Adiabatic Anionic Polymerization of Caprolactam in the Presence of *N*-Acylated Caprolactam Macroactivator: Kinetic Study

JEN-LONG YEH, JEN-FENG KUO,* and CHUH-YUNG CHEN

Department of Chemical Engineering, National Cheng-Kung University, Tainan, Taiwan 701, Republic of China

SYNOPSIS

In this study, bis ϵ-caprolactam bis-diphenyl methane diisocyanate polypropylene glycol 1000 used as the macroactivator was prepared and well characterized prior to use. The anionic polymerization of ϵ-caprolactam with the macroactivator as a function of the macroactivator concentration was adiabatically carried out. The adiabatic temperature rise method as well as the macrokinetics were used for elucidation of the kinetics of the polymerization. A nonlinear regression technique was used for determining the parameters of the macrokinetic equation. The equilibrium conversion and equilibrium time obtained were 94–96% and 2–9 min depending on the macroactivator concentration. The effects of the concentrations of macroactivator and ϵ-caprolactam on the initial rate, apparent overall reaction rate, and the empirical parameters were studied. A side reaction induced by the transfer of the proton in the isocyanurate group of the macroactivator to caprolactam anion was found. According to this finding, a new reaction kinetic model was proposed by properly modifying the macrokinetic equation. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The emergence of reaction injection molding (RIM) has been followed by the industry with mounting interest. RIM is based on the injection of monomers or reactive oligomers into a mold followed by a fast polymerization reaction. The attractiveness of the process is in saving energy and capital investments as well as the ease of molding of large, thin-walled, and complicated shapes.[1] Therefore, the RIM process has been rapidly developed by the automotive industry since Bayer AG of Germany started the Baydur System with polyurethane 20 years ago.[2-5] In 1981 Monsanto Chemical Co. of the U.S. announced that it was engaged in the development of a RIM system of Nylon 6 for exterior parts of automobiles.[5] This aroused great interest and Nylon RIM rapidly grew to be the new second RIM. The Nylon RIM system combines the characteristics of the polyurethane RIM technique and the inherent superior properties of nylon such as stiffness, abrasion resistance, and heat resistance; therefore, it is expected to find a wider range of applications than that of the polyurethane RIM.

Simulation for the kinetics of Nylon RIM is important for process design.[6,7] It is the adiabatic anionic polymerization of Nylon in nature,[6] with *N*-acylated ϵ-caprolactam as an activator and sodium or sodium hydride as a catalyst. *N*-Acylated ϵ-caprolactam, usually prepared by *in situ* polymerization, is a reaction product of ϵ-caprolactam, polyol, and isocyanate or other compounds.[8-10] The activator determines not only reaction kinetics but also product qualities. The introduction of polyol in the activator is a policy for improving the impact resistance of Nylon.[11-14] There are two approaches for the kinetics of the activated anionic polymerization of Nylon or Nylon RIM: the macrokinetics[15-19] and mechanistics.[20-23] Because of the Nylon, polymerizations are complex in mechanistic nature; the former is then used more often. The empirical equation of the macrokinetics[18,19,22,23] is a well-known one:

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 50, 1671–1681 (1993)
 CCC 0021-8995/93/101671-11

$$dX/dt = A'_o(1 - X)^n(1 + B'X)\exp(-E'_a/RT) \quad (1a)$$

where n, A'_o, B', and E'_a are empirical parameters and denote the pseudoreaction order, apparent frequency, autoacceleration factor, and apparent activation energy, respectively. For $n = 1$, the empirical equation is reduced to be the Malkin's equation.[17] These parameters in the empirical equation are determined with the data of the adiabatic temperature rise method[18,24] using regression techniques.[25,26] On the other hand, the mechanistic approach assumes a regular linear chain propagation model,[27] in which possible side reactions are neglected.

In this work the macroactivator, bis ϵ-caprolactam bis-diphenyl methane diisocyanate polypropylene glycol 1000, was prepared in this laboratory prior to use. The macroactivator then activates an anionic polymerization of ϵ-caprolactam on its two functional ends to form a Nylon-PPG-Nylon triblock copolymer. The kinetics for the polymerizations was studied as a function of the macroactivator concentration using the adiabatic temperature rise method,[18,24] and the parameters in the macrokinetic equation were evaluated using a nonlinear regression technique.[26] A possible reaction mechanism based on the observations obtained will be discussed.

EXPERIMENTAL

Reagents

ϵ-Caprolactam (Merck; Synthesis Grade) was dried *in vacuo* at 80°C overnight before use. Polypropylene glycol (PPG) 1000 (Wako; Extra Pure Reagent) was dried *in vacuo* at 80°C for 3 days. 4,4-Diphenyl methane diisocyanate (MDI) (TCI; Extra Pure Reagent) was heated to 60°C, and then the dimers and trimers in MDI were removed by decanting the melt. The catalyst, sodium hydride (Merck; Synthesis Grade), was supplied as a mixture of 80% solid with 20% mineral oil.

Macroactivator Preparation

bis-Caprolactam bis-MDI PPG1000 was used as an activator for the anionic polymerization of ϵ-caprolactam. The macroactivator was prepared in a 500-mL resin kettle under a nitrogen atmosphere. The procedure was as follows: 1 mol PPG1000 was added dropwise to 2 mol MDI at 80°C with vigorous stirring. The aim was to obtain MDI-capped PPG1000 on both ends, which was verified by the moles of isocyanate groups of the obtained product using the titration method.[28] The MDI-capped PPG further reacted with 10% excess ϵ-caprolactam to obtain *N*-acylated ϵ-caprolactam. The *N*-acylated ϵ-caprolactam obtained was further verified using the elementary analysis (Heraeus CHN-O Rapid Elemental Analyzer) and infrared spectrometry (Jasco IR-810).

Adiabatic Polymerization

Figure 1 shows the apparatus for the adiabatic anionic polymerization of ϵ-caprolactam. The apparatus consisted of a reactor, a feed flask, N_2 purging system, heaters, and a temperature control/monitor/record assembly (TCMRA).

The reactor was a 100-mL jacketed Pyrex glass flask. The thermal insulation of the reactor was obtained through evacuating the jacketed space. The reactor was equipped with a Teflon-coated stirrer, an N_2 purging tubing system, and a K-type thermocouple wires. Silicone oil was used as a heating medium. A 100-mL Pyrex glass flask with a bottom outlet was used as a feed flask. It was completely surrounded with heating tape and also equipped with a Teflon-coated stirrer, an N_2 purge tubing, and a K-type thermocouple. A Teflon inside-fitted glass tube was connected to both the reactor and feed flask for transporting molten ϵ-caprolactam and catalyst from the feed flask to the reactor.

The TCMRA consisted of an IBM AT computer with an interface card (IEE 488A) on-line with a multimeter (HP 3478A) and a scanner (CJ 180A). A BASIC program was developed to control the heating and data acquisition procedures.

Before starting polymerization, both the reactor and feed flask were evacuated and then purged with N_2. Ninety percent by weight of the predetermined amount of the ϵ-caprolactam was charged in the feed flask, and the rest of the ϵ-caprolactam and the ascribed amount of the macroactivator were added into the reactor (Fig. 1). They were then heated to 110°C for 1 h to avoid moisture in the reaction system. Then the predetermined weight of NaH was charged into the feed flask. The reactor temperature was heated to 150°C; meanwhile, the temperature of the feed flask was raised to a temperature 10°C higher than the reactor. The jacket of the reactor was evacuated by starting a vacuum pump. The N_2 inlet of the reactor and N_2 outlet of the feed flask were closed, and then the cock on the connected tube was opened. Then the molten ϵ-caprolactam and catalyst in the feed flask flowed down into the reactor to initiate polymerization. At that time, the TCMRA

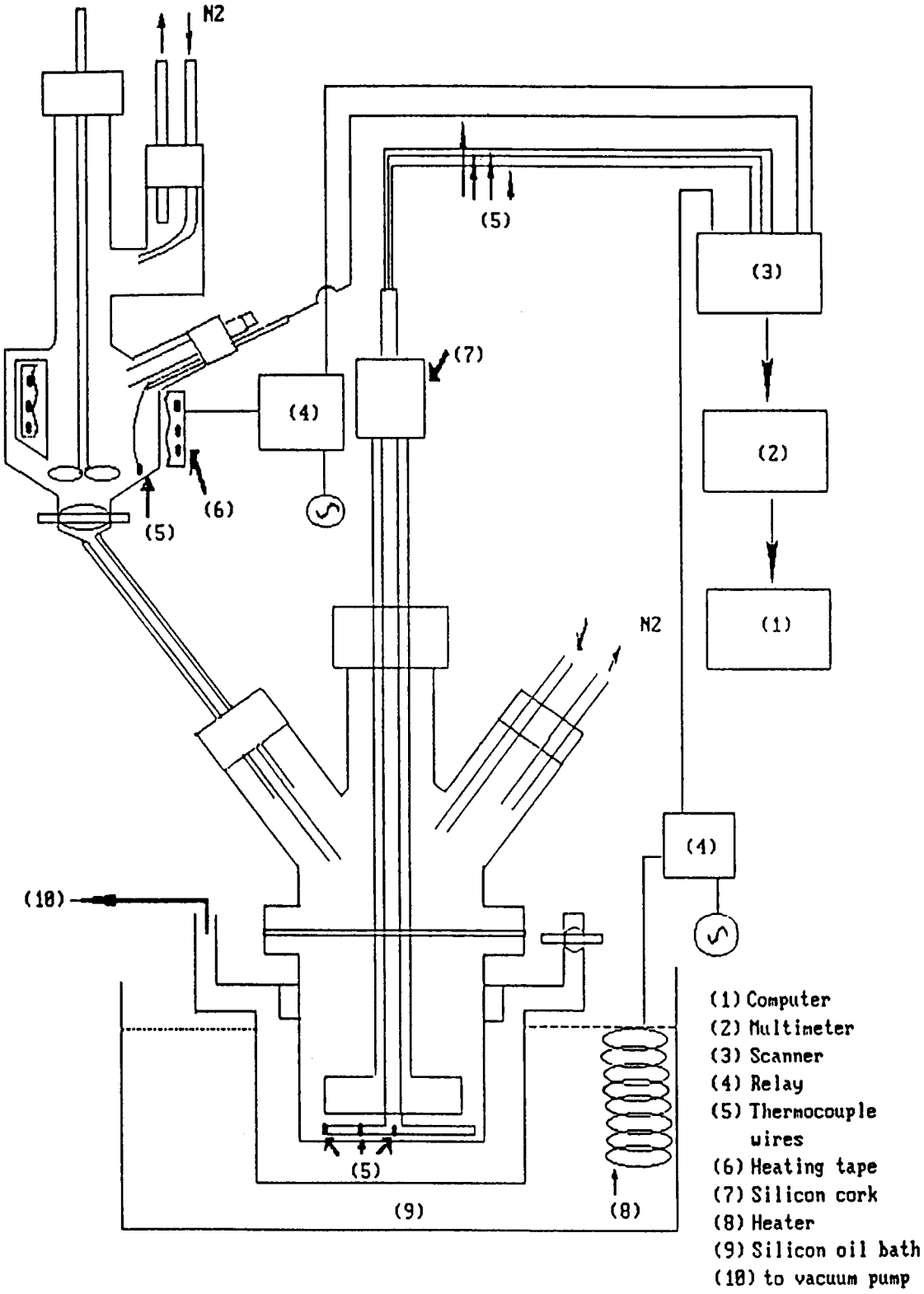


Figure 1 The apparatus for the adiabatic anionic polymerization of ϵ-caprolactam.

was started immediately. The adiabatic temperature in the reaction duration was scanned 3 points/second until a constant temperature was attained. All the runs studied were repeated three times, then the average values of them were reported.

The conversion, X, versus time data was calculated using the equation,[18,19] $X = (T - T_i)/(T_e - T_i)$ where T_i, T, and T_e denote the initial, reaction, and final temperature, respectively. To determine the equilibrium conversion, X_e, a certain amount of the polymer product was sampled from the reactor at the end of the reaction. The sample was placed in a Soxhlet extractor. It was sufficiently refluxed with methanol to extract the residual monomers. Finally the equilibrium conversion, X_e, was obtained by the equation, $X_e = (W_{c_i} - W_{c_r})/W_{c_i}$, where W_{c_i} and W_{c_r} denote the weights of initial and residual ϵ-caprolactam, respectively.

RESULTS AND DISCUSSION

Figure 2 shows the IR spectrum of the bis ϵ-caprolactam bis MDI PPG1000. The stretching vibrations of the —OH group in PPG1000 at 3500 cm^{-1} and the stretching vibration of the —NCO group in the MDI at 2270 cm^{-1} were not present in the IR spectrum. On the other hand, the characteristic absorptions of —C(=O)— in the urethane group at 1700 cm^{-1}, and of —C(=O)— in the lactam ring at 1650 cm^{-1} were observed. The results verified that the N-acylated ϵ-caprolactam macroactivator was obtained as we expected. Table I gives the weight fractions of carbon, hydrogen, and nitrogen in the bis-caprolactam bis MDI PPG1000 obtained by the elemental analysis, which were in good agreement with those calculated.

The adiabatic temperature rising experiments were conducted to study for the kinetics of polymerization of ϵ-caprolactam with macroactivator. It has been suggested that the minimum initial reaction temperature for the adiabatic homogeneous phase reaction of ϵ-caprolactam was required above 140°C.[22,29] However, in this work it was needed above 150°C. Indeed, the initial reaction temperature for various runs used here was in the range of 153–157°C. As shown in Figure 3(a), the amplitude of adiabatic temperature rise from the initial reaction

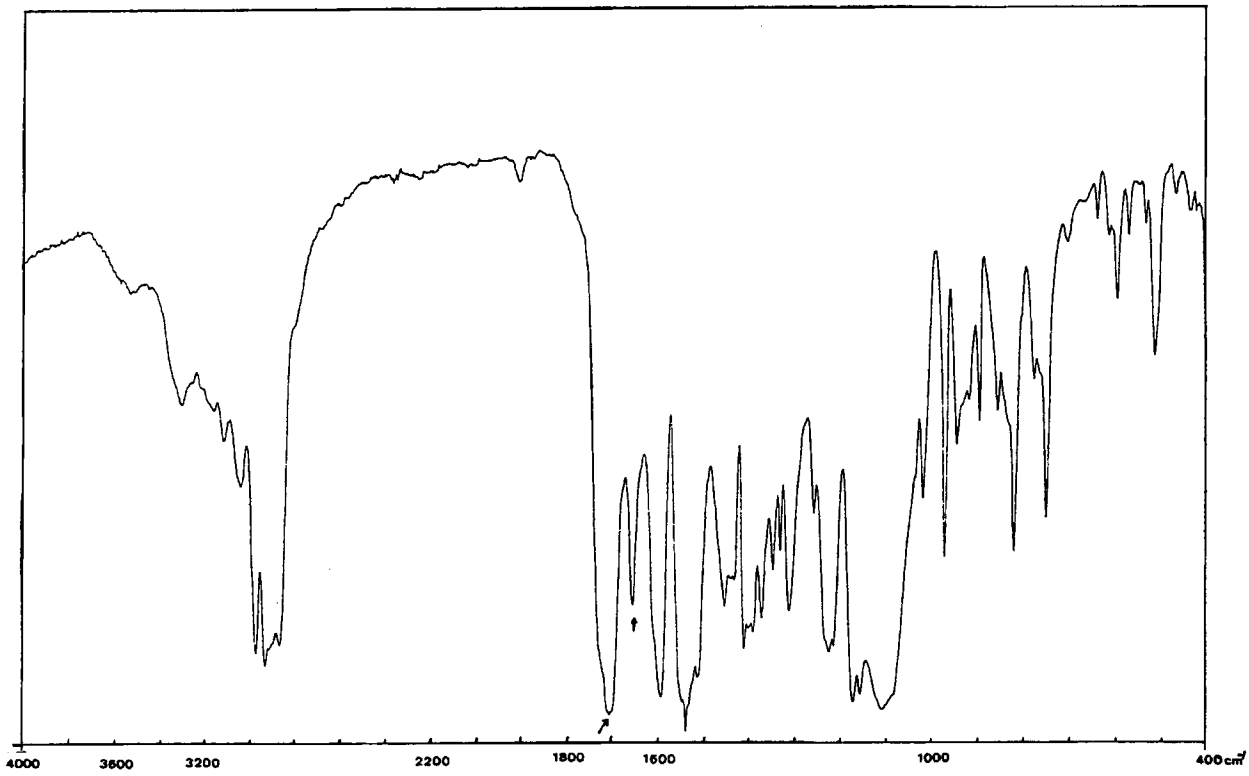


Figure 2 Infrared spectrum of bis ϵ-caprolactam bis-phenyl methane diisocyanate polypropylene glycol (activator).

Table I Result of Elemental Analysis for Composition of Macroactivator Obtained

	C (%)	N (%)	H (%)
Measured	64.68	5.08	8.39
Calculated	64.65	4.86	8.45

temperature was 32–37°C, which was close to that reported by Limtasiri et al.[14] The amplitude of temperature rise increased with a decrease in the concentration of macroactivator, except for run #3. Furthermore, utilizing the relation,[18,19] $X = (T - T_i)/(T_e - T_i)$, one obtained the corresponding conversion vs. time curves [Fig. 3(b)]. Similar to the literature reported,[16,22] the curves exhibited S-shape paths. This indicates that all the polymerization involved autoacceleration in some range of the earlier stage, and then approached equilibrium state. From the figure, the time for attaining equilibrium conversion, t_e, was 2–9 min, which was in the range of the literature value reported,[14] decreasing with the increase of the concentration of macroactivator used. Table II shows the real equilibrium conversion attained in the runs studied. They were 94–96%; the higher the macroactivator concentration, the lower the equilibrium conversion. The results were comparable to that of the homopolymerization of Nylon.[22]

As shown in Figure 4, the apparent overall reaction rate, defined as X_e/t_e, was linearly proportional to the macroactivator concentration. Whereas the initial reaction rate, $dX/dt|_{t=0}$, showed a maximum at about 0.8 mol % macroactivator.

Figure 5 shows the ratio of the apparent overall reaction rate to the initial reaction rate, that is, $(X_e/t_e)/(dX/dt|_{t=0})$, as a function of macroactivator concentrations. It showed a minimum at about 0.8 mol % macroactivator. The results infer that some side reaction induced by the macroactivator became more significant as the concentration of macroactivator was larger than 0.8 mol %.

According to the conventional kinetics of anionic polymerization of ϵ-caprolactam, the concentration dependence of the reaction rate is a first order on ϵ-caprolactam. The autocatalytic equation suggested by Malkin et al.[17]

$$dX/dt = A_o(1 - X)(1 + BX)\exp(-Ea/RT) \quad (1b)$$

was used to describe the course of polymerization mentioned above. Using a nonlinear regression method,[27] we determined the Malkin's parameters (Table II). The activation energies, Ea, fluctuated around 25 and 26 kcal/mol, close to that reported by Lin et al.[22] The autoacceleration factor, B, was smaller than the literature value reported,[14,17–19,29] and became smaller as the macroactivator concentration was less than 0.8 mol %. However, unlike the literature,[14,16] the value of B exhibited a minimum at about 0.8 mol % macroactivator used. This tendency is similar to the change of $(X_e/t_e)/(dX/dt|_{t=0})$ with the macroactivator concentration mentioned above, which yielded evidence for side reactions caused by the macroactivator at high concentrations.

In this study the parameters in the generalized

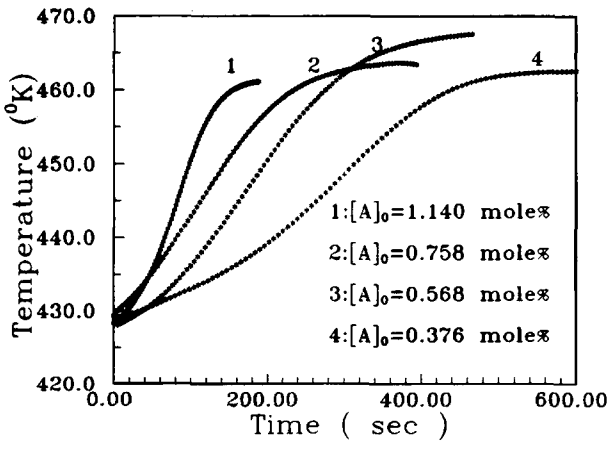


Figure 3(a) Effect of initial macroactivator concentration on the adiabatic temperature rise for an anionic polymerization of ϵ-caprolactam.

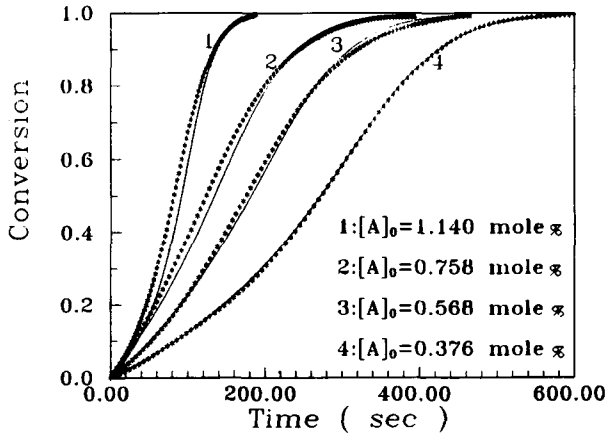


Figure 3(b) Predicted and experiment curves for adiabatic anionic polymerizations of ϵ-caprolactam and *N*-acylated macroactivator; **experimental data and (—) predicted conversion.

Table II Equilibrium Conversion and Parameters in Malkin's Equation [eq. (1b)] and Correlated Kinetic Parameter

Run No.	$[A]_o$ (mol %)	X_e (%)	Kinetic Parameters of Malkin's Equation			
			A_o (10^{-10})	B	Ea (kcal/mol)	A (10^{-13})
1	1.140	94.0	2.46 ± 0.01	0.88 ± 0.03	25.16 ± 0.05	2.10
2	0.758	93.9	2.38 ± 0.03	0.36 ± 0.04	25.43 ± 0.02	4.60
3	0.568	95.0	2.20 ± 0.01	0.42 ± 0.02	25.43 ± 0.03	7.58
4	0.376	95.8	2.01 ± 0.05	1.59 ± 0.15	26.01 ± 0.02	15.87

macrokinetics, $n \neq 1$, were also estimated. The results were shown in Table III. Obviously the autoacceleration factors, B', obtained were closer to literature values[15-18] than that obtained from the Malkin equation and almost independent of the concentration of macroactivator. The apparent reaction order on the monomer concentration was not a first order but about a 1.5 order. However, the other parameters were not significantly different from those of Table II; and the tendency for the changes of those parameters with the macroactivator concentration were just the same as those obtained based on the Malkin's kinetics, that is, eq. (1b).

As shown in Table II or III, the apparent frequency factor, A_o or A_o, increased as the concentration of macroactivator increased. By combining both the Lin's mechanistics[22] and the Malkin's macrokinetics,[17] the A_o in the Malkin's model can be correlated with the preexponential factor, A, initial concentrations of activator, $[A]_o$, and of ϵ-caprolactam, $[M]_o$, of the mechanistics[22] as follows, $A_o = A([A]_o^2/[M]_o)$. Utilizing the expression, we calculated the A value. Obviously the preexponential factor, A, decreased significantly with $[A]_o$. The similar phenomenon was also reported by Limtasiri et al.[14] Obviously, none of these two approaches can describe well the Nylon block copolymerization studied in the text.

The proton in the isocyanate group of N-acylated ϵ-caprolactam was shown to be more acidic than that in the ϵ-caprolactam. It reacted more actively with the ϵ-caprolactam anion[8] especially at the initial stage of reaction, in addition to the normal ring opening addition reaction.

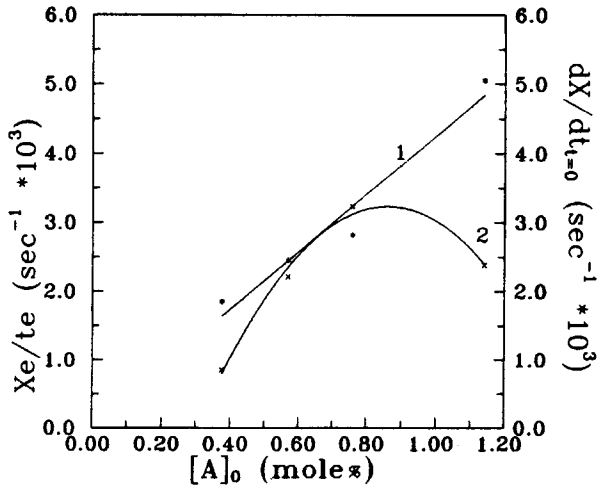


Figure 4 Changes of apparent overall reaction rate (curve 1) and initial reaction rate (curve 2) with the concentration of macroactivator for adiabatic anionic polymerization of ϵ-caprolactam.

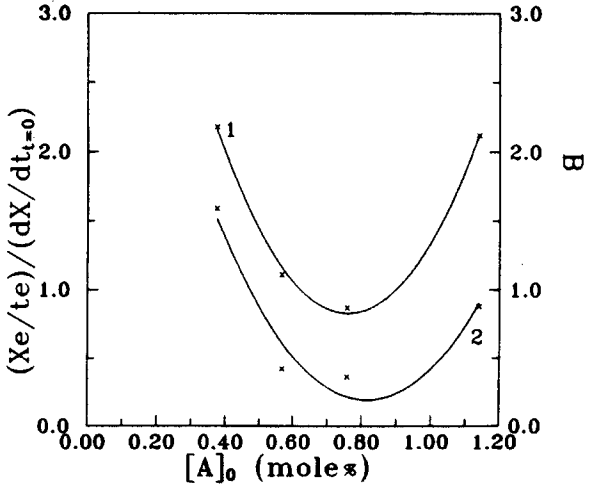
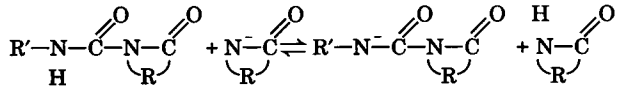
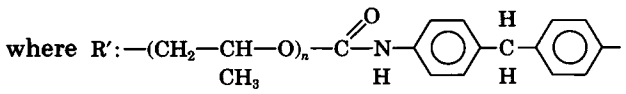


Figure 5 Comparison of the ratio of apparent overall reaction rate to initial reaction rate (curve 1) with the autoacceleration parameter (curve 2) of Malkin's equation for adiabatic anionic polymerization of ϵ-caprolactam.

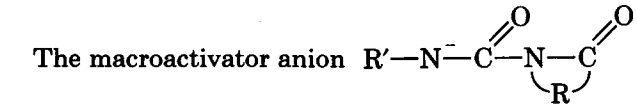
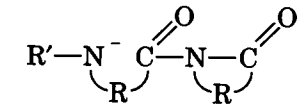
Table III Kinetic Parameters of Generalized Empirical Equation ($n \neq 1$) Obtained

Run No.	Kinetic Parameters				
	$[A]_o$ (mol %)	A'_o (10^{-10})	n	B'	E'_a (kcal/mol)
1	1.140	2.30 ± 0.04	1.50 ± 0.05	4.50 ± 0.20	25.15 ± 0.08
2	0.758	2.20 ± 0.05	1.40 ± 0.04	1.50 ± 0.08	25.20 ± 0.05
3	0.568	1.89 ± 0.04	1.60 ± 0.02	2.15 ± 0.14	25.33 ± 0.04
4	0.376	1.77 ± 0.03	1.20 ± 0.05	3.02 ± 0.08	26.00 ± 0.05

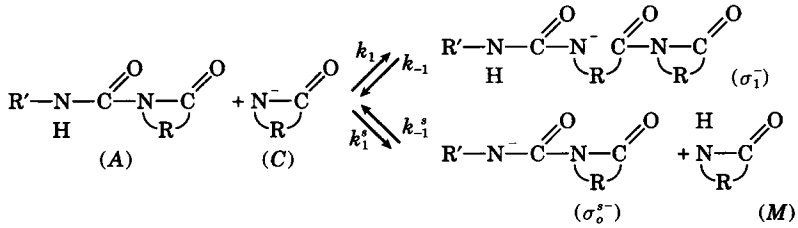


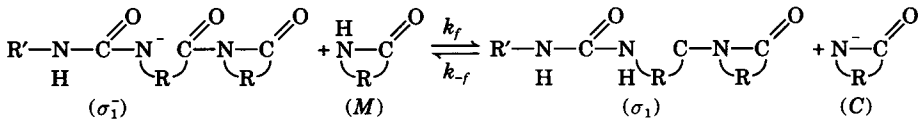
where R′: 

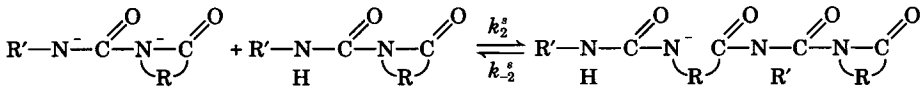
R: $-(CH_2)_5^-$

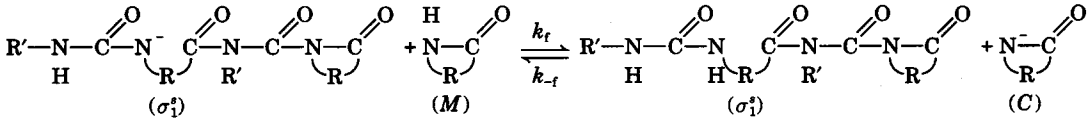
The macroactivator anion  is more resonance stable than the normal propagating anion  . Therefore, the occurrence of the macroactivator anion could slow down the reaction rate.

According to the discussion above, we propose the mechanism as follows. Initiation

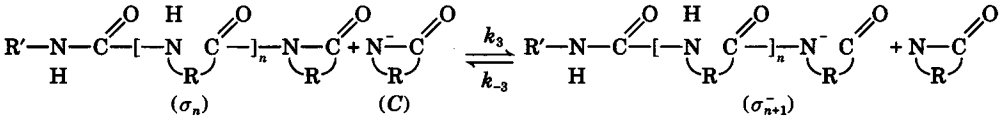


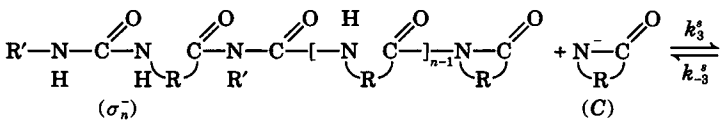


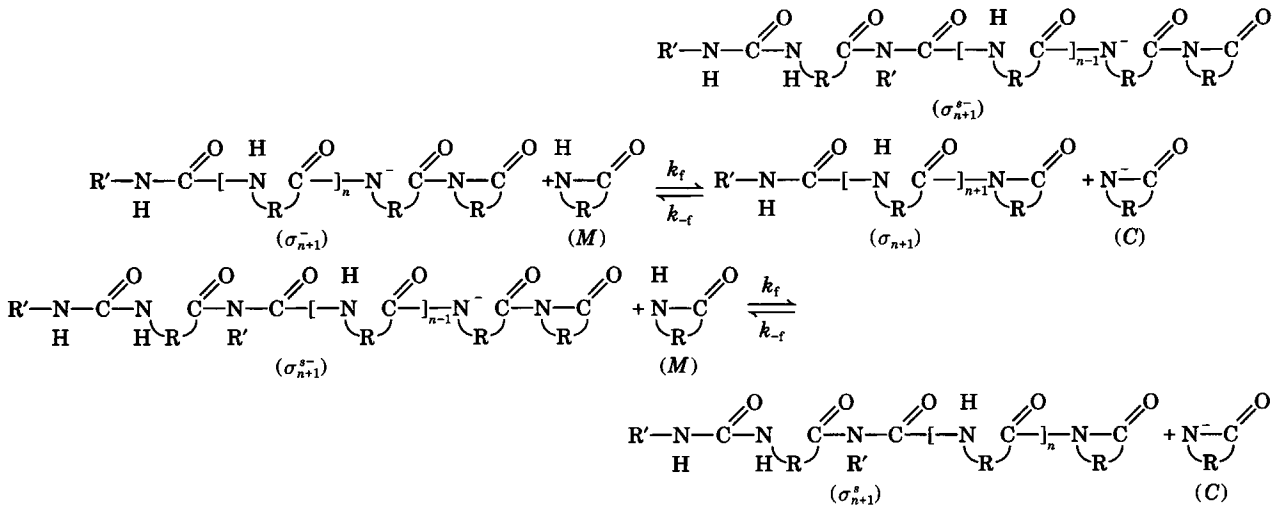




Propagation







Utilizing the above mechanism and the pseudo-steady state assumption for the intermediate ionic species, we obtained an expression for the consumption rate of ϵ-caprolactam as follows,

$$dX/dt = (-1/[M]_o)d[M]/dt = -(I + II) \quad (2)$$

where

$$I = k_1^s \frac{[A][C]}{[M]_o} + k_{-1}^s \frac{[M]}{[M]} \left(\frac{k_1^s[A][C]}{k_{-1}^s[M] + k_2^s[A]} \right)$$

$$II = \frac{[A]_o[C]_o}{[M]_o} \left\{ k_{-f} - \frac{k_f[M](k_p + k_{-f})}{(k_{-p} + k_f[M])} \right\}.$$

The derivation for eq. (2) in detail is given in the Appendix. At the initial stage of reaction, I and II can be reduced to

$$I_o = \frac{k_1^s k_2^s}{k_{-1}^s} \frac{[A]_o[C]_o}{[M]_o} \quad (2b)$$

$$II_o = -k_p[A]_o[C]_o. \quad (2a)$$

In this text we use $[A]_o = [C]_o$. Thus eq. (2) becomes,

$$dX/dt|_{t=0} = K_1 \frac{[A]_o^2}{[M]_o} - K_2 \frac{[A]_o^3}{[M]_o^2} \quad (3)$$

where

$$K_1 = k_p, \quad K_2 = \frac{k_1^s k_2^s}{k_{-1}^s} = K^s k_2^s.$$

Finally, using a linear regression method to fit the data of $dX/dt|_{t=0}$ for eq. (3), we obtained $K_1 = 13$ L mol^{-1} and $K_2 = 962$ L mol^{-1} (shown in Fig. 6). It reveals that a significant side reaction took place through transfer of the proton in the isocyanate group of activator to ϵ-caprolactam anion.

Furthermore, the initial rate expressions for both the macrokinetic and mechanistic approaches can be combined as follows,

$$dX/dt|_{x=0} = A_o \exp(-Ea/RT_o)$$

$$= \left(A \frac{[A]_o^2}{[M]_o} \right) \exp(-Ea/RT_o). \quad (4)$$

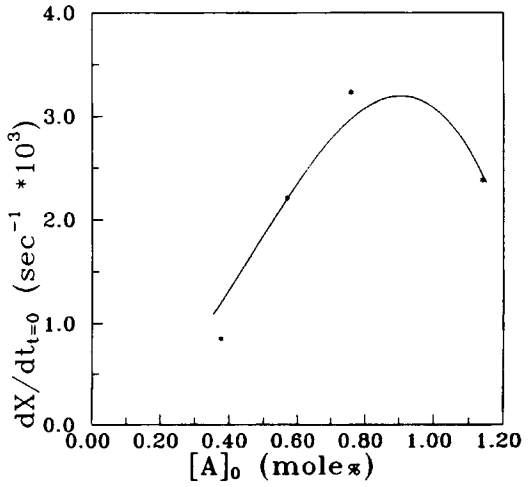


Figure 6 Initial reaction rate predicted by the kinetic model proposed, $dX/dt_{t=0} = K_1^*[A_o^2/[M]_o - K_2^*[A]_o^3/[M]_o^2$, where $K_1 = 13$ L mol^{-1}, $K_2 = 962$ L mol^{-1}.

Combining both eqs. (3) and (4) leads to

$$dX/dt_{x=0} = \left(A\frac{[A]_o^2}{[M]_o}\right)\exp(-Ea/RT_o)$$
$$= K_1\frac{[A]_o^2}{[M]_o} - K_2\frac{[A]_o^3}{[M]_o^2}.$$

Then the preexponential factor is obtained

$$A = \left(K_1 - K_2\frac{[A]_o}{[M]_o}\right)\exp(Ea/RT_o).$$

Taking the logarithm of both sides of the above equation obtains

$$\ln(A) = \ln\left(K_1 - K_2\frac{[A]_o}{[M]_o}\right) + Ea/RT_o. \quad (5)$$

According to eq. (5), recalculation of A as a function of $[A]_o$ and $[M]_o$ was made by using K_1 = 13 L mol^{-1}, K_2 = 962 L mol^{-1}, T_o = 155°C, and Ea = 25.5 kcal/mol. As shown in Figure 7, they were in good agreement with those obtained from nonlinear regression (column 6 of Table II). Therefore, we revise eq. (1) as follows,

$$dX/dt = \left(K_1\frac{[A]_o^2}{[M]_o} - K_2\frac{[A]_o^3}{[M]_o^2}\right)\exp\{-Ea/R(1/T - 1/T_o)\}(1-X)(1+BX). \quad (6)$$

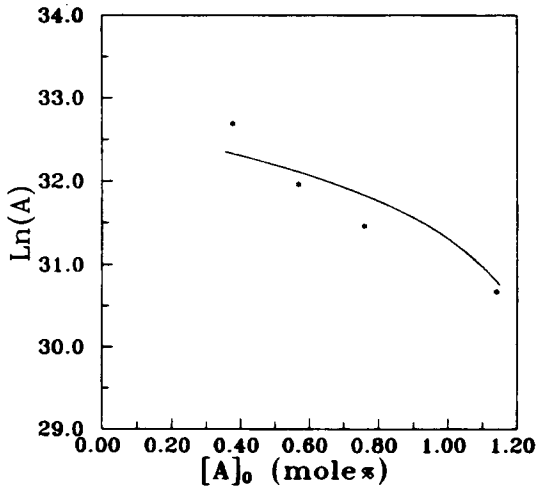


Figure 7 Preexponential factor for various concentrations of macroactivator predicted by the proposed kinetic model proposed, $\ln(A) = \ln(K_1 - K_2^*[A]_o/[M]_o) + Ea/(RT_o)$.

The good agreements between the calculated (solid lines) and experimental conversion vs. time curves were obtained [Fig. 3(b)]. In the calculation the values of K_1, K_2, T_o, Ea, $[A]_o$, and $[M]_o$ mentioned above were used in eq. (6). It means that eq. (6) could describe the kinetics of the abiabatic anionic polymerization of Nylon activated with N-acylated ϵ-caprolactam quite well.

CONCLUSION

The macroactivator studied could make the adiabatic anionic polymerization of ϵ-caprolactam for Nylon-PPG-Nylon triblock copolymer attain an equilibrium conversion of above 94% with a reaction time less than 9 min. However it also induced some side reaction somewhat retarding the rate of polymerization. The new mechanism and the modified macrokinetics proposed in the text has the advantage of predicting the preexponential factor as a function of the initial concentrations of ϵ-caprolactam and macroactivator.

We are grateful to the National Science Council of the Republic of China for financial support for this work (NSC-78-0405-E006-13).

APPENDIX

According to the mechanism suggested in the text, the consumption rate of ϵ-caprolactam is represented as follows,

$$d[M]/dt = k_1^s[A][C] - k_{-1}^s[\sigma_o^{s-}][M] - k_f[\sigma_1^-][M] + k_{-f}[\sigma_1][C] - k_f[\sigma_1^{s-}][M] + k_{-f}[\sigma_1^s][C] - k_f[M]\sum[\sigma_{n+1}^-] + k_{-f}[C] \times \sum[\sigma_{n+1}] - k_f[M]\sum[\sigma_{n+1}^{s-}] + k_{-f}[C] \times \sum[\sigma_{n+1}^s] = \frac{\{k_1^s[A][C] - k_{-1}^s[\sigma_o^{s-}][M]\}}{I} + \frac{\{k_{-f}[C]([\sigma^s] + [\sigma]) - k_f[M]([\sigma^{s-}] + [\sigma^-])\}}{II},$$

where

$$[\sigma] = \sum_{n=1}^{\infty}[\sigma_n], \quad [\sigma^s] = \sum_{n=1}^{\infty}[\sigma_n^s]$$
$$[\sigma^-] = \sum_{n=1}^{\infty}[\sigma_n^-], \quad [\sigma^{s-}] = \sum_{n=1}^{\infty}[\sigma_n^{s-}]. \quad (A1)$$

Using the steady-state assumption for those intermediate active species, one obtains

$$d[\sigma_o^{s-}]/dt = k_1^s[A][C] - k_{-1}^s[\sigma_o^{s-}][M] - k_2^s[\sigma_o^{s-}][A] + k_{-2}^s[\sigma_1^{s-}] = 0$$

$$[\sigma_o^{s-}] = \frac{k_1^s[A][C] + k_{-2}^s[\sigma_1^{s-}]}{k_{-1}^s[M] + k_2^s[A]} \quad \text{(A2)}$$

$$d[\sigma^-]/dt = k_3[\sigma][C] - k_{-3}[\sigma^-] - k_2[\sigma^-][M] + k_{-2}[\sigma][C] = 0$$

$$[\sigma^-] = \frac{(k_3 + k_{-f})[\sigma][C]}{k_{-3} + k_f[M]} \quad \text{(A3)}$$

$$d[\sigma^{s-}]/dt = k_3^s[\sigma^s][C] - k_{-3}^s[\sigma^{s-}] - k_f[\sigma^{s-}][M] + k_{-f}[\sigma^s][C] = 0 = (k_3^s + k_{-f})[\sigma^s][C] - [\sigma^{s-}](k_{-3}^s + k_f[M]) = 0$$

$$[\sigma^{s-}] = \frac{(k_3^s + k_{-f})[\sigma^s][C]}{k_{-3}^s + k_f[M]}. \quad \text{(A4)}$$

Here let $k_3 = k_3^s = k_p$ and $k_{-3} = k_{-3}^s = k_{-p}$, then

$$[\sigma^-] + [\sigma^{s-}] = \frac{(k_p + k_{-f})[C]}{k_{-p} + k_f[M]}([\sigma] + [\sigma^s]) \quad \text{(A5)}$$

$$II = k_{-f}[C]([\sigma] + [\sigma^s]) - k_f[M]\frac{[C](k_p + k_{-f})([\sigma] + [\sigma^s])}{(k_{-p} + k_f[M])} = ([\sigma] + [\sigma^s])[C]\left\{k_{-f} - \frac{k_f[M](k_p + k_{-f})}{(k_{-p} + k_f[M])}\right\}. \quad \text{(A6)}$$

Applying the material balance on the activator concentration, one obtains

$$[A]_o = [\sigma] + [\sigma^s] + [\sigma^-] + [\sigma^{s-}] + [\sigma_o^{s-}]. \quad \text{(A7)}$$

Furthermore, the concentration of the intermediate active species σ^-, σ^{s-}, and σ_o^{s-} are assumed to be much smaller than those of σ and σ^{s_o} at all times, thereby

$$([\sigma] + [\sigma^s])[C] \approx [A]_o[C]_o$$

$$II = [A]_o[C]_o\left\{k_{-f} - \frac{k_f[M](k_p + k_{-f})}{(k_{-p} + k_f[M])}\right\}$$

$$I = k_1^s[A][C] - k_{-1}^s[M]\left(\frac{k_1^s[A][C] + k_{-2}^s[\sigma_1^{s-}]}{k_{-1}^s[M] + k_2^s[A]}\right). \quad \text{(A8)}$$

$k_{-2}^s[\sigma_1^{s-}]$ in I is much smaller than $k_1^s[A][C]$, thus I becomes

$$I = k_1^s[A][C] - k_{-1}^s[M]\left(\frac{k_1^s[A][C]}{k_{-1}^s[M] + k_2^s[A]}\right) = \frac{k_1^s[A]^2[C]}{k_{-1}^s[M] + k_2^s[A]}. \quad \text{(A9)}$$

Substituting both (A8) and (A9) in (A1) results in

$$d[M]/dt = I + II = k_1^s[A][C] - k_{-1}^s[M]\left(\frac{k_1^s[A][C]}{k_{-1}^s[M] + k_2^s[A]}\right) + [A]_o[C]_o\left\{k_{-f} - \frac{k_f[M](k_p + k_{-f})}{k_{-p} + k_f[M]}\right\}. \quad \text{(A10)}$$

The consumption rate of monomer is further expressed in terms of conversion, X, defined as $[M] = [M]_o(1 - X)$, then eq. (A10) becomes

$$dX/dt = -k_1^s\frac{[A][C]}{[M]_o} + k_{-1}^s\frac{[M]}{[M]_o}\left(\frac{k_1^s[A][C]}{k_1^s[M] + k_2^s[A]}\right) - \frac{[A]_o[C]_o}{[M]_o}\left\{k_{-f} - \frac{k_f[M](k_p + k_{-f})}{k_{-p} + k_f[M]}\right\}. \quad (2)$$

At the initial stage of reaction, II may be expressed as

$$II_o = [A]_o[C]_o\left\{k_{-f} - \frac{k_f[M]_o(k_p + k_{-f})}{k_{-p} + k_f[M]_o}\right\}.$$

Because the rate of the reverse reaction of the ring opening addition is very smaller than that of H-transfer reaction at initial stage of reaction,

$$k_{-p}[\sigma^-] \ll k_f[\sigma^-][M]_o.$$

Then

$$II_o = [A]_o[C]_o\{k_{-f} - (k_p + k_{-f})\} = -k_p[A]_o[C]_o \quad \text{(2a)}$$

and

$$I_o = \frac{k_1^s k_2^s[A]_o^2[C]_o}{k_{-1}^s[M]_o + k_2^s[A]_o} = \frac{k_1^s k_2^s\frac{[A]_o^2[C]_o}{[M]_o}}{k_{-1}^s + k_2^s\frac{[A]_o}{[M]_o}}.$$

The nucleophillicity of σ_o^- is low due to its large conjugated stability, as well as the value of $[A]_o/[M]_o$ being small. I_o can be reduced to be

$$I_o = \frac{k_1^s k_2^s [A]_o^2 [C]_o}{k_{-1}^s [M]_o}. \quad (2b)$$

Consequently, the initial rate of polymerization is represented by

$$dX/dt|_{t=0} = K_1 \frac{[A]_o[C]_o}{[M]_o} - K_2 \frac{[A]_o^2[C]_o}{[M]_o^2} \quad (3)$$

where

$$K_1 = k_p, \quad K_2 = \frac{k_1^s k_2^s}{k_{-1}^s}.$$

In the case of $[A]_o = [C]_o$, eq. (3) becomes

$$dX/dt|_{t=0} = K_1 \frac{[A]_o^2}{[M]_o} - K_2 \frac{[A]_o^3}{[M]_o^2}. \quad (3a)$$

REFERENCES

1. L. M. Alberino and T. R. McClellan, in *Reaction Injection Molding*, J. E. Kresta, ed., ACS Symposium Series 270, Washington, D.C., 1985, pp. 3, 15.
2. A. von Hassell, *Plast. Tech.*, **Aug.**, 22 (1982).
3. J. A. Sneller, *Modern Plast.*, **63**, 55 (1986).
4. H. Wirtz, *J. Cellular Plast.*, **2**, 324 (1966).
5. S. Hoshino and M. Nishiyama, *Japan Plast.*, Mar.–Apr., 29 (1985).
6. G. C. Alfonso, C. Hiappori, S. Razore, and S. Russo, in *Reaction Injection Molding*, J. E. Kresta, ed., ACS Symposium Series 270, Washington, D.C., 1985, p. 163.
7. K. H. Lee and S. C. Kim, *Polym. Eng. Sci.*, **28**, 477 (1988).
8. J. Sebenda, in *Ring Opening Polymerization*, Chap. 6, K. C. Frisch and S. L. Reegen eds., Marcel Dekker, New York and London, 1969, p. 379.
9. J. Sebenda, *Prog. Polym. Sci.*, **6**, 123 (1978).
10. J. Sebenda, in *Comprehensive Polymer Science*, chairman of the editorial board, S. G. Allen, Pergamon Press, New York, 1989, pp. 3, 511.
11. W. T. Allen and D. E. Eaves, *Angew. Makro. Chem.*, **58/59**, 321 (1977).
12. J. D. Gabbert and R. M. Hedrick, *Polym. Proc. Eng.*, **4**, 359 (1986).
13. R. M. Hedrick, J. D. Gabbert, and M. H. Wohl, in *Reaction Injection Molding*, E. Kresta, ed., ACS Symposium Series 270, Washington, D.C., 1985, p. 135.
14. T. Limtasiri, S. T. Grossman, and J. C. Huang, *Polym. Eng. Sci.*, **28**, 1145 (1988).
15. A. Ya. Malkin, V. G. Frolov, A. N. Ivanova, and Z. S. Andrianova, *Polym. Sci. USSR*, **21**, 691 (1979).
16. S. A. Bolgov, A. Ya. Malkin, V. P. Begisher, and V. G. Frolov, *Polym. Sci. USSR*, **23**, 1485 (1981).
17. A. Ya. Malkin, V. G. Frolov, S. L. Ivanova, and Z. S. Andrianova, *Polymer*, **23**, 1791 (1982).
18. R. E. Gamargo, C. W. Macosko, V. M. Gonzalez, and M. Tirrell, *Rubb. Chem. Tech.*, **56**, 774 (1983).
19. P. W. Sibal, R. E. Camargo, and C. W. Macosko, *Polym. Proc. Eng.*, **1**, 147 (1984).
20. R. Z. Greenley, J. C. Stuuffer, and J. E. Kurz, *Macromolecules*, **2**, 561 (1969).
21. A. Rigo, G. Fabbri, and G. Talamini, *J. Polym. Sci. Polym. Lett. Ed.*, **13**, 469 (1975).
22. D. J. Lin, J. M. Ottino, and E. L. Thomas, *Polym. Eng. Sci.*, **25**, 1155 (1985).
23. R. A. Cimini and D. C. Sundberg, *Polym. Eng. Sci.*, **26**, 560 (1986).
24. C. W. Macosko and S. D. Lipshitz, *J. Appl. Polym. Sci.*, **21**, 2029 (1977).
25. J. L. Kuester, and J. H. Mize, in *Optimization Techniques with Fortran*, McGraw Hill, New York, 1973, p. 240.
26. F. B. Smith and D. F. Shann, *Technometrics*, **13**, 63 (1971).
27. J. Sebenda, *J. Macro. Sci. Chem.*, **A6**, 1145 (1972).
28. E. J. Malec and D. J. David, *Analytical Chemistry of Polyurethane*, D. J. David and H. B. Stalty, eds., Wiley, New York, 1969.
29. K. H. Lee and S. C. Kim, *Polym. Eng. Sci.*, **28**, 13 (1988).

Received October 20, 1992
Accepted March 14, 1993