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Improvement in aluminum complexes bearing a Schiff base in ring-opening polymerization of ε-caprolactone: the synergy of the N,S-Schiff base in a five-membered ring aluminum system†

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A series of five-membered ring aluminum complexes bearing thiol-Schiff base ligands were synthesized, and their application in the ring-opening polymerization of ε-caprolactone (CL) was investigated. The complexes exhibited dramatically higher catalytic activity than the six-membered ring $\mathbf{S^2AlMe_2}$ complex (approximately 4- to 10-fold higher) and the five-membered ring $\mathbf{L^{5\text{-}Ph}AlMe_2}$ complex (approximately 7- to 19-fold higher). Moreover, a shorter induction period was observed when the five-membered ring aluminum complexes bearing thiol-Schiff base ligands were used compared with the other types of aluminum complexes bearing Schiff base ligands. The electron-withdrawing groups enhanced the catalytic activity of the Al complexes compared with the electron donating groups. The thiol-Schiff base ligand and the five-membered ring aluminum catalysis had a synergistic effect that was stronger than the combination of their individual effects.

Introduction

Environmental problems are attracting increasing attention, and one such problem is that petrochemical plastics do not break down naturally within a short time and cause ecological damage.[1] Therefore, the development of convenient and environmentally friendly materials, such as biodegradable plastics, has become the focus of researchers. Poly(ε-caprolactone)s (PCLs) are widely used for commercial purposes because of their biodegradability, biocompatibility, and permeability; thus, they are extensively utilized in a variety of fields.[2–5] Ring-opening polymerization (ROP) is a popular method for the synthesis of PCLs because the method allows precise molecular weight control of polymers, unlike traditional polycondensation.[6] Metal catalysts act as Lewis acids to activate the carbonyl group of ε-caprolactone (CL) for conveniently conducting the ROP of CLs. Aluminum complexes are commonly selected as catalysts for ROP because of their strong Lewis acidity, convenient synthesis, and the low cost of their precursors. Among all aluminum complexes, the aluminum complexes[7] bearing Schiff base ligands have attracted the highest interest, presumably because of their many diverse substituent forms and convenient synthesis. Our recent studies revealed that using aluminum complexes with an N,S-Schiff base resulted in a significantly higher polymerization rate than using aluminum complexes with an N,O-Schiff base (5- to 12-fold for CL polymerization, Fig. 1A).[8a] Moreover, five-membered ring aluminum complexes with an N,O-Schiff base resulted in a significantly higher polymerization rate than six-membered ring aluminum complexes (two- to three-fold for CL polymerization, Fig. 1B).[8b] On the basis of our recent research, we reported the synthesis of aluminum complexes bearing aryl-ideneaminobenzenethiol (Fig. 1C) and the investigation of their catalytic reactivity during CL ROP to prove the synergy of the two aforementioned strategies.

Results and discussion

Synthesis and characterization of aluminum complexes

Aryl-2,3-dihydrobenzothiazole ligands were synthesized by the reaction of thioaniline and aryl-2-carbaldehyde in CH_2Cl_2.

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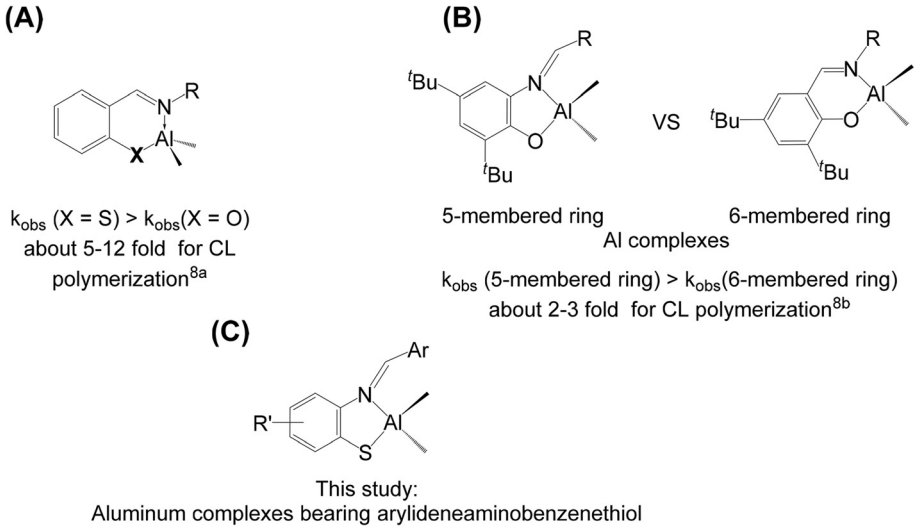


Fig. 1 (A) Use of thiol-Schiff base ligands and (B) five-membered ring aluminum complexes with an N,O-Schiff base; (C) synergy of these two strategies.

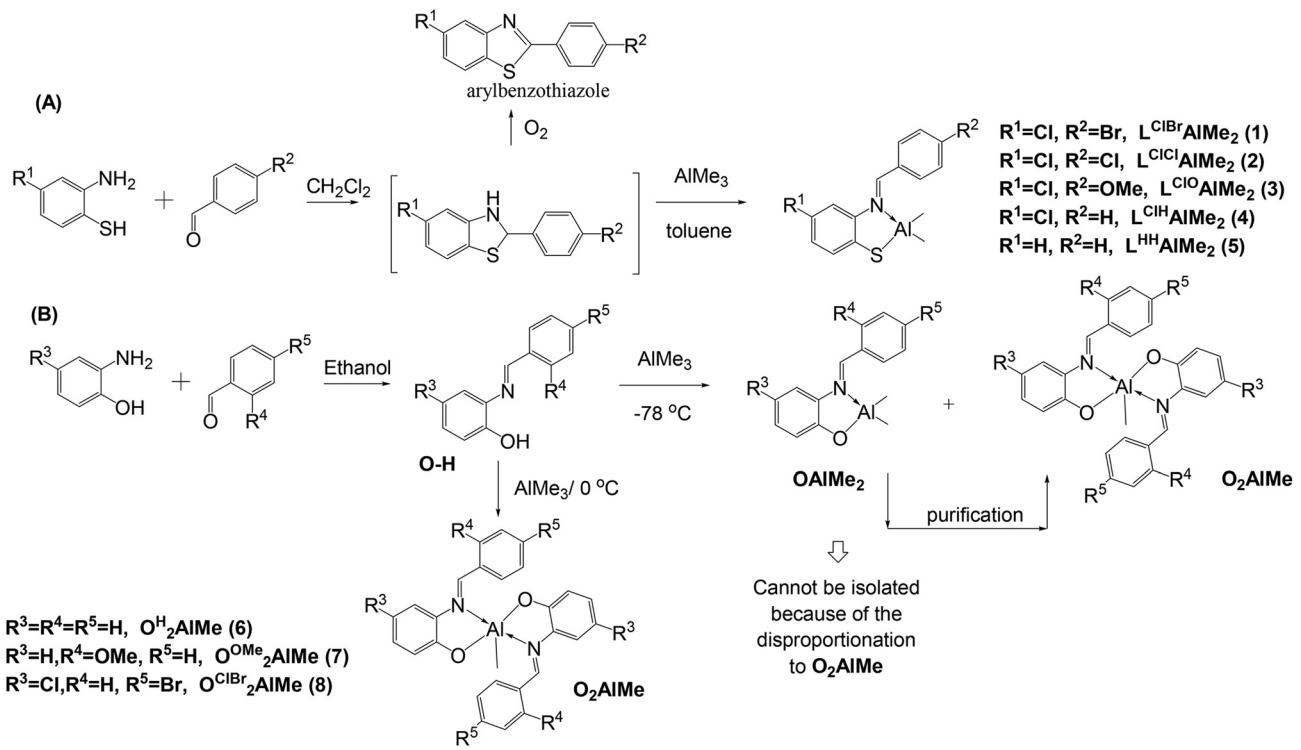


Fig. 2 Synthesis of thiol-Schiff base ligands and the associated aluminum complexes.

However, the ligands could not be isolated directly because they were further oxidized by O_2 to form arylbenzothiazole.[9] The ligand synthesis apparatus was set up in a dry box and monitored using ^{1}H nuclear magnetic resonance (NMR) (Fig. S18–S22†). When all the aryl-2-carbaldehyde had been consumed, volatile materials were removed under vacuum without isolation. All ligands reacted with a stoichiometric quantity of $AlMe_3$ in toluene at 0 °C to produce aluminum compounds (Fig. 2A). The formula and the structure were confirmed by ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, and X-ray crystal analysis. $\mathbf{L^{ClH}AlMe_2}$ **(4)** was crystallized in toluene by allowing it to stand at −20 °C. The X-ray structure of $\mathbf{L^{ClH}AlMe_2}$ **(4)** (Fig. 3, CCDC 1828535†) reveals that the Al atom has a distorted tetrahedral geometry with the two methyl groups. The aluminum atom is positioned 0.733 Å above the phenyl ring plane. The distance between the Al atom and the

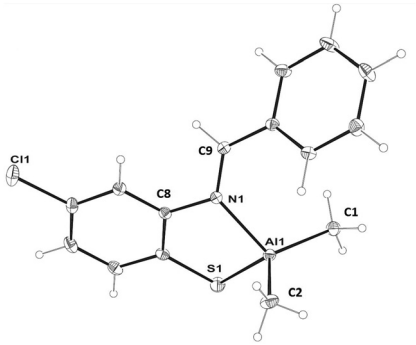
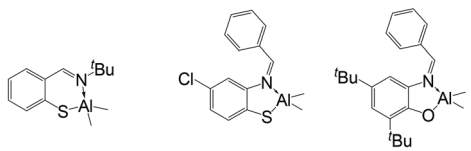


Fig. 3 Molecular structures of $L^{ClH}AlMe_2$ (4) with 30% probability ellipsoids (all of the hydrogen atoms are omitted for clarity).

Table 1 Comparisons of the selected bond lengths and angles for the three aluminum complexes



S^2AlMe_2[8a] $L^{ClH}AlMe_2$ (4) $L^{5\text{-}Ph}AlMe_2$[8b]

	S^2AlMe_2	$L^{ClH}AlMe_2$ (4)	$L^{5\text{-}Ph}AlMe_2$
Selected bond distances (Å)			
Al–S or Al–O	2.2690(7)	2.2904(8)	1.7833(15)
Al–N	1.9890(15)	2.0074(16)	2.0240(17)
Al–C	1.9655(18)	1.953(2)	1.958(2)
Al–phenyl plane	1.968(2)	1.951(2)	1.961(2)
	1.129	0.733	0.443
Selected angles (°)			
N–Al–S or N–Al–O	97.66(6)	87.46(5)	85.39(7)
C–Al–C	119.25(9)	121.65(10)	122.17(10)

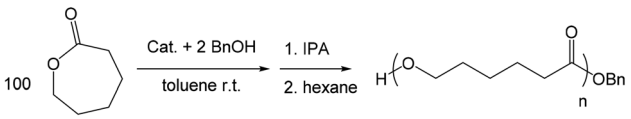
phenyl ring plane of $L^{ClH}AlMe_2$ (4) is longer than that of $L^{5\text{-}Ph}AlMe_2$ (0.443 Å, Table 1), but is shorter than that of S^2AlMe_2 (1.129 Å, Table 1). Table 1 reveals that the distances of Al–C bonds in the five-membered ring aluminum system are shorter than those in the six-membered ring aluminum system; however, the Al–N bonds in the five-membered ring aluminum system are longer. The N–Al–S (or N–Al–O) angles in the five-membered ring aluminum system are smaller than those in the six-membered ring aluminum system. The crystallography data of aluminum complexes with N,O- and N,S-Schiff base ligands display similar geometries except that the distance of the Al–O bond is shorter than that of the Al–S bond.

To compare with the five-membered ring aluminum complexes bearing thiol-Schiff base ligands, 2-benzylideneaminophenol (O^H-H), 2-(2-methoxybenzylidene)aminophenol (O^{OMe}-H), and 2-(4-bromobenzylidene)amino-4-chlorophenol (O^{ClBr}-H) (Fig. 2B) and the associated Al complexes were synthesized as displayed in Fig. 2B. However, the anticipated Al complexes (L-Al-Me_2 type) could not be isolated because they were too unstable and formed disproportionation[10] products, such as **$O^H{}_2$AlMe (6)**, **$O^{OMe}{}_2$AlMe (7)**, and **$O^{ClBr}{}_2$AlMe (8)**. Even when the temperature of the reactions of $AlMe_3$ with ligands (O^H-H, O^{OMe}-H, and O^{ClBr}-H, respectively) was reduced to −78 °C, the formation of both products (L-Al-Me_2 and L_2-Al-Me types) was observed. In the purification by using toluene and *n*-hexane as solvents, the product of the L-Al-Me_2 type was converted to one of the L_2-Al-Me type. The results revealed that the thiol-Schiff base ligands prevented the disproportionation to synthesize a highly catalytically active Al form with one ligand and two methyl groups.

Polymerization of ε-caprolactone

Polymerizations of CL were investigated by using aluminum complexes and two equivalents of BnOH as initiators in

Table 2 Polymerization of CL catalyzed using various Al complexes



Entry	Cat.	Time (min)	Conv.[a] (%)	Mn_{Cal}[b] (g mol^{-1})	Mn_{NMR}[a] (g mol^{-1})	Mn_{GPC}[c] (g mol^{-1})	PDI[c]	k_{obs} (error)[d] min^{-1}	Induction period (min)
1	**$L^{ClBr}AlMe_2$ (1)**	12	96	5600	4800	5900	1.26	0.284(12)	0.8
2	**$L^{ClCl}AlMe_2$ (2)**	12	92	5400	5600	7800	1.19	0.260(17)	1.8
3	**$L^{ClH}AlMe_2$ (4)**	20	92	5400	5200	6400	1.23	0.136(4)	0.9
4	**$L^{HH}AlMe_2$ (5)**	25	95	5500	7900	8100	1.23	0.115(8)	0.8
5	**$L^{ClO}AlMe_2$ (3)**	25	90	5200	5500	5200	1.21	0.105(4)	2.6
6[8a]	**S^2AlMe_2**	90	90	5200	5800	5100	1.04	0.028(2)	5.0
7[8b]	**$L^{5\text{-}Ph}AlMe_2$**	150	89	5200	5000	4000	1.17	0.016(1)	12.9
8	**$O^H{}_2$AlMe (6)**	144 h	81	4700	7000	5700	1.17	—	—
9	**$O^{OMe}{}_2$AlMe (7)**	145 h	90	5200	8500	11 700	1.39	—	—
10[e]	**$O^{ClBr}{}_2$AlMe (8)**	60/561	24/92	5400	6000	4200	1.25	0.005(1)	72.4

Reaction conditions: Toluene (5 mL), $[M]_0:[Cat.]_0:[BnOH]_0 = 100:1:2$, [CL] = 2.0 M, at room temperature. [a] Obtained from ^{1}H NMR analysis. [b] Calculated from the molecular weight of the monomer × $[monomer]_0/[BnOH]_0$ × conversion yield + *M*w(BnOH). [c] Obtained from GPC analysis and calibration on the basis of the polystyrene standard. Mn_{GPC} values are obtained from GPC multiplied by 0.56.[14] [d] The observed k_{obs} value is the slope of the first-order kinetic plot of ε-caprolactone polymerization *versus* time. The conversion of ε-caprolactone with time was monitored using ^{1}H NMR. [e] Toluene (5 mL), $[M]_0:[Cat.]_0:[BnOH]_0 = 100:1:2$, [CL] = 2.0 M, at room temperature.

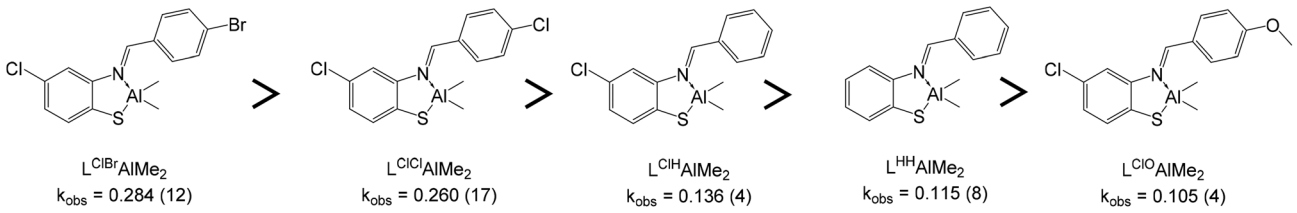


Fig. 4 Comparison of the k_{obs} of CL polymerization for various aluminum complexes.

toluene (Table 2). Table 2 reveals that all five-membered ring aluminum complexes bearing thiol-Schiff base ligands exhibited high catalytic activity in CL ROP, and the activity was slightly influenced by the ligand substituent. The catalytic rates for CL polymerization decreased in the following order (Fig. 4 and 5): **$L^{ClBr}AlMe_2$ (1)** > **$L^{ClCl}AlMe_2$ (2)** > **$L^{ClH}AlMe_2$ (4)** > **$L^{HH}AlMe_2$ (5)** > **$L^{ClO}AlMe_2$ (3)**. This ranking reveals that the presence of a greater number of electron-withdrawing groups such as chloride and bromide resulted in a higher catalytic rate. Moreover, the five-membered ring aluminum complexes bearing thiol-Schiff base ligands displayed dramatically higher catalytic activity than those of **S^2AlMe_2** (approximately 4- to 10-fold) and **$L^{5\text{-}Ph}AlMe_2$** (approximately 7- to 19-fold). Moreover, the reaction times (induction period)[10] required for forming Al benzyl alkoxide from BnOH and the dimethyl Al complex for all five-membered ring Al catalysts bearing thiol-Schiff base ligands (0–3 min) were significantly shorter than the induction periods of **S^2AlMe_2** (5 min) and **$L^{5\text{-}Ph}AlMe_2$** (13 min). The results strongly suggest that the synergy of using thiol-Schiff base ligands in a five-membered ring aluminum system is effective. Moreover, **$O^H{}_2AlMe$ (6)**, **$O^{OMe}{}_2AlMe$ (7)**, and **$O^{ClBr}{}_2AlMe$ (8)** exhibited low catalytic activity in CL polymerization at room temperature (conversion is 0% for **$O^H{}_2AlMe$ (6)**, 0% for **$O^{OMe}{}_2AlMe$ (7)**, and 24% for **$O^{ClBr}{}_2AlMe$** after 1 h by using the conditions listed in Table 2). This fact proved that using thiol-Schiff bases as ligands resulted in the formation of stable and highly catalytically active five-membered ring aluminum complexes (L–Al–Me_2 type). However, only less catalytically active five-membered ring aluminum complexes bearing N,O-Schiff base ligands (L_2–Al–Me type) were obtained.

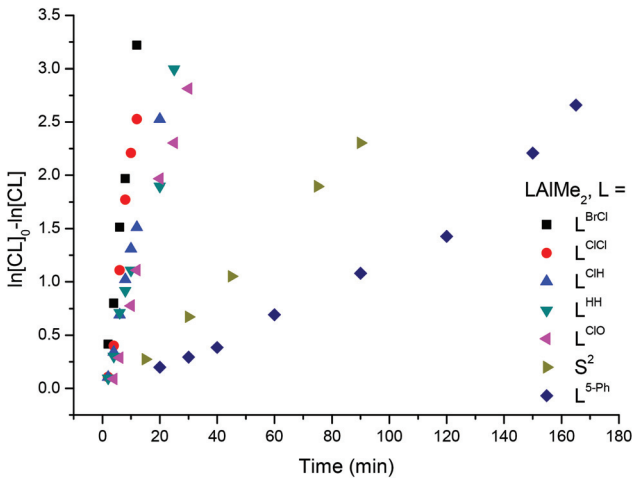


Fig. 5 First-order kinetic plots of ε-caprolactone polymerizations using various Al complexes against time.

On the basis of the results, CL polymerization using **$L^{ClBr}AlMe_2$ (1)** with the highest catalytic activity as a catalyst was systematically investigated to study the polymerization controllability (Table 3). The optimal conditions (entries 1–5, Table 3) for the optimal catalytic activity and the optimal conditions for the polymers were $[CL]_0/[Al]/[BnOH]$ = 100 : 1 : 3 and [Al] = 10 mM in toluene 5 mL. The experimental results in Table 3 revealed that the CL polymerization with this ratio

Table 3 Results of controlled CL polymerizations using **$L^{ClBr}AlMe_2$ (1)** as the catalyst

Entry	[CL]/[Al]/[BnOH]	Time (min)	Conv.[a] (%)	Mn_{Cal}[b] (g mol^{-1})	Mn_{NMR}[a] (g mol^{-1})	Mn_{GPC}[c] (g mol^{-1})	PDI[c]
1	100 : 1 : 1	46	98	11 500	10 100	26 900	1.63
2	100 : 1 : 2	12	96	5600	4800	5900	1.26
3	100 : 1 : 3	7	90	3500	5200	4300	1.14
4	100 : 1 : 4	10	80	2400	4200	2900	1.11
5	100 : 1 : 5	10	76	1800	3200	2300	1.09
6	50 : 1 : 3	5	91	1900	2700	1700	1.07
7	75 : 1 : 3	8	87	2700	3700	2700	1.10
8	150 : 1 : 3	23	92	6300	7600	6100	1.14
9	200 : 1 : 3	65	92	7100	8500	7800	1.19
10	250 : 1 : 3	110	94	12 300	11 000	13 200	1.24
11	350 : 1 : 3	180	87	11 700	16 700	16 700	1.28

Reaction conditions: Toluene (5 mL), [**$L^{ClBr}AlMe_2$**] = 0.02 M, at room temperature. [a] Obtained from ^1H NMR analysis. [b] Calculated from the molecular weight of monomer × $[monomer]_0/[BnOH]_0$ × conversion yield + *M*w(BnOH). [c] Obtained from the GPC analysis and calibration on the basis of the polystyrene standard. Mn_{GPC} values are obtained from GPC multiplied by 0.56.

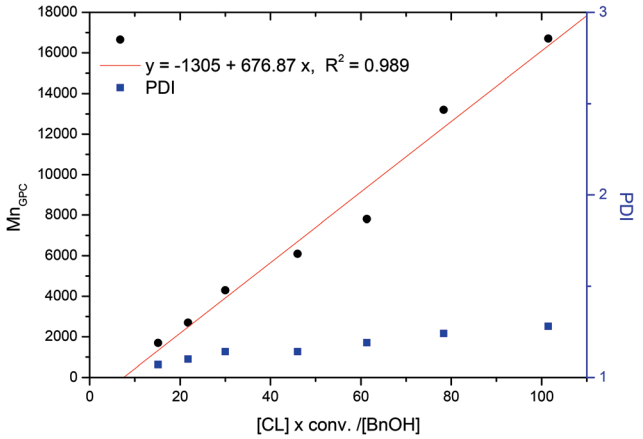


Fig. 6 Linear plot of $Mn_{(GPC)}$ *versus* $[CL]_0 \times$ conv./[BnOH], with the PDI indicated by blue squares (Table 3, entries 3, 6–11).

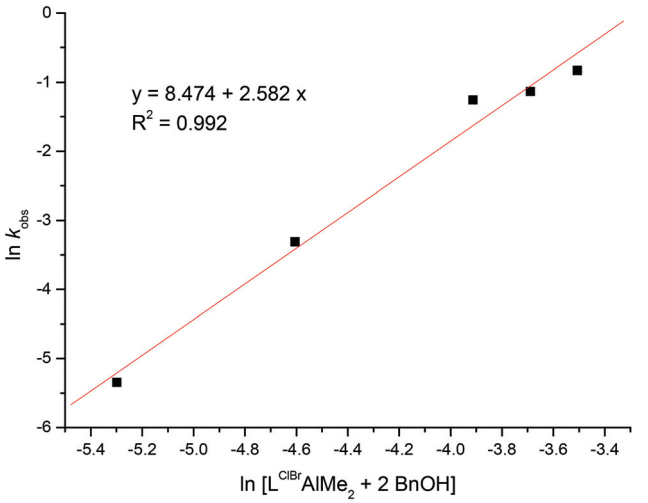


Fig. 8 Linear plot of k_{obs} *versus* $[\mathbf{L^{ClBr}AlMe_2}$ + 2 BnOH] for CL polymerization with [CL] = 2.0 M in toluene (5 mL).

([Al]/[BnOH] = 1 : 3) was controllable, as confirmed by the linear relationship between Mn_{GPC} and $[M]_0/[BnOH]_0$ (Fig. 6) with acceptable polydispersity indexes (PDIs, 1.07–1.28). The ^{1}H NMR spectrum of PCL (entry 1 of Table 3) confirmed one benzyl group (peaks a and b) and hydroxyl chain ends (peak c′) with an integral ratio of 5 : 2 : 2, suggesting that the initiation occurred through a benzyl alkoxide insertion into CL (Fig. 7). The MALDI-TOF spectrum of PCL (entry 9 of Table 3) also confirmed the presence of BnOH at the chain end of PCL (Fig. S17†).

Kinetic study of ε-caprolactone polymerization using $\mathbf{L^{ClBr}AlMe_2}$ (1)

The kinetic studies were performed at room temperature to examine the effect of the ratio of $[CL]_0/[\mathbf{L^{ClBr}AlMe_2}$ + 2 BnOH] ([CL] = 2.0 M in 5 mL of toluene) as described in Table S2 and Fig. S1.† The preliminary results indicated a first-order dependency on [CL] (Fig. S1†), and the rate of polymerization could be described as $-d[CL]/dt = k_{obs}[CL]$, where $k_{obs} = k_p[\mathbf{L^{ClBr}AlMe_2}$ + 2 BnOH$]^x$, and k_p is the propagation rate constant. By plotting $\ln k_{obs}$ against $\ln[\mathbf{L^{ClBr}AlMe_2}$ + 2 BnOH], x was found to be 2.58, and the $\ln k_p$ value was 8.474 (M^{-1} min^{-1}) (Fig. 8). Polymerizing CL by using $\mathbf{L^{ClBr}AlMe_2}$ **(1)** at room temperature resulted in the following rate law:

$$-d[CL]/dt = 4788 \times [CL][\mathbf{L^{ClBr}AlMe_2} + 2\ BnOH]^{2.58}.$$

According to the kinetic study results, the Al complex may aggregate to a new catalytic species after reacting with BnOH because the order of $[\mathbf{L^{HH}AlMe_2}$ + 2 BnOH] was larger than 2. To identify the real catalyst in the polymerization process, the reaction of $\mathbf{L^{HH}AlMe_2}$ **(5)** with 2 eq. of BnOH in $CDCl_3$ was investigated, and the results are displayed in Fig. 9. The monitoring of the disappearance of the ^{1}NMR signals of the two

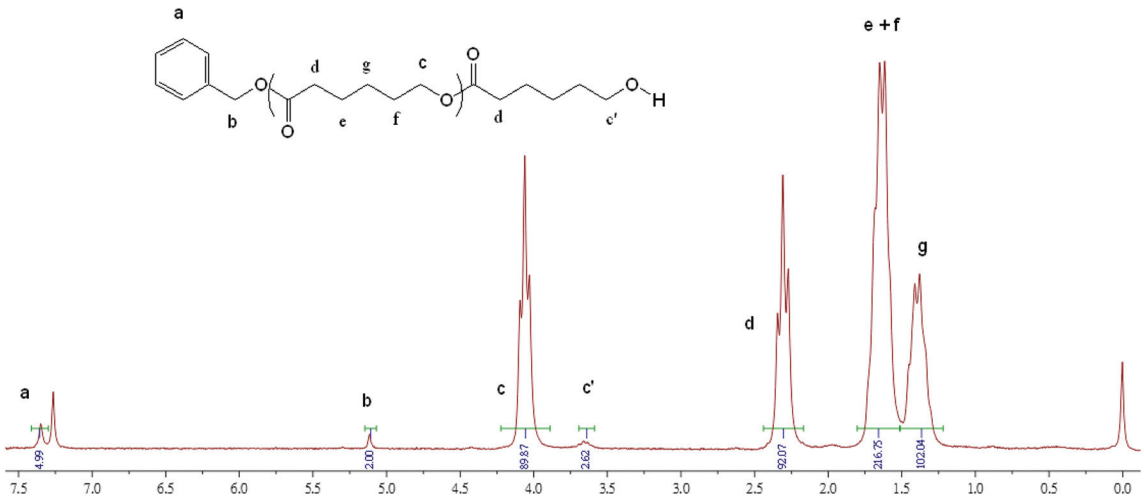


Fig. 7 ^{1}H NMR spectrum of PCL (entry 3, Table 3).

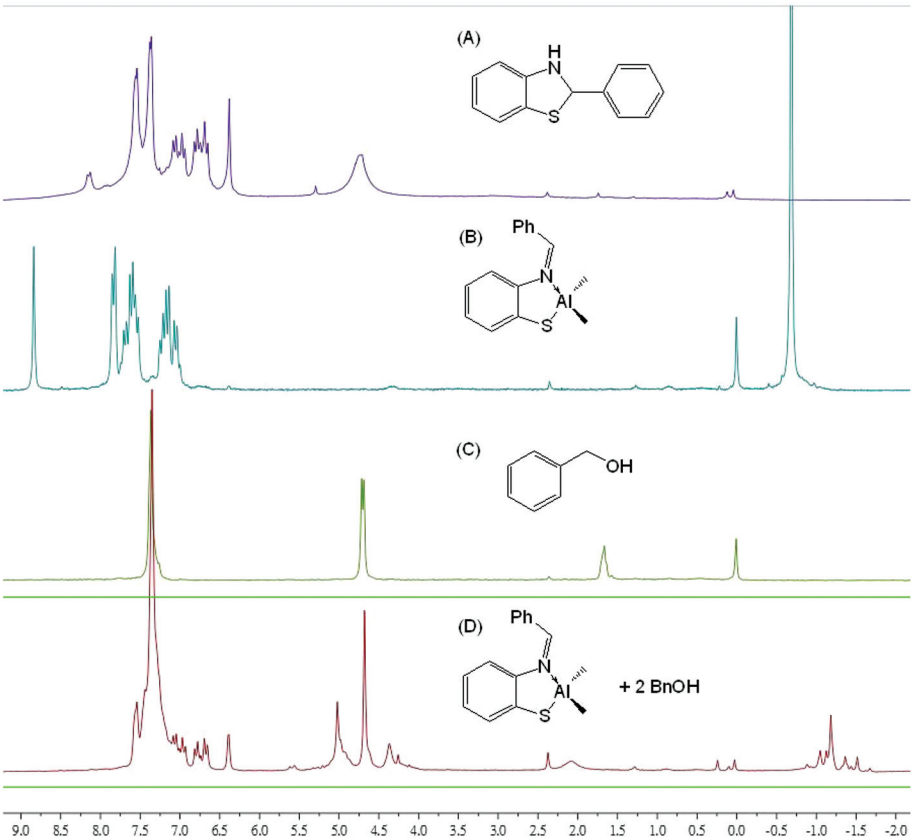


Fig. 9 The ^{1}NMR spectra of (A) L^{HH}-H, (B) $L^{HH}AlMe_2$ **(5)**, (C) BnOH, and (D) a mixture of $L^{HH}AlMe_2$ **(5)** and BnOH (1 : 2) in $CDCl_3$.

methyl groups from $L^{HH}AlMe_2$ **(5)** after reacting with benzyl alcohols and consultation of related studies[7l,t,8,10] suggest that benzyl alcohols replace the two methyl groups of $L^{HH}AlMe_2$ **(5)**. However, the imine group (8.82 ppm) of the Al complex also disappeared, and a few of the ligands appeared with benzyl alkoxide (5.02 ppm). The product could not be isolated after the purification. It is unclear so far what the real catalyst was in the polymerization, and why the order of [$L^{ClBr}AlMe_2$ + 2 BnOH] was 2.5.

Conclusions

A series of five-membered ring aluminum complexes bearing thiol-Schiff base ligands were synthesized, and their application in CL polymerization was investigated. All the five-membered ring aluminum complexes bearing thiol-Schiff base ligands exhibited dramatically higher catalytic activity than those of the six-membered ring S^2AlMe_2 complex (approximately 4- to 10-fold higher) and the five-membered ring $L^{5\text{-}Ph}AlMe_2$ complex (approximately 7- to 19-fold higher), and a shorter induction period compared with other types of aluminum complexes bearing Schiff base ligands was also observed. Moreover, the electron-withdrawing groups enhanced the catalytic activity of the Al complexes compared with the electron donating groups. Our novel approach of integrating thiol-Schiff base ligands in 5-membered ring aluminum catalysis has proven to have effective synergy.

Experimental section

Standard Schlenk techniques and a N_2-filled glovebox were used throughout the isolation and handling of all the compounds. Solvents, such as hexane, toluene, and THF, were purified by distillation after adding sodium metal and benzophenone. CH_2Cl_2 was purified by distillation after adding P_2O_5. ε-Caprolactone was purified by distillation after adding $MgSO_4$. $CDCl_3$ was used after adding molecular sieves. Deuterated chloroform, ε-caprolactone and dimethyl aluminum chloride were purchased from Acros. Benzyl alcohol, 2-aminophenol, 2-aminothiophenol, 2-amino-4-chlorobenzenethiol, benzaldehyde, 4-chlorobenzaldehyde, 4-bromobenzaldehyde, 4-methoxybenzaldehyde, and trimethylaluminum were purchased from Alfa Aesar. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini2000-200 (200 MHz for ^{1}H and 50 MHz for ^{13}C) spectrometer with chemical shifts given in ppm from the internal TMS or the center line of $CDCl_3$. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument. GPC measurements were performed on a Jasco PU-2080 PLUS HPLC pump system equipped with a differential Jasco RI-2031 PLUS refractive index detector using THF (HPLC

grade) as an eluent (flow rate: 1.0 mL min^{-1}, at 40 °C). The chromatographic column was a JORDI Gel DVB 103 Å, and the calibration curve was obtained by using primary polystyrene standards to calculate Mn(GPC). $\mathbf{O^{H}}$-**H**,[11] $\mathbf{O^{OMe}}$-**H**,[12] and $\mathbf{O^{ClBr}}$-**H**[13] were prepared following literature procedures. All the thiol-Schiff base ligands could not be isolated directly because they were further oxidized by O_2 to form arylbenzothiazole.[9]

Synthesis of $\mathbf{L^{ClBr}AlMe_2}$ (1)

A mixture of 4-bromobenzaldehyde (2.77 g, 15 mmol) and 2-amino-4-chlorobenzenethiol (2.40 g, 15 mmol) was stirred for 18 h in CH_2Cl_2 (30 mL) at room temperature in a dry box. CH_2Cl_2 of the solution was removed under vacuum to give a brown powder. Toluene (30 mL) was transferred as a solvent, and the solution was transferred to $AlMe_3$ (8 mL, 2.0 M, 16 mmol) in toluene (10 mL) at 0 °C. The solution was stirred for 18 h. Volatile materials were removed under vacuum to give a red powder and then hexane (50 mL) was transferred to the suspension. The reddish orange powder was obtained after filtering. Yield: 3.46 g (60%). ^{1}H NMR ($CDCl_3$, 200 MHz) 8.75 (s, 1H, C**H**═N), 7.77 (d, 2H, *J* = 10 Hz, *m*-**H**-*Ph*-Br), 7.69 (d, 2H, *J* = 10 Hz, *o*-**H**-*Ph*-Br), 7.47 (d, 1H, *J* = 8 Hz, *m*-**H**-*Ph*-S), 7.24 (d, 1H, *J* = 8 Hz, *o*-**H**-*Ph*-S), 7.17 (s, 1H, *m*-**H**-*Ph*-S), −0.67 (s, 6H, Al(C**H**$_3$)$_2$) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) 169.98 (**C**═N), 146.75 (*Ar***C**–N), 142.79 (*Ar***C**–S), 134.65, 132.95, 132.35, 131.97, 130.45, 130.25 (**C**–Ar), 120.08 (*Ar***C**–Cl), −7.49 (Al(**C**H$_3$)$_2$) ppm. Elemental anal. found (calcd) for $\mathbf{L^{ClBr}AlMe_2}$: $C_{15}H_{14}AlBrClNS$: N, 3.16 (3.66); C, 46.98 (47.08); H, 4.12 (3.69)%. Mp: 240 °C. Yield: 1.78 g (27%). Mp: 70 °C.

Synthesis of $\mathbf{L^{ClCl}AlMe_2}$ (2)

A method similar to that for $\mathbf{L^{ClBr}AlMe_2}$ was used, except that 4-chlorobenzaldehyde was used in place of 4-bromobenzaldehyde. Yield: 4.47 g (88%). ^{1}H NMR ($CDCl_3$, 200 MHz) 8.77 (s, 1H, C**H**═N), 7.78 (d, 2H, *J* = 10 Hz, *m*-**H**–N═C*Ph*-Cl), 7.57 (d, 2H, *J* = 8 Hz, *o*-**H**–N═C*Ph*–Cl), 7.41 (d, 1H, *J* = 10 Hz, *o*-**H**-*Ph*-S), 7.18–7.13 (m, 2H, **H**–*Ar*), −0.69 (s, 6H, Al(C**H**$_3$)$_2$) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) 169.53 (*Ar***C**═N), 146.75(*Ar***C**–N), 142.39 (*Ar***C**–S), 134.64, 133.32, 132.09, 131.63, 130.45, 130.36, 129.99, 120.33, 120.01 (*Ar*), −7.56 (Al(**C**H$_3$)$_2$) ppm. Elemental anal. found (calcd) for $\mathbf{L^{ClCl}AlMe_2}$: $C_{15}H_{14}AlCl_2NS$: N, 4.28 (4.14); C, 52.93 (53.27); H, 4.13 (4.17)%. Mp: 78 °C.

Synthesis of $\mathbf{L^{ClO}AlMe_2}$ (3)

A method similar to that for $\mathbf{L^{ClBr}AlMe_2}$ was used, except that 4-methoxybenzaldehyde was used in place of 4-bromobenzaldehyde. Yield: 1.98 g (47%). ^{1}H NMR ($CDCl_3$, 200 MHz) 8.63 (s, 1H, C**H**═N), 7.82 (d, 2H, *J* = 8 Hz, 2H, *o*-**H**–N═C*Ph*–OMe), 7.40 (d, 2H, *J* = 10 Hz, *p*-**H**–N*Ph*–Cl), 7.13–7.04 (m, 4H, *Ar*–**H**), 3.93 (s, 3H, OC**H**$_3$), −0.65 (s, 6H, Al(C**H**$_3$)$_2$) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) 167.91 (**C**═N), 165.32 (*Ar***C**–OMe), 146.79 (*Ar***C**–N), 138.92 (*Ar***C**–S), 134.02, 133.44, 129.09, 128.52, 124.50, 119.20, 114.81 (*Ar*), 55.79 (O**C**H$_3$), −7.36 (Al(**C**H$_3$)$_2$) ppm. Elemental anal. found (calcd) for $\mathbf{L^{ClBr}AlMe_2}$: $C_{16}H_{17}AlClNOS$: N, 4.03 (4.20); C, 57.08 (57.57); H, 5.11 (5.13)%. Mp: 83 °C.

Synthesis of $\mathbf{L^{ClH}AlMe_2}$ (4)

A method similar to that for $\mathbf{L^{ClBr}AlMe_2}$ was used, except that benzaldehyde was used in place of 4-bromobenzaldehyde. Yield: 2.47 g (54%). ^{1}H NMR ($CDCl_3$, 200 MHz) 8.83 (s, 3H, C**H**═N), 7.84 (d, 2H, *J* = 8 Hz, *o*-**H**–N═C*Ph*), 7.74 (t, 1H, *J* = 8 Hz, *p*-**H**–N═C*Ph*), 7.63 (d, 2H, *J* = 8 Hz, *m*-**H**–N═C*Ph*), 7.47 (d, 1H, *J* = 8 Hz, *o*-**H**–*Ph*–Cl), 7.22–7.17 (m, 2H, *Ar*–**H**), −0.68 (s, 6H, Al(C**H**$_3$)$_2$) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) 169.20 (**C**═N), 146.50 (*Ar***C**–N), 139.46 (*Ar***C**S), 135.02, 133.90, 131.91, 131.00, 129.36, 128.91, 119.38 (*Ar*), −7.63 (Al(**C**H$_3$)$_2$) ppm. Elemental anal. found (calcd) for $\mathbf{L^{ClH}AlMe_2}$: $C_{15}H_{15}AlClNS$: N, 4.55 (4.61); C, 59.95 (59.31); H, 4.94 (4.97)%. Mp: 79 °C.

Synthesis of $\mathbf{L^{HH}AlMe_2}$ (5)

A method similar to that for $\mathbf{L^{ClBr}AlMe_2}$ was used, except that benzaldehyde was used in place of 4-bromobenzaldehyde, and 2-aminothiophenol was used in place of 2-amino-4-chlorobenzenethiol. Yield: 2.54 g (62%). ^{1}H NMR ($CDCl_3$, 200 MHz) 8.82 (s, 1H, C**H**═N), 7.82 (d, 2H, *J* = 8 Hz, *o*-**H**–N═C*Ph*), 7.68 (t, 1H, *J* = 8 Hz, *p*-**H**–N═C*Ph*), 7.59 (d, 2H, *J* = 8 Hz, *m*-**H**–N═C*Ph*), 7.52 (d, 1H, *J* = 8 Hz, *Ar*–**H**), 7.22–6.98 (m, 3H, *Ar*–**H**), −0.69 (s, 6H, Al(C**H**$_3$)$_2$) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) 168.1 (**C**═N), 145.85 (*Ar***C**–N), 140.73 (*Ar* **C**–S), 134.45, 133.00, 132.18, 130.99, 130.72, 130.09, 129.16, 123.73, 119.20 (*Ar*), −7.68 (Al(**C**H$_3$)$_2$) ppm. Elemental anal. found (calcd) for $\mathbf{L^{HH}AlMe_2}$: $C_{15}H_{16}AlNS$: N, 4.96 (5.20); C, 66.99 (66.89); H, 6.37 (5.99)%. Mp: 89 °C.

Synthesis of $\mathbf{O^{H}{}_2AlMe}$ (6)

$\mathbf{O^{H}}$-**H** (1.97 g, 10 mmol) was added to toluene (40 mL) and the solution was transferred to $AlMe_3$ (2.5 mL, 2.0 M, 5 mmol) at 0 °C. The solution was stirred for 3 h. Volatile materials were removed under vacuum to give a deep red powder and then hexane (50 mL) was transferred to the suspension. The reddish orange powder was obtained after filtering. Yield: 1.58 g (73%). ^{1}H NMR ($CDCl_3$, 200 MHz) 8.90 (s, 2H, C**H**═N), 8.30 (d, 4H, *J* = 8 Hz, *o*-N═C*Ph*–**H**), 7.52–7.40 (m, 6H, *Ar*), 7.20 (d, 4H, *J* = 8 Hz, *m*-N═C*Ph*–**H**), 6.93 (d, 2H, *J* = 8 Hz, *o*-N*Ph*–**H**), 6.78 (t, 2H, *J* = 8 Hz, *p*-**H**–*Ph*O), −1.25 (s, 3H, AlC**H**$_3$) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) 160.03 (**C**═N), 158.68 (*Ar***C**–O) 136.54 (*Ar***C**–N), 133.77, 132.58, 131.83, 130.77, 128.63, 118.88, 117.52, 115.83 (**C**–Ar), −8.03 (Al(**C**H$_3$)) ppm. Elemental anal. found (calcd) for $\mathbf{L^{O}{}_2AlMe}$: $C_{27}H_{23}AlN_2O_2$: N, 6.62 (6.45); C, 74.25 (74.64); H, 5.19 (5.34)%. Mp: 120 °C.

Synthesis of $\mathbf{O^{OMe}{}_2AlMe}$ (7)

A method similar to that for $\mathbf{O^{H}{}_2AlMe}$ **(6)** was used, except that $\mathbf{O^{OMe}}$-**H** was used in place of $\mathbf{O^{H}}$-**H**. Yield: 2.04 g (83%). ^{1}H NMR ($CDCl_3$, 200 MHz) 9.29 (s, 2H, C**H**═N), 8.87 (d, 2H, *J* = 8 Hz, *o*-N═C*Ph*–**H**), 7.49–7.38 (m, 4H, N═C*Ph*–**H**), 7.20- (t, 2H, *J* = 8 Hz, *p*-N═C*Ph*–**H**), 7.03–6.89 (m, 6H, C═N–*Ar*–**H**), 6.76 (t, 2H, *J* = 8 Hz, *o*-**H**–*Ph*O), 3.89 (s, 6H, OC**H**$_3$), −1.33 (s, 3H, AlC**H**$_3$) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) 160.40 (**C**═N), 158.84 (*Ar***C**–OMe), 156.47 (*Ar***C**–O), 137.32 (*Ar***C**–N), 134.31, 132.08, 130.42, 123.30, 120.87, 118.73, 117.36, 116.40, 110.67 (*Ar*), 55.93 (O**C**H$_3$), −7.64 (Al**C**H$_3$) ppm. Elemental anal. found

(calcd) for $O^{OMe}{}_2AlMe$: $C_{29}H_{27}AlN_2O_4$: N, 5.92 (5.66); C, 70.69 (70.43); H, 5.22 (5.50)%. Mp: 134 °C.

Synthesis of $O^{ClBr}{}_2AlMe$ (8)

A method similar to that for $O^{H}{}_2AlMe$ (6) was used, except that O^{ClBr}-H was used in place of O^{H}-H. Yield: 2.11 g (64%). ^{1}H NMR ($CDCl_3$, 200 MHz) 8.76 (s, 2H, C**H**═N), 8.14 (d, 4H, J = 8 Hz, *o*-N═C*Ph*–**Br**), 7.63 (d, 4H, J = 8 Hz, *m*-N═C*Ph*–**Br**), 7.37 (s, 2H, *o*-N–*Ph*–**H**), 7.17 (d, 2H, J = 8 Hz, *p*-N–*Ph*–**H**), 6.83 (d, 2H, *m*-N–*Ph*–**H**), −1.25 (s, 3H, Al**C**$\mathbf{H_3}$) ppm. Because $O^{ClBr}{}_2AlMe$ (8) could not dissolve well in $CDCl_3$, d_6-acetone, and d_6-DMSO, the ^{13}C NMR spectrum was not available. Elemental anal. found (calcd) for $O^{ClBr}{}_2AlMe$: $C_{27}H_{19}AlBr_2Cl_2N_2O_2$: N, 3.98 (4.24); C, 49.23 (49.05); H, 3.12 (2.90)%. Mp: 147 °C.

General procedures for the polymerization of ε-caprolactone

A typical polymerization procedure was exemplified by the synthesis of entry 1 (Table 2) using the $L^{ClBr}AlMe_2$ complex as a catalyst. The polymerization conversion was analyzed by ^{1}H NMR spectroscopic studies. Toluene (5.0 mL) was added to a mixture of the $L^{ClBr}AlMe_2$ complex (0.1 mmol), BnOH (0.2 mmol), and ε-caprolactone (10 mmol) at room temperature. At indicated time intervals, 0.05 mL aliquots were removed, trapped with $CDCl_3$ (1 mL), and analyzed by ^{1}H NMR. After the solution was stirred for 12 min, the reaction was quenched by adding a drop of ethanol, and the polymer precipitated as a white solid when poured into *n*-hexane (60.0 mL). The isolated white solid was dissolved in CH_2Cl_2 (5.0 mL) and then *n*-hexane (70.0 mL) was added to obtain a purified crystalline solid. Yield: 0.91 g (80%).

Conflicts of interest

The authors declare no competing financial interest.

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