

Kinetics of Adiabatic Anionic Copolymerization of ϵ -Caprolactam in the Presence of Various Activators

KAP JIN KIM, DAE SEONG HONG, AMIYA RATAN TRIPATHY

Department of Textile Engineering, Kyung Hee University, Kyunggi-do 449-701, Korea

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ABSTRACT: Adiabatic temperature rise has been recorded as a function of polymerization time to investigate an adiabatic copolymerization kinetics of ϵ -caprolactam (CL) in the presence of several activators, considering different initial copolymerization temperatures ranging from 130 to 160°C. The copolymerization of CL and PEG-diamine has been performed using activators such as tolylene dicarbamoyl dicaprolactam (TDC), hexamethylene dicarbamoyl dicaprolactam (HDC), and cyclohexyl carbamoyl caprolactam (CCC), and sodium caprolactamate as a catalyst. The effect of PEG-diamine on the overall rate of polymerization of CL has been studied by fitting the experimental temperature rise with a new polymerization kinetic equation involving the polymerization exotherm, polymerization-induced crystallization exotherm, and the heat loss due to nonideal adiabatic condition in the experimental situation. Like homopolymerization, the net copolymerization rate is influenced by the variation of activator types in the initiation step. The temperature rise due to polymerization-induced crystallization in copolymerization is drastically decreased with the increasing initial polymerization temperature in the course of polymerization. The high molecular weight and large polydispersity index of copolymers using bifunctional activators indicate that the Claisen type condensation can occur in the course of polymerization processes. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1195–1207, 1997

Key words: adiabatic anionic copolymerization; ϵ -caprolactam; PEG-diamine

INTRODUCTION

The kinetics of activated anionic polymerization of ϵ -caprolactam (CL) using a strong base as a catalyst has been described in two different kinetic approaches.^{1–6} The first approach is based on regular mechanistic route shown in Scheme 1. Several authors^{2,3} adopted this approach for the kinetics determination. However, it has been found to be very complicated and even inconclusive due to its complex side reactions, degradation, and branching during polymerization. Con-

sequently, the result of data fitting matches poorly with the experimental facts. The second approach is mainly a formulation of an empirical rate equation such that the deviation between experimental and calculated data are to be minimized. The existing most suitable equation, applied both in isothermal and adiabatic nonisothermal polymerizations, given by Malkin et al.^{4,5} and Macosco et al.⁶ is

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

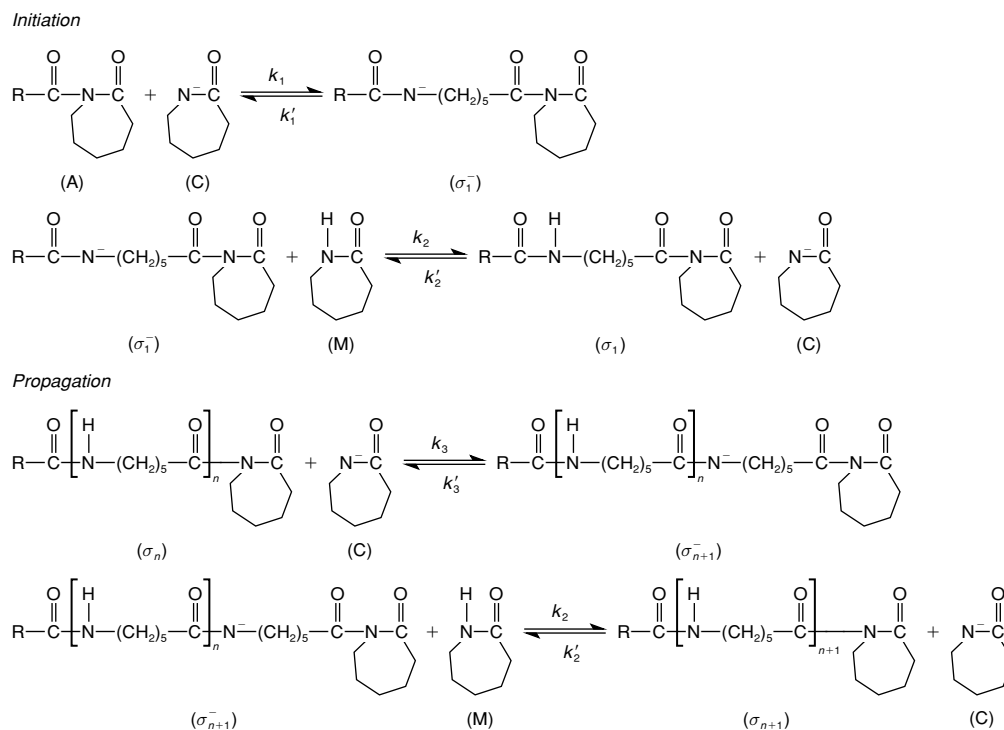
where A_0 is preexponential or frequency factor, E is apparent activation energy, n is the order of the reaction, B_0 is the autocatalytic factor and β is the degree of conversion.

Generally, the rate of the reaction is deter-

Correspondence to: K. J. Kim.

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mined by measuring the value of any convenient property that can be related to change in the composition of the system with the time. The property chosen should be reasonably easy to measure; it should change sufficiently in the course of reaction to permit an accurate distinction to be made with various compositions of the system as time passes. The degree of conversion β can be determined from the adiabatic temperature rise using the following equation in the anionic polymerization of CL because the exothermic enthalpy of polymerization is very great.

$$\beta = \frac{T_t - T_0}{T_e - T_0} \quad (2)$$

where T_t is the temperature at time t , T_0 , and T_e are initial and equilibrium temperatures, respectively.

In the determination of β from the temperature rise, almost all earlier works were based on temperature rise due to the exothermic enthalpy of polymerization, assuming the true adiabatic system. In fact, true adiabatic system would never be realized in the experimental conditions. Therefore, one should consider the heat loss due to thermal conduction for the exact determination of conversion term β . Additionally, crystallization

during activated anionic polymerization of ϵ -caprolactam in the reaction injection molding (RIM), is a widely accepted phenomenon.^{7,8} In fact, this situation is always encountered if the reaction is carried out below the melting temperature of ultimate polymer formed. As crystallization is an exothermic process, the release of heat during polymerization should also be considered for the exact determination of conversion term β . The exotherm due to polymerization-induced crystallization invokes some process-related problems such as accumulation of internal residual stress, nonuniform degree of crystallinity, and volatilization of low boiling ingredients if used, mainly in large article fabrication. To resolve these problems, required is a careful control of process parameters that strongly affect the conversion pattern, crystallization mode, as well as the whole kinetics of polymerization.

Thus, in the present study, our aim is to find out more accurate kinetic and crystallization parameters to have a better data fitting of the nonisothermal anionic polymerization of CL using several activators at their different concentration ranges in the light of enthalpy change due to polymerization, crystallization, and thermal loss. The kinetics of anionic activated copolymerization of CL with modifier, PEG-diamine, in the presence of different activator systems is also studied in this article.

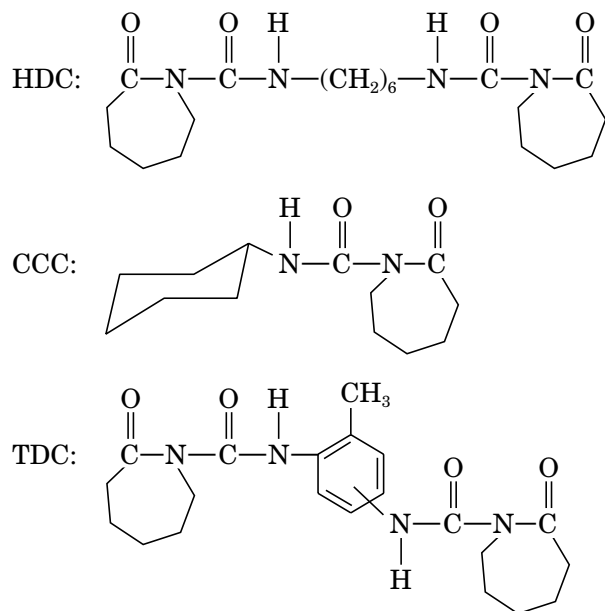
EXPERIMENTAL

Materials

CL was supplied by Kohap, Korea and sodium caprolactamate (NaCL) was from DSM, The Netherlands. 2,6-Tolylene diisocyanate (TDI) was purchased from Kokusan, Japan. Modifier, PEG-diamine (Jeffamine ED2001) was bought from Huntsman Co., USA. Hexamethylene diisocyanate (HDI) was purchased from Aldrich Chemical Co., Milwaukee, WI, and cyclohexyl isocyanate (CHI) from TCI, Japan. All the chemicals were used for polymerization without further purification.

Synthesis of Tolyene Dicarbamoyl Dicaprolactam (TDC), Hexamethylene Dicarbamoyl Dicaprolactam (HDC), and Cyclohexyl Carbamoyl Caprolactam (CCC) as Activators

CL (0.6 mol) and TDI (0.287 mol) were dissolved in 500 mL dry toluene at room temperature. It was refluxed for 8 h under dry nitrogen atmosphere. The complete consumption of isocyanate group in the reaction mixture after an 8-h reflux could be identified from the disappearance of the infrared absorption peak of NCO stretching vibration at 2270 cm^{-1} . Then the product was concentrated using a rotary vacuum evaporator and the concentrate was precipitated in a large amount of water. The white precipitate was washed with distilled water thoroughly and finally it was dried in vacuum. Synthesis of HDC and CCC has been mentioned in our earlier publication.⁹ The chemical structures of these three activators are summarized as follows:



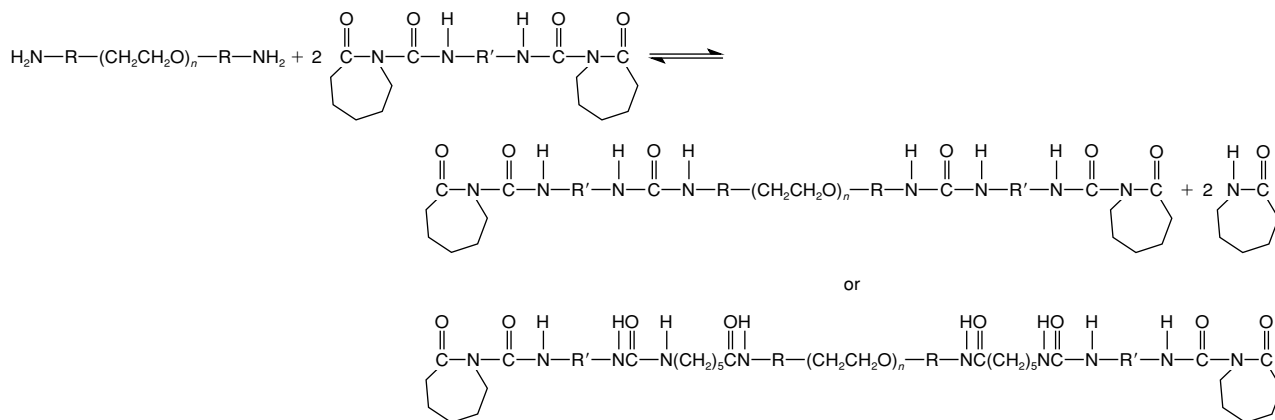
Adiabatic Copolymerization

The copolymerization of CL and modifier PEG-diamine was performed in a quasi-adiabatic reactor. The adiabatic reactor was placed on a high temperature silicone oil bath to have the initial temperature as we desired. The reactor was equipped with three K-type thermocouples to measure the temperature rise in inside, outside, and the top of the reactor with time. The thermocouples were connected with an Adam 4011 module (Avantech Co.), which was interfaced to an i-486 personal computer for data acquisition and storage in the hard disk. PEG-diamine at different weight percentage (5–20% of total copolymer) was mixed with an activator (which was taken twice mol percentage of PEG-diamine in TDC and HDC and that of four times in CCC) and CL in the adiabatic reactor under nitrogen atmosphere at 100°C for nearly half an hour. Thus, the aminolysis reaction could be performed in the reactor (Scheme 2). After aminolysis reaction, the desired initial polymerization temperature was allowed to reach accordingly varied from 130 to 160°C . Previously melted mixture of NaCL (always 1 mol percentage of total CL taken) and a small portion of CL were introduced into the reactor under the nitrogen atmosphere. Stirring was done vigorously. Thus, the copolymerization reaction (shown in Scheme 2) starts in the reactor along with adiabatic temperature rise, which was measured by K-type thermocouples as described above. When the temperature rise of the reactor starts to drop, copolymerization was stopped by removing the reactor from the adiabatic reaction vessel and quenching it to the room temperature. The sample code was designated as $X_{yyy}J_{zz}$, where X is the first letter of activator, the subscript yyy is the initial reaction temperature, J is for the PEG-diamine, and the subscript zz represents the weight percentage of modifier. For example, H140J10 indicates that HDC was used as an activator, initial polymerization temperature was 140°C , and PEG-diamine as modifier was used at 10 wt % of total copolymer.

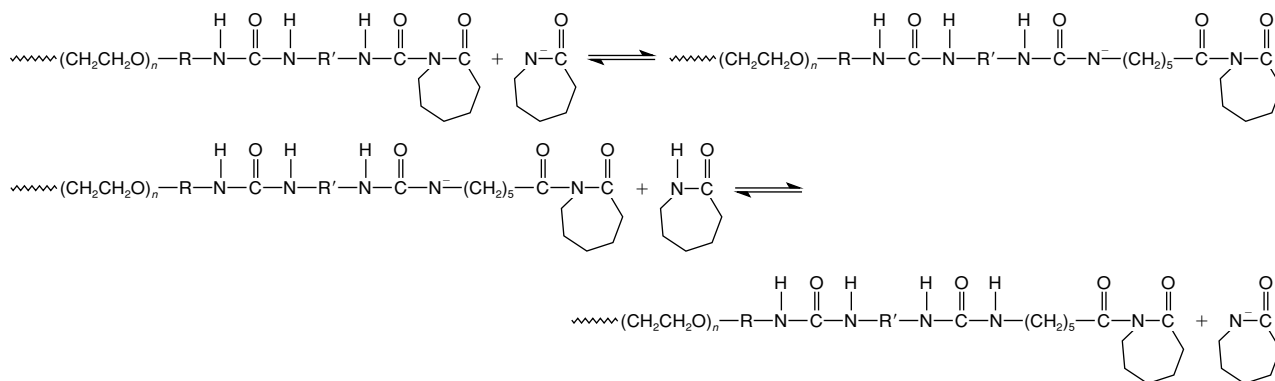
Adiabatic Homopolymerization

The initial reaction temperature was varied from 130 to 160°C . The reactor arrangement and polymerization procedure were as in copolymerization. To investigate the effect of PEG-diamine on the rate of polymerization, we have taken the same amount of catalyst and just half of the total amount of the activator used in copolymerization

Aminolysis



Copolymerization



Scheme 2 Aminolysis and subsequent copolymerization of ϵ -caprolactam.

as mentioned above. The sample code was defined as $X_{yyy}H_{zz}$, where H stands for homopolymer and the amount of X used is a half in the sample code of $X_{yyy}J_{zz}$. For example, H140H10 indicates that HDC was used as an activator, 140°C was the initial polymerization temperature, and the amount of activator HDC used in this sample is half an amount of activator used in the H140J10 sample.

Molecular Weight Distribution by GPC

Molecular weight distribution was measured by means of a Waters model 150-CV GPC with a differential refractive index detector. The unit consisting of 10^3 , 10^4 , and 10^5 Å μ -styragel HT-6E columns, was operated at 100°C temperature, using *o*-chlorophenol as an eluent as well as solvent. The injection volume was 200 μ L and the flow rate was chosen 1.0 mL/min. The system was calibrated with polystyrene standards whose molecular weights were 985,000, 475,000, 165,000, 68,000, 34,500, 22,000, 9200, 3600, and 1250, respectively.

RESULTS AND DISCUSSIONS

Polymerization Kinetics Based on Mechanistic Route

Many authors^{2,4-6} have suggested many rate equations considering their experimental facts and suggested mechanistic path (Scheme 1). Some groups adopted linear polymerization mechanism along with an irreversible disproportionation side reaction of polymer chains, while others have considered autocatalysis in addition to linear polymerization and branching to enable one to predict the conversion profiles in the rate expressions. Thus, the rate expression varies considerably from thought to thought. In an effort to pursue the autocatalytic model justifiable chemically, Reimschuessel¹¹ derived a rate expression with a pseudo-steady-state approximation on the concentration of polyamide anion $[\sigma_{n+1}^-]$ from the regular polymerization mechanism. Reimschuessel's rate equation is, further, simplified in the following form by Lin et al.,¹ assuming $[\sigma_{n+1}^-]$ is very small at all times in the equilibrium temperature range from 150 to 200°C.

$$-\frac{d[M]}{dt} = K[A]_0[C]_0 \frac{1 - \beta}{1 - B_0\beta} \quad (3)$$

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

$$K = \frac{k_2(k_3 + k'_2)}{k'_3 \left(1 + \frac{k_2}{k'_3} [M_e]\right) \left(1 + \frac{k_2}{k'_3} [M]_0\right)},$$

$$B_0 = \frac{\frac{k_2}{k'_3} [M]_0}{\left(1 + \frac{k_2}{k'_3} [M]_0\right)} \quad (4)$$

where $[M_e]$ is the equilibrium concentration of monomer. It is to be noted here that neither eq. (3) nor eq. (4) contains any k_1 or k'_1 terms, because the effect of initiation step on the overall polymerization rate has been neglected. Based on the reactive site concept, the mechanism and material balance have been considered the same, regardless of the electrophilicity of the activator; in other words, the rate of polymerization is independent of the type of activator used. However, several researches^{9,12-14} have proven that the rate of polymerization is highly dependent on the chemical structure of the activator used.

Figure 1 shows the adiabatic temperature rise vs. time for various activators at different initial polymerization temperatures for the homopolymerization of CL. The results reveal that different activators provide different rates of temperature rise. In the reaction term, the polymerization using HDC activator is highest in the rate, the CCC system is intermediate, and that of TDC is lowest. Thus, the overall polymerization rate is influenced by the chemical nature of the activators. The chemical structure of C_6 moiety (aliphatic, alicyclic, and aromatic) of N-carbamoyl caprolactam, surely affects the initiation step. Like the nucleophilic reaction, the initiation step might be involved at least three steps such as nucleophilic attack of CL anion on the carbonyl group of N-carbamoyl caprolactam, formation of an activated species, and the ring-opening mechanism. It seems that extended conjugation (aromatic ring, amide group, and caprolactam moiety in tolylene dicarbamoyl dicaprolactam) reduces the nucleophilic attack of the CL anion when TDC is used as an activator, whereas the nucleophilic attack of the CL anion has been quite easy due to the

restricted conjugation of the aliphatic chain in HDC. Consequently, the nucleophilic attack is enhanced in the order of TDC, CCC, and HDC. However, the neglect of electrophilicity of the activators in the initiation step results in an erroneous prediction of the polymerization rate. Therefore, it is highly recommended that one should modify eq. (3) to include the term representing the activity of the activator.

From Figure 1 it is also observed that the equilibrium reaches faster with the increase in polymerization temperature in all cases, which means that the activation energy has a considerably large positive value (see Table I). The rate of polymerization is observed to be faster with the increase in concentration of activator as predicted in eq. (3), but beyond 10 wt % of the activator there is no significant increase in the rate of polymerization as a function of the activator content regardless of activator types (figures are not shown here).

Copolymerization Kinetics Based on Reaction Mechanism

As mentioned above, the aminolysis reaction is allowed to take place first (otherwise, homopolymerization of CL will occur instead of forming the copolymer) and then initiation starts. But there is every possibility of having some unreacted activator, unreacted PEG-diamine, and PEG-macroactivator in the reactor before initiation occurred. As soon as sodium caprolactamate (NaCl) is added to the mixture, polymerization starts at both the PEG-macroactivator and the rest of the activator (which remains unreacted during aminolysis) to produce the copolymer and homopolymer, respectively. Figure 2 depicts the temperature rise as a function of time using different activators at 10% PEG-diamine for the copolymerization. Like homopolymerization, copolymerization is also an autocatalytic reaction (S-shaped curve) where HDC activator system shows the fastest rate of copolymerization, CCC the intermediate, and that of TDC is the slowest. As the initial temperature of polymerization increases, the rate also increases irrespective of the activator type. But, comparing Figure 1 with Figure 2, the rate of homopolymerization is faster than the copolymerization in all cases. This is attributed to a considerable increase in the viscosity of reaction medium by the addition of PEG-diamine. Moreover, the formation of PEG-dicarbamoyl dicaprolactam due to aminolysis (see Scheme 2) also contributes substantially to the viscosity of the mixture. Consequently, the reduction of the dif-

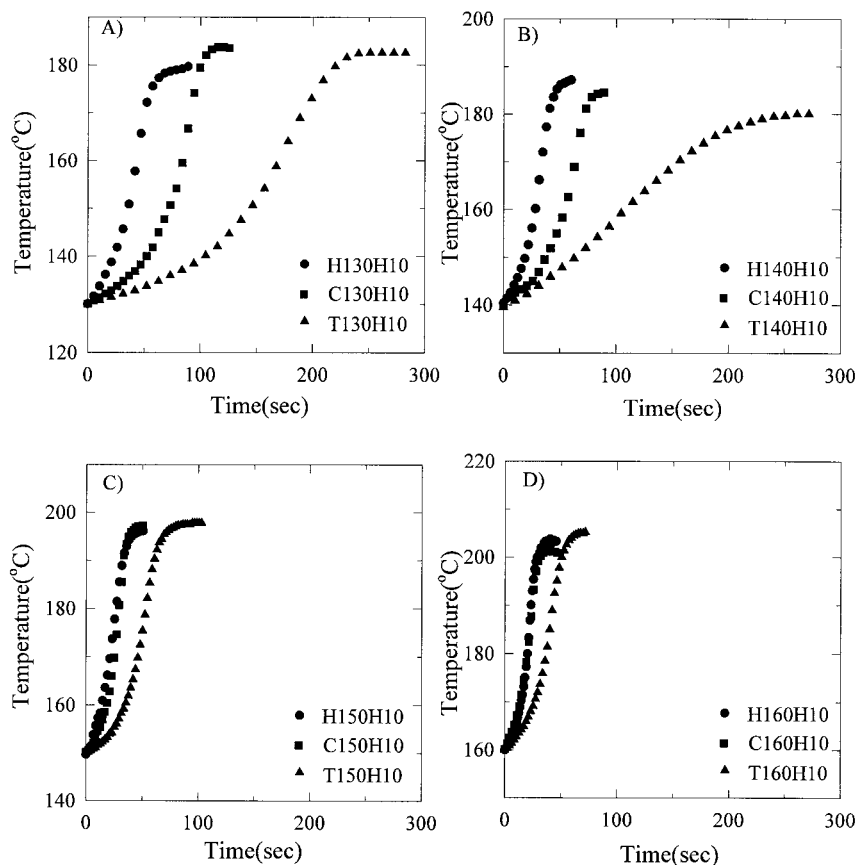


Figure 1 Temperature rise as a function of time for an adiabatic polymerization system employing various carbamoyl activator systems at different initial polymerization temperatures: (A) 130°C; (B) 140°C; (C) 150°C; (D) 160°C.

fusion of activator and NaCl results in decreasing the overall polymerization rate in the case of HxxxJ10 and TxxxJ10 samples. Like homopolymerization, the rate of the initiation step at different

activator systems plays an immense role on the overall copolymerization kinetics. This fact confirms also the importance of the initiation step in the copolymerization.

Table I A List of Average Values of Kinetic Parameters for Anionic Homopolymerization and Copolymerization with Various Activators at Different Initial Polymerization Temperatures

Samples	E (cal/mol)	n	B_0
Homopolymerization with HDC activator	17785 (428)	1.7203 (0.4836)	6.0501 (2.8965)
Copolymerization with HDC activator	17929 (547)	2.3797 (0.3895)	6.0454 (1.7871)
Homopolymerization with CCC activator	18321 (637)	1.895 (0.6749)	6.1965 (2.2524)
Copolymerization with CCC activator	18150 (502)	1.7148 (0.5709)	6.2725 (2.2115)
Homopolymerization with TDC activator	18575 (369)	1.7110 (0.9838)	6.3966 (2.7569)
Copolymerization with TDC activator	19317 (481)	2.5419 (1.2331)	6.3134 (1.7724)

Values in parentheses are standard deviations.

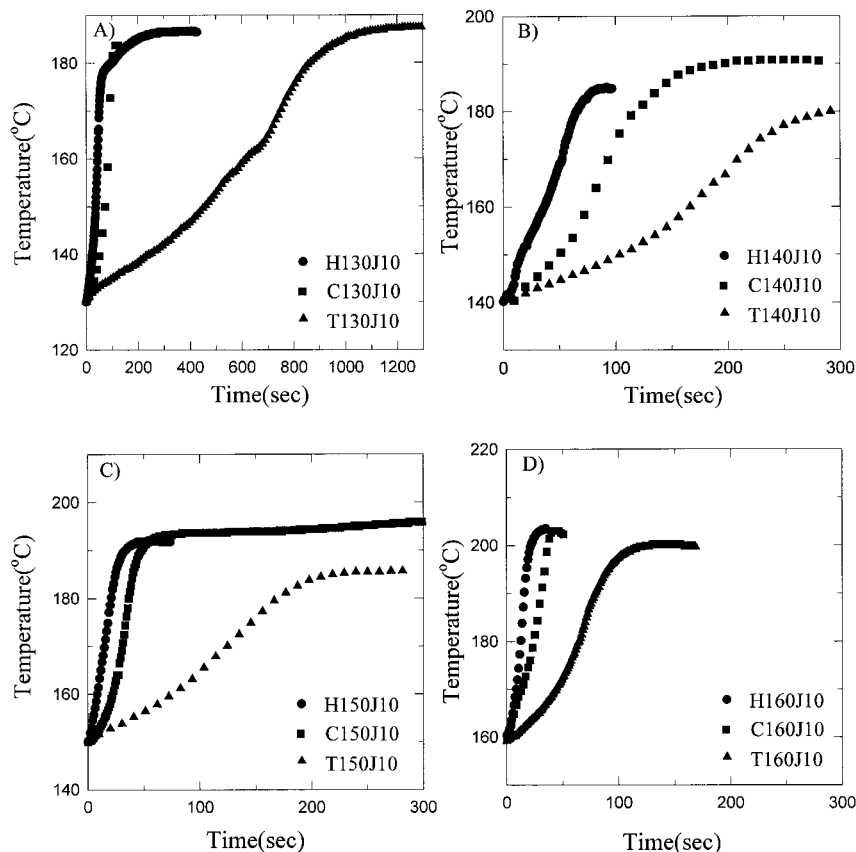


Figure 2 Temperature rise as a function of time for an adiabatic polymerization system employing various carbamoyl activator systems in the presence of PEG–diamine at different initial polymerization temperatures: (A) 130°C; (B) 140°C; (C) 150°C; (D) 160°C.

Because the increase of the PEG–diamine percentage increases the total concentration of carbamoyl moiety, the rate of polymerization is expected to be increased. However, the rate of temperature rise in the case of 10 to 20% PEG–diamine containing samples does not follow the trend of corresponding homopolymerization using same activator and equal concentration, irrespective of activator types and initial polymerization temperature (figures are not shown here). To resolve this kind of anomaly, the diffusion of the catalyst, the activator, and the monomer in the reaction mixture as well as the dilution effect should be considered in addition to the effect of the activator concentration. The effect of viscosity of the reaction mixture on the rate of polymerization is well understood when we compare the rates of polymerization with and without PEG–diamine. The rate of homopolymerization is always higher than that of the copolymerization, irrespective of the activator type and initial polymerization temperature. Furthermore, the rate of poly-

merization in the copolymers does not change in accordance to the corresponding homopolymers at the same initial polymerization temperature. This can be explained as follows: the increase of modifier percentage contributes positively in the rate of polymerization, as predicted in eq. (3). On the other hand, the increasing amount of modifier reduces the concentration of the monomers, which can be related to the dilution effect and restricts the diffusion of the reaction mixture that acts negatively on the overall rate of polymerization. However, the net effects of activator–concentration, dilution, and the viscosity of the mixture provide an optimum percentage of 10% PEG–diamine to keep a relatively higher rate of polymerization throughout the copolymerization process.

Polymerization Kinetics Based on an Empirical Approach

The total temperature change [eq. (5)] at time t in the activated anionic polymerization of CL is

a cumulative contribution of polymerization and crystallization exotherms, the heat loss due to thermal conduction, and melting endotherm as shown below:

$$T(t) = T_0 + \Delta T(t) = T_0 + (\Delta T)_p + (\Delta T)_c - (\Delta T)_{\text{loss}} - (\Delta T)_{\text{melting}} \quad (5)$$

where T_0 is the initial polymerization temperature, $(\Delta T)_p$, $(\Delta T)_c$, $(\Delta T)_{\text{loss}}$, and $(\Delta T)_{\text{melting}}$ are the temperature change due to polymerization exotherm, crystallization exotherm, thermal loss due to conduction, and melting exotherm, respectively. The melting of nylon starts at and above 200°C (obtained from nonisothermal DSC results), so one should neglect the temperature change due to melting.

The instantaneous temperature rise due to the polymerization exotherm of CL in the presence of PEG–diamine has been expressed as eq. (6) modifying the empirical equation for the anionic homopolymerization of CL proposed by Malkin et al.⁵ and Kim et al.⁹

$$\begin{aligned} \left(\frac{dT}{dt}\right)_p &= (1 - P) \frac{\Delta H_p}{C_p} \frac{d\beta}{dt} \\ &= (1 - P) \frac{\Delta H_p}{C_p} A_0 \exp(-E/RT) \\ &\quad \times (1 - \beta)^n (1 + B_0\beta) \quad (6) \end{aligned}$$

where ΔH_p is the enthalpy of polymerization of ϵ -caprolactam (ca. 33 cal/g), which is assumed almost constant in the temperature range in which reaction takes place, P is the weight fraction of PEG–diamine, and C_p is the heat capacity of the reaction mixture. As C_p varies with the conversion term β , C_p can be expressed in $(1 - P)(1 - \beta)C_{p,\text{caprolactam}} + \beta(1 - P)C_{p,\text{nylon}} + PC_{p,\text{PEG-diamine}}$, assuming that heat capacity remains constant in the experimental temperature range ($C_{p,\text{caprolactam}} = 0.5860$ cal/g·K, $C_{p,\text{nylon}} = 0.6812$ cal/g·K, and $C_{p,\text{PEG-diamine}} = 0.495$ cal/g·K). Therefore, the temperature change due to polymerization exotherm is expressed as eq. (7).

$$(\Delta T)_p = \int \left(\frac{dT}{dt}\right)_p dt \quad (7)$$

Further, the temperature change due to crystallization of formed copolymer in the experimental conditions $(\Delta T)_c$ can be modified as in eq. (8)

by introducing the weight fraction of CL, $(1 - P)$ into the previous equation suggested by Kim et al.⁹

$$(\Delta T)_c = (1 - P) \frac{\Delta H_c}{C_p} \beta \cdot X_e (1 - \exp[-K(t - \theta)]^{n_c}) \quad (8)$$

where ΔH_c is the enthalpy of crystallization of pure nylon 6 (ca. 49.5 cal/g), the crystallinity at equilibrium X_e is set to be about 0.4, n_c is the Avrami exponent, and θ is the induction period of crystallization. The heat loss due to incomplete insulation of the reactor is

$$\begin{aligned} (\Delta T)_{\text{loss}} &= \frac{U}{C_p} \left[\alpha \int_0^{(\beta)} (T - T_{\text{amb,side}}) dt \right. \\ &\quad \left. + (1 - \alpha) \int_0^{(\beta)} (T - T_{\text{amb,top}}) dt \right] \quad (9) \end{aligned}$$

where U is the overall heat transfer coefficient, $T_{\text{amb,side}}$ is the ambient temperature of the side of the reactor, $T_{\text{amb,top}}$ is the ambient temperature of the top of the reactor, and α is the area fraction of the side and the bottom of the reactor.

The measured temperatures as a function of time in the process of polymerization have been fitted with the above theoretical equations by using a nonlinear least-squares curve-fitting algorithm to verify the validity of our suggested equations. Figure 3 shows the typical curve-fitting data of the coded sample C140H10 of homopolymer using CCC as an activator. The experimental temperature rise and the calculated $(\Delta T)_i$ are matching well. The temperature rise due to pure polymerization at the end of reaction is showing around 50°C, which is slightly lower than the experimental overall temperature rise, because the contribution due to polymerization-induced crystallization (ca. 10°C) is greater than the contribution due to heat loss (ca. 6°C). Figure 4 is the data-fitting result of the coded sample T140J20 of the copolymer. The fitted curve also shows the best fitting with the experimental value mainly in higher conversion range. So, the validity of our suggested empirical equations both for homopolymerization and copolymerization of CL is established undoubtedly with the experimental results. In consequence, it is strongly recommended that one must consider the temperature change due to polymerization-induced crystallization and the heat loss owing to thermal conduction along with

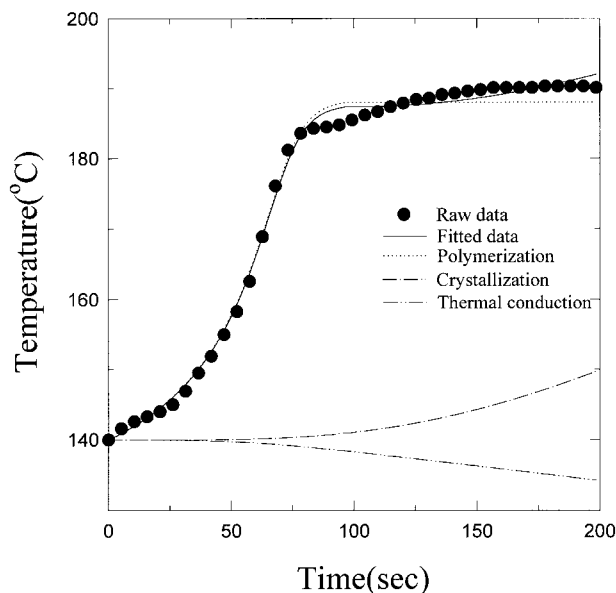


Figure 3 Typical example of kinetic model predictions vs. adiabatic data of the C140H10 sample.

apparent net temperature change in the course of polymerization of CL to extract correct polymerization kinetic parameters.

The best set kinetic parameters, representing the nonisothermal polymerization and crystallization behaviors, are shown in Table I. There is no significant difference in activation energy between homopolymers and copolymers. The average activation energy of HDC, CCC, and TDC activated copolymers are 17929, 18166, and 19317 cal/mol, respectively. Comparing three activator systems, the experimental curves (see Fig. 1) are also verified, considering the apparent activation energy obtained from empirical equations. Due to less activation energy, HDC system is fastest, CCC is intermediate, and TDC system is slowest in the reaction rates both in homopolymerization and the copolymerization. Moreover, the reaction order n is quite higher in the copolymerization than in the homopolymerization, regardless of activator types. The reaction orders in the copolymerization using HDC, CCC, and TDC are 2.4, 1.7, and 2.5, respectively, whereas those in the homopolymerization are 1.7, 1.4, and 1.7, respectively. This difference varying with the activator types is attributed to the functionalities of activators ($f = 2$ in HDC and TDC and $f = 1$ in CCC). In spite of wide difference in the chemical structure of TDC and HDC (as mentioned earlier), the reaction orders are obtained almost equal both in the TDC and HDC activated polymers. This means

that the functionality of activators plays a major role in the kinetics rather than the chemical structure of activators, and these findings are reasonably consistent with our previous results.⁹

A polymer chain degradation mechanism (as in Scheme 3) of a chain formed by the monofunctional activator has been proposed by Greenly et al.² for high-temperature anionic polymerization, which has also significance in the activated anionic polymerization of CL. It is also to be noticed that each resulting polymer chain contains imide groups, thereby, a second living chain has been created by the nucleophilic attack of CL anion, which means the increasing number of reactive sites in addition to the reactive end groups in the growing polymer chains. Therefore, the increasing number of reactive end groups must lead to the acceleration of the reaction, namely, autocatalysis. In general, the magnitude of autocatalytic parameter B_0 represents the extent of autocatalysis. An insignificant difference in B_0 values is observed irrespective of kinds of activator, activator concentration, polymerization type, initial polymerization temperature, and PEG–diamine content (see Table I). Because the origin of autocatalysis is the degradation of polymer chain during the polymerization via the reaction between the amide group in nylon 6 chain and the CL anion as shown in Scheme 3, the effect of activator type and PEG–diamine in the copolymer on autoca-

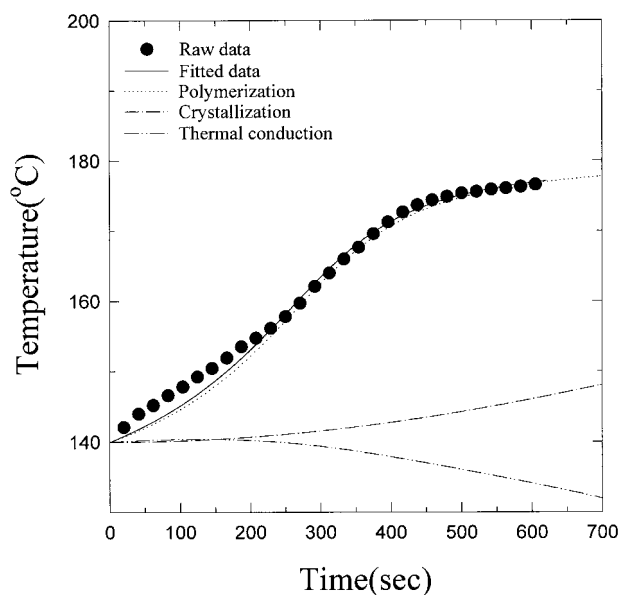
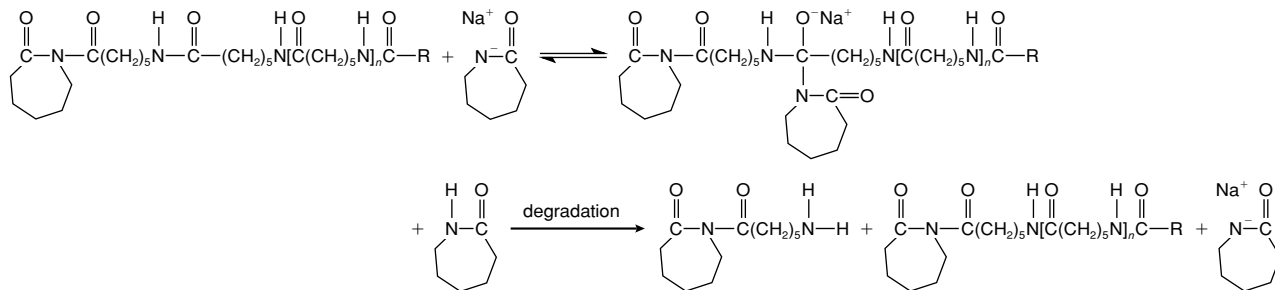


Figure 4 Typical example of kinetic model predictions vs. adiabatic data of the T140J20 sample.



Scheme 3 Degradation reaction as the origin of autocatalysis.⁵

talysis can be ignored. Moreover, the degradation reaction does not depend on the initial polymerization temperature, which means that the rate of autocatalysis remains unchanged or slightly changed in the initial polymerization temperature ranging from 130 to 160°C.

Figures 5, 6, and 7 describe the temperature change (ΔT)_c at the end of polymerization reaction, obtained from the data-fitting results due to polymerization-induced crystallization both for homopolymerization and copolymerization of CL in different temperatures of polymerization when TDC, HDC, and CCC are used as an activator, respectively. As the initial temperature of polymerization increases, the (ΔT)_c decreases drastically, irrespective of the activator types both in homopolymerization and copolymerization. This means that polymerization-induced crystallization could not take place sufficiently due to a

faster rate of polymerization until the end of polymerization reaction. Thus, one can completely ignore the crystallization contribution at the initial temperature of polymerization of 160°C or higher even for the copolymerization of CL in the presence of the modifier. This fact is very consistent with the previous results,^{9,15} in which the crystallization contribution to temperature change is negligibly small for the homopolymerization above 140°C. The effect of increased percentage of PEG–diamine on the crystallization contribution has not been consistently observed. Due to the incompleteness of polymerization-induced crystallization at the end of polymerization reaction, one should not remove the RIM-article made of CL immediately after polymerization is over. For the perfect shape and dimensional stability, longer time should be allowed even after the polymerization is finished.

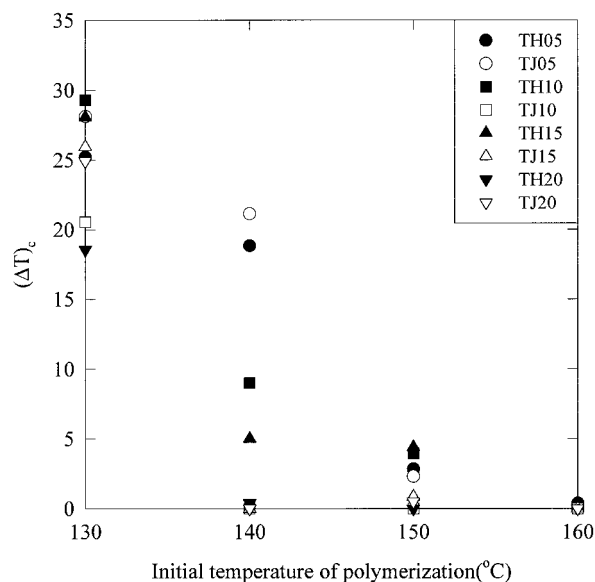


Figure 5 Temperature change due to polymerization-induced crystallization of TDC-activated polymers.

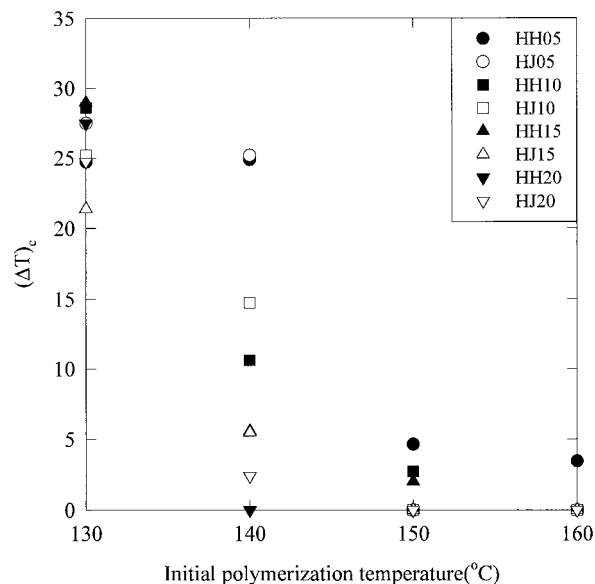


Figure 6 Temperature change due to polymerization-induced crystallization of HDC-activated polymers.

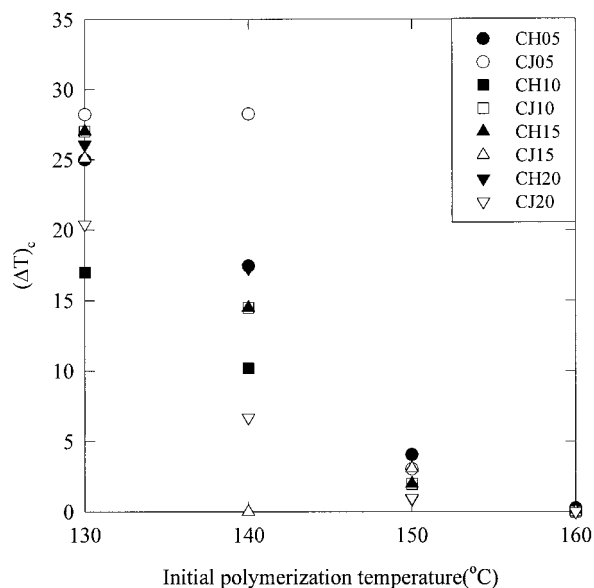


Figure 7 Temperature change due to polymerization-induced crystallization of CCC-activated polymers.

Molecular Weight Distribution and Polydispersity Index

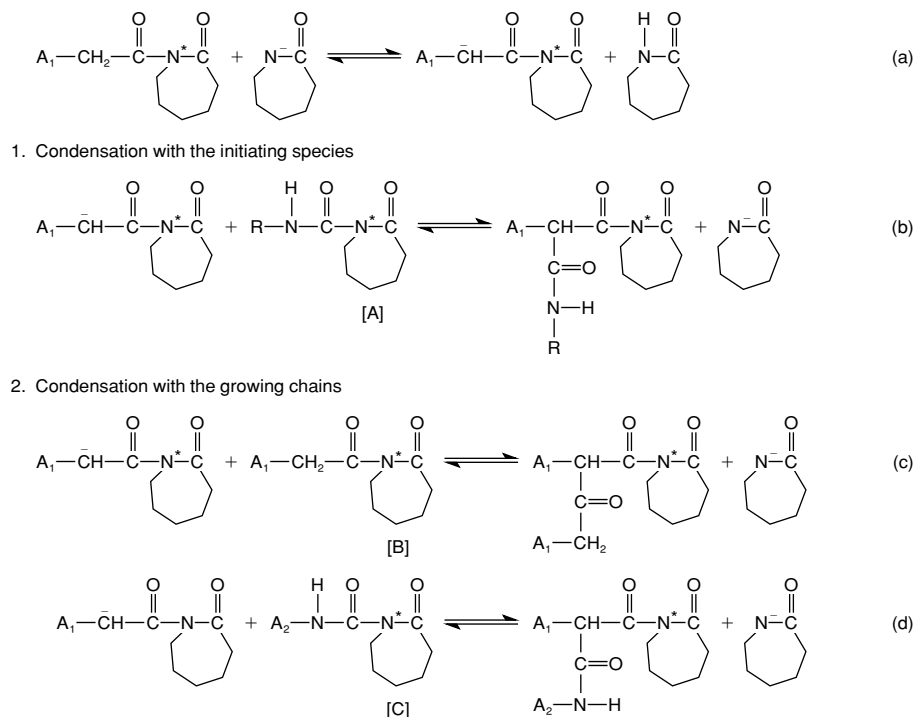
The branching or crosslinking in the activated anionic polymerization of CL has been suggested as being an important reaction as full conversion is approached.^{9,16} Petit et al.¹⁷ have observed a rapid change in the imide and lactam ion concentrations at the initial stages of polymerization, and attribute this phenomenon to a Claisen-type condensation between low molecular weight growing chains and/or initiating species (as shown in Scheme 4), which results in branching/or crosslinking reactions.

In Scheme 4, R = activator residue, $A_1 = R_1 - CO[NH - (CH_2)_5 - CO]_n - NH(CH_2)_4 -$ ($n = 0$ or few units), $A_2 = C_6H_{11} -$ in CCC, $R_1 - (CH_2)_6 -$ in HDC, and $R_1 - (CH_3)(C_6H_4) -$ in TDC, $R_1 =$ propagating species, and * represents the active site. There is also a possibility of limited thermally initiated polymerization as reaction approaches to 200°C, which can contribute in the branching reaction. Generally, the effect of branching reaction of CL polymerization has been reflected on the molecular weights and the polydispersity index of the polymers.

The number-average and the weight-average molecular weights have been obtained from GPC data. When the TDC is used as an activator, the number-average molecular weight (\bar{M}_n) and the weight-average molecular weight (\bar{M}_w) are highest, both in the homopolymers and copolymers and those of HDC and CCC activated polymers

are intermediate and lowest, respectively (see Table II). The polydispersity index of the polymers, calculated from the GPC data, also follows the above molecular weight trend. The TDC activated polymers show the highest polydispersity index, whereas the polydispersity index of HDC activated polymers is intermediate and that of CCC system is lowest. Higher value of polydispersity index for HDC activated polymers than CCC activated polymers can be interpreted to result from the occurrence of more branching and crosslinking reactions due to dominant Claisen type condensation in the course of polymerization following the eqs. (b), (c), and (d) in Scheme 4. Equation (d) is more favorable, because the electron deficiency of the exocyclic carbonyl group [C] in eq. (d) is greater due to higher electronegativity of the nitrogen atom than the exocyclic carbonyl of [B] in eq. (c). Consequently, branching through this route in eq. (d) is higher than the reaction in eq. (c). Although the reaction in eq. (b) is similar to eq. (d), eq. (b) represents the branching through the short chains at the initial level. As the functionality of CCC is one ($f = 1$), the branching reaction via the long chain can never be expected. Therefore, branching in CCC-activated polymers would mainly follow the route as in eq. (b), which produces only short branches, resulting in the lowest molecular weight and polydispersity index. In TDC-activated polymers, the branching takes place according to eq. (b) at the initial level (up to temperature 150°C). The presence of the phenyl group (electron donating) adjacent to the exocyclic nitrogen reduces the electron deficiency of the exocyclic carbonyl in [A]. Thus, the nucleophilic condensations shown in eqs. (b) and (d) in the TDC-activated polymers would also be less. Branching according to eq. (c) is the most probable route in the case of TDC system. From the above discussion, it seems that the TDC-activated polymers should give the lowest molecular weight and polydispersity index. In fact, the experimental results present the highest molecular weight and polydispersity index values. This considering resolves the thermal dissociation of TDC above a certain temperature.

TDC moiety converts into the TDI residue and CL in thermal dissociation above the temperature of 150°C.¹⁸ Once the TDI residue is formed, the reaction between the free isocyanate group and the terminal amine group of the PEG-diamine (in the case of copolymerization) can easily produce polyurea. As a result, polyureas can further be branched and/or crosslinked through the thermally dissociated isocyanate group of TDC resi-



Scheme 4 Branching via Claisen-type condensation.^{5,10}

due. The situation in the TDC activated homopolymers would be different from the copolymers, because of nonavailability of the PEG-diamine in the homopolymers. Even if the branching reaction in the homopolymer mainly follows the route as cited in eq. (c) at a higher conversion level of CL, the TDC-activated homopolymers also show very high molecular weight and polydispersity. The reason, however, is very difficult to explain.

CONCLUSION

The empirical equation presented, considering the adiabatic temperature rise due to polymeriza-

Table II Molecular Weight Data of Homopolymer and Copolymers by GPC

Sample Code	\bar{M}_n	\bar{M}_w	Polydispersity Index
T160H10	20,313	187,550	9.23
T160J10	47,371	344,759	7.29
T160J20	29,359	270,279	9.21
H160H10	21,996	121,943	5.54
H160J10	28,439	176,672	6.21
H160J10	36,663	105,690	2.88
C160H10	21,104	35,477	1.68
C160J10	11,150	20,084	1.80
C160J20	7,346	11,132	1.51

tion and polymerization-induced crystallization exotherms, and heat loss, has been proven to be better fitting with the experimental results than any other reported rate equation of activated anionic polymerization of ϵ -caprolactam. The initiation step has a profound effect on the kinetics both in the homopolymerization and copolymerization of CL. Higher is the aromatic nature of the activator, slower is the overall polymerization rate. The introduction of a soft segment like PEG-diamine into the nylon chain during copolymerization of CL does not change much in the polymerization kinetics compared with the homopolymerization. Higher values in molecular weight and polydispersity index of the activated polymerization of CL are obtained than the expected values due to branching via the Claisen-type condensation, especially in the case of bifunctional activator systems. Thermal dissociation reaction in the TDC residue also produces branching and/or some crosslinking through the formation of polyurea, besides the conventional Claisen-type condensation in the TDC-activated copolymerization. For the successful application of activated anionic polymerization of CL in the RIM, the consideration of heat change due to polymerization-induced crystallization is strongly recommended. To achieve the perfect shape and dimensional stability of the RIM article through the complete crys-

tallization, one should allow some time even after polymerization is over. Fast activator is always preferred to reduce the cycle time in the RIM of CL, as crystallization occurs simultaneously to a higher extent with the polymerization reaction when the lower initial polymerization temperature is adopted.

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