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Complete List of Authors:	Tseng, Hsi-Ching; Kaohsiung Medical University, Medicinal and Applied Chemistry Kaohsiung city Chiang, Michael, Y.; Sun Yet-Sen University, Department of Chemistry Lu, Wei-Yi; Kaohsiung Medical University, Medicinal and Applied Chemistry, Chen, Yen-Jen; Kaohsiung Medical University, Medicinal and Applied Chemistry, Lian, Cheng-Jie; Kaohsiung Medical University, Medicinal and Applied Chemistry Kaohsiung city Chen, Yu-Hsieh; Kaohsiung Medical University, Department of Medicinal and Applied Chemistry Tsai, Hsin-Yi; Kaohsiung Medical University, Department of Medicinal and Applied Chemistry Lai, Yi-Chun; Kaohsiung Medical University, Medicinal and Applied Chemistry Kaohsiung city Chen, Hsuan-Ying; Kaohsiung Medical University, Medicinal and Applied Chemistry

A Closer Look on ε-Captolactone Polymerization Catalyzed by Alkyl Aluminum Complexes: The Effect of Induction Period on Overall Catalytic Activity

Hsi-Ching Tseng,[a] Michael Y. Chiang,[a,b] Wei-Yi Lu,[a] Yen-Jen Chen,[a] Cheng-Jie Lian,[a] Yu-Hsieh Chen,[a] Hsin-Yi Tsai,[a] Yi-Chun Lai,[a] Hsuan-Ying Chen*[a]

[a] *Department of Medicinal and Applied Chemistry, Kaohsiung Medical University, Kaohsiung 80708, Taiwan, R.O.C.*
[b] *Department of Chemistry, National Sun Yat-sen University, Kaohsiung, Taiwan, 80424, R.O.C.*

Abstract

Previous studies of ring-opening polymerization of ε-caprolactone using structurally related aluminum complexes as pre-catalysts showed inconsistent trend in the total conversion time. We recognize an induction period for Al complexes to convert to real catalytic species, Al alkoxide, should be considered since the total conversion time consists of both induction period and polymer propagation time. Herein, the polymerization rate of a series of Al complexes bearing ketimine ligands was investigated. The kinetic results revealed complexes with more steric hindrance, electron-withdrawing group on ligands, or less chelating ligands demonstrated greater propagation activity. Opposite trend on these structural effects was observed on the measurement of induction periods. These features on ligands of aluminum complexes are responsible for facilitating the conversion process to Al alkoxides. The overall catalytic performance should consider both the induction period and the propagation time.

Keywords: ketimine, aluminum complex, ε-Caprolactone, Ring-opening polymerization

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* Corresponding Author: Hsuan-Ying Chen, E-mail: hchen@kmu.edu.tw
Tel.: +886-7-3121101-2585, Fax: +886-7-3125339

Introduction

Poly(lactide) (PLA) and poly(ε-caprolactone) (PCL) are popular plastic material due to their biodegradability which can reduce the pollution problem caused by disposable containers and packaging. They have also demonstrated a great deal of other applications in various fields [1] because

of their biodegradability, biocompatibility, and permeability. The most common way of their synthesis is ring-opening polymerization (ROP) of cycloesters which usually involves many metal complexes [2] as catalysts. Aluminum complexes are common catalysts for ROP because they are easily synthesized and their precursors are cheap. Surveying the literatures of ROP with aluminum complexes we found that electronic, steric and chelate effects on these complexes can account for most of their catalytic characteristics.[3-5] But several literatures showed irregular trend for catalytic performance of alkyl aluminum complexes bearing systematically varied functional ligands (*vide infra*). [3i,3p,6] It is puzzling and sometime depressing considering a lot of efforts were put in for rational design of aluminum catalyst. To solve this predicament we set out to examine the details of the rate measurement by the kinetic method. We found that the key issue was how one defined the time for conversion. Most rate studies measure the total time of conversion reaction at the onset of adding the aluminum complexes. However this practice fails to recognize the fact that time also needed to transform the aluminum complexes to the real active species, aluminum alkoxide complexes, before the real catalysis can take place (**Figure 1**). However, pure aluminum alkoxide complexes synthesized from the reaction of alkyl alcohol and alkyl aluminum complexes are not always successfully obtained because of disproportionation.[3i] In addition, alkyl aluminum complexes are suitable pre-catalysts with various initiators for the synthesis of PLA and PCL with special end chain. We report here the kinetic analysis of ROP of cycloester using alkyl aluminum complexes bearing systematically varied ketimine ligands as pre-catalysts. Steric, electronic, and chelate effects were examined for both the induction and catalytic polymer propagation period. Mechanistic evidences leading the explanation of these controlling factors were presented.

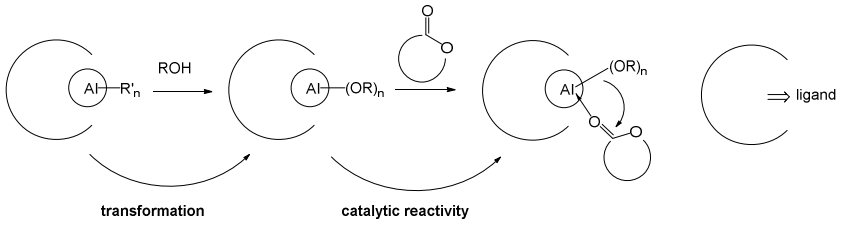


Figure 1. Schematic illustration of ROP using alkyl aluminum complex as pre-catalyst and alkyl alcohol as an initiator

Results and Discussion

Synthesis and Characterization of Al Complexes.

A series of ketimine ligands was prepared through the condensation of 2,4-pentanedione with various amines or anilines. All ligands were reacted with a stoichiometric quantity of trimethylaluminum in toluene to produce a moderate yield of Al compounds (**Figure 2**). Compound formulae and structures were confirmed by ^{1}H and ^{13}C NMR spectra, elemental analysis, and X-ray crystal analysis. The X-ray structure of $\mathbf{L^{F}AlMe_2}$ (**Figure 3a**) illustrates the tetrahedral geometry of the Al complex with the two methyl groups. Crystal-related data indicated no coordination between Al and fluorine. Compared with $\mathbf{L^{F}AlMe_2}$ (CCDC 961692), $\mathbf{L^{NMe2}AlMe_2}$ (CDCC 961691) (**Figure 3b**) and $\mathbf{L^{Py}AlMe_2}$ (CDCC 961696) (**Figure 3c**) presented a trigonal bipyramidal geometry with the two methyl groups in an equatorial plane. Selected bond distances (Å) and angles (deg) were listed in **Table 1**.

The Al-C bond of Al complexes with trigonal bipyramidal geometry, such as $\mathbf{L^{NMe2}AlMe_2}$ and $\mathbf{L^{Py}AlMe_2}$, was longer than the Al-C bond in complexes with tetrahedral geometry, such as $\mathbf{L^{F}AlMe_2}$. This is because the pendent N atom provides the Al with electrons which decreases the electron donating ability of methyl groups. Longer bond length indicates that the bond strength is weak and the weak bond strength of the Al-C bond enhances the transformation from methyl to benzyl alkoxide with benzyl alcohol.

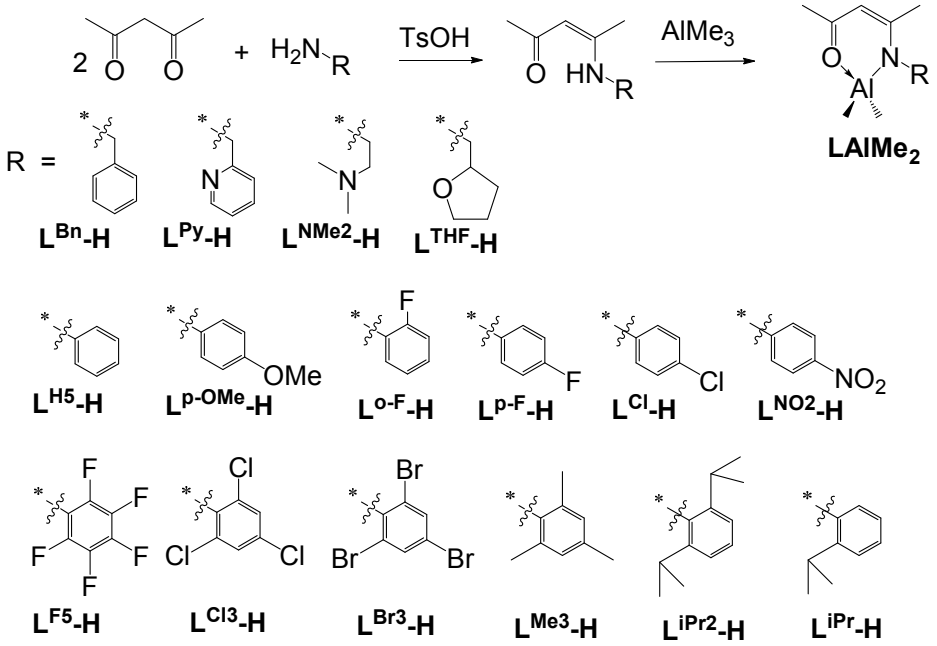


Figure 2. Synthesis of Al complexes bearing ketamine ligands prepared herein

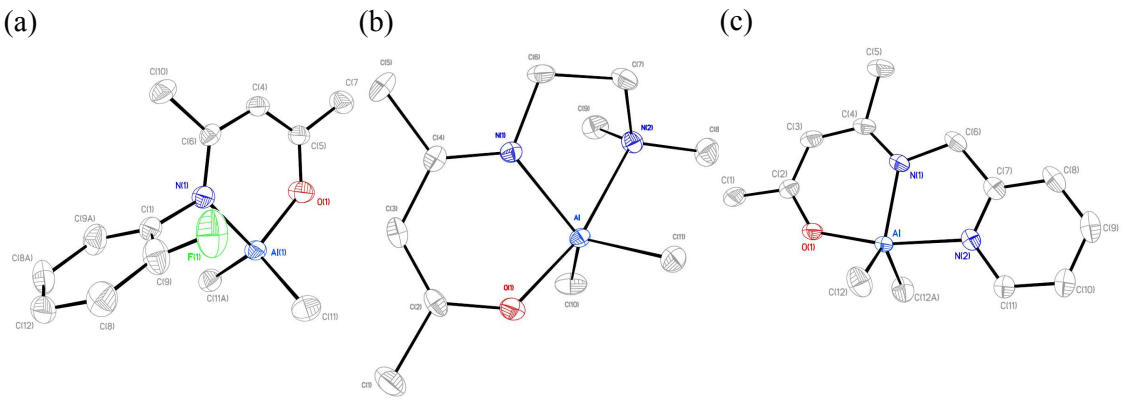


Figure 3. Molecular structures of (a) $\mathbf{L^{F}AlMe_2}$, (b) $\mathbf{L^{NMe2}AlMe_2}$, and (c) $\mathbf{L^{Py}AlMe_2}$ as 20% probability ellipsoids (all of the hydrogen atoms were omitted for clarity) (Al-C bond length: 1.964(3), 1.994(3), and 1.983(3) Å)

Table 1. Selected bond distances (Å) and angles (deg) of $\mathbf{L^{F}AlMe_2}$, $\mathbf{L^{NMe2}AlMe_2}$, and $\mathbf{L^{Py}AlMe_2}$

$\mathbf{L^{F}AlMe_2}$	$\mathbf{L^{NMe2}AlMe_2}$	$\mathbf{L^{Py}AlMe_2}$
	Selected bond distances (Å)	
Al-O(1) 1.797(3)	Al-O(1) 1.886(2)	Al-O(1) 1.881(3)
Al-N(1) 1.931(3)	Al-N(1) 1.988(3)	Al-N(1) 1.999(3)
Al-C(11) 1.964(3)Å	Al-C(10) 1.994 (3)	Al-C(12) 1.983 (3)
	Al-C(11) 1.995(3)	Al-N(2) 2.134(3)
	Al-N(2) 2.257(2)	
	Selected angles (deg)	
O(1)-Al-N(1) 95.31(12)	O(1)-Al-N(2) 166.51(10)	O(1)-Al-N(2) 167.67(12)
N(1)-Al-C(11) 109.44(9)	N(1)-Al-C(11) 116.07(12)	N(1)-Al-C(12) 119.81(9)
O(1)-Al-C(11) 109.79(9)	N(1)-Al-C(10) 121.98(12)	C(12)-Al-C(12A) 119.41(18)
C(11)-Al-C(11A) 120.22(16)	C(10)-Al-C(11) 121.31(14)	
	τ	
-	0.84	0.80

To investigate the structure of the real catalysts, $[\mathbf{L^{H5}AlOBn_2}]_2$ was synthesized from a mixture of $\mathbf{L^{H5}AlMe_2}$ and 2 equ. benzyl alcohol (BnOH) in toluene. The X-ray structure of $[\mathbf{L^{H5}AlOBn_2}]_2$ (CDCC 961693) (**Figure 4**) illustrates the triangular bipyramidal geometry of the Al complex with the four benzyl oxides in dimeric form. The axial angles of O(1)-Al-O(2) is 164.76(7) and the equatorial angles of N-Al-O(2A), O(2A)-Al-O(3), and O(3)-Al-N are 118.23(7)°, 130.09(7)°, and 111.02(8)°, respectively ($\tau = 0.90$). The distances between the Al atom and O(1), O(2), O(2A), O(3), and N are 1.8548(16)Å, 1.9091(16)Å, 1.8445(15)Å, 1.7506(16)Å, and 1.9544(18)Å, respectively. The angles of O(3)-Al-C(19) is 124.48°, which indicates the presence of a π bond between Al and O(3). This may explain why the bond of Al-O(3) is short than the others Al-O bonds.

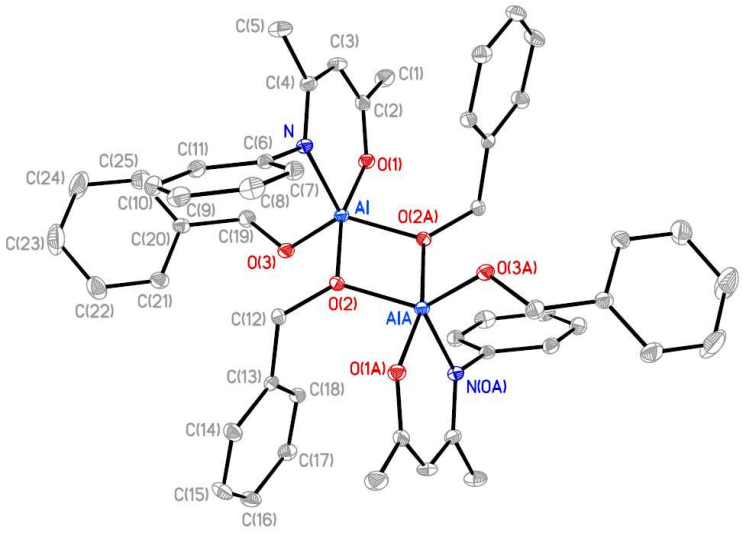


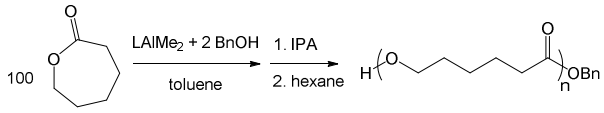
Figure 4. Molecular structures of $[\mathbf{L^{H5}AlOBn_2}]_2$ as 20% probability ellipsoids (all of the hydrogen atoms were omitted for clarity)

Polymerization of *ε*-caprolactone.

Polymerizations of *ε*-caprolactone using aluminum complexes were investigated using two equivalents of BnOH as initiator. As shown in **Table 2**, different aluminum complexes demonstrated varying degrees of catalytic activity according to type of ligands they possessed. The overall catalytic rates of aluminum complexes with different ligands (ranked by their conversion

yield over 40 mins) were found to the following order: $L^{iPr2} > L^{Me3} \sim L^{iPr} > L^{Cl3} > L^{F5} > L^{Br3} > L^{NO2} > L^{H5} \sim L^{p\text{-}F} > L^{p\text{-}OMe} > L^{p\text{-}Cl} > L^{o\text{-}F} > L^{THF} \sim L^{Py} \sim L^{NMe2} > L^{Bn}$. This order agrees neither with steric, electronic, or chelating controlling factors (e.g. $L^{p\text{-}F} > L^{p\text{-}OMe} > L^{p\text{-}Cl}$, $L^{H5} > L^{THF} \sim L^{Py} \sim L^{NMe2} > L^{Bn}$). The result was irregular and hard to draw any systematic conclusion about the electronic effect or steric effect. Similar situations with an irregular trend were reported. [3i,3p,6] The Mn_{GPC} of these polymers appeared smaller than Mn_{NMR}, except for $\mathbf{L^{NO2}AlMe_2}$, and their polydispersity index (PDI) was narrow (1.03~1.24). The explanation for $Mn_{GPC} < Mn_{NMR}$ may be that the intra-transesterification happened for the ketiminate Al system. $\mathbf{L^{iPr2}AlMe_2}$ showed no catalytic reactivity without BnOH at room temperature after 40 min (**Table 2**, entry 17[d]). Compared with one previous report[7] (**Table 2**, entry 17[e]), the addition of BnOH in catalytic process can help to improve the catalytic reactivity and control PDI, which indicates that BnO^- is a superior initiator than methyl groups.

Table 2. Polymerization of ε-caprolactone using aluminum complexes as pre-catalysts.



Entry	$LAlMe_2$ L =	Time /min	Conv.[a] /%	Mn_{Cal}[b]	Mn_{NMR}[a]	Mn_{GPC}[c]	PDI[c]
1	L^{H5}	240 (40)	68 (20)	3900	11200	5200	1.24
2	L^{F5}	180 (40)	99 (56)	5800	6800	5500	1.07
3	$L^{o\text{-}F}$	300 (40)	99 (13)	5800	10100	5200	1.09
4	$L^{p\text{-}F}$	220 (40)	84 (20)	4900	8200	4100	1.08
5	L^{Cl3}	99 (40)	99 (60)	5800	5300	4300	1.19
6	L^{Br3}	70 (40)	88 (50)	5100	9000	6400	1.04
7	$L^{p\text{-}Cl}$	180 (40)	66 (14)	3800	8900	6400	1.04
8	L^{NO2}	200 (40)	99 (29)	5800	4900	7100	1.03
9	$L^{p\text{-}OMe}$	240 (40)	53 (15)	3100	7500	7100	1.05
10	L^{Me3}	55 (40)	88 (75)	5100	5600	4700	1.19
11	L^{iPr}	55 (40)	87 (72)	5000	6100	5100	1.10
12	L^{Bn}	210 (40)	81 (7)	4700	11200	7700	1.03
13	L^{THF}	300 (40)	58 (13)	3400	14200	6200	1.20
14	L^{Py}	1280 (40)	77 (11)	4500	4300	3500	1.22
15	L^{NMe2}	1280 (40)	70 (11)	4100	9000	8100	1.04
16	L^{iPr2}	40	99	5800	9900	7000	1.05

17	$L^{iPr2(Ref.\ 7)}$	1440[e] (40[d])	93[e] (0[d])	15900	-	14100	1.64

Reaction condition: 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 monomer x $[monomer]_0/ 2[Cat]_0$ x conversion yield + *M*w(Pr^iO). [c] Obtained from GPC analysis and calibration based on the polystyrene standard. Values in parentheses are the values obtained from GPC times 0.56. [d] without BnOH. Reaction condition was the same as those listed above. [e] 300 equiv of monomer was used with [cat.] = 0.048 M and without BnOH.

This irregular trend maybe be ascribed that these aluminum complexes with two methyl groups required transformation to real active intermediates with two BnO^-, in which the induction period is the time required for transformation. Furthermore, the pendent groups of the ligands may contract the transformation time but decrease the polymerization activity of their intermediate. Therefore, the polymerization of CL by these aluminum complexes was monitored by ^{1}H NMR to determine the k_{obs} as well as the induction period for each aluminum complex catalyst (**Table 3**, **Figures S1**, and **Tables S1**). Results are illustrated in **Figures 5**, **6**, **7** and **8**.

Table 3. Kinetic study of polymerization of *ε*-caprolactone using each of the aluminum complexes as the catalysts with 2 eq. of BnOH in toluene

Entry	$LAlMe_2$	k_{obs} (min^{-1})	Induction period (min)
1	L^{H5}	0.0047 (1)	0.00
2	L^{F5}	0.0231 (19)	8.42 (406)
3	$L^{o\text{-}F}$	0.0057 (2)	32.66 (702)
4	$L^{p\text{-}F}$	0.0079 (2)	10.04 (325)
5	L^{Cl3}	0.0307 (18)	13.86 (352)
6	L^{Br3}	0.0402 (8)	17.49 (101)
7	$L^{p\text{-}Cl}$	0.0064 (2)	14.76 (338)
8	L^{NO2}	0.0096 (4)	4.36 (443)
9	$L^{p\text{-}OMe}$	0.0034 (1)	0.00
10	L^{Me3}	0.0449 (1)	8.16 (54)
11	L^{iPr}	0.0440 (15)	8.08 (108)
12	L^{Bn}	0.0099 (7)	34.76 (898)
13	L^{THF}	0.0026 (1)	0.00

14	L^{Py}	0.0029 (1)	0.00
15	L^{NMe2}	0.0024 (1)	0.00
16	L^{iPr2}	0.0664 (18)	7.00 (48)

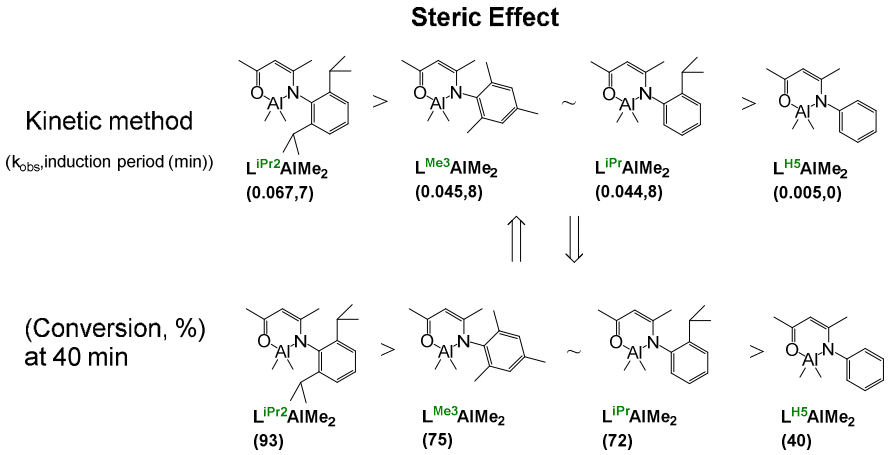


Figure 5. Comparison between the kinetic method and the conversion check at 40 min (Steric effect)

Figure 5, **6**, **7**, and **8** demonstrates that the catalytic activity of $k_{(obs)}$ was influenced by the steric, electronic, and chelating effects. In **Figure 5**, when the steric bulk of ligands increased, $k_{(obs)}$ also showed an obvious increase and the trend is similar to the method of the conversion check. In a survey of previous studies [3i-j, 5c-e] related to steric effect in cycloester polymerization by aluminum complexes, it was found that bidentate ligands, such as Schiff base, had the same tendencies in CL polymerization. The reason may be in connection with the research of Matsubara's study. Matsubara [9a] synthesized *ONO*-tridentate Schiff base ligands and associated aluminum complexes and studied their application in *rac*-lactide polymerization. That previous study demonstrated that the polymerization process was more effective in pyridine than toluene. These results can likely be explained by the transformation of the mononuclear aluminum complex into an inactive dimeric form by phenolate bridging as well as the coordination of pyridine to aluminum transformed to an active monotype. Dimerization should occur in ketiminato aluminum complexes with alkoxide bridging. However, sterically bulky ligands are able to protect aluminum against dimerization and retain the active monotype. Nomura [3i] and Carpentier [9b] reported that phenoxy-imine aluminum complexes reacted with BnOH and ^{i}PrOH to obtain disproportionation products of

bis(phenoxy-imine) aluminum complexes, with low catalytic reactivity. Sterically bulky ligands can also prevent disproportionation and maintain the catalytic reactivity of catalysts.

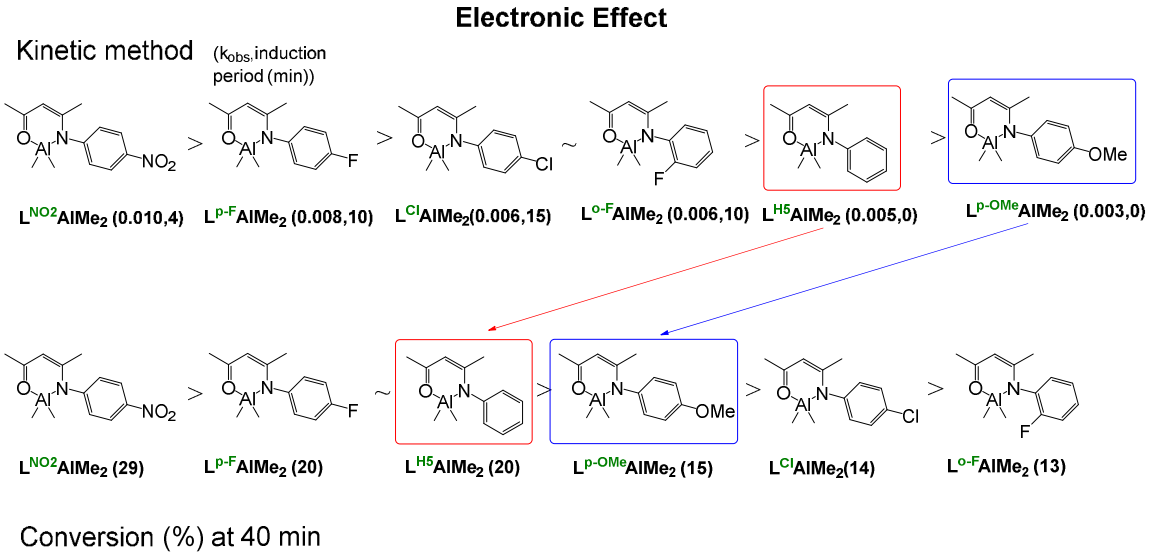


Figure 6. Comparison between the kinetic method and the conversion check at 40 min (Electronic effect)

In **Figure 6**, electron withdrawing groups, such as halide and nitro groups, also can slightly increase the catalytic activity, compared with $L^{H5}AlMe_2$. In our study, the hierarchy of catalytic rates was determined to be as follows: $L^{NO2} > L^{p\text{-}F} > L^{p\text{-}Cl} \sim L^{o\text{-}F} > L^{H5} > L^{p\text{-}OMe}$ and this trend is regular to electronic effect of ligands compared with the irregular trend under the method of the conversion check.

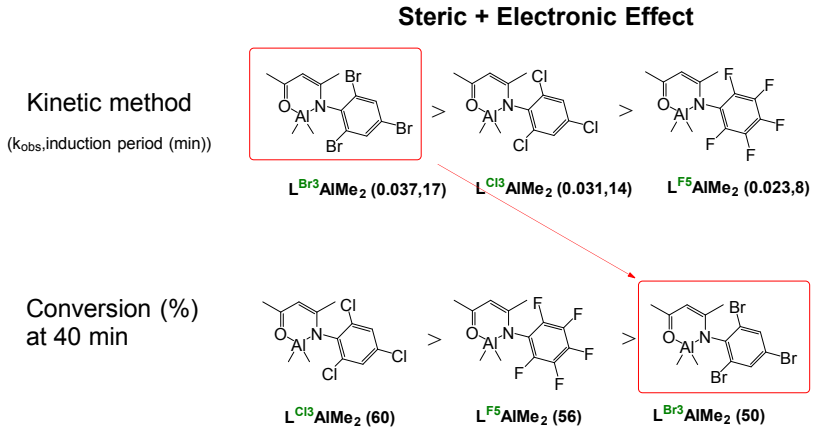


Figure 7. Comparison between the kinetic method and the conversion check at 40 min (Steric + Electronic effect)

In **Figure 7**, the steric effect is more effective than electronic effect and $L^{Br3}AlMe_2$ with largest

steric bulky ligand showed the greatest polymerization rate. But the opposite phenomenon appeared under the method of the conversion check.

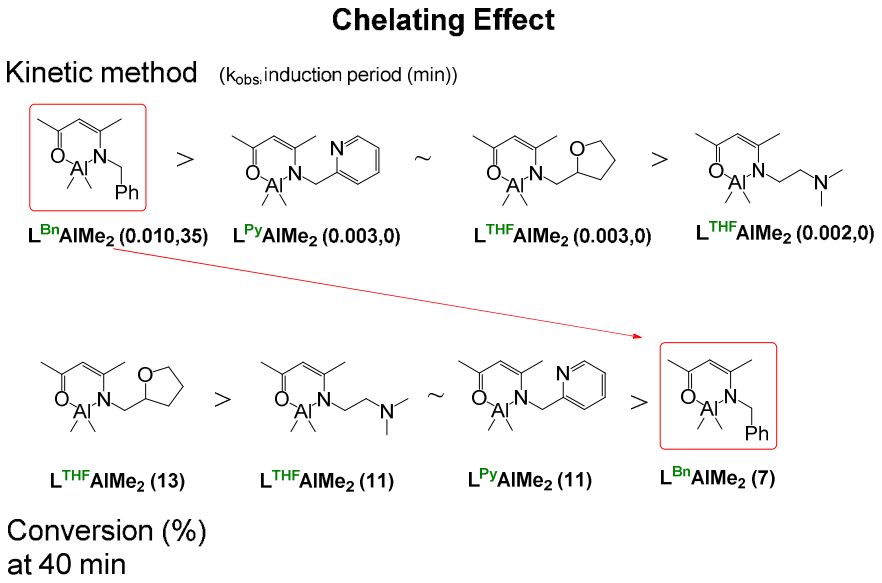


Figure 8. Comparison between the kinetic method and the conversion check at 40 min (Chelating effect)

In **Figure 8**, chelating effects, like those of 2-pyridinylmethyl, 2-tetrahydrofuranylmethyl, and 2-dimethylaminoethyl groups, decreased the catalytic rate compared with $L^{Bn}AlMe_2$. But $L^{Bn}AlMe_2$ showed the lowest rate under the method of the conversion check.

The above results showed the kinetic method was accurate analysis for the polymerization rate study compared with conventional method of the conversion check in the same time. The difference between two analytic methods is that the kinetic method can separate two parts, polymerization time and induction period, and the conversion check in the same time is the overall synthetic results. The factor of influencing induction period is that when benzyl alkoxide was used as an initiator, the weak bond strength of the Al-C bond led to increased transformation speed to real active species and decreased the induction period. According to the above data, the induction period was influenced by steric, electronic, and chelating effects. For example, sterically bulky ligands hindered BnOH from exchanging protons with methyl groups, thereby extending the induction period (induction period is 0 min for $L^{H5}AlMe_2$ but 7-8 min for $L^{ipr2}AlMe_2$, $L^{Me3}AlMe_2$, and $L^{ipr}AlMe_2$). Ligands with electron donating groups decreased the electron sharing between

aluminum and the methyl group, thereby weakening the Al-C bond, which resulted in a shorter induction period than that observed in ligands with electron withdrawing groups (induction period is 0 min for $L^{p\text{-}OMe}AlMe_2$ but 4-33 min for aluminum complexes with electron withdrawing ligands). The ligands with pendent groups including 2-pyridinylmethyl, 2-tetrahydrofuranylmethyl, and 2-dimethylaminoethyl groups showed no induction period because the pendent groups such as the electron donating groups donated electrons to aluminum and decreased the electron sharing between aluminum and the methyl group. The crystal-related data (**Figure 3**) further confirmed the relationship between the Al-CH_3 bond and the coordination effect of pendent groups (the bond length of Al-CH_3: $\mathbf{L^FAlMe_2} < \mathbf{L^{NMe2}AlMe_2}$, $\mathbf{L^{Py}AlMe_2}$). $\mathbf{L^{Bn}AlMe_2}$ showed a longer induction period than any electron withdrawing or coordinating pendent groups; however, we are currently unable to explain this result. Comparing the two methods of investigating polymerization (**Tables 2** and **3**), kinetic study elucidates the catalytic reactivity of alkyl aluminum complexes more accurately because they need to transform to the real catalytic species and the induction period confuses the real catalytic time.

Kinetic Study of the Polymerization of CL catalyzed using $\mathbf{L^{iPr2}AlMe_2}$

Kinetic studies were performed with respect to the ratio of $[CL]_0/[\mathbf{L^{iPr2}AlMe_2} + 2\ BnOH]$ ([CL] = 2.0 M in toluene) at room temperature, as shown in Table S2. Preliminary results indicate a first-order dependency on [CL] (**Figure S2**). By plotting ln k_{obs} vs. ln [$\mathbf{L^{iPr2}AlMe_2}$ + 2 BnOH], $\mathbf{L^{iPr2}AlMe_2}$ order of 1, k_{app} values of 4.28 were discovered for CL (**Figures S3**). The polymerization of CL using $\mathbf{L^{iPr2}AlMe_2}$ at room temperature demonstrated the following rate law:

$$d[CL]/dt = 4.28 \times [CL]^1[\mathbf{L^{iPr2}AlMe_2} + 2\ BnOH]^1$$

Mechanistic Studies of Polymerization

The methyl groups of the aluminum complex are not good initiators;[7] therefore, the real catalytic species, $LAlOBn_2$, was formed by the reaction of BnOH and $LAlMe_2$. The structure of the reaction product, $\mathbf{[L^{H5}AlOBn_2]_2}$ (**Figure 4a**), was isolated as a dimer. It is possible that disproportionation and dimerization may occur to form inactive species to hamper the catalytic

reaction and sterically bulky ligands inhibit these side reactions. According to the kinetic characteristics, one CL coordinated to aluminum center. Repeating the coordination of CL and initiation by alkoxide resulted in a polycaprolactone product (**Figure 9**).

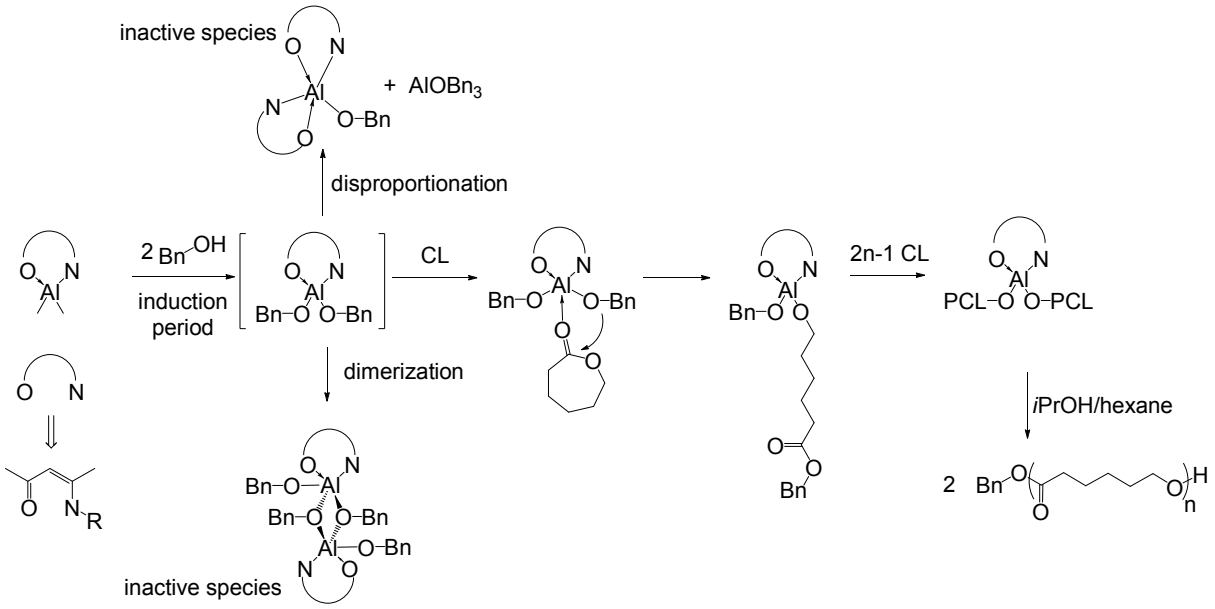


Figure 9. Possible mechanisms underlying polymerization by aluminum complex

Conclusions

This study synthesized a series of ketimines and associated aluminum complexes to catalyze the polymerization of CL and studied the catalytic activity in two methods, the kinetic method and the conversion check at the time. Through the kinetic study, the aluminum complexes bearing ketiminato ligands showed the greater catalytic reactivity for the steric bulky and electron-withdrawing groups. The pendent groups decreased the reactivity. The induction period was longer for the steric bulky and electron-withdrawing groups. The chelating effect decreased induction period by the pendent groups. But the method of the conversion check at the time sometimes showed the irregular catalytic trend which is hard to be analyzed. According to our results, the kinetic study is the great method for the research of catalytic activity of alkyl aluminum complexes because the catalytic time includes the induction period and polymer propagation and the results will be incorrect if identified the conversion for a period of time.

Experimental Section

Standard Schlenk techniques and a N_2-filled glovebox were used throughout the isolation and handling of all the compounds. Solvents, ε-caprolactone, and deuterated solvents were purified prior to use. 2,4-Pentanedione, *p*-toluenesulfonic acid, 2-flouroaniline, 4-flouroaniline, 2,3,4,5,6-pentaflouroaniline, 4-nitroaniline, 2,4,6-tribromoaniline, 2,4,6-trichloroaniline, 4-chloroaniline, aniline, 4-methoxyaniline, 2,6-diisopropylaniline, 2-isopropylaniline, 2,4,6-trimethylaniline, pyridin-2-ylmethanamine, (tetrahydrofuran-2-yl)methanamine, phenylmethanamine, *N*,*N*-dimethylethane-1,2-diamine, deuterated chloroform, and ε-caprolactone were purchased from Acros. Benzyl alcohol was purchased from Alfa. ^{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 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, at 40 °C). The chromatographic column was JORDI Gel DVB 103 Å, and the calibration curve was made by primary polystyrene standards to calculate Mn(GPC). $L^{H5}H$,[10a] $L^{F5}H$,[10b] $L^{o\text{-}F}H$,[10c] $L^{p\text{-}F}H$,[10d] $L^{Cl}H$,[10e] $L^{NO2}H$ [10f] $L^{p\text{-}OMe}H$[10a] $L^{Me3}H$,[10g] $L^{iPr2}H$,[10b] $L^{Bn}H$, [10h] $L^{Py}H$,[10i] $L^{NMe2}H$,[10j] and $L^{iPr2}AlMe_2$[7] were prepared following literature procedures.

Synthesis of $L^{Cl3}H$

A mixture of 2,4,6-trichloroaniline (9.80 g, 50 mmol) and 2,4-pentanedione (10.00 g, 100 mmol) was refluxed with *p*-toluenesulfonic acid (0.1g, 0.58 mmol) for 1 day in ethanol (150 mL). The reaction solution was cooled down in the refrigerator (0 ^{o}C) for 3 day. The solvent removed at reduced pressure to give the white powder. Yield : 12.78 g (92 %).^{1}H NMR ($CDCl_3$, 200 MHz) δ 12.00 (1H, br, N***H***), 7.42-7.40 (2H, s, Ar), 5.32 (1H, s, *β*-***H***), 2.14 (3H, s, C***H₃***C-N), 1.74 (3H, s, C***H₃***C=O) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) δ 197.25 (O=***C***CH_3), 160.78 (N***C***CH_3), 135.50 (N–***C***(Ar)), 133.52, 131.65, 128.39, 127.95 (Ar), 97.71 (*β*–***C***), 29.16 (O=C***C***H_3), 18.89 (NC***C***H_3)

ppm.

Synthesis of $L^{Br3}H$

Using a method is similar to that for $L^{Cl3}H$ except 2,4,6-tribromoaniline was used in place of 2,4,6-trichloroaniline. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 12.05 (1H, br, N***H***), 7.76, 7.49 (2H, s, Ar), 5.31 (1H, s, *β*-***H***), 2.14 (3H, s, C***H₃***C-N), 1.72 (3H, s, C***H₃***C=O) ^{13}C NMR ($CDCl_3$, 50 MHz) δ 197.05 (O=***C***CH^3), 160.48 (N***C***CH_3), 133.68 (N–***C***(Ar)), 134.68 (Ar-***m***), 125.59 (Ar-***o***), 121.60 (Ar-***p***), 97.49 (*β*–***C***), 29.21 (O=C***C***H_3), 19.08 (NC***C***H_3) ppm.

Synthesis of $L^{iPr}H$

Using a method is similar to that for $L^{Cl3}H$ except 2-*iso*prolylaniline was used in place of 2,4,6-trichloroaniline. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 12.42 (1H, br, N***H***), 7.34-7.01 (4H, m, Ar), 5.21 (1H, s, *β*-***H***), 3.27-3.06 (1H, m, C***H***$(CH_3)_2$), 2.11 (3H, s, C***H₃***C-N), 1.84 (3H, s, C***H₃***C=O), 1.23, 1.20 (6H, s, CH(C***H₃***)***₂***) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) δ 195.70 (O=***C***CH_3), 161.41 (N***C***CH_3), 144.03 (N–***C*** (Ar)), 135.80 (***C***-^{i}Pr), 126.89, 126.85, 125.96, 125.85 (Ar), 96.73 (*β*–***C***), 28.82 (***C***$(CH_3)_2$ (^{i}Pr)), 28.07 (O=C***C***H_3), 22.94 (C(***C***$H_3)_2$ (^{i}Pr)), 19.15 (NC***C***H_3) ppm.

Synthesis of $L^{THF}H$

Using a method is similar to that for $L^{Cl3}H$ except (tetrahydrofuran-2-yl)methanamine was used in place of 2,4,6-trichloroaniline. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 10.96 (1H, br, N***H***), 4.98 (1H, s, *β*-***H***), 4.02-3.92 (1H, m, NCH_2-C***H*** (THF)), 3.91-3.74 (2H, m, OC***H₂*** (THF)), 3.40-3.30 (2H, m, NC***H₂***-THF), 2.02 (3H, s, C***H₃***C-N), 1.95 (3H, s, C***H₃***C=O), 1.91-1.60 (4H, m, THF) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) δ 194.44 (O=***C***CH^3), 162.93 (N***C***CH_3), 95.25 (*β*–***C***), 77.36 (NCH_2-***C*** (THF)), 68.15 (O***C***H_2 (THF)), 46.50 (N***C***H_2-THF), 28.41 (THF), 25.57 (O=C***C***H_3), 18.69 (NC***C***H_3) ppm.

Synthesis of $L^{H5}AlMe_2$.

A mixture of $L^{H5}H$ (1.75 g, 10 mmol) and $AlMe_3$ (5 mL, 2.0 M, 10 mmol) in toluene (20 mL), was

stirred for 24 hr at 0 ^{o}C. Volatile materials were removed under vacuum to give yellow powder and then hexane (30 mL) was transferred and placed in the refrigerator (0 ^{o}C) for 1 week. The light yellow powder was obtained. Yield: 1.845 g (80 %). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.35 (2H, d, Ar-***m***), 7.24 (1H, d, Ar-***p***), 6.93 (2H, d, Ar-***o***), 5.19 (1H, s, *β*–***H***), 2.03 (3H, s, C***H*****$_3$**C-N), 1.78 (3H, s, C***H*****$_3$**C=O), -0.90 (6H, s, Al(C***H*****$_3$$)_2$**) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) δ 181.06 (O=***C***CH_3), 174.32 (N***C***CH_3), 144.01 (N–***C***(Ar)), 137.78, 129.33, 124.91, 126.42 (Ar), 99.55 (*β*–***C***), 25.71 (O=C***C***H_3), 22.59 (NC***C***H_3), -10.30 (Al(***C***$H_3$$)_2$) ppm. Elemental Anal. found (Calcd.) for : $C_{13}H_{18}AlNO$: N, 6.04 (6.06) ; C, 67.49 (67.51) ; H, 7.77 (7.85) %. Mp：62 ^{o}C.

Synthesis of $L^{F5}AlMe_2$.

Using a method is similar to that for $L^{H5}AlMe_2$ except $L^{F5}H$ was used in place of $L^{H5}H$. Yield: 2.63g (82 %). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.42 (1H, s, *β*–***H***), 2.12 (3H, s, C***H*****$_3$**C-N), 1.88 (3H, s, C***H*****$_3$**C=O), -0.92 (6H, s, Al(C***H*****$_3$$)_2$**) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) δ 186.81 ($CH_3$***C***=O), 177.21 ($CH_3$***C***–N), 144.83, 142.41, 137.35, 135.50 (Ar), 119.10 (N–***C***(Ar)), 100.77 (*β*–***C***), 26.23 (O=C***C***H_3), 22.87 (N–C***C***H_3), -11.19 (Al(***C***$H_3$$)_2$) ppm. Elemental Anal. found (Calcd.) for : $C_{13}H_{13}AlF_5NO$: N, 4.44 (4.36) ; C, 48.00 (48.61) ; H, 4.70 (4.08) %. Mp：70 ^{o}C.

Synthesis of $L^{o\text{-}F}AlMe_2$.

Using a method similar to that for $L^{H5}AlMe_2$ except $L^{o\text{-}F}H$ was used in place of $L^{H5}H$. Yield: 1.75 g (70 %). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.20 (2H, d, Ar-***m***), 7.13 (1H, d, Ar-***o***), 7.05 (1H, d, Ar-***p***), 5.26 (1H, s, *β*–***H***), 2.06 (3H, s, C***H*****$_3$**C-N), 1.83 (3H, s, C***H*****$_3$**C=O), -0.82, -0.99 (6H, s, Al(C***H*****$_3$$)_2$**) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) δ 182.55 (O=***C***CH^3), 175.88 (N***C***CH_3), 153.57 (F-***C***), 131.64 (Ar-***m***), 126.98 (N–***C***(Ar)), 124.78 (Ar-***p***), 116.66 (Ar-***o***), 116.25 (F–C-***C***(Ar-***m***)), 99.73 (*β*–***C***), 25.90 (O=C***C***H_3), 22.44 (NC***C***H_3), -11.25 (Al(***C***$H_3$$)_2$) ppm. Elemental Anal. found (Calcd.) for : $C_{13}H_{17}AlFNO$: N, 5.84 (5.62) ; C, 59.41 (62.64) ; H, 6.14 (6.87) %. The EA experiment of its single crystal was tested for 5 times but the accurate result was not obtained. The ^{1}H NMR spectrum of $L^{o\text{-}F}AlMe_2$ showed the correct structure (Figure S6). Mp: 63 ^{o}C.

Synthesis of $L^{p\text{-}F}AlMe_2$.

Using a method similar to that for $L^{H5}AlMe_2$ except $L^{p\text{-}F}H$ was used in place of $L^{H5}H$. Volatile materials were removed under vacuum to give the light yellow oil which can dissolve in hexane. Yield: 1.75 g (70 %). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.07 (2H, d, Ar-***m***), 6.94 (2H, d, Ar-***o***), 5.22 (1H, s, *β*–***H***), 2.03 (3H, s, C***H*****$_3$**C-N), 1.79 (3H, s, C***H*****$_3$**C=O), -0.91 (6H, s, Al(C***H*****$_3$$)_2$**) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) δ 181.46 (O=***C***CH^3), 163.40 (N***C***CH_3), 158.51 (F–***C***(Ar-***p***)), 139.83 (N–***C***(Ar)), 126.51, 126.34 (Ar-***o***), 116.36, 115.91 (Ar-***m***), 99.60 (*β*–***C***), 25.62 (O=C***C***H_3), 22.49 (NC***C***H_3), -10.38 (Al(***C***$H_3)_2$) ppm. Elemental Anal. found (Calcd.) for : $C_{13}H_{17}AlFNO$: N, 5.33 (5.62) ; C, 60.82 (62.64) ; H, 6.52 (6.87) %. It can not be purified with hexane because it is oil but the ^{1}H NMR spectrum of $L^{p\text{-}F}AlMe_2$ showed the correct structure (Figure S7).

Synthesis of $L^{Cl3}AlMe_2$.

Using a method similar to that for $L^{H5}AlMe_2$ except $L^{Cl3}H$ was used in place of $L^{H5}H$. Yield: 2.80 g (84 %). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.42 (2H, s, Ar-***m***), 5.38 (1H, s, *β*–***H***), 2.11 (3H, s, C***H*****$_3$**C-N), 1.77 (3H, s, C***H*****$_3$**C=O), -0.88 (6H, s, Al(C***H*****$_3$$)_2$**) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) δ 185.01 (O=***C***CH^3), 176.53 (N***C***CH_3), 138.47 (N–***C***(Ar)), 132.65, 132.51 (Ar-***m***), 128.82 (Cl–***C*** (Ar-***o***)), 123.26 (Cl–***C*** (Ar-***p***)), 100.18 (*β*–***C***), 26.14 (O=C***C***H_3), 22.68 (NC***C***H_3), -10.04 (Al(***C***$H_3)_2$) ppm. Elemental Anal. found (Calcd.) for : $C_{13}H_{15}AlCl_3NO$: N, 3.73 (4.19) ; C, 46.17 (46.67) ; H, 4.36 (4.52) %. Mp: 90 ^{o}C.

Synthesis of $L^{Br3}AlMe_2$.

Using a method similar to that for $L^{H5}AlMe_2$ except $L^{Br3}H$ was used in place of $L^{H5}H$. Yield: 3.51 g (75 %). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.77 (2H, s, Ar-***m***), 5.38 (1H, s, *β*–***H***), 2.12 (3H, s, C***H*****$_3$**C-N), 1.78 (3H, s, C***H*****$_3$**C=O), -0.84 (6H, s, Al(C***H*****$_3$$)_2$**) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) δ 185.09 (O=***C***CH^3), 176.23 (N***C***CH_3), 141.68 (N–***C***(Ar)), 135.21, 123.29 (Ar-***m***), 122.13, 120.43 (Br–***C*** (Ar-***o***)), 120.43 (Br–***C*** (Ar-***p***)), 100.31 (*β*–***C***), 26.19 (O=C***C***H_3), 22.87 (NC***C***H_3), -9.52 (Al(***C***$H_3)_2$)

ppm. Elemental Anal. found (Calcd.) for : $C_{13}H_{15}AlBr_3NO$: N, 2.63 (2.99) ; C, 33.29 (33.37) ; H, 3.07 (3.23) %. Mp: 84 ^oC.

Synthesis of $L^{p\text{-}Cl}AlMe_2$.

Using a method similar to that for $L^{H5}AlMe_2$ except $L^{p\text{-}Cl}H$ was used in place of $L^{H5}H$. Yield: 2.13 g (80 %). ^1H NMR ($CDCl_3$, 200 MHz) δ 7.33 (2H, d, Ar-***m***), 6.95 (2H, d, Ar-***o***), 5.21 (1H, s, *β*–***H***), 2.04 (3H, s, C***H₃***C-N), 1.79 (3H, s, C***H₃***C=O), -0.92 (6H, s, Al(C***H₃***)₂) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) δ 181.90 (O=***C***CH^3), 174.49 (N***C***CH_3), 142.60 (N–***C*** (Ar)), 132.21 (Ar-***m***), 129.56 (Cl–***C*** (Ar-***p***)), 126.38 (Ar-***o***), 99.70 (*β*–***C***), 25.77 (O=C***C***H_3), 22.64 (NC***C***H_3), -10.34 (Al(***C***H_3)₂) ppm. Elemental Anal. found (Calcd.) for : $C_{13}H_{17}AlClNO$: N, 5.19 (5.27) ; C, 57.81 (58.76) ; H, 6.40 (6.45) %. Mp: 70 ^oC.

Synthesis of $L^{NO2}AlMe_2$.

Using a method similar to that for $L^{H5}AlMe_2$ except $L^{NO2}H$ was used in place of $L^{H5}H$. Volatile materials were removed under vacuum to give the light brown powder. Then it was washed with hexane (30 mL) and a light brown powder was obtained after the filtration. Yield: 2.29 g (83 %). ^1H NMR ($CDCl_3$, 200 MHz) δ 8.26 (2H, d, Ar-***m***), 7.12 (2H, d, Ar-***o***), 5.28 (1H, s, *β*–***H***), 2.08 (3H, s, C***H₃***C-N), 1.83 (3H, s, C***H₃***C=O), -0.91 (6H, s, Al(C***H₃***)₂) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) δ 183.54 (O=***C***CH^3), 173.95 (N***C***CH_3), 150.42 (N–***C*** (Ar)), 146.17 (NO_2–***C*** (Ar-***p***)), 128.97, 128.17 (Ar-***m***), 126.17, 124.97 (Ar-***o***), 100.08 (*β*–***C***), 25.90 (O=C***C***H_3), 22.92 (NC***C***H_3), -10.34 (Al(***C***H_3)₂) ppm. Elemental Anal. found (Calcd.) for : $C_{13}H_{17}AlN_2O_3$: N, 9.48 (10.14) ; C, 56.71 (56.52) ; H, 6.00 (6.20) %. Mp: 110 ^oC.

Synthesis of $L^{p\text{-}OMe}AlMe_2$.

Using a method similar to that for $L^{H5}AlMe_2$ except $L^{p\text{-}OMe}H$ was used in place of $L^{H5}H$. Yield: 2.04 g (78 %). ^1H NMR ($CDCl_3$, 200 MHz) δ 6.88 (2H, d, Ar-***m***), 7.27 (2H, d, Ar-***o***), 5.17 (1H, s, *β*–***H***), 3.80 (3H, s, OC***H₃***), 2.03 (3H, s, C***H₃***C-N), 1.79 (3H, s, C***H₃***C=O), -0.91 (6H, s, Al(C***H₃***)₂) ppm.

^{13}C NMR ($CDCl_3$, 50 MHz) δ 180.76 (O=***C***CH^3), 174.88 (N***C***CH_3), 157.98 (O–***C*** (Ar-***p***)), 136.75 (N–***C*** (Ar)), 125.79 (Ar-***o***), 114.55 (Ar-***m***), 99.50 (*β*–***C***), 55.36 (O***C***H_3), 25.69 (O=C***C***H_3), 22.50 (NC***C***H_3), -10.45 (Al(***C***$H_3)_2$) ppm. Elemental Anal. found (Calcd.) for : $C_{14}H_{20}AlNO_2$: N, 4.77 (5.36) ; C, 63.61 (64.35) ; H, 6.83 (7.71) %. The ^{1}H NMR spectrum of $L^{p\text{-}OMe}AlMe_2$ showed the correct structure (Figure S12). Mp: 102 ^{o}C.

Synthesis of $L^{Me3}AlMe_2$.

Using a method similar to that for $L^{H5}AlMe_2$ except $L^{Me3}H$ was used in place of $L^{H5}H$. Volatile materials were removed under vacuum to give the deep brown oil which can dissolve in hexane. Yield: 2.41 g (88 %). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.89 (2H, s, Ar-***m***), 5.27 (1H, s, *β*–***H***), 2.27 (3H, s, C***H***$_3$ (Ar-***p***)), 2.05 (6H, s, C***H***$_3$ (Ar-***o***)), 2.07 (3H, s, C***H***$_3$C-N), 1.66 (3H, s, C***H***$_3$C=O), -0.91 (6H, s, Al(C***H***$_3)_2$) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) δ 181.04 (O=***C***CH^3), 175.69 (N***C***CH_3), 139.09 (N–***C*** (Ar)), 135.76, 131.94, 129.44 (Ar), 99.47 (*β*–***C***), 55.36 (O***C***H_3), 25.73 (O=C***C***H_3), 22.15 (***C***H_3 (Ar-***p***)), 20.79 (NC***C***H_3), 18.16 (***C***H_3 (Ar-***o***)), -9.68 (Al(***C***$H_3)_2$) ppm. Elemental Anal. found (Calcd.) for : $C_{16}H_{24}AlNO$: N, 4.16 (5.12) ; C, 65.53 (70.30) ; H, 7.73 (8.85) %. It can not be purified with hexane because it is oil and dissolve in hexane but the ^{1}H NMR spectrum of **$L^{Me3}AlMe_2$**showed the correct structure (Figure S13).

Synthesis of $L^{iPr}AlMe_2$.

Using a method similar to that for $L^{Me3}AlMe_2$ except $L^{iPr}H$ was used in place of $L^{H5}H$. Volatile materials were removed under vacuum to give the red oil which can dissolve in hexane. Yield: 2.19 g (80 %). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.36 (2H, d, Ar-***m***), 7.28 (2H, d, Ar-***m***), 7.16 (1H, d, Ar-***p***), 6.85 (1H, d, Ar-***o***), 5.23 (1H, s, *β*–***H***), 2.05 (1H, sept, C***H***C_2H_6 (Ar-***o***)), 1.24, 1.11 (6H, m, CHC_2***H***$_6$ (Ar-***o***)), 2.05 (3H, s, C***H***$_3$C-N), 1.73 (3H, s, C***H***$_3$C=O), -0.87, -0.90 (6H, s, Al(C***H***$_3)_2$) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) δ 180.94 (O=***C***CH_3), 175.40 (N***C***CH_3), 142.91 (N–***C*** (Ar)), 141.17 (***C***-^{i}Pr (Ar-***o***)), 127.14, 126.86 (Ar-***m***), 126.47 (Ar-***p***), 125.27 (Ar-***o***), 99.49 (*β*–***C***), 27.31 (***C***$(CH_3)_2$ (^{i}Pr)), 25.64 (O=C***C***H_3), 24.24, 23.69 (C(***C***$H_3)_2$ (^{i}Pr)), 22.80 (NC***C***H_3), -10.4 (Al(***C***$H_3)_2$) ppm. Elemental

Anal. found (Calcd.) for : $C_{16}H_{24}AlNO$: N, 4.59 (5.12) ; C, 66.27 (70.30) ; H, 7.46 (8.85) %. It can not be purified with hexane because it is oil and dissolve in hexane but the ^{1}H NMR spectrum of **$L^{iPr}AlMe_2$** showed the correct structure (Figure S14).

Synthesis of $L^{Bn}AlMe_2$.

Using a method similar to that for $L^{Me3}AlMe_2$ except $L^{Bn}H$ was used in place of $L^{H5}H$. Volatile materials were removed under vacuum to give the deep brown oil which can dissolve in hexane. Yield: 2.30 g (83 %). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.29 (2H, d, Ar-***m***), 7.19 (1H, d, Ar-***p***), 7.18 (2H, d, Ar-***o***), 5.10 (1H, s, *β*–***H***), 4.58 (2H, s, NC***H*****$_2$**Ph), 1.99 (3H, s, C***H*****$_3$**C-N), 1.91 (3H, s, C***H*****$_3$**C=O), -0.89 (6H, s, Al(C***H*****$_3$$)_2$**) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) δ 179.20 (O=***C***CH^3), 176.13 (N***C***CH_3), 137.00 (N–CH_2***C***(Ar)), 128.45, 128.33 (Ar-***m***), 126.86 (Ar-***p***), 126.36, 126.34 (Ar-***o***), 99.89 (*β*–***C***), 50.49 (N***C***H_2), 25.18 (O=C***C***H_3), 21.36 (NC***C***H_3), -10.43 (Al(***C***$H_3)_2$) ppm. Elemental Anal. found (Calcd.) for : $C_{14}H_{20}AlNO$: N, 5.00 (5.71) ; C, 63.17 (68.55) ; H, 8.90 (8.22) %. It can not be purified with hexane because it is oil and dissolve in hexane but the ^{1}H NMR spectrum of **$L^{Bn}AlMe_2$** showed the correct structure (Figure S15).

Synthesis of $L^{THF}AlMe_2$.

Using a method similar to that for $L^{H5}AlMe_2$ except $L^{THF}H$ was used in place of $L^{H5}H$. Volatile materials were removed under vacuum to give the colorless oil which can dissolve in hexane. Yield: 1.91 g (80 %). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.10 (1H, d, NCH_2C***H*** (THF)), 3.87 (2H, d, OC***H*****$_2$** (THF)), 3.39 (2H, d, NC***H*****$_2$**-THF), 5.05 (1H, s, *β*–***H***), 2.07 (3H, s, C***H*****$_3$**C-N), 1.94 (3H, s, C***H*****$_3$**C=O), 1.54 (4H, d, THF), -0.85, -0.88 (6H, s, Al(C***H*****$_3$$)_2$**) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) δ 178.97 (O=***C***CH^3), 175.09 (N***C***CH_3), 100.25 (*β*–***C***), 78.10 (NCH_2-***C*** (THF)), 67.73 (O***C***H_2 (THF)), 52.45 (N***C***H_2-THF), 29.54, 22.13 (THF), 25.46 (O=C***C***H_3), 20.93 (NC***C***H_3), -10.37 (Al(***C***$H_3)_2$) ppm. Elemental Anal. found (Calcd.) for : $C_{12}H_{22}AlNO_2$: N, 5.86 (5.85) ; C, 59.43 (60.23) ; H, 10.06 (9.27) %.

Synthesis of $L^{Py}AlMe_2$.

Using a method similar to that for $L^{H5}AlMe_2$ except $L^{Py}H$ was used in place of $L^{H5}H$. But the purification recrystalized with THF was carried out for 2 times. Yield: 1.99 g (81 %). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.49 (2H, d, N-C***H*** (Py-***o***)), 7.79 (1H, d, Py-***m***), 7.31 (1H, d, Py-***p***), 5.06 (1H, s, *β*–***H***), 4.77 (2H, s, NC***H₂***Py), 2.10 (3H, s, C***H₃***C-N), 1.98 (3H, s, C***H₃***C=O), -0.90 (6H, s, Al(C***H₃***)₂) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) δ 182.69 (O=***C***CH^3), 174.04 (N***C***CH_3), 154.47 (N–CH_2***C*** (Py)), 145.23 (N–***C***H (Py)), 138.12, 122.85, 120.86 (Py), 98.70 (*β*–***C***), 52.01 (N***C***H_2Py), 25.92 (O=C***C***H_3), 23.66 (NC***C***H_3), -5.83 (Al(***C***H_3)₂) ppm. Elemental Anal. found (Calcd.) for : $C_{13}H_{19}AlN_2O$: N, 11.33 (11.37) ; C, 61.33 (63.40) ; H, 8.68 (7.78) %. The EA experiment of its single crystal was tested for 4 times but the accurate result was not obtained. The ^{1}H NMR spectrum of $L^{Py}AlMe_2$ showed the correct structure (Figure S17). Its Mp. is not available because it decomposed at 110 ^{o}C.

Synthesis of $L^{NMe2}AlMe_2$.

Using a method similar to that for $L^{Me3}AlMe_2$ except $L^{NMe2}H$ was used in place of $L^{H5}H$. Volatile materials were removed under vacuum to give the brown oil which can dissolve in hexane. Yield: 1.95 g (86 %). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.03 (1H, s, *β*–***H***), 3.36 (2H, t, *J* = 3Hz, NC***H₂***$CH_2N(CH_3)_2$), 2.71 (2H, t, *J* = 3Hz, NCH_2C***H₂***$N(CH_3)_2$), 2.27 (6H, s, N(C***H₃***)₂), 1.99 (3H, s, C***H₃***C-N), 1.93 (3H, s, C***H₃***C=O), -0.92 (6H, s, Al(C***H₃***)₂) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) δ 181.93 (O=***C***CH_3), 175.04 (N***C***CH_3), 98.69 (*β*–***C***), 55.56 (NCH_2***C***$H_2N(CH_3)_2$), 45.14 (NCH_2CH_2N(***C***H_3)₂), 44.87 (N***C***$H_2CH_2N(CH_3)_2$), 25.78 (O=C***C***H_3), 22.51 (NC***C***H_3), -8.96 (Al(***C***H_3)₂) ppm. Elemental Anal. found (Calcd.) for : $C_{11}H_{23}AlN_2O$: N, 12.30 (12.18) ; C, 56.92 (58.38) ; H, 8.86 (10.24) %. After the extraction with hexane 3 times to remove insoluble impurity, the light brown oil was obtained. It can not be purified with hexane further but the ^{1}H NMR spectrum of $L^{NMe2}AlMe_2$ showed the correct structure (Figure S18).

General procedures for the polymerization of ε-caprolactone

A typical polymerization procedure was exemplified by the synthesis of entry 18 (Table 1) using complex $\mathbf{L^{iPr2}AlMe_2}$ as a catalyst. The polymerization conversion was analyzed by ^{1}H NMR spectroscopic studies. Toluene (5.0 mL) was added to a mixture of complex $L^{iPr2}AlMe_2$ (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 $CDCl_3$ (1mL), and analyzed by ^{1}H NMR. After the solution was stirred for 40 min, the reaction was then quenched by adding a drop of *iso*-propanol, and the polymer precipitated as white solid when pouring into *n*-hexane (30.0 mL). The isolated white solid was dissolved in CH_2Cl_2 (5.0 mL) and then *n*-hexane (70.0 mL) was added to give purified crystalline solid. Yield: 0.78 g (68 %). By plotting $\ln([CL]_0/[CL])$ vs. time, the slope is k_{obs} and intercept is induction period.

Electronic supplementary information (ESI) available: Polymer characterization data, and details of the kinetic study.

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Graphical abstract