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Efficient ring-opening polymerization of ε-caprolactone using anilido-imine–aluminum complexes in the presence of benzyl alcohol

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ABSTRACT

A number of new anilido-imine–Al complexes *ortho*-$C_6H_4(CH{=}NAr^1)(NAr^2)AlMe_2$ [$Ar^1 = C_6H_5$, $Ar^2 = C_6H_5$ (**2a**); $Ar^1 = 2,6\text{-}Me_2C_6H_3$, $Ar^2 = 2,6\text{-}Me_2C_6H_3$ (**2b**); $Ar^1 = 2,6\text{-}Et_2C_6H_3$, $Ar^2 = 2,6\text{-}Et_2C_6H_3$ (**2c**); $Ar^1 = 2,6\text{-}{}^i Pr_2C_6H_3$, $Ar^2 = 2,6\text{-}Me_2C_6H_3$ (**2d**); $Ar^1 = 2,6\text{-}{}^i Pr_2C_6H_3$, $Ar^2 = 2,6\text{-}Et_2C_6H_3$ (**2e**)] were synthesized, characterized and used as initiators for the ring-opening polymerization of ε-caprolactone in the presence of benzyl alcohol. The effect of initiator structure and reaction conditions, such as benzyl alcohol/Al molar ratio and reaction temperature on the reactivity, and polymer molecular weight were investigated. The polymerization of ε-caprolactone initiated by these complexes was found to take place in an immortal fashion.

1. Introduction

Poly(ε-caprolactone) (PCL) has attracted much attention due to its potential applications in medicine, pharmaceutics, and tissue engineering such as medium for the controlled release of drugs, scaffolds, and the delivery of antibodies and genes [1]. Metal complexes initiated ring-opening polymerization (ROP) of ε-caprolactone (CL) is the major method used to synthesize PCL because of its high degree control over the polymerization, and hence the formation of PCL with controlled molecular weight and narrow molecular weight distribution [2]. A large number of metal initiators, including magnesium [3], calcium [4], aluminum [5], titanium [6], iron [7], zinc [8], tin [9], and rare earth metal [10] complexes supported by various ligands have been reported. Generally, the reactivity of an initiator can be influenced by the steric and electronic characteristics of the ancillary ligand framework and therefore can be tuned by modification of the ligand. Because of high Lewis acidity and low toxicity, Al complexes were studied mostly as initiators for the ROP of CL. Recently Nomura and co-workers reported a number of highly efficient salicylaldimine–aluminum initiators for this reaction [5o]. In order to find good initiators with similar structure, we synthesize a number of anilido-imine–Al complexes, *ortho*-$C_6H_4(CH{=}NAr^1)(NAr^2)AlMe_2$ [$Ar^1 = C_6H_5$, $Ar^2 = C_6H_5$ (**2a**); $Ar^1 = 2,6\text{-}Me_2C_6H_3$, $Ar^2 = 2,6\text{-}Me_2C_6H_3$ (**2b**); $Ar^1 = 2,6\text{-}Et_2C_6H_3$, $Ar^2 = 2,6\text{-}Et_2C_6H_3$ (**2c**); $Ar^1 = 2,6\text{-}{}^i Pr_2C_6H_3$, $Ar^2 = 2,6\text{-}Me_2C_6H_3$ (**2d**); $Ar^1 = 2,6\text{-}{}^i Pr_2C_6H_3$, $Ar^2 = 2,6\text{-}Et_2C_6H_3$ (**2e**)], and examined their reactivity for the ROP of CL in the presence of benzyl alcohol (BnOH). It was found that these complexes are efficient initiators for the ROP reaction and the polymerization takes place in an immortal fashion. Herein, we report the synthesis and characterization of these Al complexes, and their properties for the ROP of CL.

2. Results and discussion

2.1. Synthesis of ligands

Anilido-imine ligands *ortho*-$C_6H_4(CH{=}NAr^1)(NHAr^2)$ [$Ar^1 = C_6H_5$, $Ar^2 = C_6H_5$ (**1a**); $Ar^1 = 2,6\text{-}Me_2C_6H_3$, $Ar^2 = 2,6\text{-}Me_2C_6H_3$ (**1b**); $Ar^1 = 2,6\text{-}Et_2C_6H_3$, $Ar^2 = 2,6\text{-}Et_2C_6H_3$ (**1c**); $Ar^1 = 2,6\text{-}{}^i Pr_2C_6H_3$, $Ar^2 = 2,6\text{-}Me_2C_6H_3$ (**1d**); $Ar^1 = 2,6\text{-}{}^i Pr_2C_6H_3$, $Ar^2 = 2,6\text{-}Et_2C_6H_3$ (**1e**); $Ar^1 = 2,6\text{-}{}^i Pr_2C_6H_3$, $Ar^2 = 2,6\text{-}{}^i Pr_2C_6H_3$ (**1f**)] were synthesized in good yields by the reaction of *ortho*-$C_6H_4F(CH{=}NAr^1)$ with corresponding $LiN(H)Ar^2$ (Scheme 1) according to the literature procedure [11]. Among these ligands, **1c** and **1e** are new compounds while **1a**, **1b**, **1d** and **1f** have been reported previously [11]. Ligands **1c** and **1e** were characterized by ^1H NMR spectroscopy along with elemental analyses. The ^1H NMR spectra of both ligands exhibit resonance about 8.30 ppm for the imino CH=N proton. The NH resonance appears at characteristically low field (10.45, 10.51 ppm). These data are similar to the corresponding values of **1a**, **1b**, **1d** and **1f**.

2.2. Synthesis of complexes

Complexes **2a**–**2f** were synthesized by alkane elimination reaction in good yields (>80%). Treatment of the ligands **1a**–**1f** with

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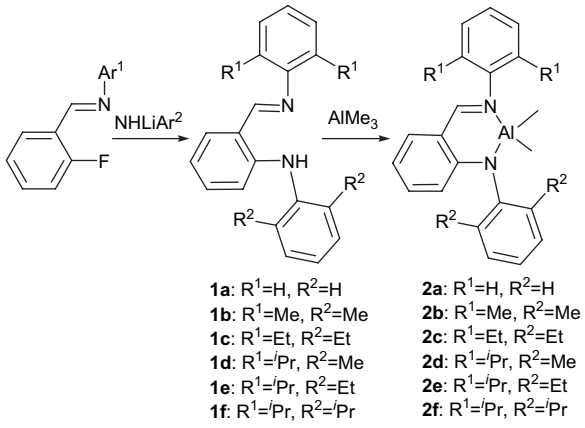


Scheme 1. Synthetic procedure of ligands **1a**–**1f** and complexes **2a**–**2f**.

$AlMe_3$ in hexane gives the desired anilido-imine–Al complexes **2a**–**2f** (Scheme 1). Complexes **2a**–**2e** are new compounds while **2f** has been reported previously [11c]. New complexes **2a**–**2e** were characterized by elemental analyses and ^1H NMR spectroscopy. The disappearance of the N–H signal of the ligands and the appearance of the resonance for protons of $AlMe_2$ in high field region (−0.60 to −1.0 ppm) demonstrate the formation of the desired complexes.

2.3. Ring-opening polymerization of ε-caprolactone initiated by *2a*–*2f* in the presence of BnOH

Polymerization reactions of CL under different conditions were studied in the presence of complexes **2a**–**2f** together with BnOH. The polymerization results are listed in Table 1. Complexes **2a**–**2f** show high reactivity for initiating the ROP of CL in the presence of BnOH, while no reaction takes place in the absence of BnOH (entries 1–4). The ^1H NMR spectrum of a typical polymer sample is shown in Fig. 1. Signals of the methylene protons (c, d, e and f) appear at 2.33, 1.66, 1.40, 4.08 ppm, and the weak signals arise from the ending benzyl group (CH_2, 5.13 ppm, b; ph, 7.37 ppm, a) and the terminal methylene protons (CH_2OH, 3.67 ppm, g). The integral ratio of the methylene protons in the terminal benzyl group (b) and the CH_2OH group (g) is close to 1. The ^1H NMR spectrum indicates that the polymer chain should be capped with a benzyl ester at one end and a hydroxyl group at the other end. The reactivity of these complexes (entries 6, 15–19) as initiators for the ROP reaction of CL under the same conditions is in the order of **2a** > **2b** > **2c** > **2d** > **2e** > **2f**, which is exactly in reverse order of the size of substituents on the two phenyl rings in their ligands. The increase in reactivity with the decrease in the size of the substituents on the two phenyl rings could be explained that the aluminum center in a complex with a less bulky ligand can be easily approached by the CL monomer. These results are in contrast to those observed in the salicylaldimine–aluminum initiator systems [5o], in which the bulkier the ligand, the higher the reactivity of the complex. To examine the effect of reaction conditions on the reactivity of the system and the molecular weight of the produced polymer, polymerization experiments under different conditions were conducted in the presence of complex **2a** and BnOH. The effect of the amount of BnOH was first studied and it was found that the highest reactivity can be obtained with the BnOH/Al molar ratio being 1/1. In all cases, the number-averaged degree of polymerization (DP_n) of the obtained polymers (calculated by ^1H NMR) is close to the CL/BnOH molar ratio, and the molecular weight (M_n) of the polymers determined by gel permeation chromatography is proportional to the $[CL]_0/[BnOH]_0$ molar ratio (Fig. 2). These results demonstrate the "living" character of the polymerization process with BnOH as a co-initiator. Similar results have been reported by Feijen and co-workers for Ca–amine initiator systems which have been described as "immortal" [4a]. The polydispersity index (PDI) of the resultant polymers ranges from 1.14 to 1.64. The narrow molecular weight distribution is a well-known feature of coordination polymerization reactions. The reactivity of complex **2a** is quite dependent on the reaction temperature and increases quickly upon elevating the reaction temperature from 20 to 70 °C. In comparison with the literature results, the reactivity of our anilido-imine–aluminum complexes is slightly lower than that of the salicylaldimine–aluminum complexes [5o].

Table 1
Ring-opening polymerization of ε-caprolactone initiated by complexes **2a**–**2f**[a]

Entry	Cat	[BnOH]/[Al]/[CL]	Temp (°C)	Time	Yield[b] (%)	TOF[c]	DP_n[d]	M_n,[e] ($\times 10^3$)	PDI[e]
1	**2a**	0:1:100	70	24 h	0	–	–	–	–
2	**2b**	0:1:100	70	24 h	0	–	–	–	–
3	**2c**	0:1:100	70	24 h	0	–	–	–	–
4	**2d**	0:1:100	70	24 h	0	–	–	–	–
5	**2a**	0.5:1:100	70	3 min	93.3	1866.0	194	45.1	1.18
6	**2a**	1:1:100	70	2 min	96.7	2901.0	100	26.4	1.20
7	**2a**	2:1:100	70	2.5 min	92.5	2220.0	55	14.9	1.23
8	**2a**	4:1:100	70	3.6 min	93.5	1558.3	27	8.2	1.10
9	**2a**	1:1:100	50	5 min	71.1	853.2	64	17.2	1.16
10	**2a**	1:1:100	20	10 min	43.0	258.0	47	13.6	1.23
11	**2a**	1:1:200	70	4.5 min	95.6	2549.3	207	48.0	1.14
12	**2a**	1:1:250	70	7 min	97.6	2091.4	256	57.9	1.26
13	**2a**	1:1:300	70	9 min	93.0	1860.0	302	76.6	1.64
14	**2a**	1:1:400	70	14 min	92.6	1587.4	410	107.0	1.56
15	**2b**	1:1:100	70	2.5 min	95.4	2289.6	99	26.1	1.21
16	**2c**	1:1:100	70	3 min	93.6	1872.0	103	27.1	1.27
17	**2d**	1:1:100	70	3.1 min	95.1	1840.6	95	25.4	1.25
18	**2e**	1:1:100	70	4.0 min	93.2	1398.0	101	26.7	1.24
19	**2f**	1:1:100	70	4.7 min	93.7	1196.2	110	27.6	1.28

[a] Polymerization conditions: catalyst, 0. 19 mmol; CL, 3.0 mol/L in toluene; a N_2 atmosphere.
[b] Isolated yield.
[c] Mole of CL consumed per mole of catalyst per hour.
[d] The number-average degree of polymerization by ^1H NMR.
[e] Obtained from GPC analysis.

According to above results and by analogy with the mechanisms accepted for the ROP of cyclic esters mediated by metal alkoxides [5i,12,13], a mechanism for our polymerization system can be proposed as shown in Scheme 2. First, BnOH reacts with the alkyl Al complex to form the active benzyloxyaluminum species. The coordination of the lactone molecule to the metal center, followed by the ring cleavage at the acyl–oxygen bond and insertion into the Al–O bond of the benzyloxyaluminum species then occurs to form a new alkoxyaluminum intermediate. Repetition of the same procedure forms the PCL chain on the Al center. The PCL chain can be removed from the Al center by reacting with BnOH (or a short chain PCL molecule) to form the PCL molecule and a new benzyloxyaluminum (or alkoxyaluminum) species that will initiate a new PCL chain. In the whole polymerization procedure, BnOH acts as a co-initiator as well as a chain transfer reagent by forming the benzyloxyaluminum complex.

To prove the formation of the benzyloxyaluminum species in the ROP of CL system, the reaction of complex **2a** with BnOH (1/1) was monitored by ^1H NMR in $CDCl_3$ at room temperature. The ^1H NMR spectrum of the reaction mixture is shown in Fig. 3. The disappearance of the resonance for one Me of the AlMe_2 moiety in high field region and the appearance of the resonance for AlOCH_2Ph protons at 4.9 ppm demonstrate the formation of the benzyloxy complex LAlMeOBn [L = *ortho*-$C_6H_4(CH{=}NC_6H_5)(NC_6H_5)$]. To confirm that the LAlMeOBn complex can initiate the ROP reaction of CL, a solution of CL in $CDCl_3$ was added to the above reaction mixture (CL/Al = 18) at room temperature and the formation of the LAlMe[$O(CH_2)_5C{=}O]_{18}OCH_2Ph$ intermediates was detected by ^1H NMR spectrum (shown in Fig. 4), in which the polymer chain shows similar resonances to those seen in the ^1H NMR spectrum of the PCL sample shown in Fig. 1.

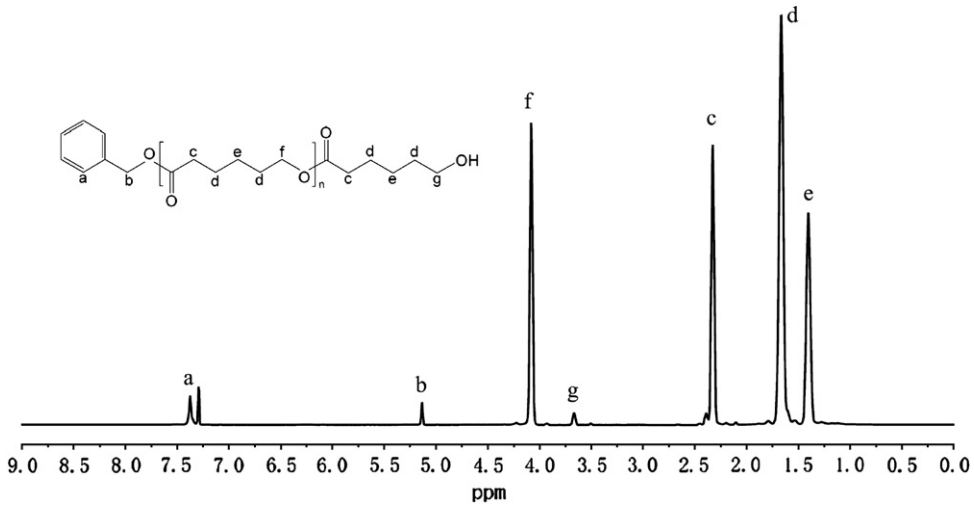


Fig. 1. ^{1}H NMR spectrum of a typical polymer sample.

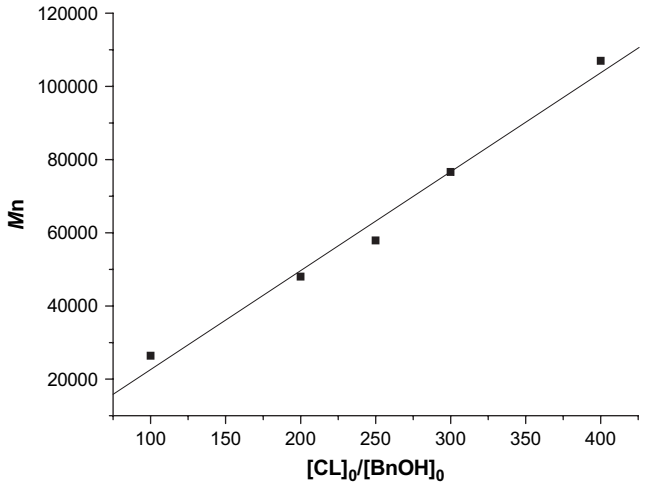


Fig. 2. Relationship between M_n of the polymer and the initial mole ratio $[CL]_0/[BnOH]_0$ for the polymerization of CL catalyzed by **2a** in toluene at 70 °C.

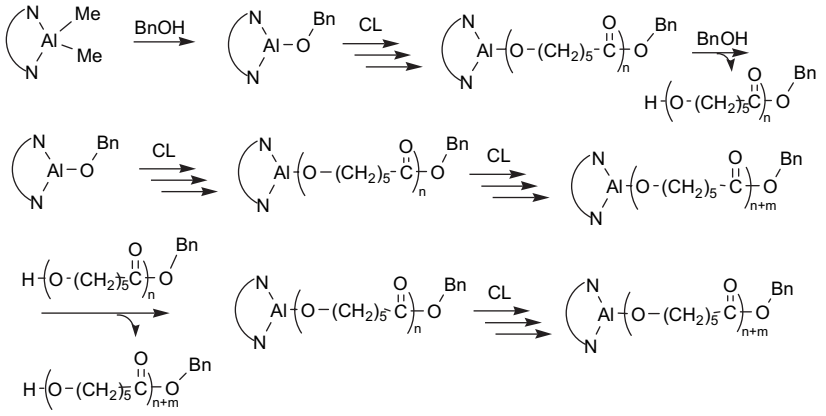
3. Experimental section

3.1. General

All reactions were performed using standard Schlenk techniques in an atmosphere of high purity nitrogen or glove box techniques. Toluene, hexane, and THF were dried by refluxing over sodium and benzophenone and distilled under nitrogen prior to use. $CDCl_3$ was dried over CaH_2 for 48 h and vacuum-transferred to an air-free flask. *n*-BuLi and $AlMe_3$ were purchased from Aldrich and used as received. ^{1}H NMR spectra were measured using a Bruker AVANCE-500 NMR spectrometer. The elemental analysis was performed on a Perkin–Elmer 2400 analyzer. The GPC measurements were performed on a Water-410 system using CH_2Cl_2 as the eluent (flow rate: 1 mL/min, at 25 °C). Molecular weights and molecular weight distributions were calculated using polystyrene as standard. ^{1}H NMR spectra of the PCL were measured using a Bruker AVANCE-500 NMR spectrometer.

3.1.1. Synthesis of ortho-$C_6H_4(CH{=}NC_6H_3Et_2$-2,6)-($NHC_6H_3Et_2$-2,6) (**1c**)

A solution of *n*-BuLi (20 mL, 20 mmol) in hexanes was added to a solution of 2,6-diethylaniline (3.1 mL, 20 mmol) in THF (30 mL) at −78 °C. The mixture was allowed to warm to room temperature and stirred overnight. The resulting solution was transferred into a solution of *ortho*-$C_6H_4F(C_6H_3Et_2$-2,6) (5.1 g, 20 mmol) in THF (40 mL) at 25 °C. After stirring for 12 h, the reaction was quenched with H_2O (25 mL), extracted with hexane, and the organic phase was evaporated to dryness in vacuo to give the crude product as yellow solid. Pure product was obtained by recrystallization from MeOH at −20 °C as yellow solid (5.0 g, 65%). Anal. Calcd for $C_{27}H_{32}N_2$ (384.56): C, 84.33; H, 8.39; N, 7.28. Found: C, 84.30; H, 8.37; N, 7.33. ^{1}H NMR (500 MHz, $CDCl_3$, 293 K): 1.13 (q, 3H, CH_2CH_3),



Scheme 2. The proposed mechanism for polymerization.

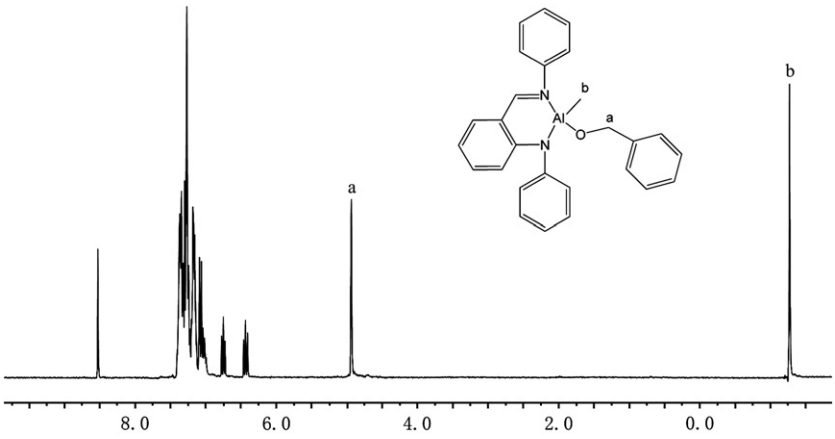


Fig. 3. ^{1}H NMR spectrum of the reaction mixture of complex **2a** and BnOH in $CDCl_3$ at room temperature.

1.14 (q, 3H, CH_2CH_3), 2.56 (m, 6H, CH_2CH_3), 2.65 (m, 6H, CH_2CH_3), 6.29 (d, 1H, Ph-*H*), 6.70 (t, 1H, Ph-*H*), 7.06–7.32 (m, 10H, Ph-*H*), 8.38 (s, 1H, C*H*═NAr), 10.51 (s, 1H, *H*NAr) ppm.

3.1.2. Synthesis of ortho-C_6H_4(CH═$NC_6H_3Et_2$-2,6)-($NHC_6H_3^iPr_2$-2,6) (**1e**)

A solution of *n*-BuLi (21 mL, 21 mmol) in hexanes was added to a solution of 2,6-diethylaniline (3.3 mL, 21 mmol) in THF (30 mL) at −78 °C. The mixture was allowed to warm to room temperature and stirred overnight. The resulting solution was transferred into a solution of *ortho*-$C_6H_4F(C_6H_3^iPr_2$-2,6) (6.0 g, 21 mmol) in THF (40 mL) at 25 °C. After stirring for 12 h, the reaction was quenched with H_2O (25 mL), extracted with hexane, and the organic phase was evaporated to dryness in vacuo to give the crude product as yellow solid. Pure product was obtained by recrystallization from MeOH at −20 °C as yellow solid (5.9 g, 68%). Anal. Calcd for $C_{29}H_{36}N_2$ (412.61): C, 84.42; H, 8.79; N, 6.79. Found: C, 84.40; H, 8.80; N, 6.80. ^{1}H NMR (500 MHz, $CDCl_3$, 293 K): 1.08 (q, 6H, CH_2CH_3), 1.12 (d, 12H, $CH(CH_3)_2$), 2.47 (m, 1H, $CH(CH_3)_2$), 2.58 (m, 1H, $CH(CH_3)_2$), 3.04 (m, 4H, CH_2CH_3), 6.21 (d, 1H, Ph-*H*), 6.63 (t, 1H, Ph-*H*), 7.05–7.27 (m, 10H, Ph-*H*), 8.27 (s, 1H, C*H*═NAr), 10.45 (s, 1H, *H*NAr) ppm.

3.1.3. Synthesis of ortho-C_6H_4(CH═NC_6H_5)(NC_6H_5) Al(Me_2) (**2a**)

$AlMe_3$ (3.7 mL, 1.0 M in hexane, 3.7 mmol) was added to the solution of **1a** (1.0 g, 3.7 mmol) in 20 mL of hexane at 0 °C with stirring. The mixture was stirred at 0 °C for 30 min and at room temperature for additional 2 h, then concentrated to about 8 mL and kept at −20 °C overnight to let the product crystallize. The product was obtained as red powder (1.1 g, 88%). Anal. Calcd for $C_{21}H_{21}AlN_2$ (328.39) C, 76.81; H, 6.45; N, 8.53. Found: C, 76.79; H, 6.44; N, 8.55. ^{1}H NMR (500 MHz, $CDCl_3$, 293 K): −0.57 (s, 6H, $AlCH_3$), 6.73 (d, 1H, Ph-*H*), 6.77 (t, 1H, Ph-*H*), 7.39–7.71 (m, 12H, Ph-*H*), 8.49 (s, 1H, C*H*═NAr) ppm.

3.1.4. Synthesis of ortho-C_6H_4(CH═$NC_6H_3Me_2$-2,6)($NC_6H_3Me_2$-2,6) Al(Me_2) (**2b**)

Compound **2b** was obtained as yellow powder analogously to the preparation of **2a**: $AlMe_3$ (2.7 mL, 2.7 mmol) and 0.90 g (2.7 mmol) of **1b**. Yield: 0.91 g, 86%. Anal. Calcd for $C_{25}H_{29}AlN_2$ (384.49): C, 78.09; H, 7.60; N, 7.29. Found: C, 78.07; H, 7.63; N, 7.28. ^{1}H NMR (500 MHz, $CDCl_3$, 293 K): −0.83 (s, 6H, $AlCH_3$), 2.31 (s, 6H, CH_3), 2.41 (s, 6H, CH_3), 6.28 (d, 1H, Ph-*H*), 6.63 (t, 1H, Ph-*H*), 7.22–7.36 (m, 8H, Ph-*H*), 8.14 (s, 1H, C*H*═NAr) ppm.

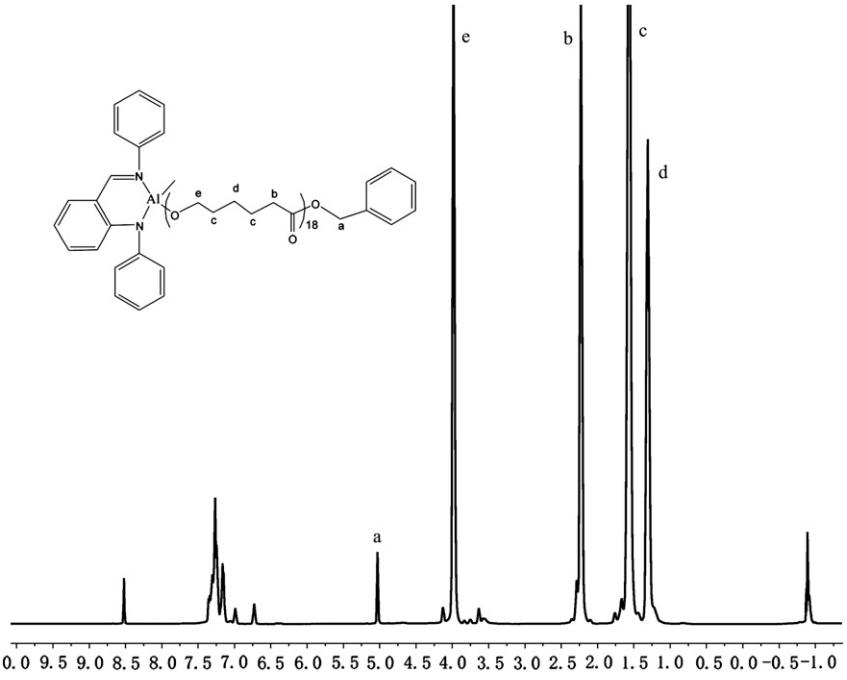


Fig. 4. ^{1}H NMR spectrum of the reaction mixture of complex **2a**, BnOH and CL in $CDCl_3$ at room temperature.

*3.1.5. Synthesis of ortho-C_6H_4(CH=$NC_6H_3Et_2$-2,6)($NC_6H_3Et_2$-2,6)Al(Me_2) (**2c**)*

Compound **2c** was obtained as yellow powder analogously to the preparation of **2a**: $AlMe_3$ (2.9 mL, 2.9 mmol) and 1.1 g (2.9 mmol) of **1c**. Yield: 1.1 g, 85%. Anal. Calcd for $C_{29}H_{37}AlN_2$ (440.60): C, 79.05; H, 8.46; N, 6.36. Found: C, 79.03; H, 8.47; N, 6.33. ^{1}H NMR (500 MHz, $CDCl_3$, 293 K): −0.98 (s, 6H, AlC*H*$_3$), 1.16 (m, 12H, CH_2CH_3), 2.60 (m, 8H, CH_2CH_3), 6.24 (d, 1H, Ph-*H*), 6.55 (t, 1H, Ph-*H*), 7.14–7.29 (m, 8H, Ph-*H*), 8.01 (s, 1H, C*H*=NAr) ppm.

*3.1.6. Synthesis of ortho-C_6H_4(CH=$NC_6H_3Me_2$-2,6)($NC_6H^i_3Pr_2$-2,6)Al(Me_2) (**2d**)*

Compound **2d** was obtained as yellow powder analogously to the preparation of **2a**: $AlMe_3$ (2.6 mL, 2.6 mmol) and 1.0 g (2.6 mmol) of **1d**. Yield: 0.93 g, 81%. Anal. Calcd for $C_{29}H_{37}AlN_2$ (440.60): C, 79.05; H, 8.46; N, 6.36. Found: C, 79.04; H, 8.46; N, 6.35. ^{1}H NMR (500 MHz, $CDCl_3$, 293 K): −0.95 (s, 6H, AlC*H*$_3$), 1.12 (d, 6H, CH(CH_3)$_2$), 1.31 (d, 6H, CH(CH_3)$_2$), 2.20 (s, 6H, CH_3), 3.25 (m, 2H, C*H*(CH_3)$_2$), 6.19 (d, 1H, Ph-*H*), 6.53 (t, 1H, Ph-*H*), 7.11–7.31 (m, 8H, Ph-*H*), 8.05 (s, 1H, C*H*=NAr) ppm.

*3.1.7. Synthesis of ortho-C_6H_4(CH=$NC_6H_3Et_2$-2,6)($NC_6H^i_3Pr_2$-2,6) Al(Me_2) (**2e**)*

Compound **2e** was obtained as yellow powder analogously to the preparation of **2a**: $AlMe_3$ (2.2 mL, 2.2 mmol) and 0.90 g (2.2 mmol) of **1e**. Yield: 0.83 g, 81%. Anal. Calcd for $C_{31}H_{41}AlN_2$ (468.85): C, 79.45 H, 8.82; N, 5.98. Found: C, 79.43; H, 8.84; N, 5.96. ^{1}H NMR (500 MHz, $CDCl_3$, 293 K): −0.90 (s, 6H, AlC*H*$_3$), 1.16 (q, 6H, CH_2CH_3), 1.22 (d, 12H, CH(CH_3)$_2$), 2.69 (m, 4H, CH_2CH_3), 3.28 (m, 2H, C*H*(CH_3)$_2$), 6.24 (d, 1H, Ph-*H*), 6.55 (t, 1H, Ph-*H*), 7.17–7.33 (m, 10H, Ph-*H*), 8.07 (s, 1H, C*H*=NAr) ppm.

3.2. Polymerization of CL

In general, polymerization was performed as the following procedures. To a rapidly stirred mixed solution of catalyst (0.19 mmol) and BnOH was added CL (3.0 mol/L), and the reaction mixture was stirred at proposed temperature for the prescribed time, during which an increase in the viscosity of the solution was observed. After the reaction was quenched by the addition of an excess of 1.0 N aqueous acetic acid solution, the polymer was precipitated into MeOH. Crude product was washed by cool MeOH three times (10 mL) and dried in vacuo up to a constant weight. ^{1}H NMR spectra of the PCL were measured using a Bruker AVANCE-500 NMR spectrometer.

4. Conclusion

In conclusion, a number of new anilido-imine–Al complexes were synthesized and characterized. All of these Al complexes are efficient initiators for the ring-opening polymerization of CL in the presence of benzyl alcohol. The reactivity of these complexes for the polymerization of CL under the same conditions is in the order of **2a** > **2b** > **2c** > **2d** > **2e** > **2f**. The DP_n of the obtained polymers is close to the monomer/initiator molar ratio in the polymerization. The polymerization reaction of CL initiated by these initiator systems takes place in an immortal fashion. The formation of benzyloxyaluminum complexes during the polymerization was confirmed by ^{1}H NMR spectroscopy.

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Appendix A. Supplementary data

NMR spectra for **1c**, **1e** and **2a**–**2e** are provided. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2008.03.035.

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