(14)–Al(1)–C(18)	120.55(10)

2h. From the above mentioned bond angles and bond lengths in these three complexes, it can be found that, the values are close for complexes **2c** and **2h** with the same substituents on the nitrogen atom of the ligands, while different alkyl groups connect the aluminum center. These results indicate that, the steric bulkiness of the *N*-substituents of the "nacnac" ligands has a more significant influence on the bond parameters than that of the groups connecting the metal atom. Furthermore, in these three complexes, the Al–N–C–C–C–N six-membered ring is nearly planar, with the deviations of the aluminum center from the ligand backbone being 0, 0, 0.0057 Å for **2a**, **2c** and **2h**, respectively. The close bond lengths of N–C and C–C bonds in the ligands of these three complexes display multiple bond character and significant delocalization in these bonds, which is consistent with the complexes with *N*-aryl substituted "nacnac" ligands.[11c]

Ring-opening polymerization of ε-caprolactone

The polymerization of ε-CL using aluminum complexes **2a–2h** as the initiators were conducted under different conditions. The polymerization results are listed in Table 2. The resulting polymers from these reactions, in the absence of alcohol, all had narrow molecular weight distributions (PDI = 1.20–1.46). In contrast, most of the aluminum alkyls could not initiate the ROP of ε-CL in the absence of alcohol,[8,9] and the limited exceptions achieved poorly-controlled polymerization process.[8,11c,d] For example, when using the dinuclear aluminum alkyl complexes bearing a piperazidine-bridged bis(phenolato) group as the initiators, the obtained polymers had broader molecular weight distributions (PDI = 1.82–2.09),[8] and the PDI values of the achieved polymers initiated by neutral three-coordinate, chelating diamide aluminum complexes were from 2.55 to 3.19.[11d] The catalytic activities of complexes **2a–2h** are significantly affected by the aliphatic *N*-substituents of the β-diketiminate ligands, and the initiators are classified to have low to good activities (Table 2) based on the review by Redshaw.[3] For instance, complex **2c** showed good activity, with 99% conversion after 30 min at 80 °C and narrow distribution (PDI = 1.27) of the obtained polymers, while **2f** displayed poor activity with trace conversion after 2 h under the same conditions. From Table 2 we can see that, the initiators bearing the *tert*-butyl group on the nitrogen atoms of the "nacnac" ligands, have higher catalytic activities than those initiators possessing smaller or larger groups in the ligands, indicating that suitable steric hindrance of ligands is beneficial for the catalytic activity. Complexes **2g** and **2h** showed moderate to

Table 2 Ring-opening polymerization of ε-CL initiated by aluminum complexes **2a–2h**[a]

Entry	Initiator	ε-CL/Al	*T*/°C	Time	Conv.[b] (%)	M_n[c] × 10^{-4}	PDI[c]	Activity[e]
1	**2a**	100	80	2 h	65	1.67	1.23	Poor
2	**2b**	100	80	2 h	90	4.12	1.21	Poor
3	**2c**	100	80	30 min	99	5.60	1.27	Good
4	**2d**	100	80	2 h	47	1.14	1.30	Poor
5	**2e**	100	80	2 h	94	3.58	1.20	Poor
6	**2f**	100	80	2 h	Trace	/	/	Low
7	**2g**	100	80	30 min	90	1.42	1.44	Moderate
8	**2h**	100	80	30 min	99	3.49	1.46	Good
9	**2c**	100	80	10 min	10	1.10	1.22	
10	**2c**	100	80	20 min	68	3.87	1.24	
11	**2c**	100	80	25 min	82	5.44	1.24	
12	**2c**	100	60	2 h	64	3.59	1.24	
13	**2c**	100	40	3 h	24	5.37	1.36	
14[d]	**2c**	100	40	3 h	Trace	/	/	
15	**2c**	200	80	1 h	99	5.64	1.19	
16	**2c**	800	80	2 h	93	5.95	1.15	Good

[a] Polymerization conditions: ε-CL, 1.0 mol L^{-1} in toluene; Ar atmosphere. [b] Determined by ^{1}H NMR spectroscopy. [c] Measured by GPC calibrated with standard polystyrene samples. [d] In CH_2Cl_2. [e] Catalytic activity (details in Table S1, ESI).

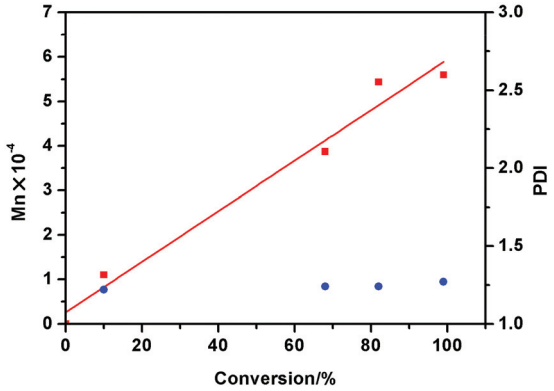


Fig. 4 Plot of M_n (■) and polydispersity (●) *versus* monomer conversion in the ROP of ε-CL initiated by **2c** (Table 2, entries 3, 9–11).

good activities, reaching 90% and 99% conversions within 30 min respectively, while the obtained polymers had smaller molecular weights and broader PDI values compared to those of **2c** (Table 2, entries 7–8). There are some reports on the catalytic activities of the metal initiators supported by *N*-aryl "nacnac" ligands in the ROP of ε-CL.[3] For instance, the diethylaluminum complexes bearing such types of ligands displayed low to poor activities at 80 °C with the monomer to metal ratio being 100 : 1,[11c] while lanthanide amides showed very high activities, for example, neodymium complex gave 96% conversion after 15 min at room temperature with a monomer to metal ratio of 1500 : 1.[17] Moreover, the tri-nuclear zinc complex bearing *N*-aryl "nacnac" ligand showed moderate polymerization activity, reaching 92% conversion after 105 min at room temperature with a monomer to metal ratio of 512 : 1.[18]

The influence of the reaction parameters on the ROP was investigated in detail using complex **2c** as the initiator, since it shows the best catalytic activity among the studied initiators. The polymerization results are listed in Table 2. As shown in Table 2 (entries 3, 9–11) and Fig. 4, a linear relationship between the monomer conversions and the number-average molecular weights (M_n) was observed with almost constant molecular weight distributions, indicating the classical feature of a living polymerization process. The polymerization temperature has a significant effect on the catalytic activity. The higher the temperature was, the faster the polymerization proceeded (Table 2, entries 3, 12–13). When the polymerization was carried out in CH_2Cl_2, complex **2c** showed a low activity with a trace of monomer conversion (Table 2, entry 14). The effect of the molar ratio of monomer to initiator (ε-CL/Al) on the catalytic behaviour was also examined (Table 2, entries 3, 15–16). With the increase of the ε-CL/Al molar ratio, higher molecular weights and narrower PDI values of the polymers were obtained (Table 2, entries 3, 15–16). From entry 16 in Table 2, we can see that even when the ε-CL/Al molar ratio was increased to 800, complex **2c** still showed good catalytic activity by 93% conversion within 2 h at 80 °C, and the resulting polymer had a narrow distribution of 1.15.

Table 3 Ring-opening polymerization of ε-CL initiated by aluminum complexes **2a–2h**/BnOH[a]

Entry	Initiator	Time	Conv.[b] (%)	M_n[c] × 10^{-4}	PDI[c]
1	**2a**	2 h	70	0.32	1.06
2	**2b**	2 h	99	0.70	1.10
3	**2c**	30 min	99	0.48	1.07
4	**2d**	2 h	70	0.37	1.18
5	**2e**	2 h	99	0.52	1.11
6	**2f**	2 h	Trace	/	/
7	**2g**	30 min	99	0.44	1.10
8	**2h**	30 min	99	0.39	1.20
9[d]	**2c**	2 h	94	0.51	1.05
10	**2c**	10 min	29	0.15	1.00
11	**2c**	15 min	60	0.28	1.04
12	**2c**	20 min	85	0.41	1.07

[a] Polymerization conditions: ε-CL, 1.0 mol L^{-1} in toluene at 80 °C; ε-CL : Al : BnOH = 100 : 1 : 1; Ar atmosphere. [b] Determined by ^{1}H NMR spectroscopy. [c] Measured by GPC calibrated with standard polystyrene samples. [d] At 60 °C.

In most cases, only the aluminum alkoxides generated *in situ* from the aluminum alkyls with alcohols can initiate the ROP of ε-CL.[8] Therefore, the ROP of ε-CL initiated by complexes **2a–2h** in the presence of BnOH was also investigated to see the effects of alcohol towards the polymerization. The representative data are summarized in Table 3. It is found that the polymerization was accelerated in the presence of BnOH using complexes **2a–2h** as the initiators, while the molecular weights of the obtained polymers were obviously smaller than those in the absence of BnOH, which was also observed in the dinuclear aluminum alkyl complex.[8] The lower temperature (entry 9 in Table 3) decreased the speed of polymerization, as it was also seen in the absence of alcohol. In addition, the resulting polymers had very narrow distributions (PDI = 1.00–1.20), and the molecular weights (M_n) increased linearly along with the monomer conversions with almost unchanged distributions (Fig. 5) in Table 3 (entries 3, 9–11), which was the same as that in the absence of alcohol.

In order to better understand the nature of ε-CL polymerization initiated by **2c** in the absence and presence of BnOH, kinetic studies were conducted in toluene at 80 °C with the

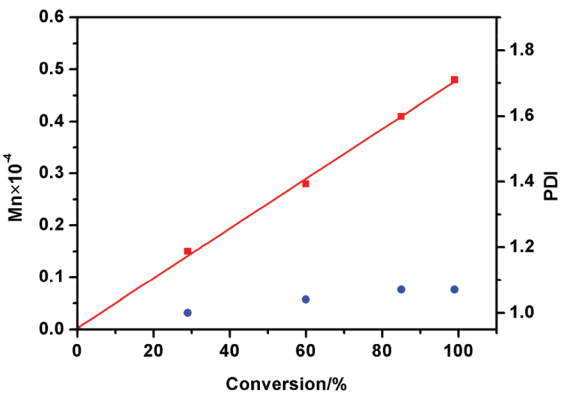


Fig. 5 Plot of M_n (■) and polydispersity (●) *versus* monomer conversion in the ROP of ε-CL initiated by **2c**/BnOH (Table 3, entries 3, 10–12).

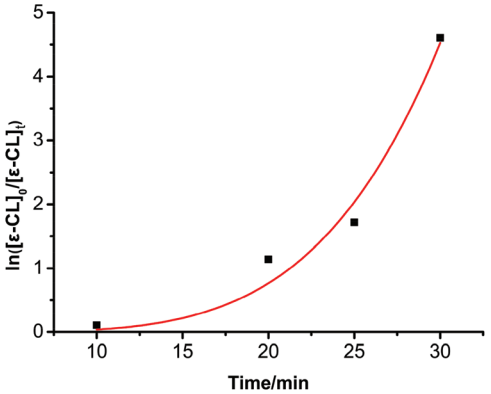


Fig. 6 Semilogarithmic plot of $\ln[[\varepsilon\text{-CL}]_0/[\varepsilon\text{-CL}]_t]$ *versus* time in the ROP of ε-CL initiated by **2c** (Table 2, entries 3, 9–11).

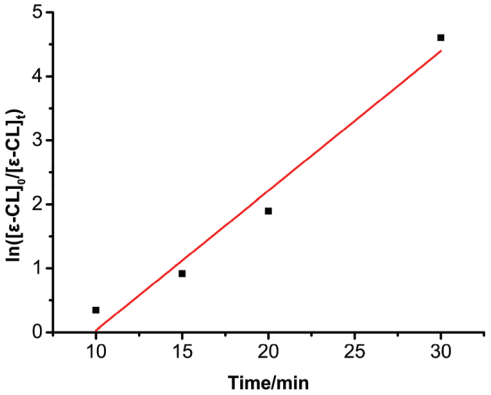
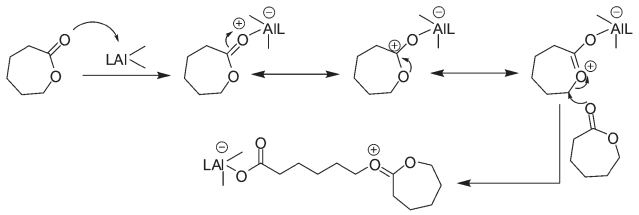


Fig. 7 Semilogarithmic plot of $\ln[[\varepsilon\text{-CL}]_0/[\varepsilon\text{-CL}]_t]$ *versus* time in the ROP of ε-CL initiated by **2c**/BnOH (Table 3, entries 3, 10–12).

monomer to initiator molar ratio being 100 : 1 (Tables 1 and 2). Semilogarithmic plots of $\ln([\varepsilon\text{-CL}]_0/[\varepsilon\text{-CL}]_t)$ *versus* reaction time for the polymerizations initiated by **2c** in the absence and presence of BnOH are shown in Fig. 5 and 6, where $[\varepsilon\text{-CL}]_0$ is the initial monomer concentration, and $[\varepsilon\text{-CL}]_t$ is the lactone concentration at a given reaction time *t*. In the absence of BnOH, the nonlinearity of the plot (Fig. 6) implies that the propagation was not first order with respect to ε-CL monomer, and an induction period was observed distinctly. While in the presence of BnOH, the linearity of the plot (Fig. 7) shows that, the polymerization rate of the ROP was first order (k_{app} = 0.218 min^{-1}) dependent upon the monomer concentration under the same conditions, and an induction period was also observed. Based on the plots (Fig. 6 and 7), the polymerization reactions should follow different mechanisms in the absence and presence of BnOH.

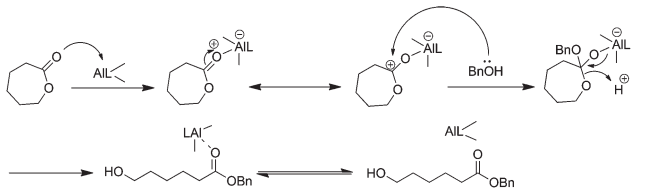
To further elucidate the mechanism, the reaction of complex **2c** with ε-CL was monitored by ^{1}H NMR with 10 : 1 and 1 : 1 ε-CL/Al ratio in C_6D_6 at 60 °C in the absence of BnOH. No obvious change for **2c** was observed in the spectrum, and the methyl groups remain attached to the Al center. In addition, no characteristic signals of the terminal methyl ($COCH_3$) group could be detected. These results



Scheme 2 A plausible mechanism for ROP of ε-CL by **2c** in the absence of BnOH *via* a cationic mechanism.

suggest that the Al–CH_3 groups do not participate in the initiation. Furthermore, no resonances were found to show that the monomer inserted into the Al–diketiminate bond. Thus, we may conclude that an insertion mechanism should be excluded, and the polymerization may operate *via* a cationic mechanism (Scheme 2).[2,19,20] Firstly, the ε-CL is coordinated to the aluminum center of complex **2c** (abbreviated as $LAlMe_2$) to form an intermediate species, then another ε-CL molecule attacks the carbocation of the intermediate species with the cleavage of an alkyl–oxygen bond to yield the initiator containing propagating species. To verify the hypothetical mechanism, the end-group analysis of the oligomers was conducted by MALDI-TOF-MS measurements. The mass spectrum (Fig. S1, ESI†) shows two sets of peak series, and each successive group of peaks exhibits a mass difference of 114 Da, corresponding to the repeating unit of ε-caprolactone. The major set of peaks might probably be assigned to the intramolecular cyclization products of ({CL}*n* + Na) (*e.g.* *n* = 7, *m*/*z* 821.4), and the minor peaks could be attributed to the protonated initiator-terminated oligomers ($nacnac^{t\text{Bu}}AlMe_2\{CL\}_n$ + H) (*e.g.* *n* = 5, *m*/*z* 837.4). When the polymerization was carried out in CH_2Cl_2 instead of toluene, the former solvent possessing a higher polarity has a stronger solvation effect on the monomer than that of toluene, which prevented the monomer from attacking the cationic species (Scheme 2), and resulted in the hindrance of the propagation for the polymerization.

In the presence of BnOH, the end-group analysis of the PCL (entry 3 in Table 3), determined by ^{1}H NMR spectrum, clearly shows the existence of aromatic benzyl protons at 7.36 ppm and the benzyl and hydroxyl methylene signals at 5.12 and 3.65 ppm (Fig. S2, ESI†), which indicates the formation of linear polymers capped with a benzyloxy group at one end and a hydroxyl group at the other. These signal assignments are consistent with those in the reported literature.[8,10a,12a,b] The above results imply that the acyl–oxygen bond cleavage of ε-CL occurred in the ROP reaction *via* either a coordination–insertion or activated monomer mechanism. To explore the mechanism further, the reactions of complex **2c** with BnOH in 1 : 1 and 1 : 4 molar ratio were monitored by ^{1}H NMR in $CDCl_3$ at room temperature. The signal of Al–OBn was not found in both cases. Instead, the resonances for ligand **1c** and unreacted **2c** appeared, which implies that BnOH system was able to decompose the aluminum alkyl complex **2c**. In addition, when the reaction of complex **2c** with BnOH in 1 : 1 molar ratio was carried out in toluene at room temperature for



Scheme 3 A plausible mechanism for ROP of ε-CL by **2c** in the presence of BnOH *via* a monomer-activated mechanism.

1 h, and ε-CL was added to the above reaction mixture at 80 °C, no polymer was isolated. The above results show that the benzyloxyaluminum intermediate was not formed, and a coordination–insertion mechanism is less plausible for the reaction. Alternatively, the polymerization in the presence of BnOH probably follows a monomer-activated mechanism (Scheme 3), which was reported by Thielemans[2] and Nomura.[21] As shown in Scheme 3, coordination of ε-CL to the aluminum initiator affords the intermediate species, which is attacked by BnOH to produce the corresponding linear ester.

Ring-opening polymerization of *rac*-lactide

In the absence of BnOH, complex **2c** was added directly to a solution of *rac*-lactide (*rac*-LA) in toluene at 80 °C with a *rac*-LA/Al ratio of 100 : 1. However no polymer could be isolated after a longer reaction time of more than 3 days. Complexes **2b**, **2d** and **2e** are also inactive in the ROP of *rac*-LA. In the presence of BnOH, when using complex **2c** as the initiator, the polymerization reaction was performed with *rac*-LA/Al/BnOH ratio of 100 : 1 : 1 in toluene at 80 °C, reaching 25% conversion after 48 h, and no further studies were conducted considering the low catalytic activity.

Conclusions

In summary, a series of aliphatic *N*-substituted β-diketiminate ligands (**1a–1f**) and their dialkylaluminum complexes **2a–2h** were synthesized and characterized by NMR and HRMS spectroscopy. The molecular structures of complexes **2a**, **2c** and **2h** were confirmed by X-ray crystallography. These dialkylaluminum complexes are efficient initiators for ring-opening polymerization of ε-caprolactone in the absence and presence of alcohol, affording narrow molecular weight distributions of the obtained polymers. The effect of the ligand substituents in complexes **2a–2h** on the catalytic activities for ROP of ε-CL was also investigated, and complex **2c** shows the highest catalytic activity with good control for the polymerization process among the studied aluminum alkyl complexes.

Experimental section

General procedures

All manipulations were performed under an argon atmosphere using standard Schlenk techniques. $AlMe_3$, $AlEt_3$ and Al^iBu_3 were purchased from Arcos and used as received. Toluene and hexane were distilled from sodium benzophenone ketyl before use. ε-Caprolactone was dried by CaH_2 for 48 h, and then distilled under reduced pressure. *Nacnac*^{R}H (R = CH_3, **1a**; ^{i}Pr, **1b**; ^{t}Bu, **1c**; Bn, **1d**) were prepared according to the published methods.[16] NMR (^{1}H, ^{13}C) spectra were recorded on a Bruker 400 Ultra Shield™ spectrometer. HRMS (EI) spectra determinations were made on a GCT-MS instrument (Micromass, England). ESI-MS spectra determinations were made on a Micromass Q-Tof (Micromass, Wythenshawe, UK) mass spectrometer. Molecular weight and molecular weight distribution (PDI) were determined against a polystyrene standard by gel permeation chromatography (GPC) on a Viscotek TDA302 instrument, and THF was used as an eluent at a flow rate of 1 mL min^{-1} at 30 °C.

Synthesis

***Nacnac*^{tBu}H (1c).** Acetylacetone (5.00 g, 50.00 mmol), *p*-TsOH (0.10 g, 0.50 mmol), and *tert*-butylamine (4.02 g, 55.00 mmol) were combined with toluene (80 mL). The resulting suspension was refluxed for 8 h with the help of Dean–Stark apparatus, and then filtered. The filtrate was dried under vacuum to afford yellow oil, which was dissolved in dried CH_2Cl_2 (60 mL). Triethyloxonium tetrafluoroborate (9.59 g, 50.00 mmol) was added to the resulting CH_2Cl_2 solution and stirred at room temperature for 2 h. Then a second equivalent *tert*-butylamine (4.02 g, 55.00 mmol) was added, and the reaction mixture was stirred at room temperature for another 3 days. Then the reaction solution was dried under vacuum and a yellow solid was obtained, which was dissolved in Et_2O. The aqueous NaOH solution was added to the Et_2O solution and stirred for 1 h. The aqueous phase of the resulting solution was extracted twice with Et_2O. The organic phases were combined and dried over Na_2SO_4. After removal of the volatiles, the residue was purified by column chromatography to give **1c** as a yellow solid. Yield: 7.36 g (70%). Anal. calcd for $C_{13}H_{26}N_2$: C, 74.23; H, 12.46; N, 13.32. Found: C, 74.20; H, 12.44; N, 13.30. ^{1}H NMR (400 MHz, $CDCl_3$): 1.34 (s, 18H, C(C*H*$_3$)$_3$), 1.99 (s, 6H, C*H*$_3$), 4.36 (s, 1H, γ-C*H*), 11.62 (brs, 1H, N-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): 22.0 (C*Me*), 30.8 (C(*C*H$_3$)$_3$), 52.7 (*C*(CH$_3$)$_3$), 96.5 (*C*H), 159.1 (N*C*Me); EI-HRMS: *m*/*z* calcd for [*M*]$^+$: 210.2096; found: 210.2103.

***Nacnac*^{CH_2CH_2Ph}H (1e).** The synthesis of **1e** was carried out by the same procedure as that of **1c**, except that 2-phenylethylamine was used. Yield: 4.10 g (62%). Anal. calcd for $C_{21}H_{26}N_2$: C, 82.31; H, 8.55; N, 9.14. Found: C, 82.30; H, 8.52; N, 9.01. ^{1}H NMR (400 MHz, $CDCl_3$): 1.85 (s, 6H, C*H*$_3$), 2.79 (t, *J* = 7.6 Hz, 4H, C*H*$_2$CH$_2$Ph), 3.46 (t, *J* = 7.6 Hz, 4H, CH$_2$C*H*$_2$Ph), 4.48 (s, 1H, γ-C*H*), 7.18–7.32 (m, 10H, Ar-*H*), 10.99 (brs, 1H, N-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): 19.3 (C*Me*), 37.9 (CH$_2$*C*H$_2$Ph), 48.3 (N*C*H$_2$CH$_2$Ph), 94.9 (*C*H), 126.0 (Ar-*C*), 128.4 (Ar-*C*), 128.9 (Ar-*C*), 140.5 (Ar-*C*), 160.7 (N*C*Me); ESI-HRMS: *m*/*z* calcd for [*M* + H]$^+$: 307.2174; found: 307.2157.

***Nacnac*^{CHPh_2}H (1f).** The synthesis of **1f** was carried out by the same procedure as that of **1c**, except that benzhydrylamine was used. Yield: 2.11 g (60%). Anal. calcd for $C_{31}H_{30}N_2$: C,

86.47; H, 7.02; N 6.51. Found: C, 86.45; H, 7.03; N, 6.50. ^{1}H NMR (400 MHz, $CDCl_3$): 1.92 (s, 6H, CH_3), 4.60 (s, 1H, γ-C*H*), 5.75 (s, 2H, C*H*Ph_2), 7.15–7.26 (m, 20H, Ar-*H*), 12.12 (s, 1H, N-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): 19.9 (C*Me*), 64.6 (*C*HPh_2), 96.3 (*C*H), 126.6 (Ar-*C*), 127.6(Ar-*C*), 128.4 (Ar-*C*), 144.4 (Ar-*C*), 160.2 (N*C*Me); ESI-HRMS: *m*/*z* calcd for $[M + H]^+$: 431.2487; found: 431.2496.

***Nacnac*^{CH_3}AlMe$_2$ (2a).** A solution of $AlMe_3$ (0.8 mL of 1.0 M solution in *n*-hexane, 0.80 mmol) was added dropwise to a solution of **1a** (0.16 g, 0.73 mmol) in *n*-hexane (10 mL) at room temperature with rapid stirring. The resulting solution was stirred overnight and filtered. The filtrate was concentrated to approximately 2 mL and kept at −30 °C for 24 h to give colorless crystals. Single crystals of complex **2a** were obtained by slowly cooling a saturated *n*-hexane solution to −7 °C. Yield: 0.09 g (70%). Anal. calcd for $C_9H_{19}AlN_2$: C, 59.31; H, 10.51; N, 15.37. Found: C, 59.33; H, 10.50; N, 15.38. ^{1}H NMR (400 MHz, $CDCl_3$): −0.90 (s, 6H, AlCH_3), 1.93 (s, 6H, CCH_3), 2.87 (s, 6H, NCH_3), 4.57(s, 1H, γ-C*H*); ^{13}C NMR (100 MHz, $CDCl_3$): −11.3 (Al*C*H_3), 21.2 (C*Me*), 33.8 (N*Me*), 95.1 (*C*H), 168.7 (N*C*Me); EI-HRMS: *m*/*z* calcd for $[M - CH_3]^+$: 167.1129; found: 167.1136.

***Nacnac*^{iPr}AlMe$_2$ (2b).** Complex **2b** was synthesized using the same procedure as that of **2a**, except that **1b** was used. Yield: 0.38 g (72%). Anal. calcd for $C_{13}H_{27}AlN_2$: C, 65.51; H, 11.42; N, 11.75. Found: C, 65.50; H, 11.41; N, 11.72. ^{1}H NMR (400 MHz, $CDCl_3$): −0.75 (s, 6H, AlCH_3), 1.26 (d, *J* = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.99 (s, 6H, CH_3), 3.86 (sept, *J* = 6.8 Hz, 2H, C*H*(CH_3)$_2$), 4.45 (s, 1H, γ-C*H*); ^{13}C NMR (100 MHz, $CDCl_3$): −4.5 (Al*C*H_3), 22.5 (C*Me*), 23.4 (CH(*C*H_3)$_2$), 49.9 (*C*H(CH$_3$)$_2$), 96.5 (*C*H), 165.7 (N*C*Me); EI-HRMS: *m*/*z* calcd for $[M - CH_3]^+$: 223.1755; found: 223.1749.

***Nacnac*^{tBu}AlMe$_2$ (2c).** Complex **2c** was synthesized using the same procedure as that of **2a**, except that **1c** was used. Single crystals of aluminum complex **2c** were obtained by slowly cooling a saturated *n*-hexane solution to 0 °C. Yield: 0.35 g (76%). Anal. calcd for $C_{15}H_{31}AlN_2$: C, 67.63; H, 11.73; N, 10.52. Found: C, 67.64; H, 11.73; N, 10.55. ^{1}H NMR (400 MHz, $CDCl_3$): −0.64 (s, 6H, AlCH_3), 1.47 (s, 18H, C(CH_3)$_3$), 2.14 (s, 6H, CH_3), 4.38 (s, 1H, γ-C*H*); ^{13}C NMR (100 MHz, $CDCl_3$): 0.9 (Al*C*H_3), 26.1 (C*Me*), 32.2 (C(*C*H$_3$)$_3$), 56.3 (*C*(CH$_3$)$_3$), 99.4 (*C*H), 166.8 (N*C*Me); EI-HRMS: *m*/*z* calcd for $[M - CH_3]^+$: 251.2068; found: 251.2055.

***Nacnac*^{CH_2Ph}AlMe$_2$ (2d).** A solution of $AlMe_3$ (2.45 mL of 1 M solution in *n*-hexane, 2.45 mmol) was added dropwise to a solution of β-diketimine **1d** (0.60 g, 2.14 mmol) in toluene (20 mL) at room temperature with rapid stirring. The reaction mixture was stirred for additional 0.5 h and then filtered. The filtrate was dried under vacuum, and the residue was dissolved with 10 mL *n*-hexane. The resulting solution was concentrated and kept at −30 °C for 24 h to give pale yellow crystals. Yield: 0.61 g (85%). Anal. calcd for $C_{21}H_{27}AlN_2$: C, 75.42; H, 8.14; N, 8.38. Found: C, 75.45; H, 8.14; N, 8.37. ^{1}H NMR (400 MHz, $CDCl_3$): −0.98 (s, 6H, AlCH_3), 1.90 (s, 6H, CH_3), 4.55 (s, 4H, CH_2Ph), 4.71 (s, 1H, γ-C*H*), 7.21–7.34 (m, 10H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): −9.9 (Al*C*H_3), 22.0 (C*Me*), 50.7 (*C*H$_2$Ph), 97.1(γ-*C*H), 126.7 (Ar-*C*), 126.8 (Ar-*C*), 128.6 (Ar-*C*), 139.8 (Ar-*C*), 170.0 (N*C*Me); EI-HRMS: *m*/*z* calcd for $[M - CH_3]^+$: 319.1755; found: 319.1750.

***Nacnac*^{CH_2CH_2Ph}AlMe$_2$ (2e).** Complex **2e** was synthesized using the same procedure as that of **2a**, except that **1e** was used. Yield: 0.12 g (73%). Anal. calcd for $C_{23}H_{31}AlN_2$: C, 76.21; H, 8.62; N, 7.73. Found: C, 76.24; H, 8.66; N, 7.72. ^{1}H NMR (400 MHz, $CDCl_3$): −0.74 (s, 6H, AlCH_3), 1.98 (s, 6H, CH_3), 2.81 (m, 4H, CH_2CH$_2$Ph), 3.46 (m, 4H, CH$_2$CH_2Ph), 4.57 (s, 1H, γ-C*H*), 7.21–7.33 (m, 10H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): −9.4 (Al*C*H_3), 20.8 (C*Me*), 37.9 (CH$_2$*C*H$_2$Ph), 49.5 (N*C*H$_2$*C*H$_2$Ph), 96.5 (*C*H), 126.4 (Ar-*C*), 128.6 (Ar-*C*), 128.7 (Ar-*C*), 139.4 (Ar-*C*), 167.7 (N*C*Me); EI-HRMS: *m*/*z* calcd for $[M - CH_3]^+$: 347.2068; found: 347.2064.

***Nacnac*^{CHPh_2}AlMe$_2$ (2f).** A solution of $AlMe_3$ (0.56 mL of 1.0 M solution in *n*-hexane, 0.56 mmol) was added dropwise to a solution of β-diketimine **1f** (0.22 g, 0.51 mmol) in toluene (5 mL) at room temperature with rapid stirring. The reaction mixture was stirred overnight and then filtered. The filtrate was dried under vacuum, and the residue was recrystallized with *n*-hexane/toluene. **2f** deposited after 24 h at −30 °C as pale yellow crystals. Yield: 0.15 g (61%). Anal. calcd for $C_{33}H_{35}AlN_2$: C, 81.45; H, 7.25; N, 5.76. Found: C, 81.43; H, 7.24; N, 5.72. ^{1}H NMR (400 MHz, $CDCl_3$): −1.48 (s, 6H, AlCH_3), 1.94 (s, 6H, CH_3), 4.81 (s, 1H, γ-C*H*), 6.17 (s, 2H, C*H*Ph_2), 7.21–7.32 (m, 20H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): −8.3 (Al*C*H_3), 24.5 (C*Me*), 65.6 (*C*HPh_2), 99.7 (*C*H), 127.1 (Ar-*C*), 128.2 (Ar-*C*), 129.2 (Ar-*C*), 141.2 (Ar-*C*), 169.1 (N*C*Me); EI-HRMS: *m*/*z* calcd for $[M - CH_3]^+$: 471.2381; found: 471.2401.

***Nacnac*^{tBu}AlEt$_2$ (2g).** A solution of $AlEt_3$ (1.20 mL of 2.2 M solution in *n*-hexane, 2.64 mmol) was added dropwise to a solution of β-diketimine **1c** (0.49 g, 2.30 mmol) in toluene (15 mL) at room temperature with rapid stirring. The reaction mixture was stirred overnight and then filtered. The filtrate was dried under vacuum, and the residue was recrystallized with *n*-hexane. **2g** deposited after 24 h at −30 °C as yellow crystals. Yield: 0.35 g (52%). Anal. calcd for $C_{17}H_{35}AlN_2$: C, 69.34; H, 11.98; N, 9.51. Found: C, 69.36; H, 11.94; N, 9.52. ^{1}H NMR (400 MHz, $CDCl_3$): −0.14 (q, *J* = 8 Hz, 4H, AlCH_2CH$_3$), 0.92 (t, *J* = 8 Hz, 6H, AlCH$_2$CH_3), 1.41 (s, 18H, C(CH_3)$_3$), 2.07 (s, 6H, CH_3), 4.31 (s, 1H, γ-C*H*); ^{13}C NMR (100 MHz, $CDCl_3$): 9.0 (Al*C*H$_2$CH$_3$), 9.1 (AlCH$_2$*C*H$_3$), 26.05 (C*Me*), 32.20(C(*C*H$_3$)$_3$), 56.22 (*C*(CH$_3$)$_3$), 99.73 (*C*H), 166.98 (N*C*Me); EI-HRMS: *m*/*z* calcd for $[M - CH_3]^+$: 265.2224; found: 265.2231.

***Nacnac*^{tBu}Al^{i}Bu$_2$ (2h).** A solution of Al^{i}Bu$_3$ (2.90 mL of 1.1 M solution in toluene, 3.19 mmol) was added dropwise to a solution of β-diketimine **1c** (0.61 g, 2.90 mmol) in *n*-hexane (12 mL) at room temperature with rapid stirring. The reaction mixture was stirred overnight and filtered. After the filtrate was dried under vacuum, the residue was recrystallized with *n*-hexane. **2h** deposited after 24 h at −30 °C as colorless crystals. Single crystals of complex **2h** were obtained by slowly cooling a saturated *n*-hexane solution to −7 °C. Yield: 0.75 g (74%). Anal. calcd for $C_{21}H_{43}AlN_2$: C, 71.95; H, 12.36; N, 7.99. Found: C, 71.96; H, 12.34; N, 8.02. ^{1}H NMR (400 MHz, $CDCl_3$): 0.01(d, *J* = 8 Hz, 4H, AlCH_2), 0.88 (d, *J* = 8 Hz, 12H, AlCH$_2$CH(CH_3)$_2$), 1.50 (s, 18H, C(CH_3)$_3$), 1.81 (sept, *J* = 8 Hz, 2H,

Table 4 Crystal data and structure refinement details for **2a**, **2c** and **2h**

	2a	2c	2h
Empirical formula	$C_9H_{19}AlN_2$	$C_{15}H_{31}AlN_2$	$C_{21}H_{43}AlN_2$
Formula weight	182.24	266.40	350.55
Crystal size/mm	0.32 × 0.30 × 0.28	0.60 × 0.22 × 0.18	0.32 × 0.26 × 0.11
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	*Pmmn*	*Fdd*2	$P2_1/c$
a/Å	9.126(7)	17.867(3)	9.8557(5)
b/Å	7.598(6)	23.885(4)	25.6952(13)
c/Å	8.267(6)	8.1825(12)	9.2957(4)
α/°	90.00	90.00	90.00
β/°	90.00	90.00	102.639(3)
γ/°	90.00	90.00	90.00
V/Å^3	573.2(8)	3491.9(9)	2297.04(19)
Z	2	8	4
D_{calcd}/Mg m^{-3}	1.056	1.013	1.014
μ/mm^{-1}	0.134	0.105	0.093
F(000)	200	1184	784
θ range for data collection/°	2.46 to 24.99	2.85 to 25.00	2.12 to 25.00
Limiting indices	$-10 \le h \le 10$ $-9 \le k \le 5$ $-9 \le l \le 9$	$-20 \le h \le 21$ $-21 \le k \le 28$ $-9 \le l \le 9$	$-11 \le h \le 11$ $-29 \le k \le 30$ $-11 \le l \le 11$
Reflns collected/unique	3094/581 [*R*(int) = 0.0252]	4727/1506 [*R*(int) = 0.0203]	14693/4031 [*R*(int) = 0.0297]
Data/restrains/parameters	581/0/54	1506/7/88	4031/11/220
Goodness-of-fit on F^2	1.000	1.076	1.000
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0360, wR_2 = 0.0809	R_1 = 0.0365, wR_2 = 0.0982	R_1 = 0.0472, wR_2 = 0.1348
R Indices (all data)	R_1 = 0.0387, wR_2 = 0.0818	R_1 = 0.0390, wR_2 = 0.1009	R_1 = 0.0621, wR_2 = 0.1435
Largest diff. peak and hole/e Å^{-3}	0.212 and −0.130	0.131 and −0.129	0.228 and −0.175

$AlCH_2CH(CH_3)_2$), 2.13 (s, 6H, CH_3), 4.36 (s, 1H, γ-C*H*); ^{13}C NMR (100 MHz, $CDCl_3$): 26.5 ($AlCH_2CH(CH_3)_2$), 27.1 ($AlCH_2CH(CH_3)_2$), 28.3 (CH_3), 31.4 ($AlCH_2CH(CH_3)_2$), 32.5 ($C(CH_3)_3$), 56.4 ($C(CH_3)_3$), 99.1 (*C*H), 167.0 (N*C*Me); EI-HRMS: *m*/*z* calcd for $[M - CH_3]^+$: 293.2537; found: 293.2543.

The ROP of ε-CL

Typical polymerization procedures in the absence of benzyl alcohol are as follows: a toluene (5 mL) solution of initiator (0.05 mmol) was added into a Schlenk tube under an argon atmosphere. The solution was stirred for 5 min at 80 °C, and then ε-caprolactone (0.57 g, 5.00 mmol) was added to the solution. After stirring for the prescribed time, the reaction mixture was withdrawn at appropriate time intervals under the protection of argon and quenched with methanol. After removal of the volatiles, the residue was subjected to ^{1}H NMR analysis. Monomer conversion was determined by observing the integration of monomer *vs.* polymer methylene resonance in the ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum. The polymer was purified by dissolving the crude samples in CH_2Cl_2 and precipitating into methanol. The obtained polymers were dried to a constant weight, and the dry polymer samples were analyzed by GPC.

Typical polymerization procedures in the presence of benzyl alcohol are as follows: a solution of complex **2c** (1.33 mL of 10 mg mL^{-1} in toluene, 0.05 mmol) and a solution of BnOH (0.54 mL of 10 mg mL^{-1} in toluene, 0.05 mmol) were mixed into a Schlenk tube, and another portion of toluene (3.13 mL) was added into the mixture, and then ε-caprolactone (0.57 g, 5.00 mmol) was added to the mixture solution. After stirring for the prescribed time, the reaction was quenched with methanol at 0 °C. The measurements for the monomer conversions, molecular weights and PDI values are the same as those in the absence of benzyl alcohol.

X-ray diffraction measurements

The crystallographic data for complexes **2a**, **2c** and **2h** were collected on a Bruker SMART APEX CCD diffractometer at 298 K with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Empirical absorption corrections were performed using the SADABS program.[22] Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2 using SHELX97.[23] All of the non-hydrogen atoms were refined with anisotropic thermal displacement coefficients. Hydrogen atoms were fitted geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms with the isotropic displacement being fixed at 1.2 and 1.5 times the aromatic and methyl carbon atoms that attached respectively. To help the refinement, the bump restraint was applied on the solvent molecules with a value of 0.02. Crystallographic data, results of structure refinements are summarized in Table 4.

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