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Aluminium complexes containing indolyl-phenolate ligands as catalysts for ring-opening polymerization of cyclic esters†

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A family of aluminium complexes supported by mono-anionic indolyl-phenolate ligands are described. Reactions of indolyl-phenolate based ligand precursors, IndHPh^{R}OH, with 1.0 or 0.5 equivalents of $AlMe_2Cl$ in toluene afforded aluminium indolyl-phenolate complexes **1–4** and aluminium bis-indolyl-phenolate complexes **5–8** respectively. The molecular structure is reported for **5**. Based on the NMR spectroscopic and X-ray crystallographic studies, a 1,3-hydrogen shift could happen from nitrogen to carbon on the five-membered ring of the indolyl group upon reacting with aluminium reagents. These novel aluminium complexes demonstrate catalytic activities toward the ring-opening polymerization of cyclic esters in the presence of alcohol.

Introduction

Due to the diverse applications of biodegradable polymers,[1–9] development of catalysts applied in preparation of such polymers has attracted attention during the past decades.[10–19] Metal-based initiators/catalysts applied in ring opening polymerization became a focus topic mainly due to their well-controlled character and promising catalytic activities.[13–19] Among these studies, the phenolate-containing ancillary ligands usually worked as efficient functionalities in preparing metal complexes, such as metal Schiff base complexes.[18,19] These metal phenolate complexes always demonstrate good catalytic activities and controlled behaviors in catalysing cyclic esters. In addition, some initiators/catalysts bearing anionic *N*-heterocyclic ligands, such as pyrrole,[20–37,43] indole[38–43] or carbazole,[44] have demonstrated catalytic activities toward the ROP of cyclic esters recently. Therefore, we intended to introduce the phenolate substituents into the indolyl ligands. We hoped the combination of phenolate and indolyl groups could work as candidates of ligand precursors. In this paper, some aluminium complexes incorporating indolyl-phenolate ligands will be reported and their catalytic activities toward the ROP of cyclic esters were also investigated.

Results and discussion

Preparations of ligand precursors and aluminium complexes

The ligand precursors IndHPh^{R}OH were prepared *via* Fischer indole synthesis reaction using phenylhydrazinium chloride and substituted 2′-hydroxy-acetophenone following the modified literature's method.[45] The synthetic route was shown in Scheme 1. The –NH signals of indole on ^{1}H NMR spectra for ligand precursors IndHPh^{H}OH, IndHPh^{Me}OH, IndHPh^{OMe}OH and IndHPh^{Br}OH were observed at δ 9.20, 9.27, 9.35 and 9.14 ppm. The –OH signals of phenol on ^{1}H NMR spectra for ligand precursors IndHPh^{H}OH, IndHPh^{Me}OH, IndHPh^{OMe}OH and IndHPh^{Br}OH were observed at δ 5.56, 5.53, 5.40 and 5.60 ppm. Compounds of IndHPh^{H}OH, IndHPh^{Me}OH, IndHPh^{OMe}OH and IndHPh^{Br}OH were characterized by elemental analyses as well.

Treatment of ligand precursors IndHPh^{R}OH with $AlMe_2Cl$ in toluene on the ratio of 1 : 1 afforded aluminium indolyl-phenolate complexes **1–4**, as shown in Scheme 1. Compared the ^{1}H NMR spectra between ligand precursors and **1–4**, the disappearance of –NH signals of indoles and –OH signals of phenols on ^{1}H NMR spectra and appearance of new Al–CH_3 proton signals as a singlet in the high field region (−0.28 to −0.30 ppm) with three protons integral intensities indicating the ligand precursors might work as mono-anionic ligands *via* alkane elimination. In addition, a multiplet appears around 4.44 ppm on ^{1}H NMR spectra and a singlet corresponding to secondary carbon appears around 41.5 ppm on ^{13}C{^{1}H} NMR spectra for each compound. This phenomenon also happens in the reactions of IndHPh^{R}OH with $AlMe_2Cl$ on the ratio of 2 : 1 affording aluminium indolyl-phenolate complexes **5–8**. A multiplet appears around 4.38 ppm on ^{1}H NMR spectra and a singlet corresponding to secondary carbon appears around

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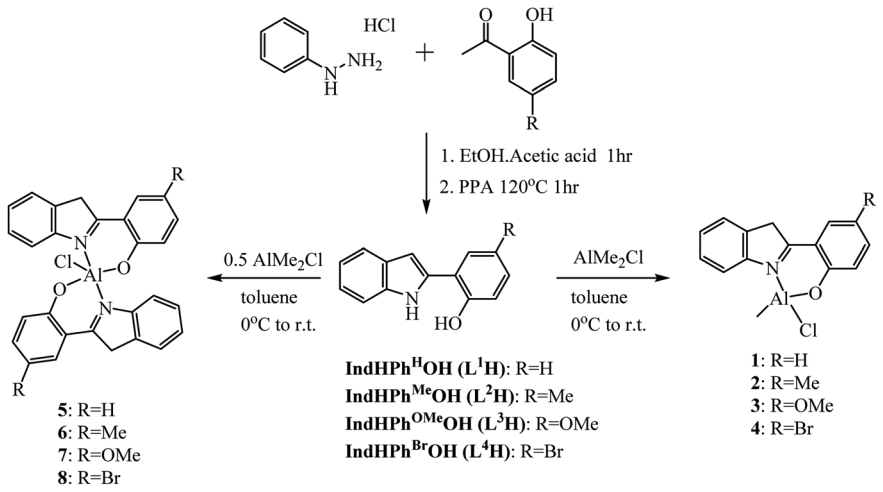

Scheme 1 The synthetic route for ligand precursors and aluminium complexes.

41.0 ppm on $^{13}C\{^1H\}$ NMR spectra for each compound. The compounds **1–8** were all characterized by elemental analyses as well.

Suitable crystals for structure determination of **5** were obtained from toluene/hexane solution. The molecular structure is depicted in Fig. 1. The solid-state structure of **5** reveals that the Al centre adopts a distorted trigonal bipyramidal geometry. Regarding coordination geometry around the Al centre, two nitrogen atoms of indole rings from different ligands are located at the axial positions of the trigonal bipyramidal geometry. The axial angle, [N–Al–N(0A), 173.65(7)°], is slightly distorted from linear, resulting in a distorted trigonal bipyramidal shape. Two oxygen atoms of phenolates from different ligands and one chloride atom form the equatorial plane. The equatorial angles around the Al centre are 125.55(8)° for O–Al–O(0A) and 117.22(4)° for O–Al–Cl. The Al–N bond length of **5** [2.015(11) Å] is longer than those [1.905(2)–1.957(4) Å] found in aluminium indolyl complexes[41,42] but within the range of those [1.9697(12)–2.183(3) Å] found in aluminium complexes containing *N*-heterocyclic ligands which the nitrogen atoms worked as dative atoms.[46–50] Therefore the Al–N bond of **5** is characteristic of coordinative covalent bond. Unlike those [1.368(2)–1.399(2) Å] C–N bond lengths found in metal indolyl complexes,[39,40,42] the C–N bond lengths C(8)–N [1.315(17) Å] and C(1)–N [1.430(17) Å] in the five-membered ring of indole group indicate one C=N double bond [C(8)–N] and one C–N single bond [C(1)–N]. In addition, there should be one C=C double bond [1.364(2)–1.391(3) Å] and one C–C single bond [1.405(3)–1.432(2) Å] around 3-position carbon of indolyl group if the indolyl part worked as mono-anionic ligand.[39,40,42] However, the C–C bond lengths C(6)–C(7) [1.493(2) Å] and C(7)–C(8) [1.508(19) Å] around 3-position carbon of indole group are characteristic of C–C single bonds. Based on those discussed above, there should be a 1,3-hydrogen shift induced by Lewis acid,[52] such as aluminium reagent, happened on the ligand precursors. Therefore, the ligand precursors worked as mono-anionic ligands to form aluminium indolyl-phenolate complexes. The Al–O bond length [1.767(10) Å] is within those [1.762(2)–1.813(2) Å] found in aluminium complexes containing phenolate *N*-heterocyclic ligands reveals the characteristic of σ-bonding.[46,48–50] The Al–Cl bond length [2.194(8) Å] is close to those [2.0978(13)–2.1935(8) Å] found in aluminium chloride complexes.[53,54]

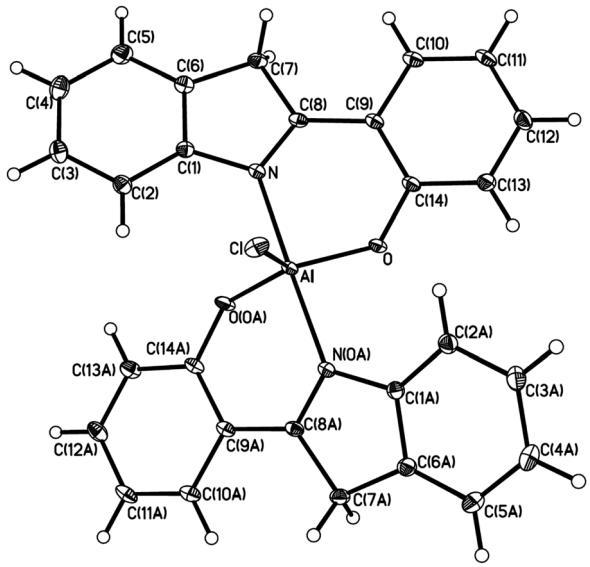

Fig. 1 Molecular structure of **5**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Al–N, 2.015(11); Al–O, 1.767(10); Al–Cl, 2.194(8); C(8)–N, 1.315(17); C(1)–N, 1.430(17); C(6)–C(7), 1.493(2); C(7)–C(8), 1.508(19); N–Al–N(0A), 173.65(7); O–Al–O(0A), 125.55(8); O–Al–Cl, 117.22(4).

Ring-opening polymerization

Due to the encouragement of some aluminium *N*-heterocyclic-phenolate-based complexes demonstrating catalytic activities toward the ROP of cyclic esters,[46–51] the new aluminium indolyl-phenolate complexes **1–8** were examined as catalysts for the ROP of ε-caprolactone in the presence of one equivalent of

Table 1 Polymerisation of cyclic esters using compounds **1–8** as catalysts in toluene if not otherwise stated[a]

Entry	Catalyst	$[Monomer]_0 : [cat.]_0 : [ROH]_0$	ROH	T (°C)	t (min)	Conv.[b] (%)	M_n[c] (calcd)	M_n[d] (obsd)	$Đ$[e]
1[f]	**1**	100 : 1:1	BnOH	80	60	81	9400	9700	1.06
2[f]	**1**	100 : 1 : 1	^{i}PrOH	80	60	77	8900	10 700	1.06
3[f]	**1**	100 : 1 : 1	9-AnOH	80	60	27	3200	5600	1.01
4[f,g]	**1**	100 : 1 : 1	BnOH	70	75	58	6700	5700	1.01
5[f]	**1**	100 : 1 : 1	BnOH	80	75	98	11 300	12 000	1.09
6[f]	**2**	100 : 1 : 1	BnOH	80	75	88	10 200	10 900	1.08
7[f]	**3**	100 : 1 : 1	BnOH	80	75	68	7900	9600	1.06
8[f]	**4**	100 : 1 : 1	BnOH	80	75	63	7300	7500	1.14
9[f]	**5**	100 : 1 : 1	BnOH	80	75	33	3900	5900	1.02
10[f]	**6**	100 : 1 : 1	BnOH	80	75	43	5000	6200	1.06
11[f]	**7**	100 : 1 : 1	BnOH	80	75	60	7000	6900	1.03
12[f]	**8**	100 : 1 : 1	BnOH	80	75	28	3300	6000	1.04
13[f]	**1**	200 : 1 : 1	BnOH	80	150	91	20 900	19 600	1.13
14[f]	**1**	300 : 1 : 1	BnOH	80	240	84	28 900	25 700	1.20
15[f]	**1**	200 : 1 : 2	BnOH	80	90	99	11 400	12 500	1.09
16[f]	**1**	400 : 1 : 4	BnOH	80	150	89	10 300	9000	1.05
17[h]	**1**	100 : 1 : 1	BnOH	80	360	15	—	—	—
18[h]	**1**	100 : 1 : 1	BnOH	80	1800	46	6700	7700	1.06
19[h]	**1**	100 : 1 : 1	BnOH	100	2880	74	10 800	12 000	1.12
20[h]	**1**	100 : 1 : 1	BnOH	110	2880	91	13 200	18 600	1.33

[a] Reaction conditions: 15 mL toluene, $[cat.]_0 = 0.125$ mmol, ROH = BnOH for ε-caprolactone; 10 mL toluene, $[cat.]_0 = 0.05$ mmol, ROH = BnOH for L-LA. [b] The values are obtained from ^{1}H NMR analysis. [c] $[ε\text{-CL}]_0/[ROH]_0 \times 114 \times$ conv. (%) + M(ROH) for ε-caprolactone; $[L\text{-LA}]_0/[ROH]_0 \times 144 \times$ conv. (%) + M(ROH). [d] Data obtained from GPC analysis and calibrated by polystyrene standard. The values are obtained from GPC times 0.56 for PCL; the values are obtained from GPC times 0.58 for PLA. [e] Obtained from GPC analysis. [f] Monomer = ε-caprolactone. [g] In 15 mL THF. [h] Monomer = L-LA.

alcohols under a dry nitrogen atmosphere and the results are shown in Table 1. Prescribed equivalent ratios on the catalyst precursor (0.125 mmol), ε-caprolactone and alcohol were introduced in 15.0 mL solvent. After several trials on running polymerization with various solvents (toluene or tetrahydrofuran) and alcohols [benzyl alcohol (BnOH), 2-propanol (^{i}PrOH) and 9-anthracenemethanol (9-AnOH)], the conditions were optimized to be toluene at 80 °C in the presence of BnOH for the polymerization of ε-caprolactone (entries 1–4). The same conditions were applied to examine the catalytic activities of the other seven catalysts (entries 5–12). Experimental results show the aluminium mono-substituted complexes (entries 5–8) demonstrate better catalytic activities than the aluminium di-substituted complexes (entries 9–12). This might result from the steric crowded environment around the metal center and the poor efficiency of chloride as initiating group. Due to the enhancement of Lewis acidity on the metal center caused by the electron-withdrawing substituent on *para*-position of the phenyl group, decreases of catalytic activities were found between **3** and **4** (entries 7–8). Based on the better catalytic activities demonstrated by **1** under the optimized condition, compound **1** was subjected to demonstrate controlled behavior (entries 13–16). Compound **1** exhibits living and immortal characters. The linear relationship between the number-average molecular weight (M_n) and the monomer-to-initiator ratio ($[ε\text{-CL}]_0/[Al]_0$ = 100–300) was demonstrated in Fig. S1† (Table 1, entries 5, 13–14, $Đ$s = 1.09–1.20). The "immortal" character was examined using 2 and 4 equivalents BnOH as chain transfer agent to produce polymers with reasonable M_n values (entries 15–16, comparing with entry 5). Based on the ^{1}H NMR spectroscopy, polymers are capped with benzyl alkoxyl group, as shown in Fig. S2.† Compared with the catalytic activities in catalyzing ROP of ε-CL demonstrated by aluminium complexes, **1** exhibits compatible activities to some complexes bearing Schiff base ligands[18,19,51] but worse activities to some complexes bearing pyrazolylephenolate ligands[48] or 2-(1,10-phenanthrolin-2-yl)phenolate ligands.[50] Polymerization of L-lactide employing **1** as catalyst in the presence of benzyl alcohol has been investigated under a dry nitrogen atmosphere as well (entries 17–20). However, compound **1** exhibits 74% conversion even though running the reaction at 100 °C with time up to 48 h (entry 19). The conversion can reach 91% at 110 °C with time up to 48 h (entry 20). Similar to the PCLs prepared above, the PLAs are capped with benzyl alkoxyl group, as shown in Fig. S3.† Due to the poor efficiency of chloride as initiating group, the polymerization mechanism of the aluminium mono-substituted complexes could be coordination–insertion mechanism[55] whereas the aluminium di-substituted complexes could be monomer-activated mechanism.[56]

Conclusion

A series of aluminium indolyl-phenolate complexes **1–8** has been synthesized and fully characterized by NMR spectroscopic studies and elemental analyses. Due to the 1,3-hydrogen shift happening on the indolyl part, the ligand precursors work as mono-anionic ligands. The hydrogen shifts from the nitrogen to 3-position carbon of indolyl part upon reacting with aluminium reagent resulting in the formation of 3*H*-indolyl phenolate ligands. This phenomenon has been confirmed by NMR

spectroscopic and X-ray crystallographic studies. Compounds **1–8** demonstrate catalytic activities in catalysing ROP of ε-caprolactone in the presence of benzyl alcohol. Under optimized condition, **1** demonstrated both living and immortal characters. However, the crowded environment around the metal centre of di-substituted complexes **5–8** might prevent the coordination of monomers or alcohols and result in the poor catalytic activities. Compound **1** also exhibits catalytic activities in catalysing the ROP of L-lactide in the presence of benzyl alcohol with conversion up to 91% at 110 °C after 48 h.

Experimental

General conditions

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

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded either on Varian Mercury-400 (400 MHz) or 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 an Elementar Vario EL III instrument. The GPC measurements were performed in THF at 35 °C with a Waters 1515 isocratic HPLC pump, a Waters 2414 refractive index detector, and Waters Styragel column (HR4E). Molecular weights (M_n) and molecular weight distributions (PDIs) were calculated using polystyrene as standard.

2′-Hydroxyacetophenone (Alfa Aesar), 2′-hydroxy-5′-methylacetophenone (Alfa Aesar), 2′-hydroxy-5′-methoxyacetophenone (Alfa Aesar), 5′-bromo-2′-hydroxyacetophenone (Matrix Scientific), phenylhydrazinium chloride (Alfa Aesar), polyphosphoric acid (SHOWA), 9-anthracenemethanol (9-AnOH, Acros) and dimethylaluminium chloride (0.9 M in heptane, Acros) were used as supplied. Benzyl alcohol (TEDIA), ε-caprolactone (Acros) and isopropanol (J.T. Baker) were dried over CaH_2 and distilled before use. L-Lactide (Bio Invigor) was recrystallized from dry toluene prior to use. IndPh^{H}OH (**L^{1}H**), IndPh^{Me}OH (**L^{2}H**) and IndPh^{Br}OH (**L^{4}H**) were prepared according to previously reported procedures.[45]

Preparations

IndPh^{H}OH (L^{1}H). The ligand precursor was prepared by following the modified literature's method using phenylhydrazinium chloride (0.72 g, 5.0 mmol) and 2′-hydroxyacetophenone (0.60 mL, 5.0 mmol) in refluxed ethanol with the presence of several drops of AcOH for 1 h. After cooled to room temperature, all the volatiles were removed under reduced pressure. Polyphosphoric acid (PPA, 10.00 mL) was added and the mixture was heated at 120 °C for 1 h. The mixture was neutralized with 2 M NaOH and extracted with EtOAc. The combined organic layer was concentrated under reduced pressure. The residue was purified by column chromatography (ethyl acetate : *n*-hexane = 1 : 5) followed by recrystallization (CH_2Cl_2/hexane) to afford pale-yellow solid. Yield, 0.58 g, 55%. ^{1}H NMR (400 MHz): δ 9.20 (s, 1H, N*H*), 7.76–7.60 (m, 2H, Ar–*H*), 7.45–7.37 (m, 1H, Ar–*H*), 7.24–7.10 (m, 3H, Ar–*H*), 7.03 (t, J = 7.7 Hz, 1H, Ar–*H*), 6.80–6.90 (m, 2H, Ar–*H*), 5.56 (s, 1H, O*H*). Anal. calc. for $C_{14}H_{11}NO$: C, 80.36; H, 5.30; N, 6.69. Found: C, 80.35; H, 5.27; N, 6.68%.

IndPh^{Me}OH (L^{2}H). This compound was prepared in a similar method to that for **L^{1}H** by using phenylhydrazinium chloride (0.72 g, 5.0 mmol) and 2′-hydroxy-5′-methyl-acetophenone (0.75 g, 5.0 mmol) instead to afford pale-yellow solid. Yield, 0.30 g, 27%. ^{1}H NMR (400 MHz): δ 9.27 (s, 1H, N*H*), 7.64 (d, J = 7.8 Hz, 1H, Ar–*H*), 7.49 (s, 1H, Ar–*H*), 7.39 (d, J = 8.1 Hz, 1H, Ar–*H*), 7.19 (t, J = 7.5 Hz, 1H, Ar–*H*), 7.13 (d, J = 7.4 Hz, 1H, Ar–*H*), 7.02–6.95 (m, 1H, Ar–*H*), 6.84 (d, J = 0.9 Hz, 1H, Ar–*H*), 6.77 (d, J = 8.2 Hz, 1H, Ar–*H*), 5.53 (s, 1H, O*H*), 2.33 (s, 3H, CH_3). Anal. calc. for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.63; H, 5.79; N, 6.24%.

IndPh^{OMe}OH (L^{3}H). This compound was prepared in a similar method to that for **L^{1}H** by using phenylhydrazinium chloride (0.72 g, 5.0 mmol) and 2′-hydroxy-5′-methoxy-acetophenone (0.83 g, 5.0 mmol) instead to afford pale-yellow solid. Yield, 0.73 g, 61%. ^{1}H NMR (400 MHz): δ 9.35 (s, 1H, N*H*), 7.68–7.59 (m, 1H, Ar–*H*), 7.37 (m, 1H, Ar–*H*), 7.24–7.20 (m, 1H, Ar–*H*), 7.20–7.15 (m, 1H, Ar–*H*), 7.12 (m, 1H, Ar–*H*), 6.83 (d, J = 2.1 Hz, 1H, Ar–*H*), 6.74 (t, J = 1.6 Hz, 2H, Ar–*H*), 5.40 (s, 1H, O*H*), 3.80 (s, 3H, OCH_3). Anal. calc. for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85. Found: C, 75.23; H, 5.36; N, 5.94%.

IndPh^{Br}OH (L^{4}H). This compound was prepared in a similar method to that for **L^{1}H** by using phenylhydrazinium chloride (0.72 g, 5.0 mmol) and 5′-bromo-2′-hydroxy-acetophenone (1.08 g, 5.0 mmol) instead to afford pale-yellow solid. Yield, 0.85 g, 59%. ^{1}H NMR (400 MHz): δ 9.14 (s, 1H, N*H*), 7.78 (d, J = 2.4 Hz, 1H, Ar–*H*), 7.67–7.62 (m, 1H, Ar–*H*), 7.41 (d, J = 8.1 Hz, 1H, Ar–*H*), 7.28 (d, J = 8.6 Hz, 1H, Ar–*H*), 7.22 (d, J = 8.2 Hz, 1H, Ar–*H*), 7.17–7.10 (m, 1H, Ar–*H*), 6.85 (d, J = 2.1 Hz, 1H, Ar–*H*), 6.78 (d, J = 8.6 Hz, 1H, Ar–*H*), 5.60 (s, 1H, O*H*). Anal. calc. for $C_{14}H_{10}BrNO$: C, 58.36; H, 3.50; N, 4.86. Found: C, 58.40; H, 3.43; N, 4.83%.

[IndHPh^{H}O]Al(CH$_3$)Cl (1). To a flask containing **L^{1}H** (0.21 g, 1.0 mmol) and 20 mL toluene under nitrogen, 1.3 mL $AlMe_2Cl$ (1.17 mmol, 0.9 M in heptane) was injected *via* a syringe at 0 °C. The mixture was stirring and warmed to room temperature for 1 hour. The resulting solution was concentrated and layered hexane to afford a pale orange solid. Yield 0.12 g, 42%. ^{1}H NMR (600 MHz) δ 7.71 (d, J = 7.8 Hz, 1H, Ar–*H*), 7.60 (d, J = 9.0 Hz, 1H, Ar–*H*), 7.55 (d, J = 7.2 Hz, 1H, Ar–*H*), 7.48–7.43 (m, 2H, Ar–*H*), 7.34 (t, J = 7.2 Hz, 1H, Ar–*H*), 7.03 (d, J = 8.4 Hz, 1H, Ar–*H*), 6.86 (t, J = 7.8 Hz, 1H, Ar–*H*), 4.41 (m, 2H, CH_2), −0.30 (s, 3H, Al–CH_3). ^{13}C{^{1}H} NMR (150 MHz) δ 181.4, 163.2, 149.8, 131.4, 116.8 (*tert-C*), 137.6, 130.5, 128.9, 127.2, 124.2, 122.8, 119.0, 117.9 (Ar–*C*H), 41.4 (*C*H$_2$), −10.3 (Al–*C*H$_3$). Anal. calc. for $C_{15}H_{13}AlClNO$: C, 63.06; H, 4.59; N, 4.90. Found: C, 63.09; H, 5.25; N, 4.49%.

[IndHPh^{Me}O]Al(CH$_3$)Cl (2). This compound was prepared in a similar method to that for **1** by using **L^{2}H** (0.22 g, 1.0 mmol), 15 mL toluene and 1.3 mL $AlMe_2Cl$ (1.17 mmol, 0.9 M in heptane) instead to afford pale-yellow solid. Yield, 0.09 g, 30%.

^{1}H NMR (600 MHz) δ 7.71 (d, J = 7.8 Hz, 1H, Ar–*H*), 7.57 (d, J = 7.2 Hz, 1H, Ar–*H*), 7.46 (t, J = 7.2 Hz, 1H, Ar–*H*), 7.39 (s, 1H, Ar–*H*), 7.35 (t, J = 15 Hz, 1H, Ar–*H*), 7.31–7.33 (m, 1H, Ar–*H*), 6.95 (d, J = 8.4 Hz, 1H, Ar–*H*), 4.44 (m, 2H, CH_2), 2.31 (s, 3H, CH_3), −0.30 (s, 3H, Al–CH_3). ^{13}C{^{1}H} NMR (150 MHz) δ 181.3, 161.2, 149.7, 131.3, 128.1, 116.3 (*tert-C*), 139.1, 129.9, 128.8, 127.0, 124.2, 122.5, 117.8 (Ar–*C*H), 41.4 (*C*H$_2$), 20.4 (*C*H$_3$), −10.1 (Al–*C*H$_3$). Anal. calc. for $C_{16}H_{15}AlClNO$: C, 64.11; H, 5.04; N, 4.67. Found: C, 65.07; H, 5.31; N, 4.39%. Despite repeated attempts, a satisfactory elemental analysis could not be obtained.

[IndHPh^{OMe}O]Al(CH$_3$)Cl (3). This compound was prepared in a similar method to that for **1** by using **L^{3}H** (0.24 g, 1.0 mmol), 15 mL toluene and 1.3 mL $AlMe_2Cl$ (1.17 mmol, 0.9 M in heptane) instead to afford yellow solid. Yield, 0.11 g, 35%. ^{1}H NMR (600 MHz) δ 7.72 (d, J = 8.4 Hz, 1H, Ar–*H*), 7.58 (d, J = 7.2 Hz, 1H, Ar–*H*), 7.47 (t, J = 7.8 Hz, 1H, Ar–*H*), 7.37 (t, J = 7.8 Hz, 1H, Ar–*H*), 7.21–7.19 (m, 1H, Ar–*H*), 7.08 (d, J = 3.0 Hz, 1H, Ar–*H*), 7.01 (d, J = 9.6 Hz, 1H, Ar–*H*), 4.44 (m, 2H, CH_2), 3.87 (s, 3H, OCH_3), −0.28 (s, 3H, Al–CH_3). ^{13}C{^{1}H} NMR (150 MHz) δ 180.8, 158.3, 149.7, 131.3, 128.2, 116.2 (*tert-C*), 128.9, 127.3, 126.6, 124.3, 123.9, 117.9, 113.0 (Ar–*C*H), 57.3 (O*C*H$_3$), 41.6 (*C*H$_2$), −9.9 (Al–*C*H$_3$). Anal. calc. for $C_{16}H_{15}AlClNO_2$: C, 60.87; H, 4.79; N, 4.44. Found: C, 62.39; H, 5.63; N, 4.09%. Despite repeated attempts, a satisfactory elemental analysis could not be obtained.

[IndHPh^{Br}O]Al(CH$_3$)Cl (4). This compound was prepared in a similar method to that for **1** by using **L^{4}H** (0.29 g, 1.0 mmol), 15 mL toluene and 1.3 mL $AlMe_2Cl$ (1.17 mmol, 0.9 M in heptane) instead to afford pale yellow solid. Yield, 0.13 g, 36%. ^{1}H NMR (600 MHz): δ 7.74–7.73 (overlap, 2H, Ar–H), 7.59 (d, J = 8.4 Hz, 1H, Ar–*H*), 7.56–7.54 (m, 1H, Ar–*H*), 7.49 (t, J = 7.8 Hz, 1H, Ar–*H*), 7.40 (t, J = 7.2 Hz, 1H, Ar–*H*), 6.95 (d, J = 9.0 Hz, 1H, Ar–*H*), 4.45 (m, 2H, CH_2), −0.29 (s, 3H, Al–CH_3). ^{13}C{^{1}H} NMR (150 MHz) δ 180.2, 161.9, 149.5, 131.3, 118.2, 110.4 (*tert-C*), 140.0, 132.3, 129.1, 127.6, 124.7, 124.3, 118.1 (Ar–*C*H), 41.5 (*C*H$_2$), −10.2 (Al–*C*H$_3$). Anal. calc. for $C_{15}H_{12}AlBrClNO$: C, 49.41; H, 3.32; N, 3.84. Found: C, 48.90; H, 4.09; N, 3.42%.

[IndHPh^{H}O]$_2$AlCl (5). To a flask containing **L^{1}H** (0.42 g, 2.0 mmol) and 15 mL toluene under nitrogen, 1.1 mL $AlMe_2Cl$ (1.0 mmol, 0.9 M in heptane) was injected *via* a syringe at 0 °C. The mixture was stirring and warmed to room temperature for 12 h. The resulting solution was concentrated and layered hexane to afford a white solid. Yield 0.21 g, 44%. ^{1}H NMR (600 MHz) δ 8.13 (d, J = 8.4 Hz, 1H, Ar–*H*), 7.70–7.69 (m, 1H, Ar–*H*), 7.56 (d, J = 7.2 Hz, 1H, Ar–*H*), 7.45–7.39 (m, 2H, Ar–*H*), 7.32 (t, J = 7.2 Hz, 1H, Ar–*H*), 6.90 (t, J = 7.2 Hz, 1H, Ar–*H*), 6.86 (d, J = 8.4 Hz, 1H, Ar–*H*), 4.41 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (150 MHz) δ 177.4, 162.6, 152.5, 132.3, 118.0 (*tert-C*), 135.5, 129.9, 128.2, 126.0, 123.2, 122.0, 121.6, 118.4, (Ar–*C*H), 41.0 (*C*H$_2$). Anal. calc. for $C_{28}H_{20}AlClN_2O_2$: C, 70.22; H, 4.21; N, 5.85. Found: C, 70.47; H, 4.61; N, 5.34%.

[IndHPh^{Me}O]$_2$AlCl (6). This compound was prepared in a similar method to that for **5** by using **L^{2}H** (0.45 g, 2.0 mmol), 15 mL toluene and 1.1 mL $AlMe_2Cl$ (1.0 mmol, 0.9 M in heptane) instead to afford white solid. Yield, 0.19 g, 37%. ^{1}H NMR (600 MHz) δ 8.11 (d, J = 7.2 Hz, 1H, Ar–*H*), 7.54 (br, 1H, Ar–*H*), 7.46–7.42 (overlap, 2H, Ar–*H*), 7.30–7.21 (overlap, 2H, Ar–*H*), 6.78 (d, J = 7.2 Hz, 1H, Ar–*H*), 4.38 (m, 2H, CH_2), 2.34 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (150 MHz) δ 177.3, 160.6, 152.6, 132.4, 127.3, 117.5 (*tert-C*), 136.7, 129.5, 127.9, 125.9, 123.1, 121.7, 121.6 (Ar–*C*H), 41.0 (*C*H$_2$), 20.5 (*C*H$_3$). Anal. calc. for $C_{30}H_{24}AlClN_2O_2$: C, 71.08; H, 4.77; N, 5.53. Found: C, 70.79; H, 4.58; N, 5.54%.

[IndHPh^{OMe}O]$_2$AlCl (7). This compound was prepared in a similar method to that for **5** by using **L^{3}H** (0.48 g, 2.0 mmol), 15 mL toluene and 1.1 mL $AlMe_2Cl$ (1.0 mmol, 0.9 M in heptane) instead to afford pale yellow solid. Yield, 0.25 g, 46%. ^{1}H NMR (600 MHz) δ 8.13 (d, J = 8.4 Hz, 1H, Ar–*H*), 7.54 (d, J = 7.8 Hz, 1H, Ar–*H*), 7.43 (t, J = 7.8 Hz, 1H, Ar–*H*), 7.31 (t, J = 7.2 Hz, 1H, Ar–*H*), 7.10 (d, J = 3.0 Hz, 1H, Ar–*H*), 7.07–7.05 (m, 1H, Ar–*H*), 6.81 (d, J = 9.0 Hz, 1H, Ar–*H*), 4.37 (m, 2H, CH_2), 3.84 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (150 MHz) δ 177.0, 157.4, 152.5, 151.5, 132.3, 117.2 (*tert-C*), 127.9, 126.0, 123.5, 123.2, 122.8, 121.7, 112.2 (Ar–*C*H), 56.1 (O*C*H$_3$), 41.0 (*C*H$_2$). Anal. calc. for $C_{30}H_{24}AlClN_2O_4$: C, 66.86; H, 4.49; N, 5.20. Found: C, 66.77; H, 3.98; N, 5.25%.

[IndHPh^{Br}O]$_2$AlCl (8). This compound was prepared in a similar method to that for **5** by using **L^{4}H** (0.58 g, 2.0 mmol), 15 mL toluene and 1.1 mL $AlMe_2Cl$ (1.1 mmol, 0.9 M in heptane) instead to afford white solid. Yield, 0.26 g, 41%. ^{1}H NMR (600 MHz) δ 8.08 (d, J = 7.8 Hz, 1H, Ar–*H*), 7.79 (d, J = 2.4 Hz, 1H, Ar–*H*), 7.57 (d, J = 7.2 Hz, 1H, Ar–*H*), 7.46–7.43 (overlap, 2H, Ar–*H*), 7.36–7.34 (m, 1H, Ar–*H*), 6.74 (d, J = 9.6 Hz, 1H, Ar–*H*), 4.38 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (150 MHz) δ 176.1, 161.4, 152.1, 132.2, 119.4, 109.9 (*tert-C*), 138.0, 128.1, 126.5, 123.9, 123.4, 121.7 (Ar–*C*H), 41.0 (*C*H$_2$). Anal. calc. for $C_{28}H_{18}AlBr_2ClN_2O_2$: C, 52.82; H, 2.85; N, 4.40. Found: C, 53.49; H, 3.44; N, 4.39%.

Polymerization procedure of ε-caprolactone. Typically, to a flask containing prescribed amount of 0.125 mmol catalyst precursor was added 14 mL toluene followed by the addition of 1.0 mL benzyl alcohol solution (0.125 M in toluene) and 1.4 mL (12.5 mmol) ε-caprolactone. The reaction mixture was stirred at prescribed temperature for the prescribed time. After the reaction was quenched by the addition of 5.0 mL acetic acid solution (0.35 N), the resulting mixture was pumped to dryness. Crude products were recrystallized from THF/hexane and dried *in vacuo* up to a constant weight.

Polymerization procedure of L-lactide. Typically, to a flask containing prescribed amount of L-lactide and 0.05 mmol catalyst precursor was added 9.6 mL toluene followed by the addition of 0.4 mL benzyl alcohol solution (0.125 M in toluene). The reaction mixture was stirred at prescribed temperature for the prescribed time. After the reaction was quenched by the addition of 5.0 mL acetic acid solution (0.35 N), the resulting mixture was pumped to dryness. 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 (**5**) by the two layers method and isolated by filtration. Crystal was mounted onto a glass fiber using perfluoropolyether oil- "oil-drop" method and cooled rapidly in a stream of cold nitrogen gas to collect diffraction data at 150 K using Bruker APEX2

diffractometer, and intensity data were collected with ω scans. The data collection and reduction were performed with the SAINT software[57] and the absorptions were corrected by SADABS.[58] 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 and refined with SHELXTL package.[59] All non-H atoms were located from successive Fourier maps, and hydrogen atoms were treated as a riding model on their parent C atoms. 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 S1.† Crystallographic data for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers, CCDC no. 2196220 for compound **5**.

Conflicts of interest

There are no conflicts to declare.

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