ELSEVIER

S0032-3861(96)00567-8

Polymer Vol. 38 No. 4, pp. 939–947, 1997

0032-3861/97/$17.00 + 0.00

Polyamides from lactams via anionic ring-opening polymerization: 2. Kinetics*

Raj S. Davét
Fish and Richardson PC, 601 13th Street NW, Washington, DC 20005, USA

and Robert L. Kruse, and Lionel R. Stebbins
Bayer Corporation, Polymers Division‡, 800 Worcester Street, Springfield, MA 01151, USA

and Kishore Udipi
Monsanto Company, Fibers Division, 3000 Old Chemstrand Road, Contonment, FL 32533, USA
(Received 16 February 1994; revised 7 February 1996)

This paper summarizes a study of the kinetics of the anionic polymerization of caprolactam employing a bisimide (isophthaloyl-bis-caprolactam) as the initiator and caprolactam–magnesium-bromide as the catalyst. The early part of this investigation was devoted to the study of phenomenological polymerization kinetics via the adiabatic reactor method. Kinetic constants were determined by regression analysis using Malkin's autocatalytic model. The adiabatic temperature rise normally occurs in two stages. The first rise of about 50°C is due to the polymerization exotherm and is followed by a second, smaller temperature rise of about 10°C attributed to the polymer crystallization. (For the purpose of comparison, it should be noted that the typical adiabatic temperature rise of either polyester or vinyl-ester resin is about 150°C). The onset of crystallization is typically preceded by an induction period. The magnitude of temperature rise and the onset of crystallization (including the induction period) is dependent upon the initial polymerization temperature. In the 117–140°C temperature range, the correlation between the experimental and predicted polymerization and crystallization exotherms was excellent. At higher initial temperature (157°C), the polymerization exotherm was only 40°C and the crystallization exotherm was not observed.

(Keywords: anionic polymerization; kinetics; crystallization)

INTRODUCTION

This paper is the second of the three-part series on polyamides from lactams via anionic ring-opening polymerization[1,2]. The ring-opening polymerization of caprolactam is an important method for synthesis of nylon 6 and its copolymers[3]. This study was undertaken primarily in support of a reaction injection pultrusion project. Anionic ring-opening polymerization of caprolactam to nylon 6 is uniquely suited to form a thermoplastic matrix for pultruded fibre-reinforced composites. The fast reaction kinetics with no by-products and the crystalline nature of the nylon so produced make anionic polymerization of caprolactam a compelling choice for the reaction injection pultrusion process.

Although a large number of initiators are described in the literature[4,5] to anionically polymerize caprolactam, the primary choice of the catalyst has been sodium (Na), except in the studies at the Monsanto Company by Hedrick and coworkers[3,6] and Greenley *et al.*[7]. In the above studies, caprolactam–magnesium-bromide and isophthaloyl-bis-caprolactam were used as the catalyst and initiator, respectively. In this study too, caprolactam–magnesium-bromide and isophthaloyl-bis-caprolactam were used as the catalyst and initiator for several reasons: stability and ease of handling of caprolactam–magnesium-bromide compared to sodium, and the proven efficiency of isophthaloyl-bis-caprolactam in earlier studies at the Monsanto Company. Much of the data base available within the Monsanto Company on anionic polymerization of caprolactam using caprolactam–magnesium-bromide and isophthaloyl-bis-caprolactam as the catalyst and initiator involves block copolymerization of caprolactam with end-functional polyethers and polydienes[3,6]. Due to the lack of basic information in the literature on the anionic polymerization of caprolactam in the presence of caprolactam–magnesium-bromide and isophthaloyl-bis-caprolactam, a systematic effort was exerted to develop the type of information necessary to support the pultrusion effort. It is important to note that the information available in the open literature is based on initiator/catalyst systems different from those employed here. The initiator/catalyst combinations used in prior published kinetic studies are: Na/tetraacetyl hexamethylene diisocyante[8], Na/*N*–acetylcaprolactam[7,9–12], Na/hexamethylene-1,6-bis-carbamidocaprolactam[12–14], Na/phenylisocyanate[9,11,14,15], Na/toluenediisocyanate[11], Na/1,4-diphenylmethanediisocyanate[11], Na/triphenylmethanediisocyanate[11], Na/trimer of toluenediisocyanate[11], Na/

* Work done at Monsanto Plastics Technology, Springfield, MA. Release for publication, obtained from Monsanto Plastics
† To whom correspondence should be addressed; formerly with Bayer and Monsanto Corps
‡ Formerly, Monsanto Plastics Division

phenylcarbamoyl caprolactam[12], Na/2,4-toluene-bis-carbamoyl caprolactam[12], Na/4,4-diphenylmethane-bis-carbamoyl caprolactam[12], Na/hexamethylene-bis-carbamoyl caprolactam[12], and caprolactam–magnesium-bromide/*N*-acetylcaprolactam[7].

The objective of this research was to measure the basic kinetic parameters for anionic polymerization of caprolactam using caprolactam–magnesium-bromide/isophthaloyl-bis-caprolactam as the catalyst/initiator system. The variables studied include: (a) initial polymerization temperature; (b) concentration of the initiator; (c) concentration of the catalyst.

EXPERIMENTAL

The monomer, catalyst and initiator handling procedures for drying and storage, polymerization techniques, and data acquisition are described in a previous paper[1]. Also in ref. 1, we have described the procedure for measuring the monomer–polymer conversion by Soxhlet extraction. In this paper, we describe the equipment for adiabatic polymerization.

Adiabatic reaction set-up

Adiabatic polymerization was conducted in a heavily insulated, 250 ml glass jar with lid (*Figure 1*) that was set up in an air circulating oven. The front door of the oven had two handholes, similar to a glove box, for inserting the experimenter's hands into the oven. This enabled the catalyst and initiator solutions to be combined in a glass beaker, vigorously stirred, and poured into the reaction vessel by working through the two handholes without opening the oven. The glass polymerization vessel and the catalyst and initiator solutions in caprolactam were preheated to the initial reaction temperature in the oven. After pouring the mixture of the catalyst and initiator solutions into the beaker, a lid with a copper–constantan thermocouple (*Figure 1*) was placed on the beaker. The total time for mixing and pouring the catalyst and initiator solutions and covering the beaker with the lid was minimized to less than a couple of seconds. The temperature of the oven as well as inside the glass polymerization vessel were continually monitored and stored by the data acquisition equipment described previously. The samples remained in the adiabatic reactor for at least 30 min to ensure complete reaction and crystallization.

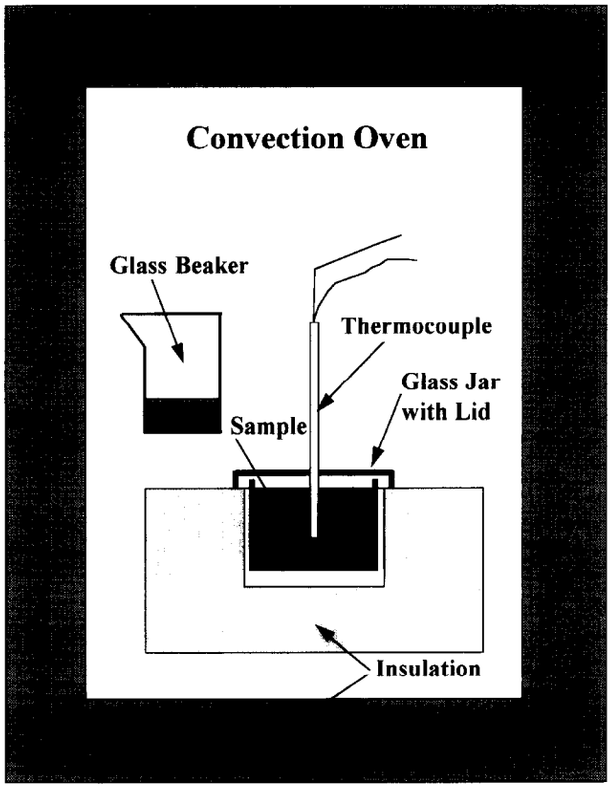


Figure 1 Apparatus for measurement of adiabatic temperature rise during anionic polymerization of nylon 6

KINETICS OF ANIONIC POLYMERIZATION OF CAPROLACTAM

Chemistry of anionic ring-opening polymerization of caprolactam

The chemistry of anionic ring-opening polymerization reaction is complex[4,16–20]. Anionic ring-opening polymerization involves several reversible and irreversible reactions in which the active species are consumed and regenerated[4]. Many side reactions have been reported to participate in the polymerization process–especially at elevated temperatures[4,21,22]. The reaction scheme for the anionic ring-opening polymerization of caprolactam is shown in the first paper in this series[1].

The reaction mechanism of ring-opening homopolymerization of caprolactam consists primarily of two transacylation reactions: initiation and propagation. The initiation occurs by the addition reaction between initiator and catalyst (described in ref. 1). The propagation then occurs by repeating the addition and hydrogen abstraction reactions. According to Sabenda[4], such a 'regular' reaction scheme is presented 'for the sake of simplicity'. In reality, deactivation, branching, and a series of reversible transacylation reactions occurring during the anionic ring-opening polymerization of caprolactam produce side reaction products, heterogeneities in the resultant polymer structure, and a broad molecular weight distribution[4].

The low temperature ($\sim$ 140°C) anionic ring-opening polymerization is further complicated by the crystallinity in nylon 6. Magill[23] has reported that the temperature for maximum crystallization rate in nylon 6 is about 140–145°C. Above 145°C, the nucleation rate is low while below this temperature viscous effects hinder crystal growth. Consequently, at about 140–145°C, heterogeneous reaction conditions can be encountered (as we have seen in this study) if there is simultaneous polymerization of caprolactam and crystallization of the nylon 6 formed during polymerization.

Reaction kinetics

The phenomenological kinetics of the isophthaloyl-bis-caprolactam initiated anionic polymerization of caprolactam was obtained by the adiabatic reactor method. Principles of the method have been discussed elsewhere[24,25]. Under adiabatic conditions, assuming constant heat capacity, constant heat of reaction, and homogeneous reaction, temperature rise data yields fractional conversion[25]:

$$X = \frac{[\mathrm{M}]_0 - [\mathrm{M}]}{[\mathrm{M}]_0} = \frac{H}{H_{\mathrm{tot}}} = \frac{(T - T_0)}{(T_f - T_0)} \qquad (1)$$

Table 1 Nomenclature

[A]	Activator, acyllactam concentration, mol l^{-1}
b	Autocatalytic term, l mol^{-1}
[C]	Catalyst, caprolactam–magnesium-bromide, concentration, mol l^{-1}
H	Heat of polymerization, J mol^{-1}
H_{tot}	Total heat of polymerization, J mol^{-1}
k	Pre-exponential or front factor, l mol^{-1} s^{-1}
M	Monomer concentration, mol l^{-1}
M_0	Initial monomer concentration, mol l^{-1}
R	Universal gas constant, J mol^{-1} K^{-1}
T	Temperature, K
T_0	Initial polymerization temperature, K
T_f	Final adiabatic temperature, K
t	Time, s
U	Activation energy, J mol^{-1}
X	Fractional conversion

The terms in equation (1) are described in *Table 1*. The condition of constant heat capacity can be relaxed if accurate data is available for heat capacity as a function of both conversion and temperature.

In the past, two approaches to kinetic modelling have been used: mechanistic models[7–9,13,15,26] and overall models[10–12,14]. The mechanistic models have attempted to individually account for each possible reaction. Although propagation reactions in caprolactam polymerization consists of only a few types of transacylation reactions, their detailed mechanism, as well as kinetics, are not yet well understood[4]. In seeking a better kinetic model capable of describing the polymerization process and reflecting the chemistry as well, Cimini and Sundberg[26] modified a rate equation originally derived mechanistically by Reimschuessel[27]. Subsequently, Provaznik *et al.*[28] have shown the fundamental importance of changes of the reaction medium on the individual polymerization reactions. Consequently, appropriate corrections concerning the detailed reaction mechanism and kinetics can be expected in the future, but so far the mechanistic models have had a limited success in predicting the anionic ring-opening polymerization of caprolactam. This approach has been found to be severely hindered by the complex nature of this anionic ring-opening polymerization. Although mechanistic models are highly desirable, in the absence of accurate information about the intermediate steps and the possibilities of side reactions like catalyst deactivation and branching, these models are complicated and impractical. On the other hand, the overall models lump all reactions into a single reaction step that accounts for the overall reaction profile like the initial rise in the reaction rate with conversion followed by a decrease in the reaction rate.

In this study, we have used an autocatalytic model originally proposed by Malkin *et al.*[2]. Bolgov *et al.*[11] found that the originally proposed autocatalytic model[12], which was valid for equal concentration of initiator and catalyst during the anionic polymerization of caprolactam, can be modified for unequal concentration of the initiator and catalyst by an autocatalytic equation of type

$$\frac{dX}{dT} = k \exp\left(\frac{U}{RT}\right) \frac{[A]\,[C]}{[M_0]} (1 - X) \times \left\{1 + \frac{b}{([A]\,[C])^{1/2}} X\right\} \quad (2)$$

The terms in equation (2) (Malkin's autocatalytic model) are described in *Table 1*. In Malkin's autocatalytic model, the concentration of the activator, [A], is defined as the concentration of the initiator times the functionality of the initiator. For a difunctional initiator, e.g. isophthaloyl-bis-caprolactam, the concentration of the activator (acyllactam) is twice the concentration of the initiator. The term [C] is defined as the concentration of the metal ion that catalyses the anionic polymerization of caprolactam. In the magnesium-bromide catalysed system, the concentration of the metal ion is the same as the concentration of caprolactam-magnesium bromide ('catalyst') because the latter is monofunctional.

Malkin's autocatalytical model is an extension of the first order reaction to account for the rapid rise in reaction rate with conversion. Equation (2) does not obey any mechanistic arguments because it was derived by an empirical approach of fitting the calorimetric data to the rate equation such that the deviations between the experimental data and the predicted data are minimized. The model, however, not only gives a good fit to the experimental data but yields a single pre-exponential factor (also called the front factor[14]), k, activation energy, U, and autocatalytic term, b. The value of the front factor k allows a comparison of the efficiency of various initiators in the initial polymerization of caprolactam[12]. On the other hand, the value of the autocatalytic term b describes the intensity of self-acceleration effect during chain growth[12].

RESULTS AND DISCUSSION

Verification of Malkin's autocatalytic model

In this study, the catalyst and initiator system was comprised of caprolactam–magnesium-bromide and isophthaloyl-bis-caprolactam, respectively. We have determined the optimum values of the kinetic parameters in Malkin's autocatalytic model (equation (2)) which consist of k, U, and b, by regression analysis.

The kinetic parameters in equation (2) were obtained by regression analysis. Equation (2) was linearized by transposing (1 – X) and the autocatalytic term to the left and then taking the logarithms of both sides of the equation. Fixing the value of b, a linear regression was performed for k and U. This procedure was repeated for several values of b, and an optimum value of b was

Table 2 Kinetic constants for anionic polymerization of caprolactam with different catalyst and initiator systems

System (catalyst/initiator)	Source	Model	Analytical method	U (kJ mol^{-1})	k (l mol s^{-1})	b (l mol^{-1})
MgBr + /IBT[a]	This study	Malkin's autocatalytic model	Adiabatic temperature analyzed by regression analysis	30.2	1.49×10^4	2.17
Na/HMCC1[b]	Malkin *et al.*[10]	"	"	63 ± 6	4.17×10^8	0.066
Na/HMCC1[b]	Sibal *et al.*[14]	"	"	63.8 ± 0.5	2.23×10^8	1.15 ± 0.5
$MgBr^+$/NAC[c]	Greenley *et al.*[7]	Greenley's mechanistic model	Assuming pseudo-first order, isothermal reaction during low conversion	46	N/A	N/A
$MgBr^+$/IBT[a]	This study	First order rate dependence on monomer concentration	"	40.6	7.62×10^5	N/A

[a] Magnesium-bromide–caprolactam/isophthaloyl-bis-caprolactam
[b] Sodium/hexamethylene-1,6,-bis-carbamidocaprolactam
[c] Magnesium-bromide–caprolactam/*N*-acetylcaprolactam
N/A, not available or not applicable

chosen that gave the 'best fit' straight line to the linearized equation. The corresponding values of k and U obtained from the 'best fit' straight line were chosen as the optimum.

The values of the activation energy, U, the front factor k, and the autocatalytic term b, for the caprolactam–magnesium-bromide/isophthaloyl-bis-caprolactam system, as well as other catalyst/initiator systems, are shown in *Table 2*. The values of the kinetic constants for the caprolactam–magnesium-bromide/isophthaloyl-bis-caprolactam system are based on the adiabatic temperature rise data in *Figure 2* with initial polymerization temperatures of 117 and 136°C. It is important to note that the activation energy of magnesium catalysed system is considerably lower (30.2 kJ mol^{-1} vs about 65 kJ mol^{-1}) than that for the sodium catalysed system[10,14]. This is because the magnesium cation is less electropositive than the sodium cation. Therefore, the magnesium cation, compared to the sodium cation, is less tightly bound to the caprolactam anion.

In the only other reported study on the kinetics of anionic ring-opening homopolymerization of caprolactam–magnesium-bromide, Greenley *et al.*[7] determined the value of the activation energy by making the following assumptions: (1) the reaction is pseudo-first order; (2) the reaction is isothermal – consequently, their experimental data were below 20% conversion due to the need for pseudo-isothermal conditions; (3) there is a half order dependence on the initial catalyst concentration. The third assumption was made in the derivation of the rate equation to obtain a better fit.

The role of the isothermal and pseudo-first order reaction assumptions on the observed value of activation energy was assessed to allow comparison of our data to previous work by modifying Malkin's autocatalytic equation so that the autocatalytic term, b, is equal to zero. The values of the activation energy and front factor were calculated using short-time, low conversion data. By making b equal to zero, the modified Malkin autocatalytic model becomes a first order rate reaction. *Table 2* shows that by assuming pseudo-first order, isothermal reaction during low conversion, the values of the activation energy for the caprolactam–magnesium-bromide catalysed ring-opening homopolymerization of caprolactam are calculated to be nearly the same by Greenley *et al.*[7] and by us (46 kJ mol^{-1} vs 40.6 kJ mol^{-1}). As a matter of fact, even the value of the activation energy calculated by Greenley *et al.*[7] for sodium/*N*-acetylcaprolactam system assuming pseudo-first order, isothermal reaction during low conversion is much larger than the activation energy reported by other investigators[9–11] for the same catalyst/initiator system (92 kJ mol^{-1} vs about 65 kJ mol^{-1}). Based on the above calculations, the implication of assuming pseudo-first order reaction, i.e. neglecting the autocatalytic term, and using only the low conversion data in the determination of the activation energy is likely to

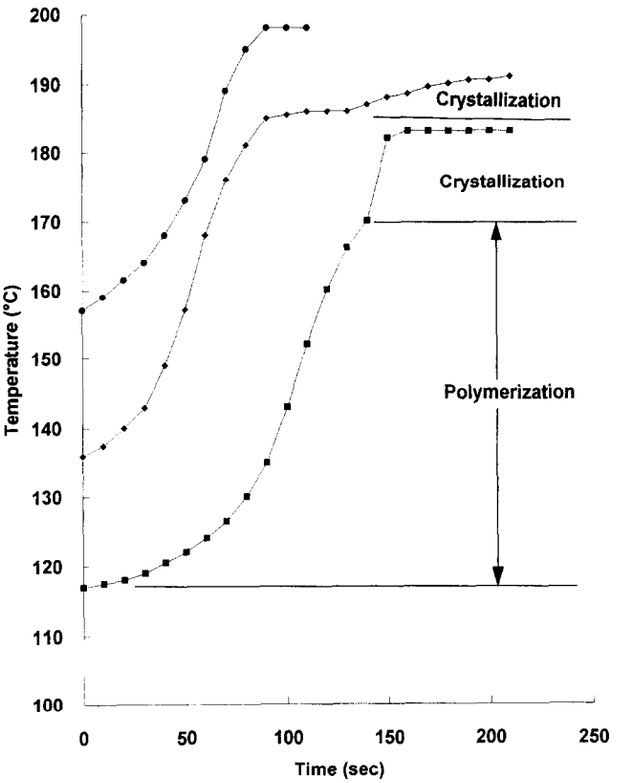
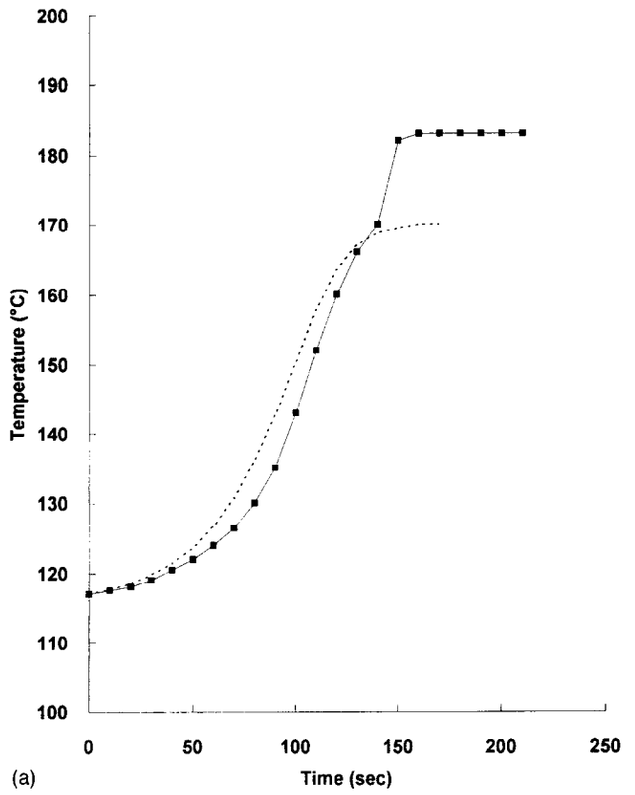
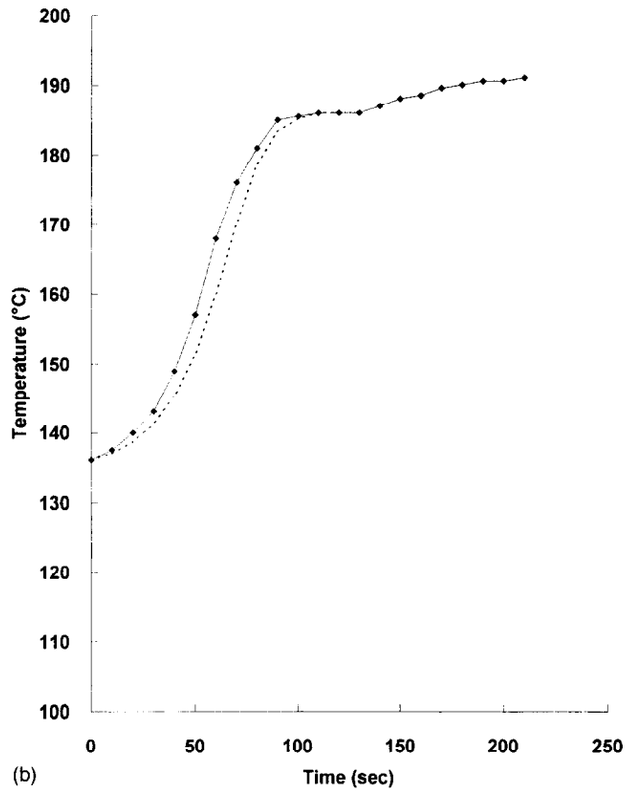


Figure 2 Adiabatic conversion of nylon 6: experimental data for initial polymerization temperatures of 117°C (lower line), 136°C (middle line), and 157°C (top line) with acyllactam and caprolactam–magnesium-bromide concentrations of 70 and 108 mmol l^{-1}, respectively





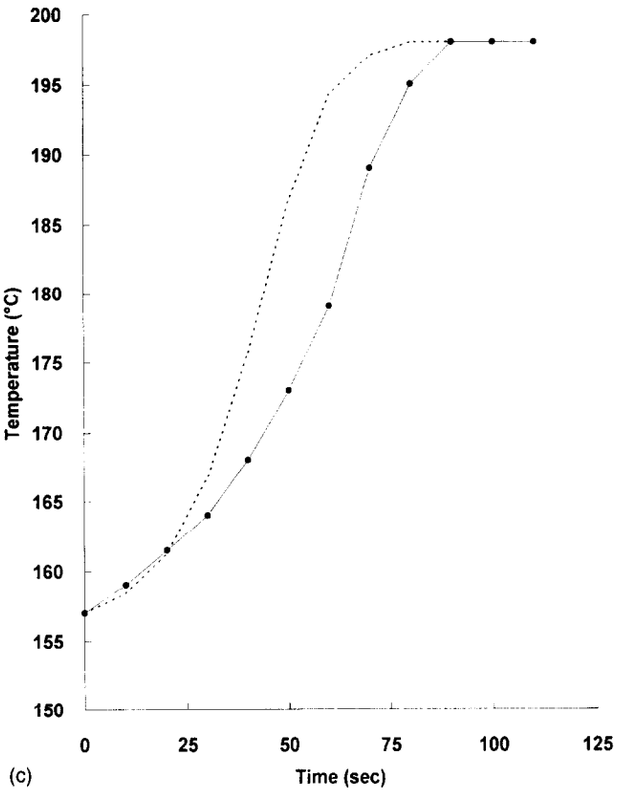


Figure 3 Adiabatic conversion of nylon 6: model prediction (dashed line) vs experimental data (solid line) for initial polymerization temperature of: (a) 117°C; (b) 136°C; (c) 157°C with acyllactam and caprolactam–magnesium-bromide concentrations of 70 and 108 mmol l^{-1} respectively

result in gross over-prediction in the value of the activation energy.

It appears that most activation energy values in the literature for sodium catalysed anionic ring-opening homopolymerization of caprolactam are in the range of 63–71 kJ mol^{-1} despite the variety of initiators used[8–11,14]. This indicates that the value of activation energy is probably independent of the initiator used and dependent only on the catalyst used in the anionic-ring opening polymerization of caprolactam. The results of this study, as well as the study by Greenley *et al.*[7], add further credence to the last statement that the activation values for caprolactam–magnesium-bromide catalysed system is much lower than the activation energy values for the sodium catalysed system (30 kJ mol^{-1} vs about 65 kJ mol^{-1}).

In this study, the calculated values of U, k and b for the caprolactam–magnesium-bromide/isophthaloyl-bis-caprolactam system are 30.2 kJ mol^{-1}, 1.49×10^4 l mol^{-1}, and 2.17 l mol^{-1}, respectively. These optimized values were used in the next study for comparing model predictions with experimental data obtained from adiabatic polymerization under different conditions.

Effect of initial polymerization temperature

The effect of initial polymerization temperature was examined with a constant catalyst/initiator concentration of 108 mmol caprolactam–magnesium-bromide and 35 mmol of the difunctional initiator iosphthaloyl-bis-caprolactam per litre of caprolactam. (Note: 35 mmol l^{-1} of isophthaloyl-bis-caprolactam is 70 mmol l^{-1} equivalent of acyllactam because isophthaloyl-bis-caprolactam is difunctional.) We selected an excess of caprolactam–magnesium-bromide over acyllactam (108 mmol vs 70 mmol) to ensure complete reaction even if trace amounts of moisture remained in

the polymerizing system. (Water deactivates the caprolactam–magnesium-bromide catalyst on a one-to-one mole basis.)

The data from the adiabatic temperature rise experiment (*Figure 2*) shows that the adiabatic temperature rise occurs in two stages when the initial temperature is below 140°C. The first rise of 50°C is due to the reaction exotherm, which is in agreement with values reported in earlier studies[12,14]. A second smaller rise of about 10°C occurs after the first rise. The second temperature rise is due to the heat of crystallization of the polymer formed. No attempts were made in this study to model the temperature rise due to crystallization. The delay between completion of polymerization and onset of crystallization is the induction period. In *Figure 2*, the induction period is clearly defined when the initial polymerization temperature is 136°C, while it is barely visible for 117°C.

When the initial polymerization temperature was 157°C, an adiabatic temperature rise of only 40°C (instead of 50°C due to polymerization with initial polymerization temperatures of 117 and 136°C) was observed and there was no further rise in temperature due to crystallization. This is a result of two factors: (1) as the temperature approaches the melting temperature of nylon 6, depolymerization[21] or other side reactions[4,21] that are not accounted for in the scheme of kinetic modelling may occur; (2) the absence of crystallization temperature rise is due to a negligible rate of crystallization above 190°C for nylon 6 homopolymer[23].

Figures 3a–c compare experimental data of adiabatic temperature rise with model predictions for initial polymerization temperatures of 117, 136, and 157°C. The model predictions for the reaction exotherm compare well with experimental data for 117 and 136°C. Note that the model does not predict the second temperature rise due to crystallization. For initial polymerization temperature of 157°C (*Figure 3c*), the adiabatic temperature rise lags model prediction, indicating that the reaction mechanism for high temperature polymerization is affected by depolymerization or other side reactions (see discussion above) unlike that for the lower temperature polymerization.

The effect of polymerization temperature on conversion was also examined. Monomer conversion was measured by the Soxhlet extraction procedure previously described[1]. The initial polymerization temperature range examined for monomer conversion by adiabatic polymerization was 110–210°C. Results are given in *Table 3*. The temperature rise in each polymerization run was monitored for 6 min even though, typically, there was no increase in temperature after 3–4 min.

Since caprolactam polymerizes by a ring-opening mechanism, the ring-chain equilibrium prevails and the conversion of the monomer to polymer does not reach 100%. Therefore, it is important to know the percent monomer conversion. The equilibrium conversion is typically 94%. Analysis of the data shows that there is a sharp drop in conversion between 130 and 120°C.

Above 130°C, nylon attains its equilibrium conversion. Below 130°C, the polymerization was too slow because the reactive sites were trapped in the simultaneous diffusion controlled crystallization process that resulted in 'gel' formation in the polymerizing system. Similar results were also obtained with a monofunctional initiator (described in ref. 1).

Table 3 Monomer conversions by adiabatic polymerization as a function of initial polymerization temperature for acyllactam and caprolactam–magnesium-bromide concentrations of 70 and 108 mmol l^{-1}

Initial polymerization temperature (°C)	Monomer conversion (%)
110	64.4
120	67.8
130	89.7
140	92.8
160	93.6
210	92.5

Effect of initiator concentration

Malkin's autocatalytic model predicts the reaction rate to be proportional to the concentration of the activator and catalyst. The effect of activator concentration will be discussed in this section.

Figure 4 shows the adiabatic temperature rise for isophthaloyl-bis-caprolactam levels of 20, 35, and 50 mmol l^{-1} of caprolactam, i.e. acyllactam concentration of 40, 70, and 100 mmol l^{-1} of caprolactam. The initial polymerization temperature and catalyst levels were held constant at 136°C and 108 mmol l^{-1}, respectively. For acyllactam concentrations of 70 and 100 mmol l^{-1}, the typical temperature rise due to the reaction exotherm followed by the crystallization exotherm was observed. The adiabatic temperature rise in the case of 40 mmol l^{-1} of acyllactam was quite different, however. The expected temperature rise was observed for the first 50 s followed by

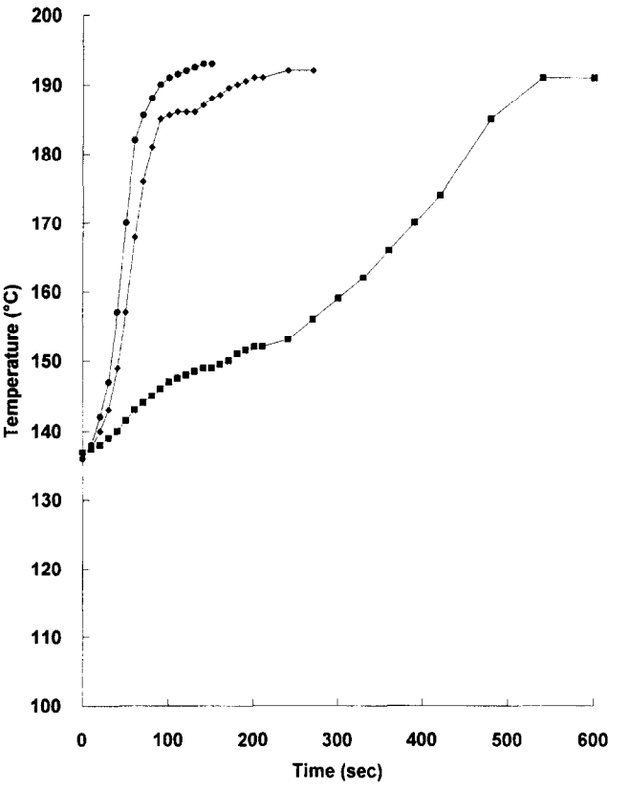
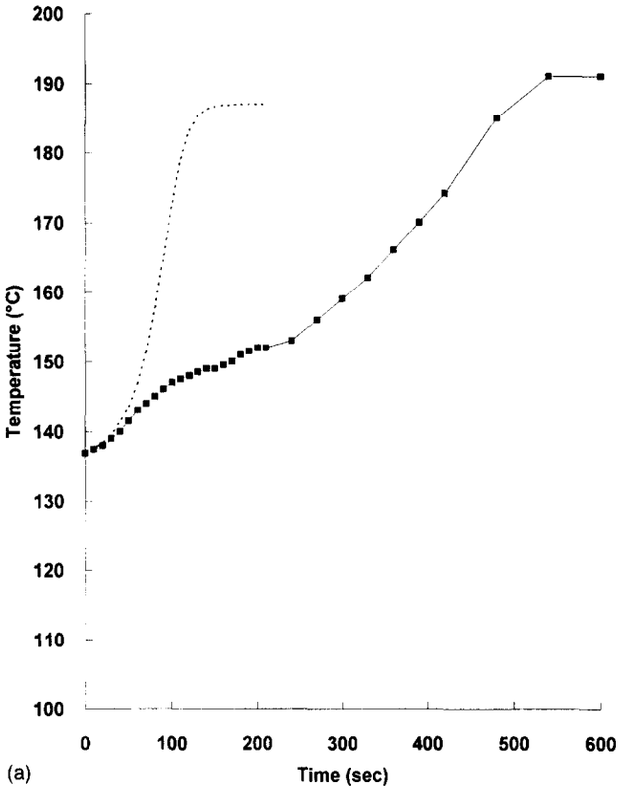
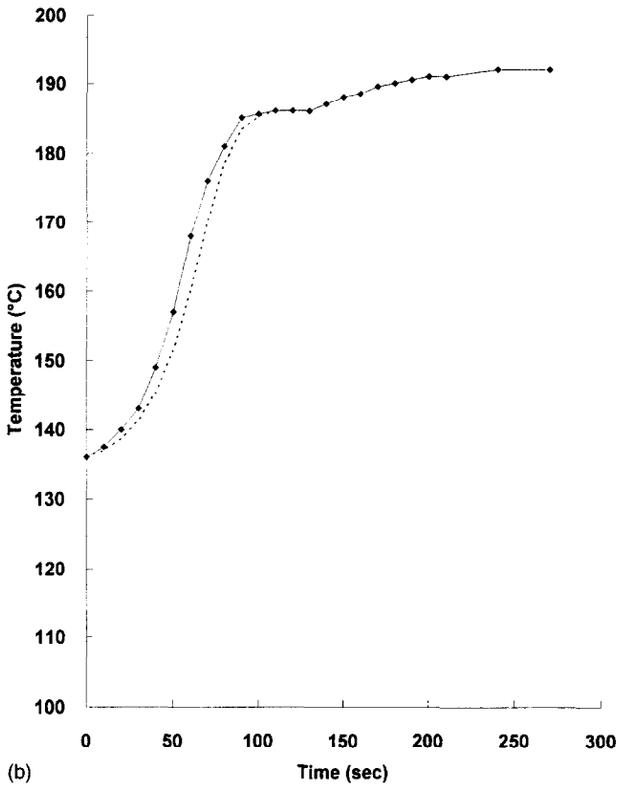


Figure 4 Adiabatic conversion of nylon 6: experimental data for initial polymerization temperature of 136°C with acyllactam concentrations of 40 mmol l^{-1} (lower line), 70 mmol l^{-1} (middle line), and 100 mmol l^{-1} (top line) and caprolactam–magnesium-bromide concentration of 108 mmol l^{-1}





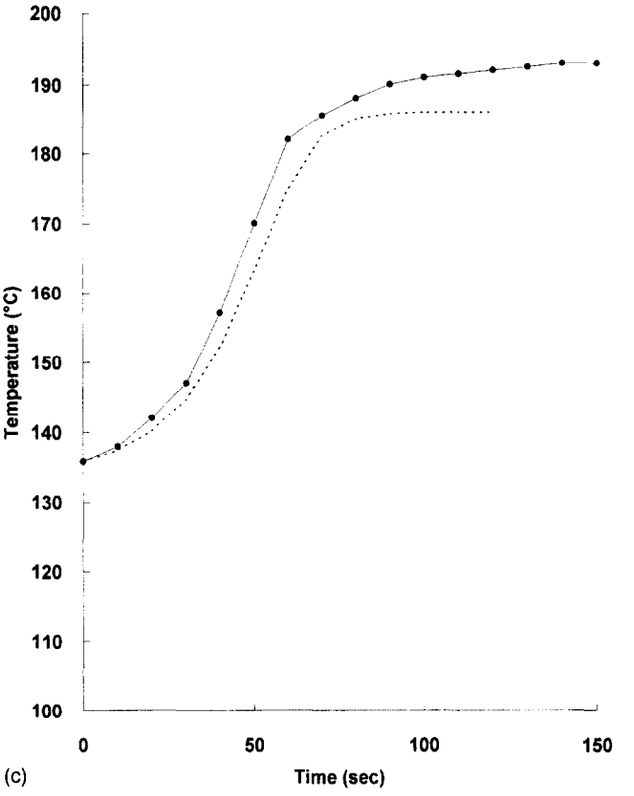


Figure 5 Adiabatic conversion of nylon 6: model prediction (dashed line) vs experimental data (solid line) for initial polymerization temperature of 136°C with acyllactam concentrations of: (a) 40 mmol l^{-1}; (b) 70 mmol l^{-1}; (c) 100 mmol l^{-1} and caprolactam-magnesium-bromide concentration of 108 mmol l^{-1}

a sudden change in the slope of the exotherm curve. (*Figure 5a* compares the experimental data with model predictions.) After 50 s, the adiabatic temperature rise was very sluggish and the total time for a 50°C rise was about 600 s instead of the typical 120 s. Three possible explanations are offered to explain this anomaly. First, there exists a competition between polymerization and crystallization particularly when the initial polymerization temperature is below the maximum crystallization rate temperature of about 140–145°C. If the polymerization rate is slow, then crystallization of the growing chains can lead to entrapment of restricted mobility of the active end of the growing molecules, thereby suppressing the active ends from propagation. Second, the formation of a gel-like network could cause the reaction to shift from kinetic to diffusion controlled mechanism. In the anionic polymerization of caprolactam, the molecular weight is inversely proportional to the activator concentration. With low activator concentrations, long chains are formed at low conversion. The presence of long entangled chains in a low viscosity monomer can create a gel-like structure. Third, the concentration of acyllactam (40 mmol l^{-1}) is too far below the stoichiometric requirements for a monofunctional catalyst concentration of 108 mmol l^{-1}. Greenley *et al.*[7] have suggested that two imide functions of the initiator may occupy coordination sites around one catalyst molecule. Therefore, there may be simultaneous growth of two polymer molecules from a catalyst site if an activator-to-catalyst ratio of two is employed. They suggested that if ratios of less than two are employed (as in the case of the polymerizing system containing 40 mmol l^{-1} of acyllactam and 108 mmol l^{-1} of caprolactam–magnesium-bromide) or the polymer chain with its imide group is removed from the catalyst, degradative and branching processes should be enhanced due to the ability of the polymer amide groups to compete more favourably

Table 4 Monomer conversion as a function of acyllactam (activator) concentration for initial polymerization temperatures of 150°C and caprolactam–magnesium-bromide (catalyst) concentration of 108 mmol l^{-1}

Acyllactam concentration (mmol l^{-1})	Conversion at end of polymerization (%)
40	84
70	90
100	93

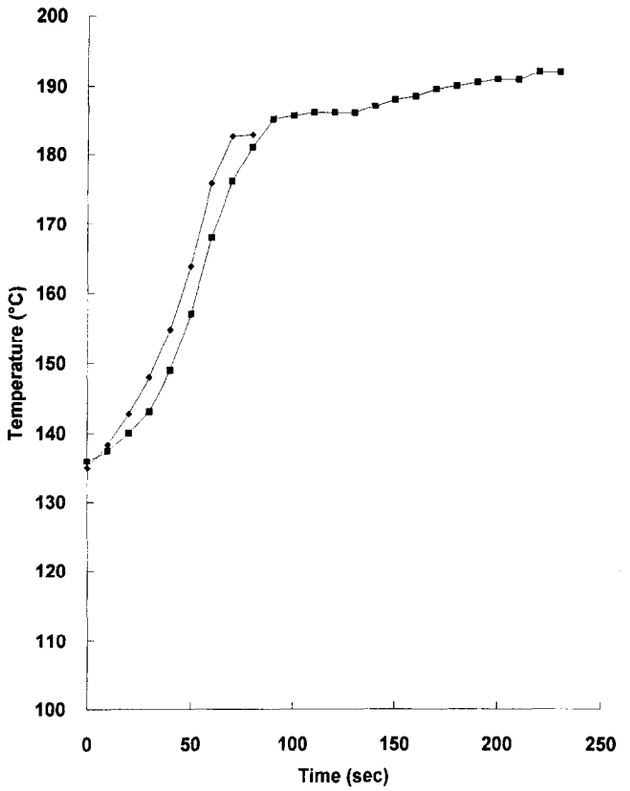


Figure 6 Adiabatic conversion of nylon 6: experimental data for initial polymerization temperature of 135°C with acyllactam concentration of 70 mmol l^{-1} and caprolactam–magnesium-bromide concentration of 108 mmol l^{-1} (lower line) and 150 mmol l^{-1} (top line)

with monomer for coordination sites than they could with imide functions.

Figures 5a–c compare the experimental data of adiabatic temperature rise with model predictions for three levels of acyllactam concentrations. The model results compare favourably with experimental data when the acyllactam concentration is 70 mmol l^{-1} or higher. The suspected cause of the anomaly with 40 mmol l^{-1} of acyllactam has been described above. The conversion of monomer to polymer is also affected by acyllactam concentration (*Table 4*).

In the range of acyllactam concentration examined, with the initial polymerization temperature and concentration of caprolactam–magnesium-bromide held constant at 150°C and 108 mmol l^{-1}, the percent conversion increases with acyllactam concentration between 40 and 70 mmol l^{-1}, but reaches equilibrium conversion between 70 and 100 mmol l^{-1}. The lower conversion achieved for the acyllactam concentration of 40 mmol l^{-1} is likely to be due to the long polymerization time. With a slow rate, the system is more apt to become diffusion controlled and equilibrium conversion cannot be obtained.

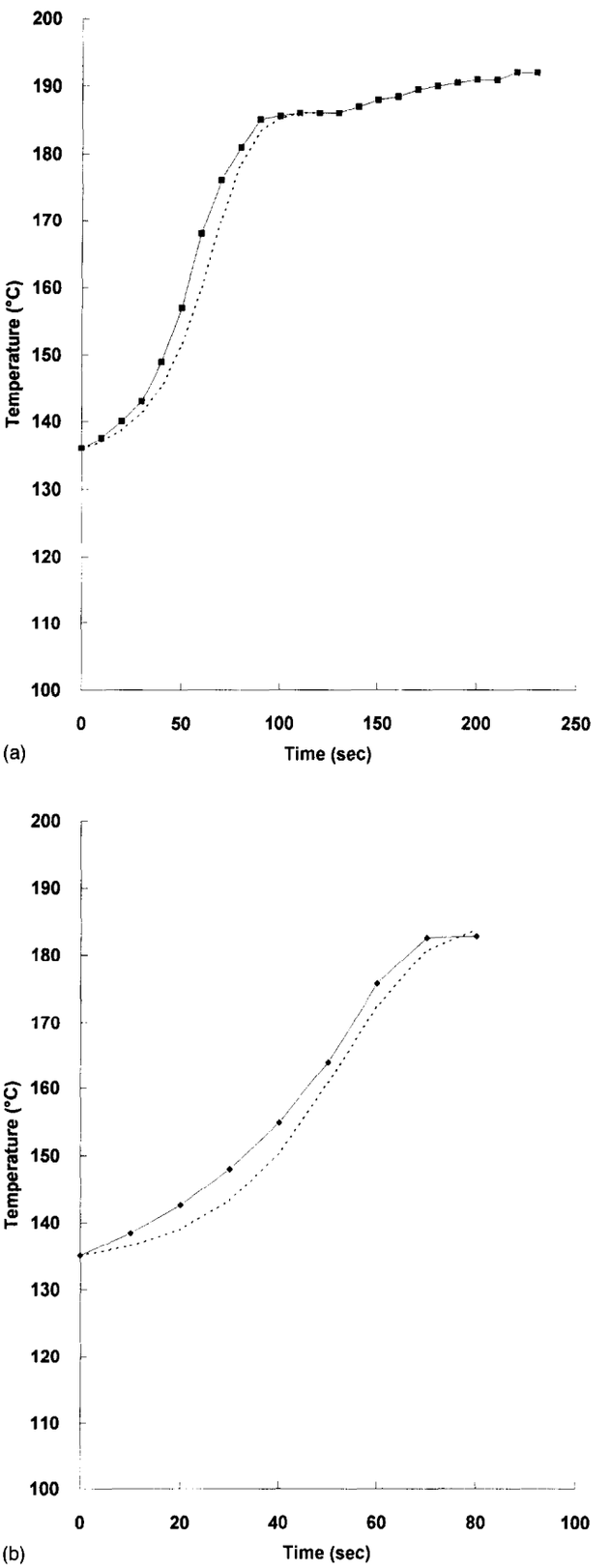


Figure 7 Adiabatic conversion of nylon 6: model prediction (dashed line) vs experimental data (solid line) for initial polymerization temperature of 135°C with acyllactam concentration of 70 mmol l^{-1} and caprolactam–magnesium-bromide concentration of: (a) 108 mmol l^{-1}; (b) 150 mmol l^{-1}

Effect of catalyst concentration

Figure 6 shows the adiabatic temperature rise for catalyst levels of 108 and 150 mmol l^{-1}. The initial polymerization temperature and acyllactam concentration were held constant at 135°C and 70 mmol l^{-1}, respectively. The adiabatic temperature rise showed no unexpected characteristics.

Figures 7a and *b* compare the experimental data of adiabatic temperature rise with model predictions for two catalyst levels. The model results compare favourably with the experimental data.

CONCLUSIONS

In this study we have described the kinetics of anionic ring-opening polymerization of caprolactam, which is initiated by isophthaloyl-bis-caprolactam and catalysed by caprolactam–magnesium-bromide, using Malkin's autocatalytic model, and demonstrated a satisfactory fit between the experimental data and the model. The calculated value of the overall apparent activation energy for the isophthaloyl-bis-caprolactam/caprolactam–magnesium-bromide as the initiator/catalyst system is 30.2 kJ mol^{-1} vs about 65 kJ mol^{-1} for Na/hexamethylene–1,6,–bis-carbamidocaprolactam as the initiator/catalyst system. Increasing the polymerization temperature causes the rate of polymerization to increase.

The reaction rate is proportional to the product of acyllactam (activator) and caprolactam–magnesium-bromide (catalyst) concentrations within the limits studied. When the acyllactam and caprolactam–magnesium-bromide concentration concentrations are 40 and 108 mmol l^{-1}, respectively, and the initial polymerization temperature is about 140°C, the initial polymerization rate is extremely slow due to simultaneous polymerization and crystallization. Consequently, the conversion of caprolactam to nylon 6 is lower than that obtained by polymerizations with a higher ratio of acyllactam to caprolactam–magnesium-bromide concentration (84% vs 90–93%).

ACKNOWLEDGEMENTS

Financial support and release for publication were provided by Monsanto Company, Plastics Technology. The authors wish to thank Allen Padwa for proofreading this manuscript.

REFERENCES

1 Udipi, K., Davé, R. S., Kruse, R. L. and Stebbins, L. R. *Polymer* 1997, **38**, 927
2 Davé, R. S., Udipi, K., Kruse, R. L. and Williams, D. E. *Polymer* 1997, **38**, 949
3 Hedrick, R. M., Gabbert, J. D. and Lockwood, M. H. 'Reaction Injection Molding' (Ed. J. Kresta), *ACS Symp. Ser.* 1985, **270**, 135
4 Sebenda, J. in 'Lactam-Based Polyamides' (Eds R. Puffr and V. Kubanek), Vol. 1, CRC Press, Boca Raton, Florida, 1991, p. 29
5 Sekiguchi, H. in 'Ring-Opening Polymerization' (Eds K. J. Ivin and T. Saegusa), Vol. 2, Elsevier, London, 1984, p. 809
6 Gabbert, J. D. and Hedrick, R. M. *Polym. Process Eng.* 1986, **4**, 359
7 Greenley, R. Z., Stauffer, J. C. and Kurz, J. E. *Macromolecules* 1969, **2**, 561
8 Sittler, E. and Sebenda. J. *Coll. Czech. Chem. Commun.* 1968, **33**, 270
9 Rigo, A., Fabbri, G. and Talamini, G. *J. Polym. Sci., Polym. Lett. Edn.* 1975, **13**, 469
10 Malkin, A. V., Frolov, V. G., Ivanova, A. N. and Andrianova, Z. S. *Polym. Sci. USSR* 1979, **21**, 691
11 Bolgov, S. A., Begishev, V. P., Malkin, A. Y. and Frolov, V. G. *Polym. Sci. USSR* 1981, **23**, 1485
12 Malkin, A. V., Ivanova, S. L., Frolov, V. G., Ivanova, A. N. and Adarinova, Z. S. *Polymer* 1982, **23**, 1791
13 Wittmer, P. and Gerrens, H. *Makromol. Chem.* 1965, **89**, 27
14 Sibal, P. W., Camargo, R. E. and Macosko, C. W. *Polym. Process Eng.* 1984, **1**, 147
15 Lin, J. D., Ottino, J. M. and Thomas, E. L. *Polym. Eng. Sci.* 1985, **25**, 1155
16 Yeh, J. L., Kuto, J. F. and Chen, C. Y. *J. Appl. Polym. Sci.* 1993, **50**, 1671
17 Pufr, R. and Vladimirov, N. *Makromol. Chem.* 1993, **194**, 1765
18 Mateva, R. and Dencheva, N. *J. Polym. Sci. Part A, Polym. Chem.* 1992, **30**, 1449
19 Slomkowski, S. and Duda, A. in 'Ring-Opening Polymerizations' (Ed. D. J. Brunelle), Hanser Publishers, New York, 1993, p. 117
20 Natova, M., Cheshkov, V., Aushorov, N. R., Usmanova, M. M. and Veksel'man, A. *Eur. Polym. J.* 1993, **29**, 205
21 Cawthon, T. M. and Smith, E. C. *Am. Chem. Soc., Div. Polym. Chem.*, Am. Chem. Soc., Washington, DC, 1960, New York City Meeting, p. 98
22 Reimschuessel, H. K. *J. Polym. Sci., Macromol. Rev.* 1977, **12**, 65
23 Magill, J. H. *Polymer* 1962, **3**, 655
24 Lipshitz, S. D. and Macosko, C. W. *J. Appl. Polym. Sci.* 1977, **21**, 2029
25 Camargo, R. E., Gonzalez, V. M., Macosko, C. W. and Tirrell, M. V. 'Proc. 2nd Int. Conf. Reactive Polym. Processes' (Ed. J. T. Lindt), University of Pittsburgh Press, Pittsburgh, PA, 1982, p. 126
26 Cimini, R. A. and Sundberg, D. C. *Polym. Eng. Sci.* 1986, **26**, 560
27 Reimschuessel, H. K. in 'Ring Opening Polymerization' (Eds K. C. Frisch and S. L. Reegan), Marcel Dekker, New York, 1969, chapter 7
28 Provaznik, M., Puffr, R. and Sebenda, J. *Eur. Polym. J.* 1988, **24**, 511