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# Aluminium metal complexes supported by amine bis-phenolate ligands as catalysts for ring-opening polymerization of ε-caprolactone

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A family of aluminium complexes supported by dianionic amine bis(phenolate) ligands are described. Treatment of ligand precursors $H_2O_2NN^{Py}$ or $H_2O_2NN^{Me}$ [$H_2O_2NN^{Py}$ = $(2\text{-}C_5H_4N)CH_2N(CH_2\text{-}2\text{-}HO\text{-}3,5\text{-}C_6H_2(^tBu)_2)_2$; $H_2O_2NN^{Me}$ = $Me_2NCH_2CH_2N(CH_2\text{-}2\text{-}HO\text{-}3,5\text{-}C_6H_2(^tBu)_2)_2$] with 1.1 molar equivalent of $AlMe_3$ in toluene affords $MeAl(O_2NN^{Py})$ (**1**) and $MeAl(O_2NN^{Me})$ (**2**) as five-coordinate aluminium methyl complexes, which further react with one equivalent of benzyl alcohol affording $(C_6H_5CH_2O)Al(O_2NN^{Py})$ (**3**) and $(C_6H_5CH_2O)Al(O_2NN^{Me})$ (**4**) as five-coordinate aluminium benzyloxy complexes. The molecular structures are reported for compounds **1** and **4**. Compounds **3** and **4** show excellent catalytic activity toward the ring-opening polymerization of ε-caprolactone.

## Introduction

Poly(ε-caprolactone) (PCL), poly(lactide) (PLA) as well as their co-polymers are the most important synthetic biodegradable polymers, and have attracted considerable attention mainly due to their biomedical and pharmaceutical applications.[1] One of the promising methodologies for the syntheses of those polymers is the ring-opening polymerisation employed the metal alkoxides as initiators. Some excellent initiators or catalysts have been reported, and many afford materials with narrow molecular weight distribution and high yield.[2–7] Aluminium alkoxide based system seems to be active and suitable in preparing the well-defined polyesters due to their high Lewis acidity and low toxicity.[2–6] The "living" and "immortal" properties exhibited by bis(phenolate)aluminiumalkoxides in ring-opening polymerisation reaction also encourage researcher to develop novel bulky (phenolate)aluminiumalkoxides, which are expected to yield polymers with a narrow molecular weight distribution.[4–6]

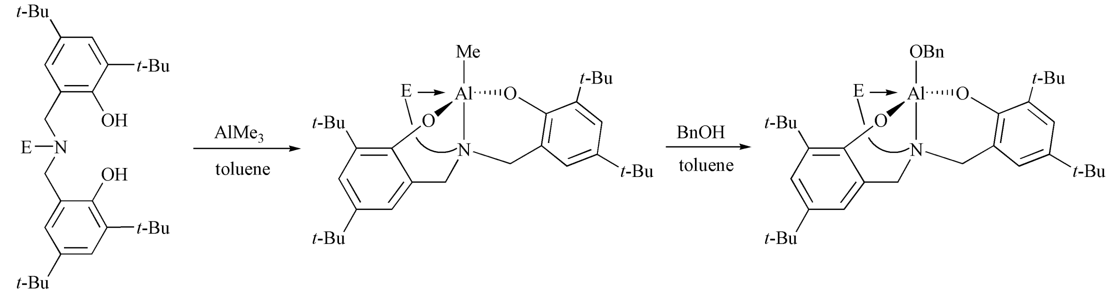
Amine bis(phenolate) ligand precursors are known for several decades, and can be easily prepared by a modified Mannich reaction.[8] Recently their application in syntheses of metal complexes have been reported by the groups of Ng,[9] Yamauchi,[10] Kol and Goldschmidt,[11–13] and Mountford.[14,15] Once the pendant functionality formed, the amine bis(phenolate) ligand precursors have the potential to create a bowl-shaped environment around the metal center and to prevent complexes from dimerisation. Some catalytic chemistry of group 4 complexes with pendant amine bis(phenolate) ligand has been explored.[11–13] The application of amine bis(phenolate) aluminium complexes in ring-opening polymerisation, on our knowledge, has not been reported.

In this paper, we report several aluminium complexes supported by the bulky amine bis(phenolate) ligands. The catalytic activities of aluminiumalkoxide complexes toward ring-opening polymerisation of ε-caprolactone are also presented.

## Results and discussion

### Syntheses and characterization of aluminum amine bis(phenolate)s

Treatment of ligand precursors $H_2O_2NN^{Py}$ or $H_2O_2NN^{Me}$ [$H_2O_2NN^{Py}$ = $(2\text{-}C_5H_4N)CH_2N(CH_2\text{-}2\text{-}HO\text{-}3,5\text{-}C_6H_2(^tBu)_2)_2$; $H_2O_2NN^{Me}$ = $Me_2NCH_2CH_2N(CH_2\text{-}2\text{-}HO\text{-}3,5\text{-}C_6H_2(^tBu)_2)_2$] with 1.1 molar equivalent of $AlMe_3$ in toluene produces $MeAl(O_2NN^{Py})$ (**1**) and $MeAl(O_2NN^{Me})$ (**2**), as shown in Scheme 1. Further reactions of **1** or **2** with one equivalent of benzyl alcohol afford $(C_6H_5CH_2O)Al(O_2NN^{Py})$ (**3**) and $(C_6H_5CH_2O)Al(O_2NN^{Me})$ (**4**), respectively. All of those compounds were isolated as colorless crystalline solids and were characterized by spectroscopic studies as well as microanalyses. $^1H$ and $^{13}C\{^1H\}$ NMR spectra of **1** and **3** are indicative of a highly symmetric species in solution, with a conformational flexibility of the N–C*H*$_2$-aryl moiety due to two broadened signals corresponding to the methylene protons of N–C*H*$_2$-aryl found around 3.4–3.9 ppm. Those resonances commence to split into several broadened signals (253 K) and then resharpen as six doublets along with two sets of split signals corresponding to the *tert*-butyl protons and two sets of split signals



$H_2O_2NN^{Py}$ E= $CH_2Py$
$H_2O_2NN^{Me}$ E= $CH_2CH_2NMe_2$

**1:** E= $CH_2Py$
**2:** E= $CH_2CH_2NMe_2$

**3:** E= $CH_2Py$
**4:** E= $CH_2CH_2NMe_2$

**Scheme 1**

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

| | | | |
|---|---|---|---|
| Al–O(1) | 1.7516(15) | Al–O(2) | 1.7573(14) |
| Al–N(1) | 2.2150(16) | Al–N(2) | 2.0570(18) |
| Al–C(37) | 1.981(2) | | |
| O(1)–Al–O(2) | 124.22(8) | O(1)–Al–N(2) | 116.53(7) |
| O(2)–Al–N(2) | 114.58(8) | C(37)–Al–N(1) | 172.99(9) |

**Table 2** Selected bond lengths (Å) and angles (°) for **4**

| | | | |
|---|---|---|---|
| Al–O(1) | 1.748(3) | Al–O(2) | 1.768(3) |
| Al–O(3) | 1.743(3) | Al–N(1) | 2.186(4) |
| Al–N(2) | 2.096(4) | | |
| O(1)–Al–O(2) | 124.44(16) | O(1)–Al–N(2) | 116.96(16) |
| O(2)–Al–N(2) | 116.81(16) | O(3)–Al–N(1) | 166.37(16) |

corresponding to the phenoxide protons upon cooling both samples in toluene-$d_8$ to 223 K. Suitable crystals of **1** for structural determination were obtained from toluene/hexane solution. The molecular structure is shown in Fig. 1, and selected bond lengths and angles are listed in Table 1. The structure confirms a symmetric and monomeric structure with penta-coordinated aluminium center, including two six-membered amine-phenolate metalla-rings and one amine-pendant functionality metalla-ring. The central Al atom adopts distorted trigonal bipyramidal geometry with distorted axes, C37–Al–N1 (172.99(9)°). The O1, O2 and N2 atoms reside equatorially, forming angles subtended by aluminium of ~120°. The Al–O bond lengths (1.7516(15) and 1.7573(14) Å) for the chelate are between those (1.692(1)–1.738(2) Å) for aluminium bridged-phenoxide and those (1.754(3)–1.854(2) Å) for aluminium phenoxide.[5,6] The Al–C bond length (1.981(2) Å) is slightly longer than those (1.936(4)–1.966(5) Å) found in a four-coordinated aluminium bridged-phenoxide,[5,6] but compatible with those (1.975(2)–1.982(3) Å) found in a five-coordinated aluminium phenoxide.[16] The Al–N bond length (2.0570(18) Å) of the pendant arm is shorter than those observed in a pendant benzamidinate aluminium complex (2.218(6) Å)[17] and a pendant imino-alkoxide aluminium complex (2.254(2) Å).[16] The Al–N bond length (2.2150(16) Å) of the amine donor is between that (2.011(4) Å) for four-coordinated and those (2.245(4) and 2.265(4) Å) for five-coordinated pendant triazacyclononanate aluminium.[18] $^1$H NMR spectroscopy of **2** in $CD_2Cl_2$ showed two doublets, at $\delta$ 3.59 and 3.76 ppm, which can be assigned to the two diastereotopic methylene protons of N–C$H_2$-aryl groups. However, these signals in **4** are broader than those in **2**, indicating a higher conformational flexibility of the two six-membered amine-phenolate metalla-rings in **4**. A suitable crystal of **4** for structural determination was grown from toluene–hexane solution. The molecular structure is shown in Fig. 2, and selected bond lengths and angles are listed in Table 2. Basically, the chelate of compound **4** is quite similar to compound **1** except for datively bonded $CH_2NMe_2$ instead of $C_5H_4N$ for **1**. The central Al atom adopts distorted trigonal bipyramidal geometry to form a five-coordinate aluminium complex. Bond lengths of Al–O$_{phenoxide}$ and Al–N$_{amine}$ and the bond angles around the central Al atom are similar to those discussed above. The Al–N bond length (2.096(4) Å) of the pendant arm is compatible with that (2.0929(16) Å)[19] observed in a pendant benzamidinate aluminium complex but shorter than that (2.413(5) Å)[16] observed in a pendant imino-alkoxide aluminium complex. The Al–O bond length (1.743(3) Å) of benzyl alkoxide is compatible with bond lengths of Al–O$_{phenoxide}$ (1.748(3)–1.768(3) Å) observed in compounds **1** and **4**. Severe disorder is found for the carbon atoms on the benzyl moiety of the benzyloxy group.

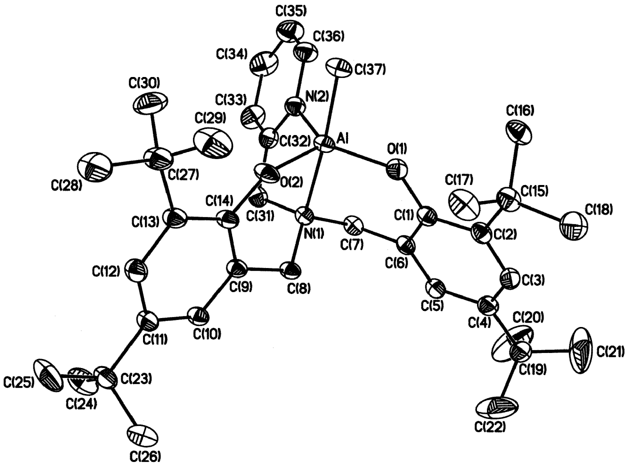


**Fig. 1** Molecular structure of MeAl(O$_2$NN$^{Py}$) (**1**). Hydrogen atoms on carbon atoms are omitted for clarity.

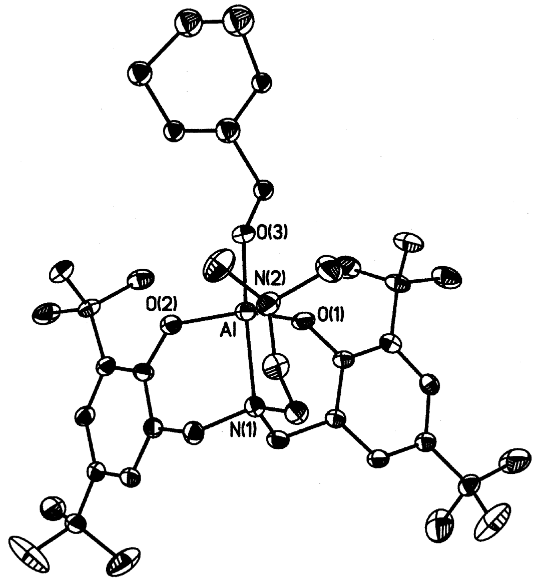


**Fig. 2** Molecular structure of ($C_6H_5CH_2O$)Al(O$_2$NN$^{Me}$) (**4**). Hydrogen atoms on carbon atoms are omitted for clarity. Only the major part of the disorder is shown.

### Ring-opening polymerisation of ε-caprolactone initiated by 3 and 4

Since several aluminium bridged-phenoxides derivatives have demonstrated efficient catalytic activities toward the ROP of lactones,[4–6] the benzyloxy derivatives **3** and **4** were expected to work as initiators toward the ROP of ε-caprolactone. In general, polymerization reactions were carried out in toluene (30 ml) at 50 °C with prescribed equivalent ratios of the initiators (0.25 mmol), monomers and benzyl alcohol for the prescribed time. After the reaction was quenched with an excess aqueous acetic acid solution, the polymer was precipitated in *n*-heptane. The results of the polymerization of ε-CL initiated by **3** and **4** under different reaction conditions are summarized in Table 3. As judged by the low molecular weight distribution values of polyesters (1.02–1.07), both five-coordinated aluminium complexes **3** and **4** behave in a controlled manner. The linear relationship between the number-average molecular weight ($M_n$) and the monomer-to-initiator ratio ($[M]_0/[I]_0$), as shown in Fig. 3 (entries 1–5) and Fig. 4 (entries 9–13), implies the 'living' character of the polymerization process. This was further confirmed by the resumption experiment (entries 8 and 17), which was performed by the addition of another portion of ε-CL monomer after the polymerization of the first addition had gone to completion. The molecular weight increases from the first polymer ($M_n$ = 8770 for **3**; 11700 for **4**) to the final polymer ($M_n$ = 20300 for **3**; 21600 for **4**). The 'immortal' character of **3** and **4** is also investigated using benzyl alcohol as the chain transfer agent (entries 6

**Table 3** Ring-opening polymerization of ε-caprolactone initiated by complexes **3** and **4** at 50 °C

| Entry | Initiator | [M] : [Al] : [BnOH] | Time/h | $M_n$ (obs.)[a] | $M_n$ (calc.)[b] | $M_n$ (NMR)[c] | Conv.[c] (%) | Yield[d] (%) | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | **3** | 25 : 1 : 0 | 2 | 4970 | 2840 | 2780 | 96 | 57 | 1.07 |
| 2 | **3** | 50 : 1 : 0 | 2 | 8770 | 5510 | 5660 | 95 | 67 | 1.05 |
| 3 | **3** | 75 : 1 : 0 | 3 | 14600 | 8260 | 10200 | 95 | 84 | 1.04 |
| 4 | **3** | 100 : 1 : 0 | 3 | 16900 | 10800 | 10900 | 93 | 88 | 1.04 |
| 5 | **3** | 150 : 1 : 0 | 6 | 30000 | 16900 | 18500 | 98 | 81 | 1.05 |
| 6 | **3** | 100 : 1 : 1 | 4 | 9270 | 5470 | 4920 | 94 | 90 | 1.05 |
| 7 | **3** | 150 : 1 : 2 | 18.5 | 8600 | 5300 | 6700 | 90 | 67 | 1.05 |
| 8 | **3** | 50 (50) : 1 : 0 | 2 (2) | 20300 | 10600 | 11900 | 93 (92) | 80 | 1.04 |
| 9 | **4** | 25 : 1 : 0 | 0.25 | 5300 | 2690 | 2780 | 90 | 28 | 1.06 |
| 10 | **4** | 50 : 1 : 0 | 0.50 | 11700 | 5710 | 6290 | 98 | 86 | 1.04 |
| 11 | **4** | 75 : 1 : 0 | 1 | 18900 | 8600 | 8400 | 99 | 83 | 1.03 |
| 12 | **4** | 100 : 1 : 0 | 1 | 20000 | 11100 | 12000 | 96 | 82 | 1.02 |
| 13 | **4** | 150 : 1 : 0 | 3 | 37400 | 16900 | 17600 | 98 | 87 | 1.07 |
| 14 | **4** | 100 : 1 : 1 | 0.5 | 10800 | 5600 | 8000 | 96 | 86 | 1.04 |
| 15 | **4** | 150 : 1 : 2 | 7 | 9700 | 5500 | 6500 | 95 | 92 | 1.04 |
| 16 | **4** | 200 : 1 : 3 | 14 | 10100 | 5700 | 5500 | 99 | 96 | 1.04 |
| 17 | **4** | 50 (50) : 1 : 0 | 0.5 (0.5) | 21600 | 11000 | 15400 | 99 (95) | 85 | 1.04 |

[a] Obtained from GPC analysis. [b] Calculated from [$M$(lactone) × $[M]_0/[Al]_0$ × conversion yield/([ROH] + 1)] +$M$(BnOH). [c] Obtained from $^1H$ NMR analysis. [d] Isolated yield.

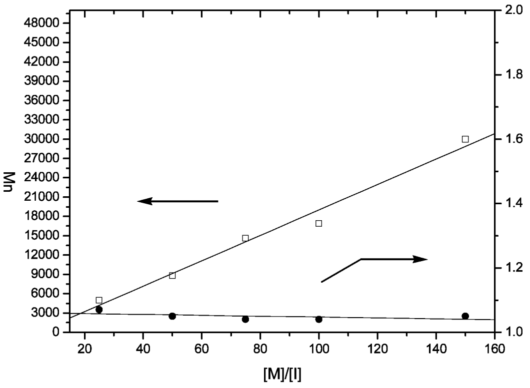


**Fig. 3** Polymerization of ε-CL initiated by **3** in toluene at 50 °C.

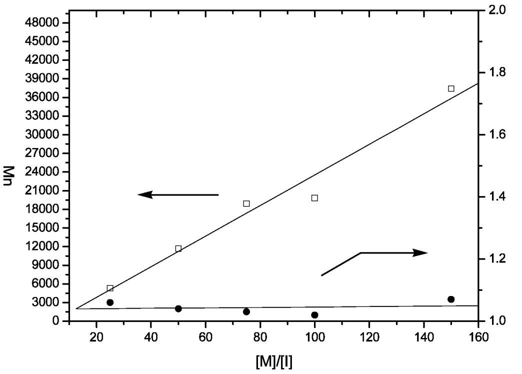


**Fig. 4** Polymerization of ε-CL initiated by **4** in toluene at 50 °C.

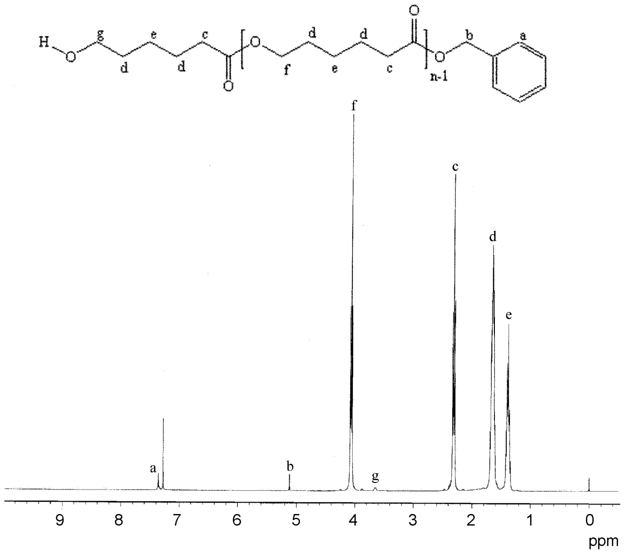


**Fig. 5** $^1H$ NMR spectrum of PCL-50 initiated by **4** in $CDCl_3$.

and 14). The $M_n$ of the polymer in each case became half of that found in the reaction without addition of one equivalent of benzyl alcohol. This character can be further confirmed by using different [M] : [Al] : [BnOH] ratios in each case (entries 7 and 15–16).

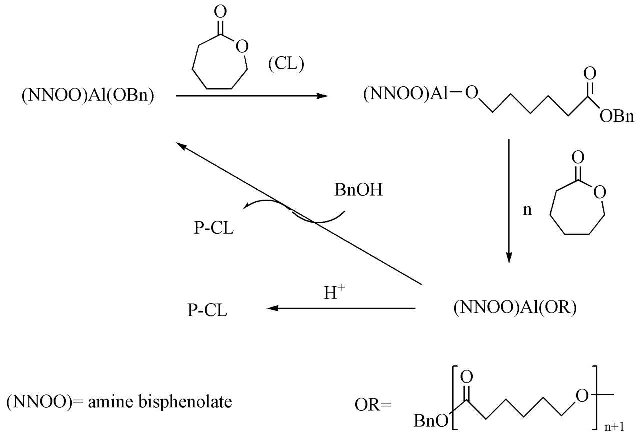
For the end group analysis, a polymer produced from ε-CL and **4** ($[M]_0/[I]_0$ = 50) was purified from THF–hexane, and subjected to $^1H$ NMR spectroscopy. As shown in Fig. 5, peaks are assignable to repeating $-C(O)(CH_2)_5O-$ units (c–f) and terminals $PhCH_2O$(a), $PhCH_2O$(b), and $HOCH_2$(g), respectively. The intensity ratio between $H_b$ ($CH_2$ from PCL at the benzyl alkoxy chain end) and $H_g$ ($CH_2$ from PCL at the hydroxy end) is close to 1, indicating the ring cleavage of a lactone occurs between the acyl-oxygen bond to form an aluminium alkoxide intermediate, which further reacts with excess lactones to form polyesters. On the basis of these results and by analogy with the mechanisms accepted for the ROP of cyclic esters mediated with metal alkoxides,[4,5,20,21] the first step is a coordination of the monomer to the metal center to form the monomeric adduct, followed by the attack of the activated OBn ligand to the carbonyl carbon of the coordinated monomer to cleave the acyl-oxygen bond and to form the Al-alkoxo polymer end. Continuous coordination and insertion of the monomer yields linear polymer. Polyesters can be released by the addition of benzyl alcohol or acidic solution, as shown in Scheme 2.

## Conclusion

A family of monomeric five-coordinate aluminium complexes supported by dianionic amine bis(phenolate) ligands have been prepared and fully characterized. Complexes **3** and **4** were found to catalyze the polymerization of ε-caprolactone with very narrow PDIs. They also exhibit both 'living' and 'immortal' characters. Fine-tuning of the ligands and further application to the polymerization of other monomers are currently being undertaken.

## Experimental

All manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk-line or drybox techniques. Solvents were refluxed over the appropriate drying agent and



**Scheme 2**

distilled prior to use. Deuterated solvents were dried over molecular sieves.

$^1$H and $^{13}$C{$^1$H} NMR spectra were recorded either on a Varian Mercury-400 (400 MHz) or a Varian Inova-600 (600 MHz) spectrometers in chloroform-d at ambient temperature unless stated otherwise and referenced internally to the residual solvent peak and reported as parts per million relative to tetramethylsilane. Elemental analyses were performed by a Heraeus CHN-O-RAPID instrument. The GPC measurements were performed on a Hitachi L-7100 system equipped with a differential Bischoff 8120 RI detector using THF (HPLC grade) as eluent. Molecular weights and molecular weight distributions were calculated using polystyrene as standard.

Benzyl alcohol and ε-caprolactone were purified before use. $AlMe_3$ (2 M in toluene, Acros) was used as supplied. The compounds $H_2O_2NN^{Py}$ and $H_2O_2NN^{Me}$ were prepared according to previously reported procedures.[12]

### Preparations

**$MeAl(O_2NN^{Py})$ (1).** To a solution of $H_2O_2NN^{Py}$ (4.4 g, 8 mmol) in 50 ml toluene, 4.4 ml $AlMe_3$ (2 M, 8.8 mmol) was added dropwise at room temperature. After 20 hours of stirring, the reaction mixture was filtered. All the volatiles were removed under reduced pressure, and the residue was washed with 25 ml hexane to afford a white powder. Yield, 4.2 g, 89%. $^1$H NMR (600 MHz): $\delta$ −0.40 (s, Al–$CH_3$, 3H), 1.26 (s, $C(CH_3)_3$, 18H), 1.38 (s, $C(CH_3)_3$, 18H), 3.60–3.90 (br, Ar$CH_2$, 6H), 6.80 (d, CH-phenoxide, 2H, $J$ = 2.4 Hz), 7.20 (d, CH-phenoxide, 2H, $J$ = 2.4 Hz), 7.35 (d, CH-Py, 1H, $J$ = 8 Hz), 7.49 (m, CH-Py, 1H), 7.95 (m, CH-Py, 1H), 8.98 (d, CH-Py, 1H, $J$ = 5.2 Hz). $^{13}$C{$^1$H} NMR (150 MHz): $\delta$ −5.8 (s, Al–$CH_3$), 29.3, 31.8 (s, $C(CH_3)_3$), 34.0, 34.9 (s, $C(CH_3)_3$), 56.7 (s, $CH_2$Py or N($CH_2$)Ph), 59.7 (br, $CH_2$Py or N($CH_2$)Ph), 123.4, 123.6 (s, Ph), 123.6, 124.2, 141.6, 149.8 (s, Py), 120.6, 137.9, 138.1, 155.9, 156.7 (s, *tert*-C). Anal. Calc. for $C_{37}H_{53}AlN_2O_2$: C, 76.0; H, 9.1; N, 4.8. Found: C, 75.4; H, 9.3; N, 5.2%.

**$MeAl(O_2NN^{Me})$ (2).** To a solution of $H_2O_2NN^{Me}$ (2.62 g, 5 mmol) in 35 ml toluene, 2.8 ml $AlMe_3$ (2 M, 5.5 mmol) was added dropwise at room temperature. After 11 hours of stirring, the reaction mixture was filtered. All the volatiles were removed under reduced pressure, and the residue was washed with 15 ml hexane to afford a white powder. Yield, 2.2 g, 79%. $^1$H NMR (600 MHz, $CD_2Cl_2$): $\delta$ −0.60 (s, Al–$CH_3$, 3H), 1.28 (s, $C(CH_3)_3$, 18H), 1.41 (s, $C(CH_3)_3$, 18H), 2.46 (s, $NMe_2$, 6H), 2.73 (t, $CH_2$, 2H, $J$ = 6.0 Hz), 2.88 (t, $CH_2$, 2H, $J$ = 6.0 Hz), 3.59 (d, $CH_2$, 2H, $J$ = 12.6 Hz), 3.76 (d, $CH_2$, 2H, $J$ = 12.6 Hz), 6.87 (d, CH-phenoxide, 2H, $J$ = 2.4 Hz), 7.23 (d, CH-phenoxide, 2H, $J$ = 2.4 Hz). $^{13}$C{$^1$H} NMR (150 MHz, $CD_2Cl_2$): $\delta$ −8.4 (s, Al–$CH_3$), 29.4, 31.7 (s, $C(CH_3)_3$), 34.1, 35.0 (s, $C(CH_3)_3$), 47.3 (s, NMe), 50.0, 55.3 (s, $(CH_2)_2$), 58.7 (s, N($CH_2$)Ph), 123.9, 124.0 (s, Ph), 121.4, 137.8, 138.9, 155.6 (s, *tert*-C). Anal. Calc. for $C_{35}H_{57}AlN_2O_2$: C, 74.4; H, 10.2; N, 5.0. Found: C, 73.8; H, 10.3; N, 5.0%.

**$(C_6H_5CH_2O)Al(O_2NN^{Py})$ (3).** A mixture containing **1** (2.3 g, 4 mmol) and 0.42 ml benzyl alcohol (0.44 g, 4 mmol) in 40 ml toluene was stirred at room temperature for 2 hours. All the volatiles were removed under reduced pressure, and the residue was washed with 10 ml hexane to yield a white powder. Yield, 2.35 g, 87%. $^1$H NMR (600 MHz): $\delta$ 1.32 (s, $C(CH_3)_3$, 18H), 1.47 (s, $C(CH_3)_3$, 18H), 3.78–3.86 (br, Ar$CH_2$, 6H), 5.45 (s, Ph$CH_2$O, 2H), 6.88 (d, CH-phenoxide, 2H, $J$ = 1.8 Hz), 7.25 (t, *p*-$C_6H_5$, 1H, $J$ = 7.2 Hz), 7.29 (d, CH-phenoxide, 2H, $J$ = 1.8 Hz), 7.35 (d, CH-Py, 1H, $J$ = 7.8 Hz), 7.39 (m, *m*-$C_6H_5$, 2H $J$ = 7.2 Hz), 7.43 (t, CH-Py, 1H, $J$ = 7.2 Hz), 7.63 (d, *o*-$C_6H_5$, 2H, $J$ = 6.0 Hz), 7.92 (m, CH-Py, 1H), 9.86 (d, CH-Py, 1H, $J$ = 6.0 Hz). $^{13}$C{$^1$H} NMR (150 MHz): $\delta$ 29.5, 31.7 (s, $C(CH_3)_3$), 34.0, 35.0 (s, $C(CH_3)_3$), 56.7 (s, $CH_2$Py or N($CH_2$)-Ph), 59.5 (br, $CH_2$Py or N($CH_2$)Ph), 65.6 (s, Ph$CH_2$O), 123.6, 123.9 (s, Ph), 123.1, 124.2, 141.8, 152.8 (s, Py), 125.3, 126.6, 127.7 (s, *o,m,p*-$C_6H_5CH_2O$), 120.6, 138.1, 138.5, 147.7, 155.9, 156.1 (s, *tert*-C). Anal. Calc. for $C_{43}H_{57}AlN_2O_3$: C, 76.3; H, 8.5; N, 4.1. Found: C, 76.5; H, 8.8; N, 4.6%.

**$(C_6H_5CH_2O)Al(O_2NN^{Me})$ (4).** A mixture containing **2** (2.1 g, 3.7 mmol) and 0.39 ml benzyl alcohol (0.41 g, 3.7 mmol) in 40 ml toluene was stirred at room temperature for 2 hours. All the volatiles were removed under reduced pressure, and the residue was washed with 10 ml hexane to yield a white powder. Yield, 2.0 g, 81%. $^1$H NMR (600 MHz, $CD_2Cl_2$): $\delta$ 1.30 (s, $C(CH_3)_3$, 18H), 1.45 (s, $C(CH_3)_3$, 18H), 2.71 (s, $CH_2$, 2H), 2.78 (s, $NMe_2$, 6H), 2.94 (s, $CH_2$, 2H), 3.55–3.80 (br, Ar$CH_2$, 4H), 5.30 (s, Ph$CH_2$O, 2H), 6.88 (d, CH-phenoxide, 2H, $J$ = 1.8 Hz), 7.18 (t, *p*-$C_6H_5$, 1H, $J$ = 6.6 Hz), 7.26 (d, CH-phenoxide, 2H, $J$ = 2.4 Hz), 7.33 (t, *m*-$C_6H_5$, 2H, $J$ = 7.2 Hz), 7.52 (d, *o*-$C_6H_5$, 2H, $J$ = 7.8 Hz). $^{13}$C{$^1$H} NMR (150 MHz, $CD_2Cl_2$): $\delta$ 29.5, 31.7 (s, $C(CH_3)_3$), 34.1, 35.1 (s, $C(CH_3)_3$), 49.2 (s, NMe), 49.5, 55.8 (s, $(CH_2)_2$), 58.9 (s, N($CH_2$)Ph), 66.0 (s, Ph$CH_2$O), 123.8, 123.9 (s, Ph), 125.3, 126.4, 127.7 (*o,m,p*-$C_6H_5CH_2O$), 121.4, 137.9, 138.9, 148.3, 155.6 (s, *tert*-C). Anal. Calc. for $C_{41}H_{61}AlN_2O_3$: C, 75.0; H, 9.4; N, 4.3. Found: C, 74.4; H, 9.4; N, 4.5%.

### Polymerization studies

The conditions using in this paper are similar to those employed by Lin and co-workers.[5] Typically, to a rapid stirring solution of catalyst (0.25 mmol) in toluene (30 ml) was added a prescribed amount of ε-CL. The reaction mixture was stirred at 50 °C for the prescribed time. After the reaction was quenched by the addition of an excess acetic acid solution, the resulting mixture was poured into excess *n*-heptane to precipitate PCL (poly-ε-caprolactone). Crude products were recrystallized from THF–hexane and dried *in vacuo* up to a constant weight.

### Crystal structure data

Crystals were grown from toluene/hexane solution, and isolated by filtration. Suitable crystals of **1** or **4** were sealed in thin-walled glass capillaries under a nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. The absorption correction was based on the symmetry equivalent reflections using the SADABS program. The space group determination was based on a check of the Laue symmetry and systematic absences and was confirmed using the structure solution. The structure was solved by direct methods using a SHELXTL package. All non-H atoms were located from successive Fourier maps, and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms. Some details of the data collection and refinement are given in Table 4.

**Table 4** Summary of crystal data for compounds **1** and **4**

| | **1** | **4** |
|---|---|---|
| Formula | $C_{37}H_{53}AlN_2O_2{\cdot}0.5\ C_7H_8$ | $C_{41}H_{61}AlN_2O_3$ |
| $M_w$ | 630.36 | 656.90 |
| $T$/K | 293(2) | 293(2) |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $P2_1/c$ |
| $a$/Å | 15.7989(10) | 19.9123(19) |
| $b$/Å | 15.3016(10) | 11.7193(12) |
| $c$/Å | 17.3809(11) | 18.5419(17) |
| $\alpha$/° | 90 | 90 |
| $\beta$/° | 109.8530(10) | 113.582(2) |
| $\gamma$/° | 90 | 90 |
| $V$/Å$^3$ | 3952.1(4) | 3965.6(7) |
| $Z$ | 4 | 4 |
| $D_c$/Mg m$^{-3}$ | 1.059 | 1.100 |
| $\mu$(Mo-Kα)/mm$^{-1}$ | 0.084 | 0.088 |
| Reflections collected | 21971 | 22096 |
| No. of parameters | 415 | 407 |
| $R1^a$ | 0.0571 | 0.0874 |
| $wR2^a$ | 0.1737 | 0.2472 |
| GoF$^b$ | 1.252 | 1.088 |

[a] $R1 = [\Sigma(|F_o| - |F_c|)/\Sigma|F_o|]$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $w = 0.10$.
[b] $\mathrm{GoF} = [\Sigma w(F_o^2 - F_c^2)^2/(N_{\mathrm{rflns}} - N_{\mathrm{params}})]^{1/2}$.

CCDC reference numbers 213986 and 213987.

See http://www.rsc.org/suppdata/dt/b3/b307365c/ for crystallographic data in CIF or other electronic format.

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