Mechanism and Kinetics of Adiabatic Anionic Polymerization of ε-Caprolactam In the Presence of Various Activators

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SYNOPSIS

Nylon 6 was prepared by adiabatic anionic polymerization of ε-caprolactam using hexamethylene dicarbamoyl dicaprolactam (HDC), cyclohexyl carbamoyl caprolactam (CCC), or phenyl carbamoyl caprolactam (PCC) as activators and sodium caprolactamate (NaCL) as a catalyst at various initial reaction temperatures ranging from 130 to 160°C. Adiabatic temperature rise was recorded as a function of polymerization time to investigate polymerization kinetics. Kinetic parameters for polymerization, which are more accurate than data reported to date, could be obtained by fitting the temperature rise data with a new polymerization kinetic equation involving crystallization exotherm and thermal conduction. The polymerization rate highly depended on the chemical structure of the activator used, which indicates that the initiating step where the activator is attacked nucleophilically by NaCL is a very important reaction step, affecting the overall polymerization rate. CCC showed the fastest polymerization rate, whereas HDC and PCC showed the medium and the slowest rate, respectively. The contributions of crystallization exotherm and thermal conduction to the resultant temperature rise during polymerization were significant, when the initial reaction temperature was lower than 140°C. In all cases, the molecular weight obtained from intrinsic viscosity measurement was greater than the expected molecular weight. This may be attributed to the branching and/or crosslinking reaction through Claisen-type condensation reactions. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The kinetics of the anionic polymerization of ε-caprolactam using a strong base catalyst and an activator has been analyzed, mainly using two different approaches.[1-6] One is based on the dominant reaction mechanism.[2,3] This approach has been found to be severely complicated by the complex side reactions present during anionic polymerization, and, hence, was limited to adopting a kinetic equation derived from a simplified reaction mechanism for data-fitting calculation. Consequently, the data-fitting results were rather poor. The other is basically an empirical approach to formulate a rate equation such that the deviations between the experimental and the predicted data are minimized. The empirical equation, proposed by Malkin et al.[4,5] and Macosco et al.[6,7], is most suitable for describing both isothermal and nonisothermal adiabatic polymerizations. The equation is written in the form:

$$\frac{d\beta}{dt} = A_0 \exp(-E/RT)(1-\beta)^n(1+B_0\beta) \quad (1)$$

where A_0 is the preexponential constant, β the fractional conversion, E the apparent activation energy, n the order of dependence on the monomer concentration, and B_0 the autocatalytic parameter.

The fractional conversion β cannot be determined from direct measurement of the concentration of the unreacted residual ε-caprolactam because the anionic polymerization is finished within several minutes. However, β can be obtained indirectly from the adiabatic temperature rise by the relation:

$$\beta = \frac{T - T_0}{T_e - T_0} \qquad (2)$$

where T is the temperature at time t, T_0 and T_e are initial temperature and equilibrium temperature at which the equilibrium conversion is reached, respectively.

Because the anionic polymerization of ϵ-caprolactam is initiated at a temperature below the melting temperature of the polymer produced and the true adiabatic system can never be realized experimentally, the effects of crystallization and partial melting of the polymer produced and thermal conduction upon the temperature rise during the polymerization must be taken into consideration in order to measure the correct conversion β as a function of time and, hence, obtain the correct polymerization kinetic parameters. In this study, we could obtain more accurate polymerization kinetic parameters for various activator systems and understand the crystallization behavior and thermal conduction during the polymerization by considering the contribution of crystallization and thermal conduction.

EXPERIMENTAL

Synthesis of Activators

ϵ-Caprolactam (CL, 2.2 mol) and 1,6-hexamethylene diisocyanate (1.0 mol) were reacted in bulk under a dry nitrogen atmosphere at 75°C for 6 h. The product was dissolved in acetone and then poured into an excess of water with mechanical stirring. The precipitate was washed thoroughly with fresh water to obtain the pure product (hexamethylene dicarbamoyl dicaprolactam, HDC). It was predried at 50°C for 1 day, and then dried in vacuum (ca. 1–2 mmHg) at 40°C for 3 days to form fine powder. Cyclohexyl carbamoyl caprolactam (CCC), which is a viscous liquid at room temperature, was obtained from the reaction between CL (1.2 mol) and cyclohexyl isocyanate (1.0 mol) at 95°C for 13.5 h under a continuous dry nitrogen flow. No further purification was made. Phenyl carbamoyl caprolactam (PCC) was obtained from the reaction between CL (1.2 mol) and phenyl isocyanate (1.0 mol) at 70°C for 3.5 h in bulk under a dry nitrogen atmosphere. The purification of PCC was performed in the same manner as in the case of HDC. All the products obtained above were kept in a vacuum desiccator before use.

Adiabatic Polymerization

CL, generously provided by Kohap, Korea, was dried under vacuum, below 1 mmHg at room temperature for more than 3 weeks before use. Sodium caprolactamate (NaCL) catalyst, generously provided by DSM, the Netherlands, was used without further purification. CL and NaCL were charged first into an adiabatic reactor, which consisted of a double-walled reaction vessel, a stirrer, a nitrogen gas inlet, and a K-type thermocouple.[8] When the mixture reached the desired initial reaction temperature, activator was added with vigorous stirring under a dry nitrogen atmosphere, and the temperature of the mixture as a function of time was continuously recorded on an X-Y recorder for kinetic analysis. The amount of the catalyst, [C], ranged from 0.6 to 1.0 mol %. The amount of activator, [A], was chosen to satisfy the following relation, $f[A] = [C]$, where f is the functionality of activator. Polymerization was stopped by removing the reactor from the adiabatic reaction vessel and quenching it to room temperature when no further temperature rise was observed. The initial reaction temperature ranged between 130°C and 160°C. Sample code was defined as Xyyy/zz, where X is the first letter of the activator, yyy is the initial temperature, and zz is the concentration of the catalyst in mol %. For example, C130/08 indicates that the anionic polymerization was carried out with the initial temperature at 130°C, using CCC as an activator and 0.8 mol % of NaCL as a catalyst. Polymer yield was measured after soxhlet extraction of the powdered polymer with water for a day.

Intrinsic Viscosity and GPC Measurements

Intrinsic viscosity was measured at 20°C with aqueous formic acid (85%) as a solvent using a Ubbelohde viscometer. The number-average molecular weight was calculated from the intrinsic viscosity data using the equation,[18] $[\eta] = 75 \times 10^{-3} \overline{M_n}^{0.7}$. Molecular weight distribution was measured by means of a Waters Model 244 GPC. The unit, consisting of 10^3, 10^4, and 10^5 Å μ-Styragel columns, was operated at room temperature, using a mixture of m-cresol and chloroform (1/4 v/v) as an eluent. The system was calibrated with polystyrene standards whose molecular weights were 2.3×10^6, 2.4×10^5, 5×10^4, 9×10^3, and 1.8×10^3, respectively.
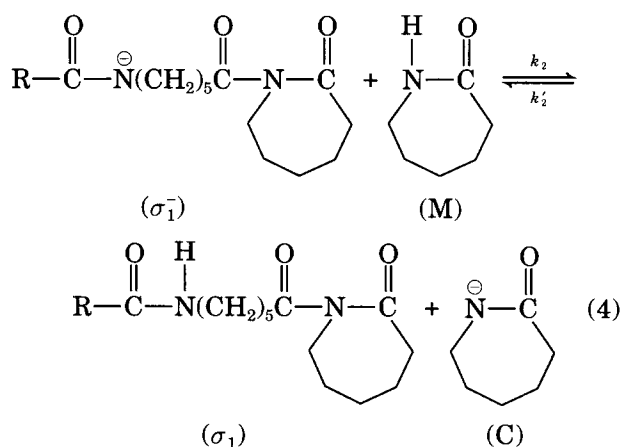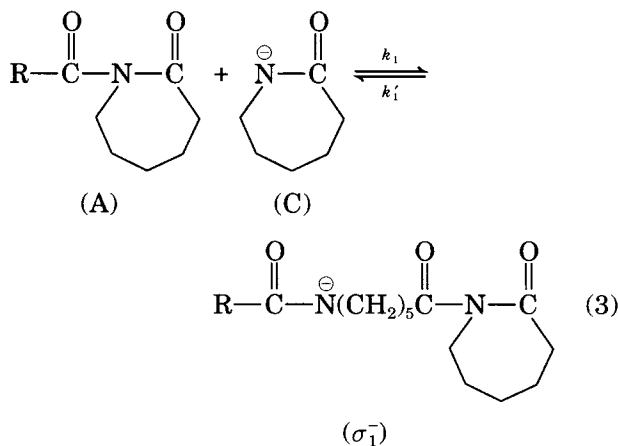
RESULT AND DISCUSSION

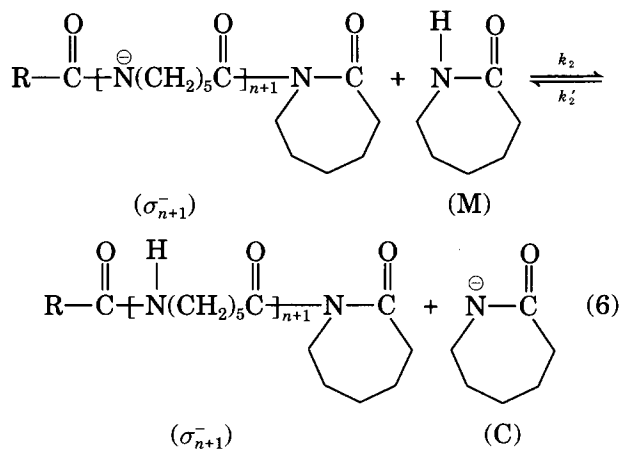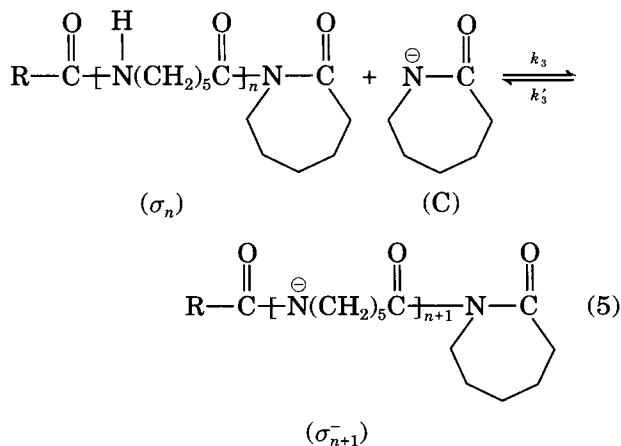### Polymerization Kinetics Based on Reaction Mechanism

When one does not consider side reactions, the major reaction scheme responsible for linear polymer chain

propagation using carbamoyl caprolactam or acyl caprolactam as an activator is given below:[1]

Initiation

$$R-C-N-C \ + \ N-C \ \underset{k_1'}{\overset{k_1}{\rightleftharpoons}}$$

(A)　　　(C)

$$R-C-N(CH_2)_5C-N-C \quad (3)$$

(σ_1^-)

$$R-C-N(CH_2)_5C-N-C \ + \ N-C \ \underset{k_2'}{\overset{k_2}{\rightleftharpoons}}$$

(σ_1^-)　　　(M)

$$R-C-N(CH_2)_5C-N-C \ + \ N-C \quad (4)$$

(σ_1)　　　(C)

Propagation

$$R-C-N(CH_2)_5C\overline{}_nN-C \ + \ N-C \ \underset{k_3'}{\overset{k_3}{\rightleftharpoons}}$$

(σ_n)　　　(C)

$$R-C-N(CH_2)_5C\overline{}_{n+1}N-C \quad (5)$$

(σ_{n+1}^-)

$$R-C-N(CH_2)_5C\overline{}_{n+1}N-C \ + \ N-C \ \underset{k_2'}{\overset{k_2}{\rightleftharpoons}}$$

(σ_{n+1}^-)　　　(M)

$$R-C-N(CH_2)_5C\overline{}_{n+1}N-C \ + \ N-C \quad (6)$$

(σ_{n+1}^-)　　　(C)

Many different equations for the anionic polymerization rate have been derived using the linear reaction mechanism shown above. Reimschuessel[9] derived the following rate equation with a pseudo-steady-state approximation on the concentration of polyamide anion, $[\sigma_{n+1}^-]$.

$$-\frac{d[M]}{dt} = k_2' \frac{[M]}{[M_e]} [\sigma][C]$$

$$\times \left\{ \frac{1 + \dfrac{k_2}{k_3'}[M_e]}{1 + \dfrac{k_2}{k_3'}[M]} - \frac{[M_e]}{[M]} \right\} \quad (7)$$

where $[M_e]$ is the equilibrium monomer concentration. Lin et al.[1] modified eq. (7) with further assumption that $[\sigma_{n+1}^-]$ are small at all times.

$$\frac{d\beta}{dt} = K[A]_0[C]_0 \frac{1-\beta}{1-B_0\beta} \quad (8)$$

where $[A]_0$, $[C]_0$ are the initial concentrations of the activator and the catalyst respectively, and

$$K = \frac{k_2(k_3 + k_2')}{k_3'\left(1 + \dfrac{k_2}{k_3'}[M_e]\right)\left(1 + \dfrac{k_2}{k_3'}[M]_0\right)}, B_0$$

$$= \frac{\dfrac{k_2}{k_3'}[M]_0}{\left(1 + \dfrac{k_2}{k_3'}[M]_0\right)} \quad (9)$$

Cimini and Sundberg[3] derived eq. (10) under the assumption that $k_1 = k_3$, $k_1' = k_3'$, and $k_2' = 0$.
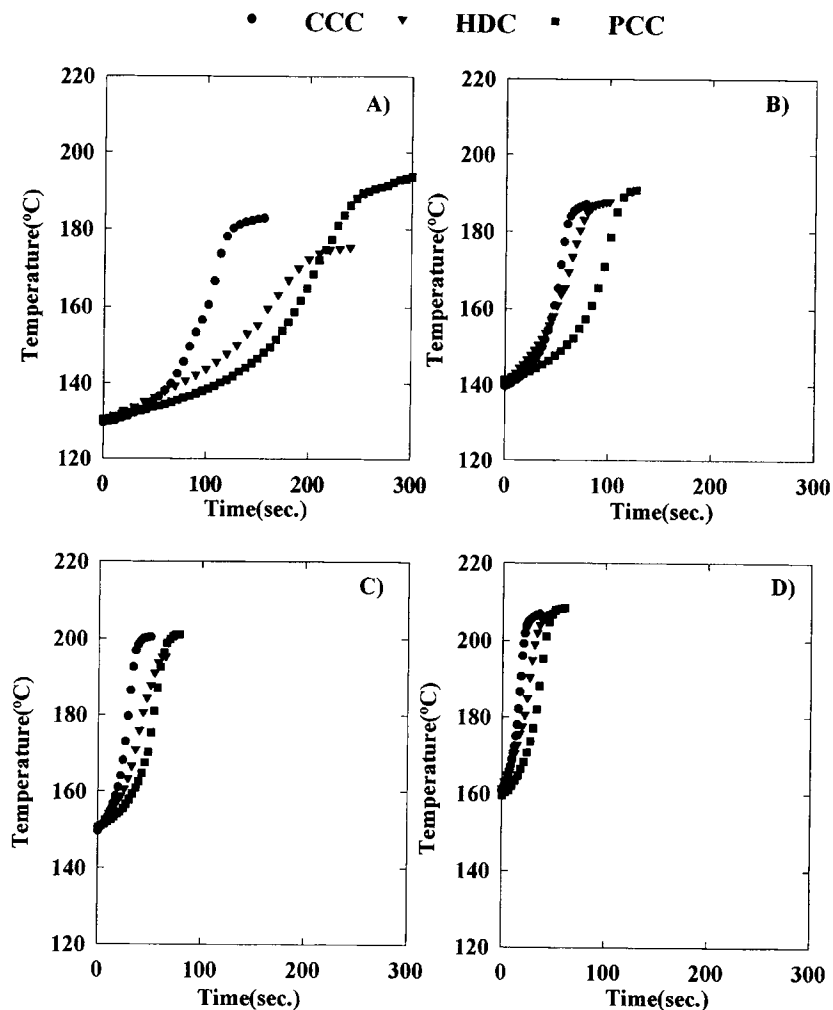
Figure 1 Adiabatic experimental data plots for various carbamoyl activator systems using 1 mol % NaCL at various initial polymerization temperatures.

$$-\frac{d[M]}{dt} = \frac{k_2 k_3 [C]^{1/2} [M][A]_0}{k_3' + k_2[M]} \qquad (10)$$

No equations reported to date include the terms k_1 and k_1' associated with eq. (3), because the effect of the initiation step by activators on the overall polymerization rate has been considered negligibly small. Thus, the rate of polymerization was predicted to be independent of the kind of activator adopted. However, the rate of polymerization has been found to be highly dependent on the chemical structure of the activator.[3,10-12] Carbamoyl caprolactams (phenyl carbamoyl caprolactam, tolylene dicarbamoyl dicaprolactam, cyclohexyl carbamoyl caprolactam, etc.) showed much faster polymerization rates than N-acyl caprolactam (acetyl caprolactam) did.[10-12] Such difference in reaction rates is attributed to the different level of electronegativity of N-substituents

of the caprolactam ring in the activator. Because an N-carbamoyl residue is more electronegative than an N-acyl residue, the N-carbamoyl substituent makes the carbonyl group of caprolactam more electron-deficient than the N-acyl group does. Thus, N-carbamoyl caprolactam is more readily attacked nucleophilically by the lactam anion in the initiation step. Similarly, cyclohexyl carbamoyl caprolactam was the fastest activator among the carbamoyl caprolactams.

Figure 1 shows the adiabatic temperature rise as a function of polymerization time for the various activators used in this study. CCC shows the fastest reaction rate, whereas HDC and PCC show the medium and the slowest rate, respectively. This result indicates again that the initiation step, which depends on the chemical structure of activators used, is the most important in determining the overall
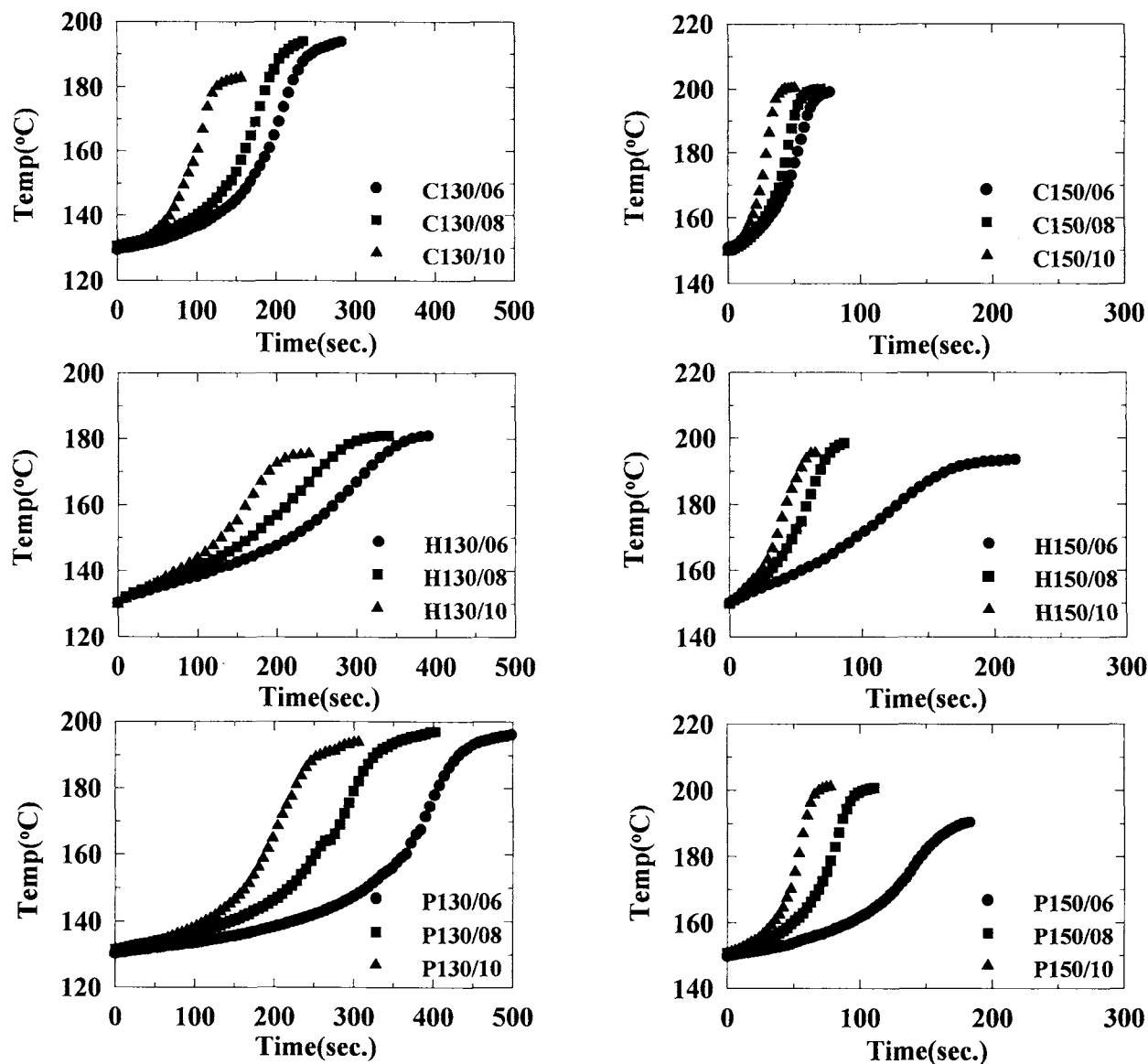
Figure 2 Adiabatic experimental data plots for various carbamoyl activator systems at the initial temperatures of 130 and 150°C.

polymerization rate. The neglect of nucleophilic attack of lactam anion towards an activator results in an erroneous prediction of the polymerization rate. Therefore, a polymerization rate equation derived from the reaction mechanism must include the rate-constant terms associated with eq. (3) in order to get better result. Unfortunately, such an equation has not been reported because of difficulties in solving the equation. Consequently, the empirical equation for polymerization rate has been used more frequently in analyzing the anionic polymerization kinetics of ε-caprolactam. The increase in the initial reaction temperature decreases the time at which the conversion reaches an equilibrium value in all

cases. The rate of polymerization was found to become faster with increasing concentration of the catalyst and / or activator, as predicted in the above equations [eqs.(8) and (10)] in all cases (see Fig. 2).

Polymerization Kinetics Based on an Empirical Approach

The temperature change as a function of polymerization time is attributed to the polymerization exotherm, the crystallization exotherm, the heat loss by thermal conduction, and the partial melting endotherm, as shown in eq. (11).

$$T(t) = T_0 + \Delta T(t) = T_0 + (\Delta T)_p$$

$$+ (\Delta T)_c - (\Delta T)_{\text{loss}} - (\Delta T)_{\text{melting}} \quad (11)$$

where T_0 is the initial temperature and $(\Delta T)_p$, $(\Delta T)_c$, $(\Delta T)_{\text{loss}}$, and $(\Delta T)_{\text{melting}}$ are the contributions of the polymerization exotherm, crystallization of the polymer produced, thermal conduction, and melting of the polymer produced, respectively. The onset temperature of the melting transition of the polymer obtained, T_{mo}, was found to be about 200°C (473 K). When one chooses the temperature fitting range from T_0 and T_{mo}, one can neglect the contribution of the partial melting endotherm to the observed temperature of the reactor.

Autocatalytic behavior is clearly observed in the early stages, as seen in Figure 1. This autoacceleration is attributed to an increase in the concentration of N-acyl caprolactam due to a polymer chain degradation mechanism proposed by Greenly et al.[2] Cimini and Sundberg[3] derived equations including the term responsible for the polymer degradation mechanism to express the autocatalytic behavior. Lin et al.[1] derived a kinetic model including the autocatalytic parameter from a regular, linear reversible reaction mechanism [eqs.(3)–(5)] without taking into consideration the polymer degradation mechanism proposed by Greenly et al.[2] to explain the autocatalytic character. However, these two equations did not fit the experimental data well. On the other hand, Malkin et al.[4,5] suggested the empirical kinetic equation [eq.(1)] including the autocatalytic parameter. This equation exhibited better data fitting than the two previous equations did. Thus, in this study, the temperature rise attributed to the polymerization exotherm will be expressed with the empirical equation for the polymerization rate proposed by Malkin et al.[4,5]

$$(\Delta T)_p = \int \left(\frac{dT}{dt} \right)_p dt \quad (12)$$

$$\left(\frac{dT}{dt} \right)_p = \frac{\Delta H_p}{C_p} \cdot \frac{d\beta}{dt}$$

$$= \frac{\Delta H_p}{C_p} \cdot A_0 \exp(-E/RT)(1 - \beta)^n (1 + B_0\beta) \quad (13)$$

where ΔH_p is the enthalpy of polymerization of ϵ-caprolactam (ca. 33 cal/g), which is almost constant in the temperature range in which the reaction takes place, and C_p is the heat capacity of the reaction mixture. Because C_p varies with the conversion β,

C_p can be expressed as $C_p = (1 - \beta)C_{p,caprolactam} + \beta C_{p,nylon6}$, under the assumption that the heat capacities are constant in the experimental temperature range ($C_{p,caprolactam} = 0.5860$ cal/g·K and $C_{p,nylon6} = 0.6812$ cal/g·K).

The correct equation for nonisothermal polymerization-induced crystallization has not been established yet. Malkin et al.[13] proposed a new crystallization equation of the self-acceleration type that can be applied to both iso- and nonisothermal cases. Lee and Kim[14] used the same equation [eq.(14)], as proposed by Malkin et al.[10,13], to analyze polymerization-induced crystallization with extensive experimental data on the formation of nylon 6 through anionic ring-opening polymerization of ϵ-caprolactam.

$$\frac{dX_c(t)}{dt} = K_0 \exp(-E_D/RT) \exp\left(-\frac{\psi T_m^\circ}{T(T_m^\circ - T)} \right)$$

$$\times X_c(t)^{2/3}(X_e - X_c(t)) \quad (14)$$

where $X_c(t)$ is the degree of crystallinity at time t, K_0 the preexponential constant based on the formation of three-dimensional spherulites, E_D the activation energy for transportation of the amorphous phase to the crystalline interface, ψ the constant that is related to the free energy of formation of a critical nucleus, T_m° the equilibrium melting temperature, and X_e the equilibrium crystallinity. The values of parameters T_m°, E_D, and ψ must be determined as a function of fractional conversion β experimentally to apply eq. (14) to our system. The job of determining the parameters experimentally is very tedious and may result in large errors. However, we cannot directly use the values of the parameters obtained by Lee and Kim,[14] because the magnitudes of E_D and ψ may be highly dependent on the kind and the concentration of activator used.[10]

Avrami's equation, shown in eq. (15), is often used to characterize the nonisothermal crystallization of several polymers without any modification, under the oversimplifying assumption that the rate constant of crystallization K and the Avrami exponent n_c are constant in the temperature range to be investigated.

$$X_c(t) = X_e(1 - \exp(-Kt^{n_c})) \quad (15)$$

The curve fitting of the nonisothermal crystallization data by the Avrami equation showed very good results up to crystallinity of about 90%.[15–17] Thus, we adopted the simplified Avrami's equation

in characterizing the nonisothermal reaction-induced crystallization to avoid the difficulty in determining several parameters experimentally. However, because the portion to be crystallized during polymerization is the polymer produced and the crystallization does not take place up to the time θ, one can introduce the conversion β and the crystallization induction period θ to eq. (15), and the temperature rise attributed to the crystallization exotherm can be expressed as shown in eq. (16).

$$(\Delta T)_c$$

$$= \frac{\Delta H_c}{C_p} \cdot \beta \cdot X_e \{1 - \exp[-K(t - \theta)^{n_c}]\} \quad (16)$$

where ΔH_c is the enthalpy of crystallization of pure nylon 6 (ca. 49.5 cal/g) and X_e is set to be about 0.4.

The heat loss via the thermal conduction due to incomplete insulation can be written as

$$(\Delta T)_{loss} = \frac{U}{C_p} \int_0^{t(\beta)} (T - T_{amb}) dt \quad (17)$$

where U is the overall heat transfer coefficient and T_{amb} is the ambient temperature.

A best set of kinetic parameters, representing the nonisothermal polymerization and crystallization behaviors, was determined by the nonlinear least-squares curve-fitting method using eqs. (12), (13), (16), and (17). Figure 3 shows the typical curve-fitting result for the adiabatic polymerization coded as P130/10. The experimental and calculated temperature rises show a very good data fitting, which indicates that eqs. (13), (16), and (17) are appropriate in describing the nonisothermal polymerization, the nonisothermal reaction-induced crystallization, and the thermal conduction in this study. In this case, the total contributions of crystallization exotherm and thermal loss to the final reaction temperature are 23°C and −7.9°C, respectively, during polymerization. Thus, subtraction of the effects due to crystallization and thermal loss can result in the correct kinetic parameters for pure polymerization. The kinetic parameters for polymerization under various conditions are summarized in Table I.

The overall activation energy for polymerization and the autocatalytic parameter have nearly same values of about 18,400 cal/mol and around 5, respectively, regardless of the kind of activator used. The reaction order for CCC and PCC is about 0.65, whereas that for HDC is 1.21. This difference in
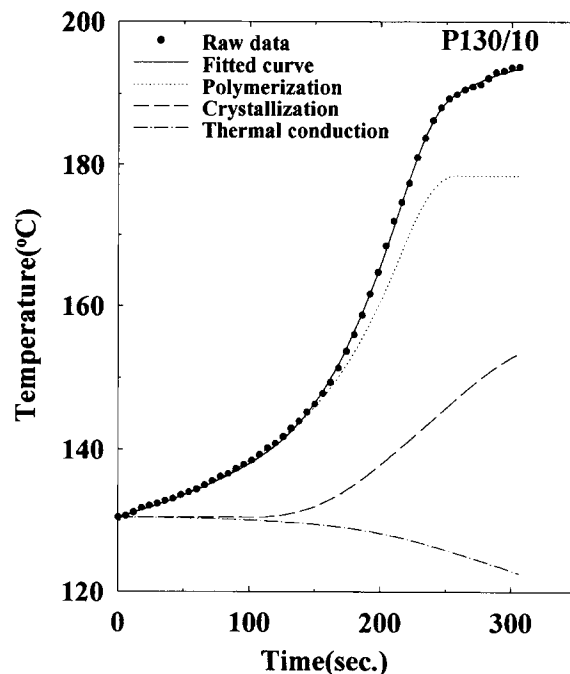

Figure 3 Typical example of predictions based on the kinetic model vs. adiabatic data: 1 mol % PCC system. Initial reaction temperature is 130°C.

the reaction order seems to be attributed to the difference between the functionality of CCC and PCC ($f = 1$) and that of HDC ($f = 2$). The total contribution of polymerization exotherm, $(\Delta T)_p$, for the CCC and PCC activator systems are in the range of 47 to 48°C, whereas $(\Delta T)_p$ for the HDC activator system shows a slightly lower value (ca. 43 to 47°C). This is attributed to the result that the total polymerization exothermic enthalpy in the case of HDC is less than in the other cases, because the polymer yield of the HDC system is less than that of the CCC and PCC systems, as can be seen in Table II.

Polymerization-Induced Crystallization Behavior

Figure 4 shows the curve-fitting result for P160/10. Because this reaction was completed six times faster than in the case of P130/10, the rate of crystallization is slowed down significantly due to the difficulty in forming a nucleus of critical size during such a short period at the small degree of undercooling and, thus, the total contributions of crystallization and thermal loss are very small when the extent of polymerization reaches the equilibrium state. In general, when the polymerization is completed within 100 s or the initial reaction temperature is greater than 140°C in all cases, the crystal-

Table I   A List of Kinetic Parameters for Polymerization Under Various Conditions

Sample	$A_0(\times 10^7)(s^{-1})$	E(cal/mol)	n	B_0
C130/06	1.049898	18602	0.4432	4.9903
C130/08	0.925823	18416	0.6575	5.7072
C130/10	1.118246	18029	0.6226	4.4982
C140/06	1.082631	18498	1.6070*	5.7787
C140/08	1.213678	18390	0.6101	5.0734
C140/10	1.173843	18043	0.5851	5.4651
C150/06	1.226421	18494	0.6890	4.7754
C150/08	1.050151	18273	0.6279	6.0458
C150/10	1.417343	18054	0.7237	5.0598
C160/06	1.208497	18472	0.8391	5.2909
C160/08	1.161916	18380	0.7675	7.1210
C160/10	1.275560	18040	1.1243*	6.8092
Average		18308	0.6566	5.5513
H130/06	0.75362	18445	1.0513	3.3891
H130/08	1.079972	18390	1.6123*	3.4093
H130/10	1.012446	18111	1.1954	3.2190
H140/06	1.068115	18502	1.3413	4.2507
H140/08	1.071774	18041	1.1194	4.5000
H140/10	1.113292	17889	1.1219	4.0347
H150/06	1.118906	18896	2.0357*	5.7103
H150/08	1.023162	18226	0.9852	3.7784
H150/10	1.012299	17995	1.1665	4.5987
H160/06	1.090790	18740	1.4111	4.2059
H160/08	1.296750	18369	1.5056	5.6237
H160/10	1.241579	18109	1.1579	3.2949
Average		18359	1.2056	4.1679
P130/06	0.659519	18674	0.6143	4.2872
P130/08	0.952278	18729	0.9011	4.3237
P130/10	0.966596	18472	0.7956	4.3577
P140/06	0.953358	19280	0.7120	5.3987
P140/08	0.863399	18740	0.8335	5.0345
P140/10	0.929379	18392	0.4128	4.6481
P150/06	0.927155	19078	1.0140*	5.8872
P150/08	1.061913	18743	0.4729	4.6900
P150/10	1.007471	18394	0.4217	4.9311
P160/06	1.183118	19304	0.7378	5.8869
P160/08	1.118969	16903	0.4740	4.8213
P160/10	1.017958	18393	0.7034	5.1063
Average		18591	0.6436	4.9477

* Not used in the calculation of the average value.

lization occurring simultaneously with polymerization can be neglected, regardless of the initial polymerization temperature and the kind and concentration of activator. This is very consistent with the previous study of Wittmer and Gerrens,[18] which suggests that a minimum initial temperature of 140°C is usually required for adiabatic reaction conditions without crystallization.

When one can ignore the effects of reaction-induced crystallization and thermal conduction, the maximum temperature rise due to the perfect polymerization of caprolactam is expected to be about 51°C.[18] When the observed temperature rise exceeds about 50°C in the temperature-time plot, crystallization during polymerization is always expected. As seen in Figure 2, the contribution of exothermic crystallization for C130/06 and C130/08 can be expected to be much greater than for C130/10 even without the data-fitting procedure (cf. Fitting result: ΔT_{crys} for C130/06 = 22.5°C, ΔT_{crys} for C130/08

= 20.2°C, and ΔT_{crys} for C130/10 = 10°C). Similarly, the contribution of exothermic crystallization for H130/06 and H130/08 is greater than for H130/10 (cf. Fitting result: ΔT_{crys} for H130/06 = 14.5°C, ΔT_{crys} for H130/08 = 16.7°C, and ΔT_{crys} for H130/10 = 4°C), whereas the contribution of crystallization is similar for the P130/yy series (ΔT_{crys} = 26°C). The contribution of exothermic crystallization for polymerization starting at 150°C is expected to be negligibly small, regardless of the kind and concentration of the activator. In conclusion, the contribution of crystallization at equilibrium conversion is less with greater polymerization rates at a higher initial temperature or higher concentrations of a catalyst and activator.

These polymerization-induced crystallization behaviors under various conditions, however, suggest that in the RIM process of nylon 6 one should not remove the product from a mold as soon as the polymerization is finished, but prolong the molding time considerably until the crystallization can be completed in the mold to obtain good dimensional stability after molding. We obtained the time ($t_{0.95}$) required to reach 0.95 of the equilibrium crystallinity using the crystallization kinetic parameters from the curve fitting of the raw data. Figure 5 shows the plot of $t_{0.95}$ against the initial reaction temperature for the Xyyy/10 series. The crystallization for the H series shows the slowest rate, whereas the crystallization for the C series is the fastest. The C140/10 and C150/10 systems seem to be the most appropriate to shorten the cycling time of the RIM process.

Polymer Yield and Molecular Weight

Data for the yield of polymerization are listed in Table II. All the cases showed very high yield. The
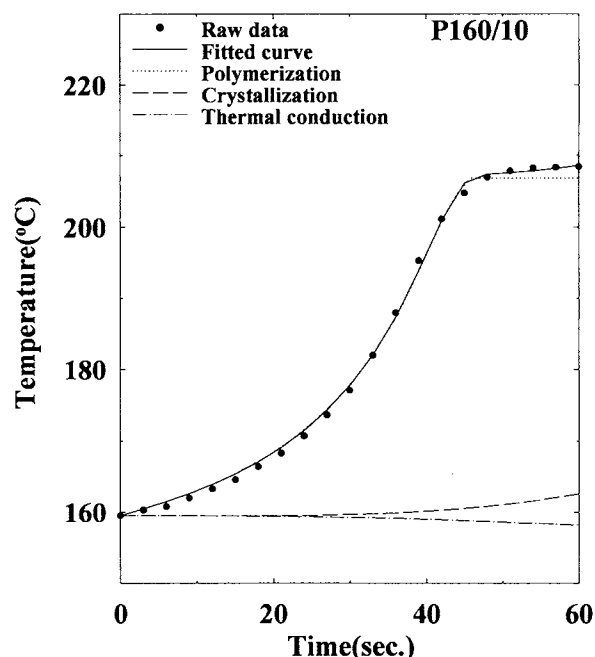

Figure 4 Example of kinetic model predictions vs. adiabatic data: 1 mol % PCC system. Initial reaction temperature is 160°C.

yields for polymerization at high initial temperatures (150 and 160°C) are relatively low. This result can be explained by the fact that the temperature at which limited thermally initiated polymerization is possible is reached more quickly, and deactivation of catalyst results in incomplete conversion of the monomer.[3]

The expected number-average molecular weight, $(\overline{M_n})_{expected}$, of the polymer produced can be calculated from eq. (18), under the assumptions that no termination reaction is present and all

Table II   Yields of Polymerization

| Sample	Yield (%)	Sample	Yield (%)	Sample	Yield (%)
C130/06	98.6	H130/06	97.9	P130/06	98.9
C130/08	98.4	H130/08	98.1	P130/08	99.0
C130/10	97.6	H130/10	97.9	P130/10	98.9
C140/06	98.9	H140/06	98.1	P140/06	97.4
C140/08	98.0	H140/08	97.7	P140/08	98.1
C140/10	98.5	H140/10	97.8	P140/10	98.1
C150/06	97.1	H150/06	96.6	P150/06	98.3
C150/08	97.5	H150/08	96.8	P150/08	97.9
C150/10	97.5	H150/10	97.7	P150/10	97.7
C160/06	96.6	H160/06	97.4	P160/06	97.3
C160/08	96.6	H160/08	96.5	P160/08	97.5
C160/10	96.7	H160/10	96.7	P160/10	97.5

Table III Molecular Weight Data of the Polymers Produced

Sample	$(\bar{M}_n)_{expected}$	Sample	$(\bar{M}_n)_{expected}$	Sample	$(\bar{M}_n)_{expected}$
Cyyy/06	18,980	Hyyy/06	37,980	Pyyy/06	18,900
Cyyy/08	14,260	Hyyy/08	28,460	Pyyy/08	14,270
Cyyy/10	11,440	Hyyy/10	22,800	Pyyy/10	11,440
Sample	$\bar{M}_n$	Sample	$\bar{M}_n$	Sample	$\bar{M}_n$
C130/06	37,600	H130/06	98,300	P130/06	33,800
C130/08	24,000	H130/08	66,700	P130/08	29,400
C130/10	17,400	H130/10	48,200	P130/10	23,500
C140/06	30,800	H140/06	102,400	P140/06	29,000
C140/08	27,000	H140/08	68,900	P140/08	28,300
C140/10	22,600	H140/10	51,400	P140/10	27,200
C150/06	37,800	H150/06	102,700	P150/06	32,100
C150/08	24,000	H150/08	68,900	P150/08	29,400
C150/10	16,300	H150/10	65,100	P150/10	21,800
C160/06	25,700	H160/06	112,400	P160/06	33,500
C160/08	21,500	H160/08	69,200	P160/08	30,900
C160/10	19,400	H160/10	48,700	P160/10	27,300

activators are effective in initiating polymerization.

$$(\overline{M_n})_{expected} = \frac{\text{No. of mole of CL}}{\text{No. of mole of activator}}$$

$$\times\ 113.6 + \text{molecular weight of activator} \quad (18)$$

The expected and measured number-average molecular weights of the polymers produced are listed in Table III. In all cases, the molecular weight obtained from intrinsic viscosity measurement shows a greater value than the expected molecular weight does. This is attributed to the branching and/or crosslinking reaction via the Claisen type condensation reaction as shown in eq. (19), irrespective of the kind of activator.[3]
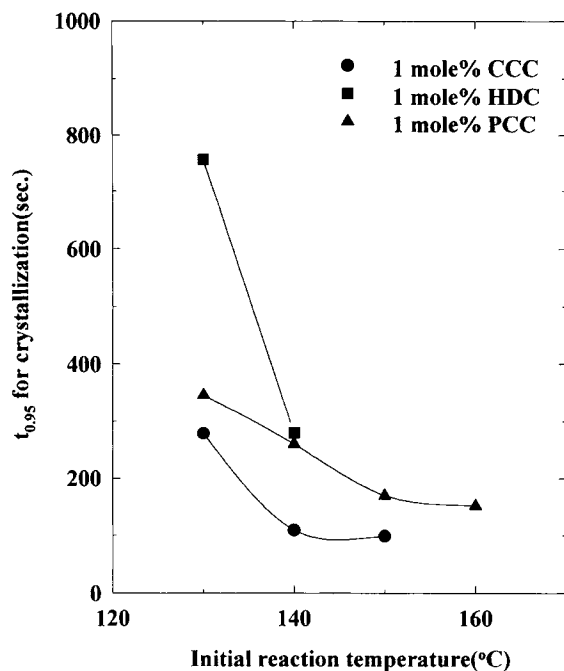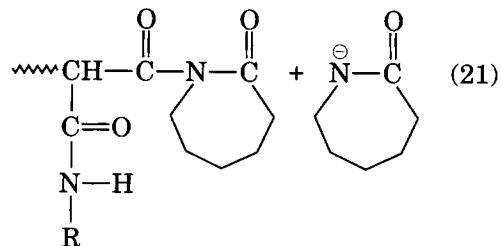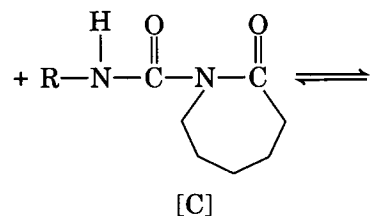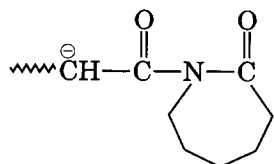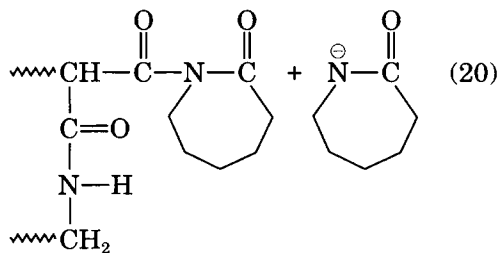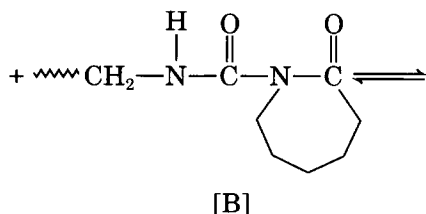

[A]

(19b)

(19a)
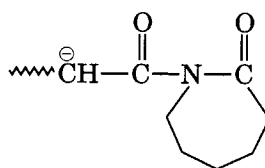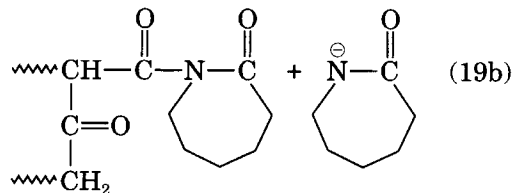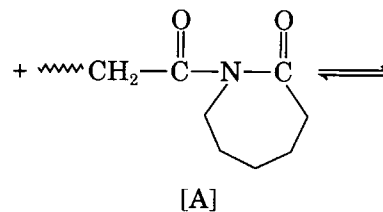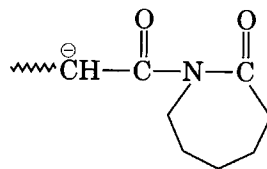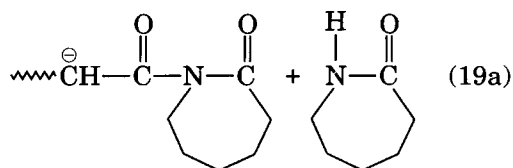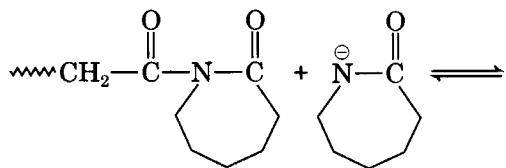
Figure 5 The plot of $t_{0.95}$ for crystallization vs. the initial temperature for $[NaCL]_0 = 1$ mol %.

where $R = C_6H_{11}$— or C_6H_5—.

The difference between the expected and the observed molecular weights is the greatest for the HDC activator system. This indicates that in addition to the branching and/or crosslinking reaction via the Claisen type condensation reaction as shown in eq. (19), eq. (20) is also favorable for the HDC activator system. The reaction in eq. (20) is favored more than the reaction in eq. (19), because electron-deficiency of the exocyclic carbonyl group of [B] in eq. (20) is greater than the exocyclic carbonyl group of [A] in eq. (19). Even though the reaction [eq. (21)] similar to eq. (20) is also possible with the CCC and PCC activator systems, only short branches can be expected rather than long branches expected for the HDC activator system. The polydispersity index of the polymers calculated from GPC data is around 1.5 for the CCC and PCC activator systems, whereas the HDC system shows a slightly higher value (ca. 1.7). This result can also be interpreted to be attributed to the occurrence of more branching and crosslinking reactions due to the dominant Claisen type condensation reaction, which are not expected for the CCC and PCC activator systems, as shown in eq. (20).

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