

Ring-Opening Polymerization of ϵ -Caprolactone and Cyclohexene Oxide Initiated by Aluminum β -Ketoamino Complexes: Steric and Electronic Effect of 3-Position Substituents of the Ligands

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Abstract: A series of aluminum complexes supported by β -ketoamino, ligand-bearing, 3-position substituents LAlEt_2 ($\text{L}=\text{CH}_3\text{C}(\text{O})\text{C}(\text{Cl})=\text{C}(\text{CH}_3)\text{NAr}$ (L_1), $\text{L}=\text{CH}_3\text{C}(\text{O})\text{C}(\text{H})=\text{C}(\text{CH}_3)\text{NAr}$ (L_2), $\text{L}=\text{CH}_3\text{C}(\text{O})\text{C}(\text{Ph})=\text{C}(\text{CH}_3)\text{NAr}$ (L_3), and $\text{L}=\text{CH}_3\text{C}(\text{O})\text{C}(\text{Me})=\text{C}(\text{CH}_3)\text{NAr}$ (L_4), $\text{Ar}=2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$) were synthesized in situ and employed in the ring-opening polymerization (ROP) of ϵ -caprolactone (ϵ -CL) and cyclohexene oxide (CHO). The 3-position substituents on the β -ketoamino ligand backbone of the aluminum complexes influenced the catalyst activity remarkably for both ROP of ϵ -CL and CHO. Aluminum β -ketoamino complexes displayed different catalytic behavior in ROP of ϵ -CL and CHO. The order of the catalytic activity of LAlEt_2 was $\text{L}_1\text{AlEt}_2 > \text{L}_2\text{AlEt}_2 > \text{L}_3\text{AlEt}_2 > \text{L}_4\text{AlEt}_2$ for ROP of ϵ -CL, being opposite to the electron-donating ability of the 3-position substituents on the β -ketoamino ligand, while the order of the catalytic activity for ROP of CHO was $\text{L}_1\text{AlEt}_2 > \text{L}_3\text{AlEt}_2 > \text{L}_4\text{AlEt}_2 > \text{L}_2\text{AlEt}_2$. The effects of reaction temperature and time on the ROP were also investigated for both ϵ -CL and CHO.

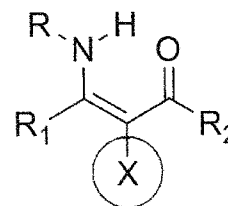
Keywords: ring-opening polymerization, ϵ -caprolactone, cyclohexene oxide, aluminum β -ketoamino complexes.

Introduction

Mono-anionic β -ketoamino ligand has emerged as one of the most versatile ligands in coordination chemistry for their strong metal-ligand bonds¹⁻¹¹ and for their relatively facile tunability to access derivatives containing a range of substituents around the ligands' skeleton. In the past, most work paid their attentions to the steric and electronic effects of substituents (R) on the nitrogen donor atom and side groups (R_1 and/or R_2) of these ligands backbone (see the Scheme I) of metal complexes on the catalyst behavior.⁴⁻⁹ However, few investigations were focused on the effect of the substituents (X) on the 3-position of the β -ketoamino ligands skeleton.¹⁰

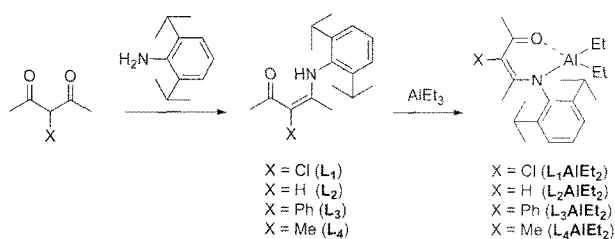
The aluminum complexes draw considerable attention for both organic synthesis¹² and polymerization,¹³ due to their strong Lewis acidity, relatively low toxicity, and ready

availability. Up to date, many kinds of ligands with sterically bulky have been used in organo-aluminum chemistry to form aluminum complexes. However, few studies have focused on the aluminum complexes with mono-anionic bidentate β -ketoamino ligand as the catalyst for the application in polymerization and small molecule activation.¹¹ The polymerization activity of metal complexes can be influenced by the steric and electronic characteristics of the ancillary ligand framework. The effect of electronic perturbations of the supporting ligand (particularly in systems that



Scheme I. A general structure of β -ketoamino ligand.

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Scheme II. Synthesis of aluminum β -ketoamino complexes.

exhibit parity with respect to steric effects) on the rate of propagation is quite complicated, depending on the catalyst system itself and the monomer in the polymerization. For example, Gibson and coworkers¹⁴ have shown that the introduction of electron-withdrawing substituent on phenoxy forms of ancillary salen ligand affords a more active aluminum initiator for the ROP of lactide. Coates and coworkers¹⁵ observed that electron withdrawing substituents on the supporting ligand greatly improved the catalytic efficiency of the Zn β -diketiminato complex used for the copolymerization of carbon dioxide with epoxide. A similar activity-electronic effects trend has been recently reported by Nomura *et al.*¹⁶ in the ROP of ϵ -CL with salicylaldimine-aluminum complexes. On the other hand, Hillmyer and Tolman¹⁷ have observed an opposite tendency for the ROP of ϵ -CL with five-coordinate aluminum alkoxide initiators supported by bis(phenoxy)-bis(amine) ligands. Some heterogeneous zinc catalysts were also tried for ring opening polymerization of epoxide monomers.¹⁸

In present work, to understand these phenomena and establish the relationship between electronic and steric effects and polymerization activity for the ROP of ϵ -CL and CHO by aluminum β -ketoamino complexes, we have synthesized a family of aluminum complexes supported by β -ketoamino ligand with various 3-position substituents *in situ* (Scheme II) and estimated their activities in ROP of ϵ -CL and CHO. Two folds were emphatically paid in the present study: (i) the effect of 3-position substituents on the β -ketoamino ligands of the aluminum complexes on the catalytic activities and properties of resulting polymers; (ii) the different catalytic behavior of the β -ketoamino aluminum complexes in the ROP of ϵ -CL and CHO.

Experimental

Materials. All works involving air-and/or moisture-sensitive compounds were carried out under dry, high purity nitrogen using standard Schenk techniques. Toluene was refluxed and distilled from Na-benzophenone under dry nitrogen. ϵ -caprolactone (ϵ -CL) (99%, Aldrich) was dried over calcium hydride under nitrogen at 25 °C for 4 days, distilled under reduced pressure before use. Cyclohexene oxide (99%, Aldrich) was refluxed over calcium hydride and distilled under nitrogen. AlEt₃ (1.1 M, in toluene), 2,4-

pentanedione, 3-chloride-2,4-pentanedione, 2,6-diisopropyl-aniline, 3-methyl-2,4-pentanedione and 3-phenyl-2,4-pentanedione were purchased from Aldrich and used without purification.

Measurements. The ¹H-NMR and ¹³C-NMR spectra of the β -ketoamino ligands were recorded on a Varian Gemini-2000 (300 MHz, 75 MHz) spectrometer in a general way. Chemical shifts are reported in per million (ppm) using tetramethylsilane as internal reference for all NMR spectra. Elemental analyses were performed on a Flash EA 1112 series, CE Instrument. The molecular weight and polydispersity of the resultant polymers were measured by gel permeation chromatography (GPC) on a Waters-400 spectrometer using polystyrene as standard and tetrahydrofuran (THF) as eluent. The glass transition temperature (T_g) was determined from Perkin-Elmer 7 differential scanning calorimeter under nitrogen from room temperature to 180 °C at a heating rate of 10 °C/min. All T_g were taken from the second scan to eliminate the difference in sample history. The thermogravimetry was measured on American Du Pont 2000 analytic instrument from 50 to 700 °C at a heating rate of 10 °C/min. Melting point (mp) of the β -ketoamino ligands was measured without corrected.

Synthesis of β -Ketoamino Ligands (L_1 - L_4). (2,6-ⁱPr₂C₆H₃)-NHC(CH₃)=C(Cl)C(O)C(CH₃) (L_1). To a stirred solution of 3-chloride-2,4-pentanedione (4.68 mL, 40.0 mmol) in toluene (50.0 mL) was added 2,6-diisopropyl aniline (12.68 mL, 60.0 mmol) and *p*-toluene sulfonic acid hydrate as catalyst. The reaction mixture was stirred and refluxed 24 h in a Dean-Stark apparatus under N₂. After it cooled to room temperature, the dark yellow solution was concentrated in vacuo and extracted with diethyl ether (35.0 mL). The ether layer was washed with saturated aqueous bicarbonate followed by brine. The ether layer was separated, dried with Na₂SO₄, and filtered. The solvent was removed by distillation. The residue was dried in vacuo (4 mmHg) at 120.0 °C for 5 h to remove any remaining free 2,6-diisopropylaniline and afforded a brown-yellow solid. The solid was collected and recrystallized in hexane, giving 4.50 g (38.3%) of a pale yellow solid. Mp=112.0-114.0 °C. Anal. Calcd for C₁₇H₂₄ClNO: C, 69.49; H, 8.23; N, 4.77; O, 5.45. Found: C, 69.77; H, 8.29; N, 4.77; O, 5.55%. ¹H-NMR (300 MHz, CDCl₃), δ (ppm): 1.15-1.21 (12H, ⁱPr-CH₃), 1.57 (3H, C-CH₃), 1.89 (3H, C(O)-CH₃), 2.38 (3H, C=C(NH)-CH₃), 3.02 (2H, ⁱPr-CH), 7.19 (8H, Ar-H), 12.43 (1H, NH). ¹³C-NMR (75 MHz, CDCl₃), δ (ppm): 194.24, 161.41, 146.21, 135.37, 128.78, 123.87 (split), 102.73, 28.57 (split), 24.51, 22.82, 17.92.

(2, 6-ⁱPr₂ C₆H₃)NHC(CH₃)=CHC(O)C(CH₃) (L_2). L_2 was prepared in a similar way to L_1 . Yield = 63.5%. Mp = 45.0-47.0 °C (lit²⁰, 43.0-46.0 °C). ¹H-NMR (300 MHz, CDCl₃), δ (ppm): 1.14-1.23 (12H, 12H, ⁱPr-CH₃), 1.64 (3 H, C-CH₃), 2.13 (3H, C(O)-CH₃), 3.00-3.05 (2H, ⁱPr-CH), 5.21(1H, -CH=), 7.16-7.33 (3H, Ar-H), 12.06 (1H, NH).

(2, 6-ⁱPr₂ C₆H₃)NHC(CH₃)=C(Ph)C(O)C(CH₃) (L_3). L_3

was prepared in a similar way to **L**₁. Yield = 52.2%. Mp = 170.0-172.0 °C. Anal. Calcd for C₂₃H₂₉NO: C, 82.34; H, 8.71; N, 4.18; O, 4.77%. Found: C, 82.31; H, 8.71; N, 4.17; O, 4.78%. ¹H-NMR (300 MHz, CDCl₃), δ (ppm): 1.15-1.21 (12H, ⁱPr-CH₃), 1.57 (3H, C-CH₃), 1.89 (3H, C(O)-CH₃), 1.93 (3H, C=C(NH)-CH₃), 3.06 (2H, ⁱPr-CH), 7.19 and 7.50 (m, Ar-H), 13.18 (1H, NH). ¹³C-NMR (75 MHz, CDCl₃), δ (ppm): 195.56, 162.55, 146.24, 140.24, 134.09, 132.27, 128.21 (split), 126.73, 123.67, 110.15, 29.31 (split), 24.70, 22.85, 17.94.

(**2**, 6-ⁱPr₂ C₆H₃)NHC(CH₃)=C(CH₃)C(O)C(CH₃) (**L**₄). **L**₄ was prepared in a similar way to **L**₁. Yield = 45.4 %. Anal. Calcd for C₁₈H₂₇NO: C, 79.07; H, 9.95; N, 5.12; O, 5.85. Found: C, 79.14; H, 9.78; N, 5.15; O, 5.85%. ¹H-NMR (300 MHz, CDCl₃), δ (ppm): 1.13-1.19 (12H, ⁱPr-CH₃), 1.70 (3H, C-CH₃), 1.92 (3H, C(O)-CH₃), 2.24 (3H, C=C(NH)-CH₃), 3.00 (2H, ⁱPr-CH), 7.16-7.34 (8H, Ar-H), 13.16 (1H, NH). ¹³C-NMR (75 MHz, CDCl₃), δ (ppm): 195.94, 161.80, 146.37, 135.42, 128.78, 123.87, 98.73, 28.50 (split), 24.56, 22.83, 16.63, 14.78.

In Situ Synthesis of Aluminum-Complex Bearing β -Ketoamino Ligands (L₁AlEt₂). All aluminum complexes were prepared according to the literature.^{11a} For *in situ* synthesis of **L**₁AlEt₂, AlEt₃ (0.53 mL, 1.9 M, 1.0 mmol) was added to a stirred solution of **L**₁ (0.2938 g, 1.0 mmol) in 5.0 mL of toluene at 0 °C. The mixture was then allowed to warm to room temperature and stirred for overnight. The resulting solution was directly used in the following ring-opening polymerization.

L₂AlEt₂, **L**₃AlEt₂, and **L**₄AlEt₂ were prepared in a manner analogous to that described for **L**₁AlEt₂ by the simple replacement of ligand **L**₁ with ligands **L**₂, **L**₃, and **L**₄, respectively.

Ring-opening Polymerizations of ε -CL and CHO. Under nitrogen protection, toluene (2.0 mL) was added with a syringe to the catalyst solution in Schlenk flask and heated to the desired temperature followed by the addition of ε -CL. The reactions were carried out in desired conditions and quenched with 5% HCl methanol solution (v/v). Solid was obtained by filtration, washed with methanol to remove excess metal catalysts, and dried under vacuum. Cyclohexene oxide (CHO) polymerizations were also performed in a similar way only by the replacement of ε -CL with CHO.

Results and Discussion

Synthesis of Ligands (L**₁-**L**₄) and Aluminium β -Ketoamino Complexes.** In addition to the strongly electrophilic character of the metal atom itself of metal complexes, the supporting ligands can be used to fine-tune both the steric and electronic properties at the metal center.¹⁹ In this regard, the β -ketoamino ligands (**L**₁-**L**₄) with various substituents on 3-position were prepared. Ligands **L**₁-**L**₄ could be prepared easily by the condensation reaction of the correspond-

ing β -diketone with 2,6-diisopropyl aniline in toluene containing *p*-toluenesulfonic acid hydrate as catalyst in a moderate yield. The resulting ligands are white or pale yellow solids. When the molar ratio of the substituted diketone (R=Me, Ph and Cl) in the 3-position to the amine was changed from 1:1 to 1:2, or even to 1:3, we could not obtain the corresponding β -diimine ligand; the final compounds was still β -ketoamino ligands. In general, three tautomeric forms, ketoamine and enoimine, are present in the resulting β -ketoimine ligand. The ketoamine structure of the ligands was predominant over the other two, which can be confirmed from not only the weak signals at 12.43, 12.06, 13.19, and 13.17 ppm in ¹H-NMR spectra of **L**₁-**L**₄, respectively, being assigned to the proton of NH group, but also the carbonyl resonance signals in the region of 195.0 ppm in the ¹³C-NMR spectra.

Aluminum complexes (**L**₁AlEt₂, **L**₂AlEt₂, **L**₃AlEt₂, **L**₄AlEt₂) were obtained by the reaction of the ligands **L**₁-**L**₄ with AlEt₃ overnight in 1:1 molar ratio at room temperature in toluene *in situ*. The reactions proceed along with the elimination of 1 equiv. of ethane. Their catalytic activities toward heteroatom monomers (ε -CL and CHO) were estimated directly using the resulting solution containing *in situ* generated catalysts in desired amount without separation.

The ROP of ε -CL and CHO. ROP of ε -CL were carried out with a catalyst loading of previous prepared aluminum β -ketoamino complexes in desired conditions. The 3-position substituent of the ligand significantly affected the behavior of the catalysts, such as their activity and product properties as summarized in Table I. The efficacy of these catalysts decreases in the order of **L**₁AlEt₂ > **L**₂AlEt₂ > **L**₃AlEt₂ > **L**₄AlEt₂, ranging from 45.9 to 76.2% in a period of 3 h. These polymerization results can be explained by using Hammett σ values of the 3-position substituents. The Hammett σ values of Me, Ph, H, and Cl are -0.170, -0.010, 0.000 and 0.227, respectively.²⁰ As is well known, the Hammett σ value is a measurement of the electronic effect of the substituent groups to a certain extent, the bigger positive σ value, the stronger electron-withdrawing ability of substituents is, whereas the smaller negative σ value, the stronger electron-donating ability of substituents is. As shown in Table I, the electron-withdrawing chlorine group at the 3-position on the β -ketoamino ligands backbone resulted in an enhancement of catalytic activity, whereas electron-donating methyl and phenyl group in the 3-position reduces their catalytic activities. The incorporation of electron-withdrawing substituents onto the ligands is expected to lead to a more electrophilic aluminum center, which is beneficial to coordinating ε -CL and subsequently leading to ε -CL activated.

The 3-position substituents also have a significant effect on the number average molecular weight of resulting poly(ε -CL). As shown in Table I, the M_n value of poly(ε -CL) obtained by **L**₃AlEt₂ records the lowest, 0.73×10^4 and the M_n value of poly(ε -CL) obtained by **L**₄AlEt₂ records the

Table I. Effects of 3-Position Substituent on β -Ketoamino Ligands of Aluminum Complexes on the Ring-Opening Polymerization of ε -Caprolactone (ε -CL)^a and Cyclohexene Oxide (CHO)^b

Entry	Catalyst	Monomer	Temp. (°C)	Time (h)	M_n ($\times 10^{-4}$)	M_w/M_n	Yield (%)
1	L₁AlEt₂	ε -CL	50	3	1.91	2.06	44.8
2			60	3	4.56	2.18	76.2
3			70	3	4.67	2.28	89.8
4	L₂AlEt₂		60	3	0.73	2.63	71.6
5	L₃AlEt₂		60	3	2.44	2.06	64.8
6	L₄AlEt₂		60	3	1.84	1.92	45.9
7	L₁AlEt₂	CHO	50	1	2.49	2.66	65.9
8			60	1	1.82	2.32	68.9
9			70	1	1.93	2.69	72.4
10	L₂AlEt₂		60	1	1.24	2.20	22.1
11	L₃AlEt₂		60	0.5	1.68	2.42	20.0
12			60	1.0	1.82	2.33	40.8
13			60	2.0	1.85	2.41	58.2
14			60	3.0	1.56	2.84	69.0
15			60	3.0 ^c	2.50	2.23	50.9
16	L₄AlEt₂		60	1	1.68	2.22	30.1

^aConditions of ε -CL polymerization: solvent = 1.80 mL; ε -CL = 1.700 \pm 0.005 g; aluminum complexes = 0.25 mL (1 mmol/5.53 mL).

^bConditions of CHO polymerizations: toluene solvent = 1.80 mL; CHO = 2.000 \pm 0.028 g; aluminum complexes = 0.25 mL (1 mmol/5.53 mL).

^cAluminum complexes = 0.25 mL.

highest, 4.56×10^4 . Apart from poly(ε -CL) obtained by **L₄AlEt₂**, the order of molecular weight of poly(ε -CL) is parallel to the steric nature of 3-position substituents. The steric hindrance of the substituents might reduce the chain-transfer rate yielding high-molecular weight polymer. Evidently, the electron-withdrawing group at 3-position onto β -ketoamino ligands of aluminum complexes improves both catalyst activity and molecular size of resulting poly(ε -CL).

Herein, aluminum β -ketoamino complexes were also firstly employed in CHO polymerizations. It was found that aluminum complexes catalyze ROP of CHO in highly efficient way, as shown in Table I. As for catalyst activity, it can be found that the effect of 3-position substituents on the ROP of CHO is different from that of ε -CL. Unlike the ROP of ε -CL, the activity trend of CHO polymerization cannot fit with the Hammett σ values of the 3-position substituents; however, it is said that the electron-withdrawing nature of 3-position substituents is much better than that of electron donating substituents in enhancing the catalyst activity. The type of 3-position substituents on β -ketoamino ligands backbone of aluminum complexes show no apparent effect on the molecular size of resulting poly(cyclohexene oxide) (PCHO).

The effect of reaction temperature on the ROP of ε -CL and CHO catalyzed by **L₁AlEt₂** is also observed. Table I summarizes the results of polymerization of ε -CL and CHO carried out at 50, 60, and 70 °C. The period of polymeriza-

tion for ε -CL and CHO is 3 h and 1 h, respectively. It is clear that polymerization temperature has much influence on the conversion of ε -CL, whose conversion increases from 44.8 to 89.8% with the temperature rising from 50 to 70 °C. However, polymerization temperature has no obvious effect on the conversion of CHO. The conversion is 65.9% at 50 °C, 68.9% at 60 °C and 72.4% at 70 °C. The effect of temperature on the degree of polymerization of ε -CL and CHO shows the similar trend, that is, the temperature has a more effect on molecular weight of poly(ε -CL) than that of PCHO.

Figure 1 displays the conversion versus time plots of ε -CL polymerization by **L₁AlEt₂** and CHO polymerization by **L₃AlEt₂**. The conversions increase linearly at the early period of polymerization and then approach to the asymptotic value at high conversions. It is of interest that the molecular weight of resulting PCHO has no an apparent change with the variation of polymerization time (Table I, entries 11-14) which is the typical characteristics of the chain polymerization. Comparing entry 14 to 15 in Table I, the low catalyst concentration is beneficial for the improvement of the PCHO molecular weight as expected.

Thermal Properties of Resultant Polymers. The thermal properties of the resulting polymer were investigated by TGA and DSC. The melt temperature (T_m) of poly(ε -CL) obtained with **L₁AlEt₂**, **L₂AlEt₂**, **L₃AlEt₂**, **L₄AlEt₂** varied

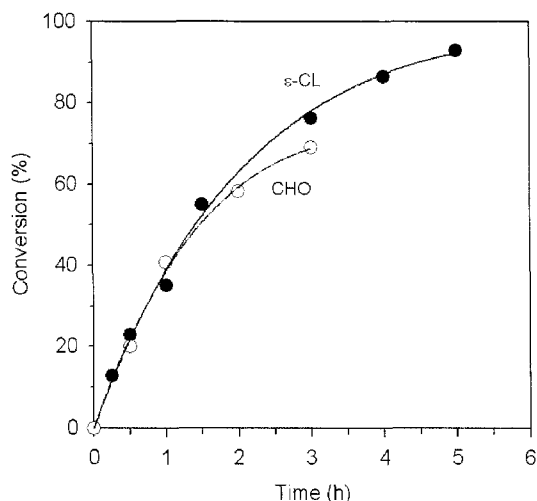


Figure 1. The effect of reaction time on the conversion of ϵ -caprolactone and cyclohexene oxide.

from 57.7 to 64.5 °C, most probably due to the variation of their molecular weights (see Table I) even though there are no definite relationship between T_m and M_n within our experimental range. The glass transition temperature of PCHO is around 68.4 °C, not much obviously influenced by their molecular weights. The typical maximum weight loss temperatures are around 437 °C for PCHO and at 457 °C for poly(ϵ -CL), respectively.

Conclusions

A series of aluminum complexes containing β -ketoamino ligands with variety of 3-position substituents have been successfully synthesized. All the complexes are found to be active toward the ROP of ϵ -CL and CHO, particularly, towards the CHO. The electron withdrawing nature of 3-position substituents is benefit for improving the both catalytic activity and molecular weight for both the ROP of ϵ -CL and CHO. A mechanistic study of the ring-opening polymerization as well as the steric effects of the substituents of the aluminum alkyl groups is our current investigation. The thermal properties of resultant polymer are also varies with the structure of the catalysts, but no definite relationship between them.

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