Kinetics of anionic polymerization of lactams. (Solution of non-isothermal kinetic problems by the inverse method)

A. Ya. Malkin, S. L. Ivanova and V. G. Frolov
Research Institute of Plastics, Perovsky pr. 35, Moscow, USSR 111112

and A. N. Ivanova and Z. S. Andrianova
The Chernogolovka Branch of the Institute of Chemical Physics of the USSR Academy of Sciences, Chernogolovka Moscovskaya oblast, USSR 142432

(*Received* 11 *January* 1980; *revised* 11 *April* 1981)

Wide use has been made of non-isothermic studies for obtaining kinetic data on the anionic polymerization of ϵ-caprolactam and ω-dodecalactam. Data are obtained by measuring changes in reaction temperature, under conditions of heat exchange with the surroundings and by solving the inverse thermophysical problem. This solution yields kinetic constants, which when substituted into heat conduction and kinetic equations minimize the deviations of calculated temperature dependences on time and the deviations in experimental data. Thus, we have studied qualitatively the polymerization of lactams. Numerical values of the basic kinetic constants in the macrokinetic scheme have been determined. Some new effects, such as self-acceleration in the polymerization of caprolactam and the increase of the apparent activation energy at high degrees of conversion in the polymerization of dodecalactam were detected. The approach may be useful in studying other polymerizations.

Keywords Polymerization, kinetics; lactams; polyamides; non-isothermal; activator

INTRODUCTION

The general method for constructing macrokinetic models of polymerization is to measure the way in which the concentrations of the various reactants or reaction products change with time under isothermal conditions.

In practice, the method is tedious, especially if the reaction proceeds with significant heat changes and goes to completion in a short time.

Development of methods based on continuous monitoring of a chosen parameter under non-isothermal conditions with subsequent mathematical treatment of experimental data[1] have therefore become important.

The temperature of the reaction mass is the simplest property to measure. If the reaction takes place under adiabatic conditions, then the change in temperature is directly related to the degree of conversion (extent of reaction).

However, if the heat of reaction is partly dissipated to the surroundings, then polymerization does not proceed *uniformly* throughout the volume of the reaction vessel, and a spatial distribution of temperatures and degrees of conversion arises. This type of non-isothermal scheme (with heat removal) is undesirable in industry since it yields inhomogeneous polymers. But it is experimentally attractive for studying reaction kinetics since the measuring technique is greatly simplified (although the treatment of the results is complicated and requires special computing techniques).

Here, we discuss the possibilities of the non-isothermal method, using, as example, the anionically activated polymerization of lactams (*AAPL*) choosing ε-caprolactam (C_6) and ω-dodecalactam (C_{12}), which polymerize to nylon-6 and nylon-12, respectively. We aim to generalize earlier experimental data[2-4].

The *AAPL* reaction makes is practically possible to produce finished products directly from monomers, omitting any processing stage.

THEORY

When a polymerization reaction takes place in a certain volume (below we consider the case of a spherical reactor) the state of the system is characterized by the temperature $T(r,t)$ and by the degree of conversion $\beta(r,t)$, which are functions of the space coordinate, r, and time, t. Below we consider reactions for which β is the *only* parameter characterizing the degree of conversion (extent of reaction), so that during the reaction β changes from 0 to 1.

Variations in the functions $T(r,t)$ and $\beta(r,t)$ are described by the following system of equations:

$$\frac{\partial T}{\partial t}=a\left(\frac{\partial^2 T}{\partial r^2}+\frac{2}{r}\frac{\partial T}{\partial r}\right)+\frac{Q}{c}\frac{\partial \beta}{\partial t} \tag{1}$$

$$\frac{\partial \beta}{\partial t}=K_0 f(\beta)\mathrm{e}^{-U/RT} \tag{2}$$

where Q is the heat of reaction at $\beta=1$; U is the activation energy for polymerization; R is the gas constant; K_0 is a constant called the pre-exponential factor; $f(\beta)$ is a kinetic function which depends on the reaction mechanism; a is

0032-3861/82/121791-10$3.00

the thermal conductivity; and c is the heat capacity.

Boundary conditions are as follows.

At $r = R_0$:

$$T = T_0 \text{ and } \frac{\partial T}{\partial r} = -\frac{B}{R_0}(T - T_0)$$

At $t = 0$:

$$T = T_0 \text{ and } \beta = 0$$

where R_0 is the radius of the reactor; B is the Biot number characterizing the extent of heat exchange with the surroundings; T_0 is the temperature of the thermostat housing the reactor—polymerization starts at T_0.

For a known reaction (i.e. one for which the values of the constants Q, K_0, U and the function $f(\beta)$ are known) the functions $T(r,t)$ and $\beta(r,t)$ can be found. Determination of these functions is directly achieved by solving the system of equations (1) and (2).

In kinetic studies the inverse problem is of prime interest. The function $T(t)$ is measured at several points (i.e. at different values of r). Values of Q, K_0, U and $f(\beta)$ are then required which can be substituted into equations (1) and (2): subsequent solution of these equations gives values of the functions $T(t)$ (at the points chosen) in best agreement with actual experimental kinetics. Choice of $f(\beta)$ is, of course, the most complicated task.

Measurements of $T(t)$ can be carried out at a small number of points. We confined ourselves to measurements two points: $r = 0$ and $r = R_0$. The experiment thus gave rise to values of the functions $T_c = T_c^e(0,t)$ and $T_R = T_R^e(R,t)$, where the superscript e means 'experimentally-measured'. Calculations using equations (1) and (2) give theoretical values of the functions $T_c^t = T_c^t(0,t)$ and $T_R^t = T_R^t(R_0,t)$, where the superscript t signifies 'calculated values'.

This problem is a member of the class of inverse problems. Its solution relies on the introduction of a function to characterize the standard deviation of the theoretical curves obtained by solving equations (1) and (2) from the corresponding experimental data. The solution to the problem lies in finding the values of the constant for which the standard deviation is lower than a certain value (as a rule, the experimental error). Such a solution is, of course, ambiguous. However, if a set of solutions lie in a defined narrow region, then the problem is considered to have been solved.

Generally speaking, the standard deviation can be chosen in various ways. In the present work we chose it as follows:

$$\Phi = \frac{1}{n}\sum_{i=1}^{n}\left(\sum_{k=1}^{m}\frac{\lambda_k}{4(t_{k+1} - t_k)}\int_{t_k}^{t_{k+1}}\left\{\left[1 - \frac{T_c^t(t)}{T_c^e(t)}\right]^2 + \left[1 - \frac{T_c^e(t)}{T_c^t(t)}\right]^2 + \left[1 - \frac{T_R^e(t)}{T_R^t(t)}\right]^2 + \left[1 - \frac{T_R^t(t)}{T_R^e(t)}\right]^2\right\}\mathrm{d}t\right)^{1/2} \tag{3}$$

where n is the number of sets of measurements (obtained, for example, at different initial temperatures); m is the number of segments resulting from the division of the integration interval; λ_k are the weights of individual segments inside the integration interval (all $\lambda_k = 1/m$ in the simplest case, but this is not always the most convenient example; introduction of various values of λ_k such that:

$$\sum_{k=1}^{m}\lambda_k = 1$$

enables us artificially to enhance the role of the various time intervals—say, at the start or at end of the process).

Success in solving the inverse problem depends both on correct choice of the mathematical model and on the nature and amount of experimental data, i.e. on the informative value of the data. To solve a particular inverse problem it is therefore necessary to separate these two factors and to investigate the informative value of the available set of experimental data either qualitatively or with the aid of a computer with respect to the chosen mathematical model, which is presumed to be exact.

As a numerical experiment, a set of $T(t,0)$ and $T(r,R_0)$ found from equations (1) and (2), at fixed values of K, U, Q and B, and various T_0, are taken as experimental data for the inverse problem. Solution is then sought for by minimizing the function of Φ.

In such an experiment, errors in the model are eliminated, leaving the problem of finding the constants in the specified model. Since the solution is known, the result of the numerical experiment must show if local minima are present in Φ and if the constants (ΔK, ΔU, ΔQ, ΔB) have been accurately enough determined: this latter is shown by the magnitude of Φ. These estimates serve as: (i) criteria for eliminating ambiguities; (ii) criteria for estimating the accuracy of the solution for a real experiment based on this mathematical model; and (iii) as the basis for deciding how accurate is the solution. The inaccuracy here exceeds the estimate of inaccuracy made for the real experiment by the model.

We therefore carried out a computer simulation. The function $f(\beta)$ was assumed to be linear, $f(\beta) = 1 - \beta$. Numerical integration of equations (1) and (2) was carried out by an implicit difference scheme with linearization of $(1 - \beta)\exp(-U/RT)$ for each layer, and solving the corresponding linear system by the fitting method.

Preliminary analysis showed that for the values of the constants to be determined there must be two curves, $T(t,0)$ and $T(t_1,R_0)$, representing two possible different values of T_0. (Data set close together are mainly used to determine the complex quantity $K_0{\cdot}\exp(-U/RT_0)$, as will be shown below for two numerical experiments.)

The initial 'experimental' data used were $T_c^e(0,t)$ and $T_R^e(R_0,t)$ calculated for $B = 0.9$ from equations (1) and (2) using values of K_0, Q and U obtained by adiabatic experiment.

Instead of the required quantities K_0 and U, we chose their combinations, $\hat{K} = K_0{\cdot}\exp(-U/RT_*)$ and $\hat{U} = U/RT_*^2$, which allowed us to avoid frequently-encountered ravines in the minimization of Φ. Here T_* is a particular normalizing temperature. $T_* = T_0$ for a single experiment and if several experiments are involved in the search for the parameters, then T_* is equal to one of the temperatures T_0 (or is the average temperature).

Exact solution of equations (1) and (2), gives $\hat{K} = 0.15$; $\hat{U} = 0.032$ ($U = 12$ kcal mol^{-1}); $B = 0.9$; $Q = 43$ J cm^{-3}; $T_* = 160$°C.

In the first numerical experiment, the experimental data chosen were the functions $T_c^e(0,t)$ and $T_R^e(R_0,t)$ at $T_0 = 160$° and 190°C, and $T_* = 160$°C; in the second experiment, use was made of the functions at initial temperatures:

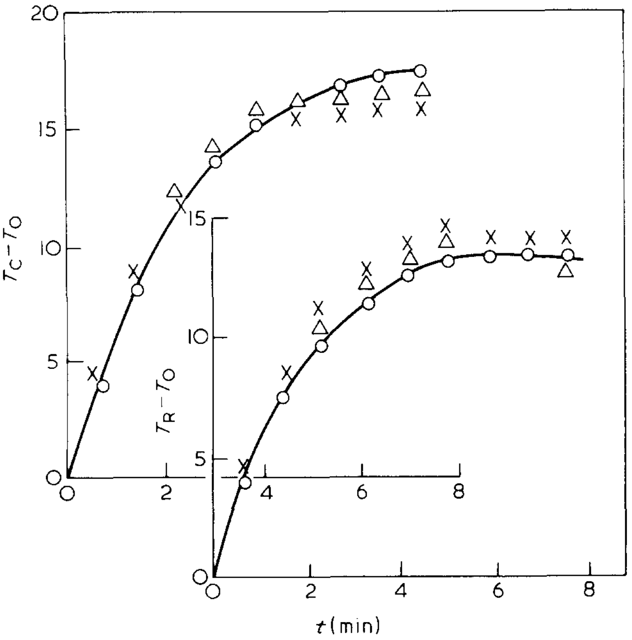


Figure 1 Example illustrating the effect of accuracy (characterized by φ) on the agreement between experimental data (——) and calculation. Values of φ: X, 0.11; △, 0.06; ○, 0.02

$T_0=180°C$ and $190°C$, and $T_*=160°C$.

As a starting point for computations we used values far from the true values: $\hat{K}=0.01$, $\hat{U}=0.1$, $B=0.04$, $Q=2$ J cm^{-3}, which gave $\Phi=73.5$.

Solution of the inverse problem in the first numerical experiment gave: $\hat{K}=0.15$, $\hat{U}=0.0331$, $Q=42.7$ J cm^{-3}, $B=0.878$ and $\Phi=0.01$.

Comparison of the theoretical and initial 'experimental' data is given in *Figure 1*. The following data characterize the accuracy of determining the constants as a function of the standard deviation Φ obtained during minimization:

$\hat{K}$	$\hat{U}$	B	Q	Φ
0.15	0.04	0.575	35.7	0.11
0.15	0.0385	0.5775	39.27	0.06
0.15	0.0339	0.706	41.17	0.02

From this it follows that if the initial experimental data are obtained with an error greater than 6%, the error in the determination, say, of U will be: $U=14.2$ kcal mol^{-1} (calculated); $U=12$ kcal mol^{-1} (true value).

Note that an exact value of K is obtained even if Φ is approximately 10%. Calculations show that unambiguous determination of the Biot parameter by a kinetic experiment is possible only in accurate experiments (error $<1\%$) and hence when an exact model is used. Φ is almost insensitive to the change in Biot parameter. Changing the Biot number within reasonable limits corresponding to the experimental conditions, i.e. from approximately 0.5 to 1.5, does not affect the calculation of kinetic parameters.

Using the above values at $\Phi\approx 6\%$, Q can be determined with an accuracy of up to 10%. The error in determining U includes the error in K_0, calculated as $\Delta K_0/K_0 \propto \Delta\hat{K}/\hat{K}+\Delta\hat{U}.T_*$. The major contribution in calculating the error comes from the $\Delta\hat{U}.T_*$ term in determining K_0. In our case, $0.006\times 433\approx 2.6$ and hence, only the order of magnitude of K_0 can be determined. The model for calculations, however, incorporates K_0 and U in the combinations $\hat{K}$ and $\hat{U}$, which are found with much greater accuracy; it is the values of these combinations that must be used in theoretical calculations, say, in calculating the duration of the process.

Solution of the inverse problem in the second numerical experiment gave the following values:

$$\hat{K}=0.09645;\ \hat{U}=0.05145;\ Q=40.2;\ B=0.76;$$
$$\text{at } \Phi=0.06 \text{ and } T_*=160°C$$

In this numerical experiment the set of experimental data is not informative enough because of the closeness of the initial temperatures corresponding to different experiments. As a result, the parameters $\hat{K}$ and $\hat{U}$ cannot be found with sufficient accuracy: $\hat{K}=0.09645$ instead of 0.15, and $\hat{U}=0.05145$ instead of 0.032; there is good agreement between theoretical and experimental curves (about 6%). Parameters found in the second case make calculations possible only in the temperature region corresponding to experiments involved in the minimization of Φ. The parameters determined in the first numerical experiment make it possible to interpolate the results over a sufficiently wide temperature range.

The rate constant $K(T)$ calculated for $T_0=190°C$ from the parameters found in the first numerical experiment is in good agreement with the rate constant found in the second experiment (0.411 and 0.405).

Calculations have shown that if the experimental data are informative enough (as in the first numerical experiment), the choice of the initial point in minimizing Φ does not affect the accuracy of the determination of the parameters required. In a case where the experiment provides little information (as in the second numerical experiment), the results depend on the choice of initial point.

EXPERIMENTAL

Experiments were carried out on ε-caprolactam and ω-dodecalactam. Monomers were preliminarily dried in a vacuum cabinet at a residual pressure of 5–10 mmHg and at temperatures ranging from 50° to 55°C for 20 h. The experimental setup is shown in *Figure 2*. Each monomer was melted in vessel 1. The catalyst (sodium metal or sodium-caprolactam) was introduced in a specified quantity into the melt. A solution of the activator in the monomer was prepared in vessel 2 in a similar way. The molar concentration of active groups in both solutions was the same. This means that when a monofunctional activator was used, its concentration was equal to the catalyst concentration. When a bifunctional activator was used, its concentration was half the catalyst concentration.

The components were mixed in a connecting pipe 3 leading to a spherical reactor 4, and in the reactor itself. Reactor capacity was about 260 cm^3. Vessels used to prepare the components of the reacting mixture and the main reactor were kept in a thermostat. Prior to the experiment the entire system was purged with argon.

The main parameter to be measured was the temperature, which was determined and continuously recorded for two points, 6 and 6′.

The values of the thermophysical parameters of the system were determined in a 'blank' experiment. To do this, polymer-in-monomer solutions of different

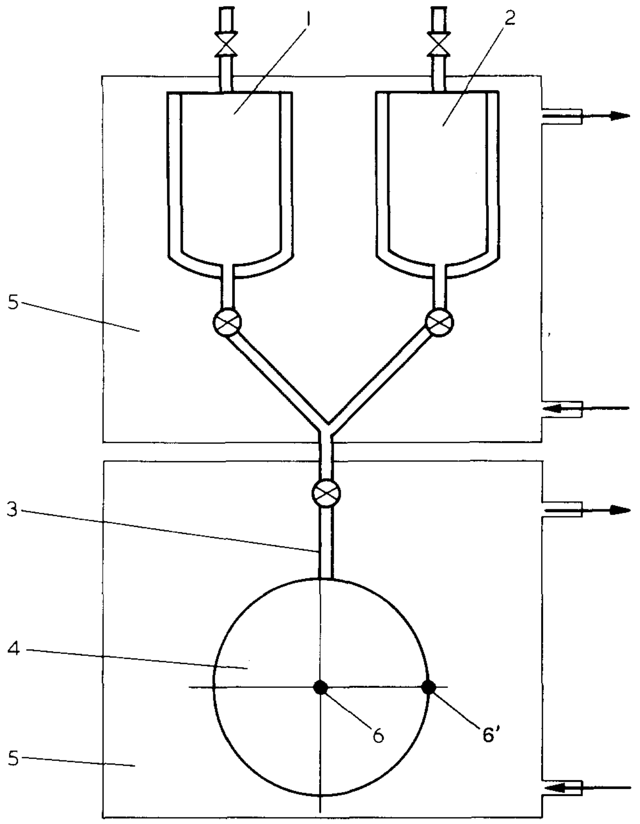


Figure 2 Schematic representation of the apparatus: 1 and 2, vessels for preparing solutions of the catalyst and activator in lactam; 3, mixing pipe; 4, main reactor; 5, thermostat; 6 and 6', thermocouple attachments made

concentration were prepared without introducing any catalyst. The reaction vessel 4 was heated to a chosen temperature, exceeding the thermostat temperature T_0 by 26°–40°C, and was then placed in the thermostat.

From the results of the temperature changes with time at $r=0$ and $r=R_0$, which are comparable with the known solutions of standard heat-exchange problems, we found the values of the thermophysical constants of the reaction mass. Values of a and B had errors of up to 10%. Changes in coefficients of the same order of magnitude arise from the changes in solution concentration (simulating the variation in polymer concentration in the reaction mass during polymerization).

The calculation shows that the variation in thermophysical constants within the limits indicated has no effect whatsoever on the determination of kinetic parameters. For this reason we considered only the average values of the thermophysical constants and neglected possible changes in them.

The only activator used for polymerizing dodecalactam was *N*-acetylcaprolactam. Polymerization of caprolactam was carried out with a number of activators (*Table 1*). Various initial temperatures T_0 were used and the catalyst concentration [C] ranged from 0.0175 to 0.075 mol l^{-1} (from 0.35 to 1.5 mol %). Activator concentration [A] was equal to $[A]=[C]/N$, where N = the functionality of the activator.

Under non-isothermal conditions, no simple relationship exists between the heat effect (as estimated from the rise of temperature) and the extent of reaction. In the special case of adiabatic polymerization, however, there is a linear correlation between the temperature increment and the extent of reaction. Thus, if the overall heat effect for polymerization reaction is Q, and the heat capacity of the reaction mass, c, then the maximum temperature rise, Δ, with respect to the initial temperature is $\Delta=Q/c$. The extent of reaction β is then related to the temperature T by a simple formula:

$$\beta=(T-T_0)/\Delta \qquad (4)$$

If the polymerization proceeds sufficiently rapidly, conditions close to adiabatic are realized in the centre of the reaction vessel, and in this case the quantity Δ measured (at $r=0$) with an error of 2–3% corresponds to the independently found heat of reaction.

If polymerization takes place sufficiently slowly, conditions close to adiabatic can be created in the following way. A follow-up system was built, which increased the temperature of the thermostat immediately after the temperature T_c changed (at $r=0$). This makes it possible to sharply reduce the heat removal from the thermostat.

Direct measurements show that when this procedure is used the heat loss with respect to Q does not exceed 4% at worst (for more detail, see ref. 2).

The adiabatic scheme for polymerization was used in the present work to control those results based on the treatment of the data from non-isothermal investigations (with heat removal). This was achieved by substantial simplification in the treatment of experimental data without avoiding the problem of heat removal, using the method described in the literature[5].

RESULTS AND DISCUSSION

Dodecalactam

In investigating the *AAPL* reaction for C_{12} the kinetic function $f(\beta)$ was assumed to be of the form: $f(\beta)=(1-\beta)$, i.e it was presumed that *AAPL* occurs by a first-order reaction. The agreement between T^e and T^t is illustrated in *Figure 3* which shows the corresponding dependences. It is clear that the inverse method of solution gives rise to

Table 1 Activators used in AAPL of caprolactam

Activator	Abbreviation	Functionality in *AAPL* reaction	T_{melt} (°C)
Phenylcarbamoyl caprolactam	PhCCl	1	67
p-Chlorophenylcarbamoyl caprolactam	*p*-ChPhCCl	1	117
m-Chlorophenylcarbamoyl caprolactam	*m*-ChPhCCl	1	74
m,p-Dichlorophenylcarbamoyl caprolactam	DChPhCCl	1	122
2,4-Toluylene-bis-carbamoyl caprolactam	2,4-TCCl	2	169.5
2,6-Toluylene-bis-carbamoyl caprolactam	2,6-TCCl	2	–
Mixture of 2,4- and 2,6-toluylene-bis-carbamoyl caprolactams (63/35)	TCCl	2	145
4,4-Diphenylmethane-bis-carbamoyl caprolactam	DPhMCCl	2	174
Hexamethylene-bis-carbamoyl caprolactam	HMCCl	2	77.5
N-Acetylcaprolactam	AcCl	1	–

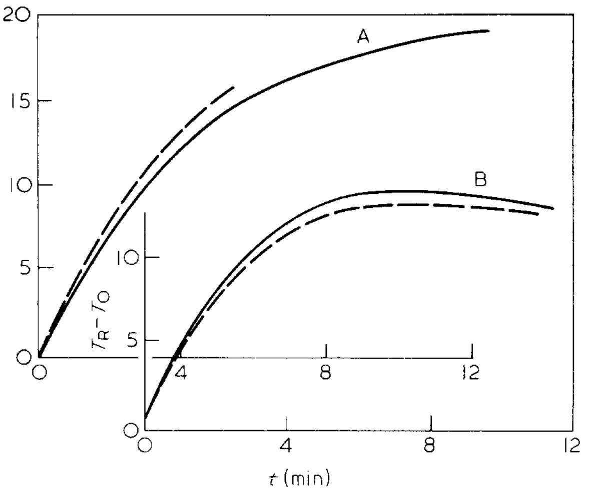


Figure 3 Comparison of experimental (——) and calculated (— — —) dependences $T(t)$ in the centre (A) and at the walls (B) of the reactor for polymerization of dodecalactam. Experimental conditions: [C] = [A] = 4.45×10^{-2} mol l^{-1}; T_0 = 190°C

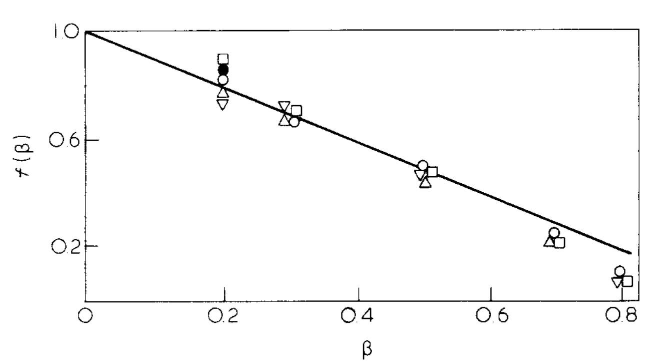


Figure 4 Determination of the kinetic function $f(\beta)$ for C_{12} *AAPL*. Straight line corresponds to $f(\beta) = 1 - \beta$. Values of [C] = [A], mol %: ●, 0.35; □, 0.5; ○, 0.75; △, 1.0; △, 1.5

satisfactory agreement between T^e and T^t and enables us to determine the kinetic constants Q, U and K_0 for the kinetic function chosen, $f(\beta)$.

According to the data obtained, $Q = 10$ kcal cm^{-3}, $U = 12$–13 kcal mol^{-1}. The resulting value of Q exceeds the value given by Schaaf[6], but Schaaf does not use a method for taking into account (or eliminating) the error associated with heat removal, so his value of Q is evidently underestimated. Using maximum catalyst concentration we obtained even higher (by 15%) values of Q. These high values are probably associated with additional heat effects due to secondary reactions.

The most controversial point here is the choice of kinetic function. To obtain independent information on this question, use was made of experimental data from the adiabatic scheme with the temperature of the thermostat being brought up to the temperature of the reaction mass. Treatment of the experimental data was as follows[5].

From the dependences $\beta(t)$ and the parallel dependences $T(t)$ there were chosen the values (at t = the same) of β and T. The values of the reaction rates $d\beta/dt$ at these times were found. Then, for a series of fixed β there can be plotted the dependences of $d\beta/dt$ on T, allowing us to calculate the activation energy U (for various β) and also to find 'from the points' the values of the kinetic function $f(\beta)$, computed with the aid of equation (2) as follows:

$$f(\beta)=\frac{1}{K_0}\frac{d\beta}{dt}e^{U/RT} \qquad (5)$$

and the constant K_0 is chosen such that the condition $f(0) = 1$ is automatically satisfied. The results of determining $f(\beta)$ based on adiabatic measurements and from equation (5) are presented in *Figure 4*.

Data obtained by the adiabatic method convincingly confirm that *AAPL* for C_{12} can be described by a first-order equation with values of β up to 0.7.

Consideration of the temperature dependence of the polymerization rate shows that, with β up to about 0.35, the activation energy is 12 kcal mol^{-1}, which is consistent with the value found by solving the inverse problem. With large degrees of conversion the apparent or Arrhenius activation energy of polymerization increases to 20 kcal mol^{-1}. This phenomenon may be insignificant in solving the inverse problem of non-isothermal kinetics since this solution gives averaged values based on equation (2), in which it is assumed before hand that U = constant. But it is important for understanding the mechanism of *AAPL*. The point is that the *AAPL* reaction starts in the homogeneous region. But, as has been shown by plotting a phase diagram for nylon-12 in dodecalactam[7] and a parallel study of the polymerization kinetics, as the polymerization proceeds the system moves to the heterogeneous region because amorphous phase separation occurs in the polymerizing mass. This may be responsible for the increase in apparent activation energy when compared with the initial value of U, corresponding to small β values.

For practical purposes, however, it may be assumed that $U = 12$ kcal mol^{-1} with a corresponding correction being introduced into the pre-exponential factor.

To complete the consideration of the *AAPL* for C_{12} the role of the activator concentration [A] must be investigated. As seen from *Figure 4*, it does not affect the form of $f(\beta)$, nor does it affect the activation energy. But [A] has a strong influence on the value of the pre-exponential factor K_0, the value of which depends on the activator concentration [A] in a linear manner, as seen from *Figure 5*, i.e.

$$K_0 = k[A] \qquad (6)$$

where $k = 5.6 \times 10^6$ l $(mol\ min)^{-1}$, i.e. *AAPL* for C_{12} has an overall order of 1.0 with respect to the activator and the catalyst (their concentrations are equal).

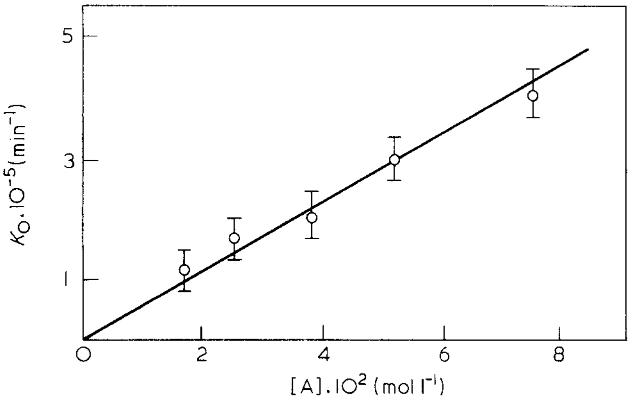


Figure 5 Dependence of the pre-exponential factor (*AAPL* of C_{12}) on activator concentration ([C] = [A])

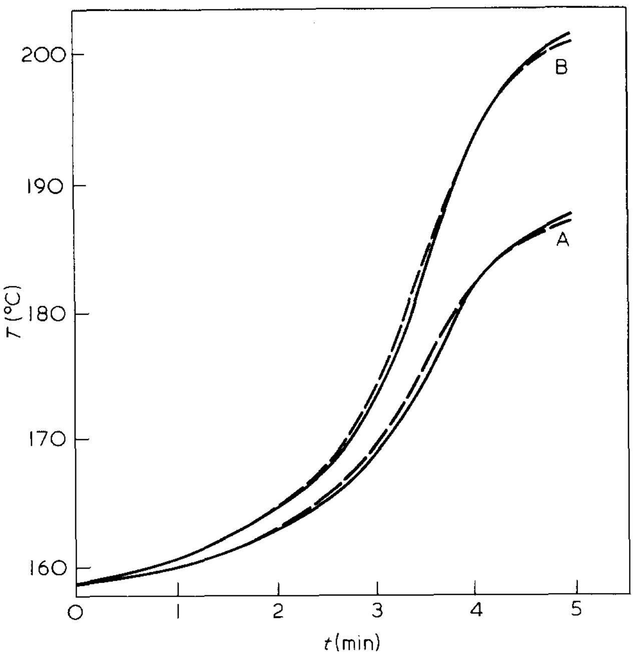


Figure 6 Comparison of experimental (——) with calculated (– – –) dependences $T(t)$ at the wall (A) and at the centre (B) of the reactor (*AAPL* of C_6) using AcCL as activator. Experimental conditions: [C] = [A] = 4.45×10^{-2} mol l^{-1}

Thus, summing up the results, it may be said that *AAPL* for C_{12} is described by the following equation:

$$\frac{d\beta}{dt} = 5.6 \times 10^6 \times [A] \times (1-\beta)e^{(-12000/RT)} \qquad (7)$$

where the activator concentration [A] is expressed in mol l^{-1}.

It should be noted, however, that the applicability of this equation (and, in particular, the separated values of the reaction order with respect to the activator and catalyst) at different catalyst–activator ratios has not been tested.

Caprolactam

In spite of the fact that *AAPL* for C_6 has long been described in sufficient detail in the literature[8] and the chemistry of this reaction has been thoroughly studied[9], the data available on the kinetics of *AAPL* for C_6 and on numerical values of the constants that characterize it are rather contradictory.

For example, in a number of investigations (see refs 10 and 11), accomplished by a sampling procedure under isothermal conditions, the activation energy ranged from 16 to 22 kcal mol^{-1}.

At the same time, when the kinetics of *AAPL* were studied by observing temperature increases[12], the values of U obtained were close to 45 kcal mol^{-1}. In all cases, the reaction order of *AAPL* for C_6 was assumed to be first order in the monomer, i.e. it was assumed, just as in the case of C_{12}, that $f(\beta) = 1 - \beta$ for caprolactam.

Solution of the inverse problem, the principal method used in the present work, has led to substantially more complicated results. If $f(\beta)$ is assumed to have the form $f(\beta) = 1 - \beta$, then more or less satisfactory agreement between $T^e(t)$ and $T^t(t)$ can be achieved, the average discrepancy between experimental and theoretical curves being about 10%. But it has been found that when a linear form for $f(\beta)$ is assumed qualitative agreement cannot be achieved between experimental and theoretical curves. In particular, the data on one of the basic kinetic characteristics of the process—the time to reach maximum reaction rate, i.e. the position of the maximum in $d\beta/dt$—and the inflection points in $T(t)$, are found to be in disagreement.

A completely analogous situation occurs if it is assumed that *AAPL* for C_6 is described by the power equation $f(\beta) = (1-\beta)^n$, where n may be either an interger or a fraction (calculations were carried out for the $n = 0.5$, 1 and 2.5). This contradiction implies that a kinetic equation of the form $f(\beta) = (1-\beta)^n$ does not represent the actual mechanism of the *AAPL* reaction for C_6. The solution of this contradiction lies in choosing a 'correct' macrokinetic function $f(\beta)$. The method of treating the experimental data by solving inverse problems provides a reliable means of separating the various functions $f(\beta)$ into those known to be incorrect, say, those of the form $(1-\beta)^n$ and those which are possible (but not necessarily true) for the observed *AAPL*. Indeed, the inverse method does not reveal the analytical form of the function $f(\beta)$ corresponding to the true molecular polymerization mechanism. However, it enables us to find an adequate macrokinetic model capable of describing (with a desirable degree of accuracy) the observed experimental data and of formally approximating the true parameters of the process with the aid of a convenient analytic expression.

In the case of the *AAPL* reaction for C_6, a function $f(\beta)$ of the following form is such a macrokinetic model, corresponding to experimental data:

$$f(\beta) = (1-\beta)(1 + C_0\beta) \qquad (8)$$

where C_0 is a new kinetic constant which characterizes the intensity of self-acceleration (autocatalysis) of the *AAPL* reaction. Only at $C_0\beta \ll 1$, i.e. in the initial stages of the process, may the *AAPL* reaction for C_6 be described by a first-order equation.

Solution of the inverse problem using equation (8) yields fairly good results, as illustrated by the example in *Figure 6*. In all other cases the results obtained by using the kinetic function $f(\beta)$ in the form (8) are as good.

Thus, self-acceleration is a new phenomenon characteristic of ε-caprolactam in the *APPL* reaction. Further discussion of the kinetic features of the reaction based on the use of various kinetic schemes and also on the temperature and concentration variations of the catalytic system should be carried out in terms using the model (8), that is, using values of the constants K_0, C_0, U and Q. For sake of comparison, we shall make use of somewhat altered constants. Equation (2) is rewritten introducing the initial monomer concentration, $[M]_0$. Then, $\beta = ([M]_0 - [M])/[M]_0$, where [M] is the instantaneous monomer concentration, and equation (2) then takes on the following form:

$$\frac{d([M]/[M]_0)}{dt} = -\bar{K}_0 \frac{[M]}{[M]_0}\left[1 + C_0\left(1 - \frac{[M]}{[M]_0}\right)\right] \qquad (9)$$

where $\bar{K}_0 = K_0[M]_0$ has the dimensions of mol (litre min)$^{-1}$.

For the activator (AcCl), the values of the kinetic constants presented in *Table 2* were obtained.

Table 2 Values of kinetic constants for the polymerization of caprolactam activated by AcCl

Concentration of catalyst						
[C] x 10^2 (mol l^{-1})	[C] (mol %)	$\bar{K}_0 \times 10^{-7}$ [mol (l min)$^{-1}$]	U (kcal mol^{-1})	Q (cal g^{-1})	C_0	$\bar{C}_0 = C_0\bar{K}_0 \times 10^{-8}$, [mol (l min)$^{-1}$]
2.67	0.3	0.58	16.8	30.5	25	1.5
4.45	0.5	1.49	15.0	29.5	22.5	3.4
6.23	0.7	2.71	13.5	28.0	15.8	4.4
8.90	1.0	6.22	16.8	30.0	8.1	5.1

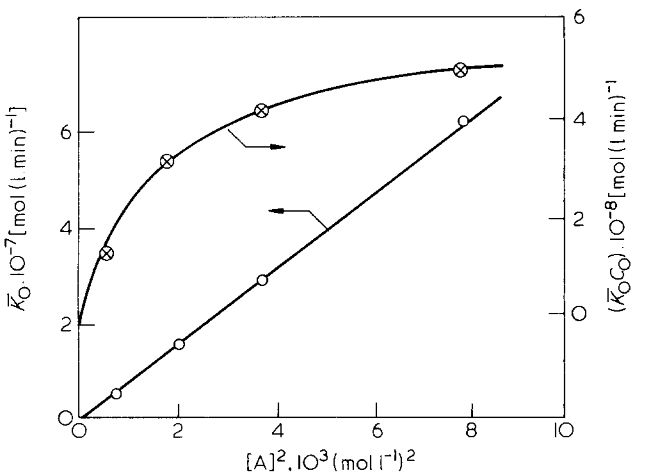


Figure 7 Dependence of kinetic constants on catalyst concentration [C] (*AAPL* of C_6). Activator used, AcCl

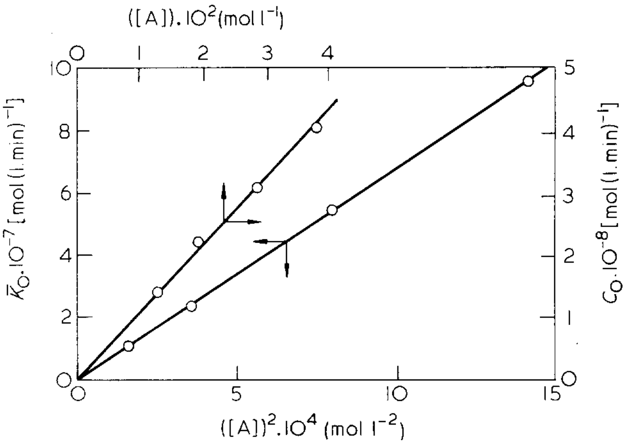


Figure 8 Dependence of kinetic constants on catalyst concentration ([C] = [A], *AAPL* of C_6). DPhCCl activator

The quantity $\bar{C}_0 = C_0\bar{K}_0$ included in *Table 2* characterizes the degree of self-acceleration of the *AAPL* reaction for C_6. As the concentration of the catalytic system increases, so does $C_0\bar{K}_0$. No substantial change in $C_0\bar{K}_0$ is observed, however, for the same catalytic concentration at different initial reaction temperatures.

It should be noted that the values of activation energy presented in *Table 2* are averaged. They were obtained assuming that the temperature dependence of the two kinetic constants are the same. This is not necessarily true in all cases, considering that the mere appearance of the second kinetic constant C_0 reflects the possible occurrence of a second reaction, apart from chain growth. The two reactions are generally characterized by the rate of reaction and, possibly, by the temperature dependence of this rate, i.e. by the activation energy. Indeed, agreement between the calculated dependences $T(t)$ and experimental data can be improved to an even larger extent if each of the constants has its own value of activation energy. Values of U are found to be somewhat different, but not by too great an amount. This effect is thus disregarded in the present treatment.

Table 3 Values of kinetic constants k and m for a number of activators

Activator	$k \times 10^{-10}$ [l (mole/min)$^{-1}$]	m (mol l^{-1})
AcCl	0.77	0.93
PhCCl	2.22	0.36
2,4-TCCl	2.70	0.70
DPhMCCl	6.70	0.16
HMCCl	10.0	0.033

The dependence of the kinetic constants on the activator concentration is shown in *Figure 7* and an example (*AAPL* activated by DMMCCL) is given in *Figure 8*. From these data it is seen that K_0 and $\bar{K}_0$ are proportional to the square of the activator concentration and $\bar{C}_0$ is proportional to the [A] (in experiments where $[A]=[C]/N$ is fulfilled). From this it follows directly that C_0 is inversely proportional to [A].

Thus, the results obtained for C_6 can be regarded as experimental proof of the applicability of the following equation for *AAPL* (at $[A]=[C]/N$):

$$\frac{d\beta}{dt}=k\frac{[A]^2}{[M]_0}(1-\beta)\left(1+\frac{m\beta}{[A]}\right)e^{-U/RT} \qquad (10)$$

where m is the proportionality constant in the dependence of C_0 on the catalyst concentration.

The value of constant k, the pre-exponential factor, allows us to compare the efficiency of using various activators in the initial stage of the process (at $\beta \ll 1$). The value of m describes the intensity of self-acceleration effect during chain growth. Values of these constants for some of the activators used are given in *Table 3*.

Thus, for all the activators chosen, *AAPL* for C_6 is characterized by a self-acceleration effect; the values of the constant C_0, which characterize its role, are high, so this phenomenon is important for the kinetics and mechanism of the reaction concerned. At the same time, the form of the function adopted here, $f(\beta)=(1-\beta)\times(1+C_0\beta)$, is nothing more than a convenient approximation.

To test the correctness of the choice of the kinetic function an attempt was made (as in the case with C_{12}) to treat the experimental data independently using adiabatic polymerization conditions by means of a method[5] which

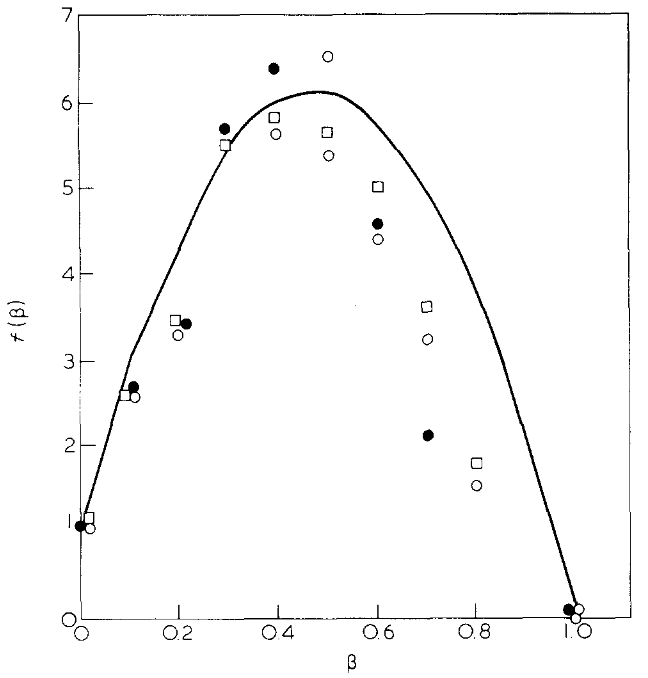


Figure 9 Comparison of kinetic function $f(\beta) = (1-\beta) \times (1 + 22.5\beta)$ derived by inverse solution of the non-isothermic kinetics (——) with values of $f(\beta)$ calculated from the data obtained by adiabatic measurements using the differential method (○, ●, ■). Data given refer to the following polymerization conditions: [C] = [A] = 4.45×10^{-2} mol l^{-1}; initial temperatures, T_0 (°C): ○, 151; ●, 159; ■, 170

does not involve an *a priori* approximation for the function $f(\beta)$. An example of the treatment of the experimental data by this scheme, described in detail for C_{12}, is shown in *Figure 9.*

The application of this calculation scheme requires a vastly larger amount of experimental data than the solution of inverse non-isothermal problems, and is limited by the errors of graphical differentiation. Nonetheless, it has an advantage in that it does not require the assignment of the function and allows us to obtain independently the values of E and $K_0[f(\beta)]$. From the example given in *Figure 9* it follows that a dependence of the form $f(\beta) = (1-\beta)(1 + C_0\beta)$ with a suitable value of the parameter C_0 *does* describe the experimental data obtained by a different method in which the function $f(\beta)$ is not specified. Naturally, the values of K_0 obtained by the different methods are found to be consistent. The activation energy obtained by this method is 15 ± 2 kcal mol^{-1}, irrespective of the concentration of the catalytic system, and this value is maintained up to high degrees of conversion. The same range of activation energy was obtained using this differential method for the other catalytic systems.

Thus, we have obtained direct agreement between results from two fundamentally different methods (the adiabatic method and the non-isothermal method with removal of heat). Thus, the results obtained and, in particular, the general conclusion that self-acceleration of the *AAPL* reaction occurs for C_6 may be considered reliable.

A different picture results when attempts are made to ust the non-isothermal method[12] specifically for *AAPL* proposed. In this method, the function $f(\beta)$ is specified *a priori* and the criterion for choosing it is the desire to linearize the experimental data in the coordinates log $[1/(T_{max} - T_0)^n(dT/dt)$ vs. T^{-1}, where n is an arbitrarily chosen reaction order. This method follows directly from the substitution of a function of the form $(1-\beta)^n$ (after replacing β by temperature) into the basic kinetic equation (2).

After separating the variables in the equation:

$$\frac{1}{T_{max}-T_0}\frac{dT}{dt}=K_0\left(1-\frac{T-T_0}{\Delta}\right)^n e^{-U/RT} \qquad (11)$$

and taking logarithms we obtain [12] an equation for calculating the kinetic constants which requires the experimental data to be represented in the above-indicated coordintes. Instead of temperature, we may use β as the variable and represent the experimental data in the coordinates log $[(1-\beta)^n(d\beta/dt)]$ vs. T^{-1}, where the choice of n is again dictated by the possibility of linearizing the experimental data.

For the experimental dependences $T(0,t)$, i.e. for the centre of the reactor, where nearly adiabatic conditions are maintained, the above graph can be plotted with $n = 2$, as seen from *Figure 10.* The activation energy calculated from this Figure is 40–50 kcal mol^{-1}, consistent with the original data[12]. From what has been said it follows, however, that such a result is erroneous because of the incorrectness of the function $f(\beta)$ adopted. A consequence of this is the sharply overestimated value of activation energy as compared with the true value which is close to 16 kcal mol^{-1}.

An essential point here is that the latter value, obtained by us using theoretical methods from non-isothermal measurements, is in good agreement with the value obtained by direct methods using the ampoule procedure under strictly isothermal conditions[10,11].

Thus, a theoretical analysis of non-isothermal *AAPL* for C_6 has enabled us to establish that the reaction takes place with self-acceleration (autocatalytically); its activation energy is 15 ± 1.5 kcal mol^{-1} up to high degrees of conversion; the initial reaction rate is proportional to the product of the activator and catalyst concentrations (the activator and the catalyst are present in the system in an equimolecular ratio).

The reaction mechanism responsible for self-

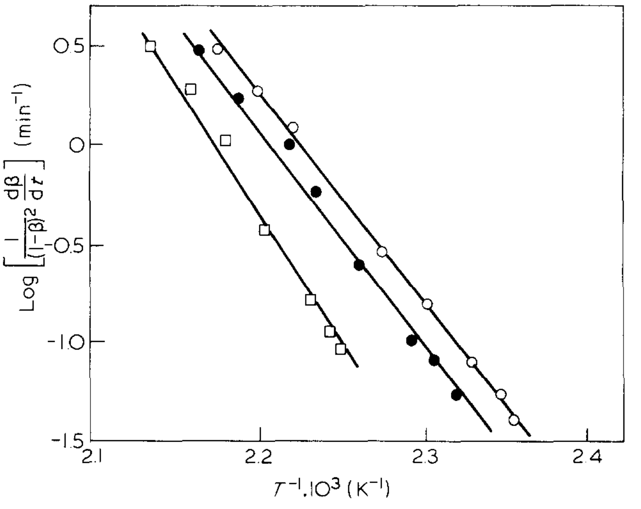


Figure 10 Calculation of activation energy for *AAPL* of C_{12} carried out as described in the literature[12]. Polymerization conditions: [C] = [A] = 2.67×10^{-2} mol l^{-1}; initial temperatures T_0 (°C): ○, 151; ●, 159; ■, 170. Activator used, AcCl

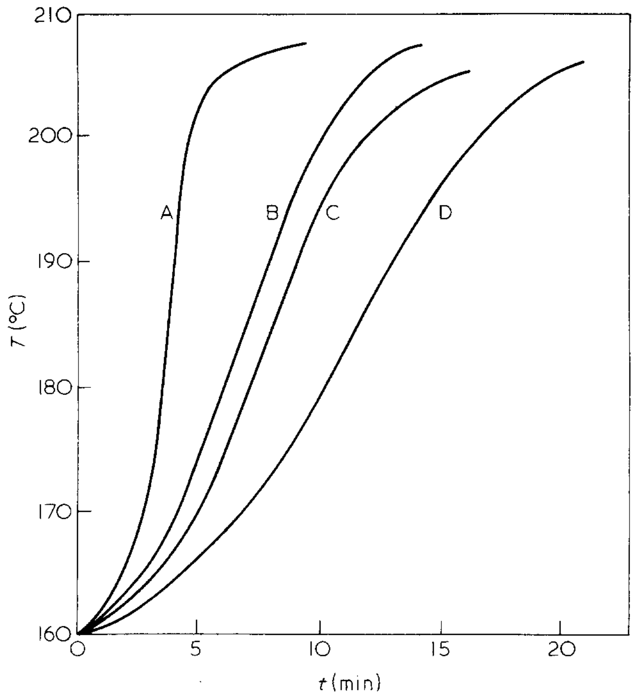
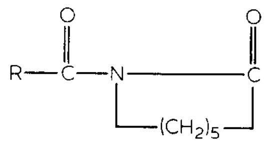


Figure 11 Comparison of the rates of variation of the temperature of the reaction mass for caprolactams. Chloro-substituted carbamoyl caprolactam activators A, PhCCl; B, p-ChPhCCl; C, *m*-ChPhCCl; D, DChPhCCl. Polymerization conditions: [C] = [A] = 2.67×10^{-2} mol l^{-1}. T_0 = 160°C

acceleration deserves special consideration, but this is beyond the scope of the present work. We shall only point out, as a first approximation, that *AAPL* may occur by a stepwise mechanism and the rate of the first elementary stem—the interaction between activator and catalyst—may differ from the rate of chain-growth which involves the addition of the lactam to the active centre formed.

The effect of the chemical structure of the activator on the rate of *AAPL* deserves a somewhat more detailed consideration. In our work we made use of activators of general formula represented as follows:



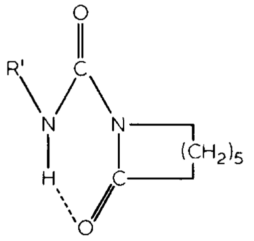
In general, the radical R exhibits electron-acceptor properties which enhance polarization of the imide group in the direction of the electrophilic substituent, facilitating nucleophilic attack of the anion of the lactam on the positively charged carbonyl group[9].

This explains why a phenyl group exerts a stronger activating effect than does an acyl group: the phenyl radical has more pronounced electron-acceptor properties.

This, however, does not exhaust the role of the activator. The activating power of adducts of aromatic diisocyanates is greater than that of AcCl or PhCCl. This can be accounted for by the mutual effects of carbamoyl groups, each of which has comparatively weak electron-accepting properties. Further increase of the electronegativity of the radical R for carbamoyllactams does not lead to a corresponding increase in the rate of polymerization; on the contrary, the reaction rate is lowered. This is well illustrated in *Figure 11*, which compares the kinetic curves for the chloro-derivatives of PhCCl. The strong electron-accepting substituent introduced not only increases the electronegativity of the radical R but also leads to an increase in the acidity of the nitrogen atom of the carbamoyl group[13], thereby reducing the basicity of the caprolactam anions and, hence, the catalytic activity.

Thus, by considering a series of aromatic carbamoyllactams as *AAPL* activators for C_6 it follows that there exists an optimum electronegativity of the substituent at which the rate of the reaction is maximized. It is interesting to note that the experiments carried out using various isomers of TCCl (i.e., 2,4- and 2,6-TCCl) and their blends have shown that the position of the second carbamoyl group does not affect the rate of *AAPL* (*Figure 12*).

Of all the activators studies, HMCCl displays the highest activating ability. This result agrees with the data for HMCCl in the literature[13]. Perhaps, the high activity of HMCCl may be explained[14] by the formation of intramolecular hydrogen bonds in alkyl carbamoyl lactams:



This leads to stabilization of the polar structure with a carbonyl bond. Otherwise, it would be difficult to account for the high activity of HMCCl since it is clear that

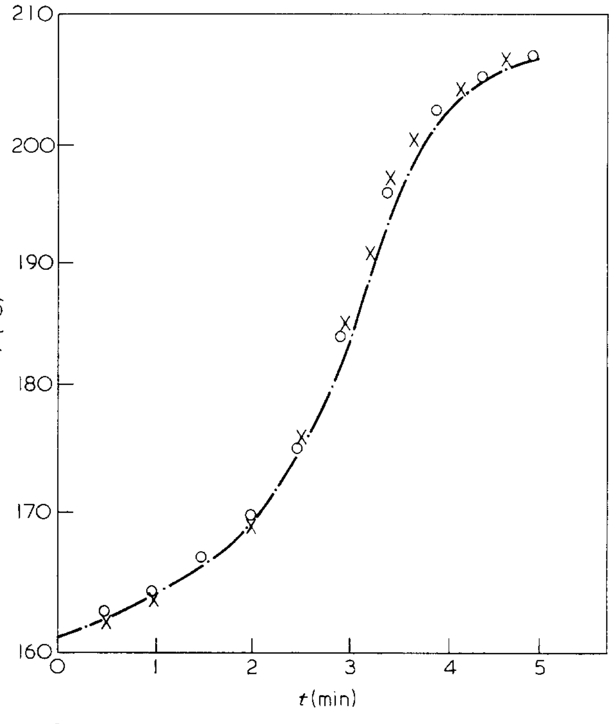


Figure 12 Comparison of rates of variation of the temperature of the reaction mass, using the following compounds used as activators: O, 2,6-TCCl; X, 2,4-TCCl; (— · — · —), blends of 2,4- and 2,6-TCCl Polymerization conditions: [C] = 2.67×10^{-2} mol l^{-1} [A] = 1.325×10^{-2} mol l^{-1}. T_0 = 160°C

aromatic isocyanates must be much more active than aliphatic isocyanates in reactions with compounds having a mobile proton.

CONCLUSIONS

Non-isothermal methods of investigation are efficient in determining the chemistry and mechanical properties of polymers[1]. With a limited amount of experimental data they furnish an incomparably larger body of information than the corresponding isothermal methods.

Furthermore, an experiment carried out under non-isothermal conditions is as a rule, simpler both in procedure and apparatus. Treatment of the data obtained by a non-isothermal method is incomparably more complicated since it is based in most cases on the use of computers.

Here, wide use has been made of the non-isothermal method for obtaining kinetic data for the anionic ally-activated polymerization of ε-caprolactam and ω-dodecalactam. Data were obtained by measuring changes in the temperature of the reaction mass which was allowed to undergo heat exchange with the surroundings. The inverse thermo-physical problem was then solved.

Such a solution yields values of the kinetic constants, which when substituted into the heat conduction and kinetics equations minimize the deviations of the calculated dependences of temperature on time and the deviation of the experimental data.

In this way we made a qualitative study of the polymerization of lactams. Numerical values of the basic kinetic constants in the macrokinetic scheme were determined, and some new effects, such as self-acceleration during the polymerization caprolactams and the increase in apparent activation at high degrees of conversion (polymerization of dodecalactam) were detected.

The approach proposed in the present paper may be useful in studying other polymerizations.

REFERENCES

1 Stolin, A. M., Malkin, A. Ya. and Merzhanov, A. G. *Polym. Eng. Sci.* 1979, **19**, 1065

2 Malkin, A. Ya., Ivanova, S. L. and Korchagina, M. A. *Vysokomol. Soedin. (A)* 1977, **19**, 2224

3 Malkin, A. Ya., Ivanova, A. N., Ivanova, S. L. and Andiranova, Z. S. *Inzh.-Fiz. Zhurn.* 1978, **34**, 636

4 Malkin, A. Ya., Ivanova, A. N., Frolov, V. G. and Andrianova, Z. S. *Vysokomol. Soedin. (A)* 1979, **21**, 632

5 Merzhanov, A. G., Abramov, V. G. and Abramova, L. T. *Doklady Akad. Nauk SSSR* 1966, **171**, 901

6 Schaaf, S. *Kunststoffe-technol.* 1969, **12**, 455

7 Kulichikhin, S. G. and Malkin, A. Ya. *Vysokomol. Soedin. (B)* 1979, **21**, 444

8 Heikens, D. *Makromol. Chem.* 1956, **19**, 62

9 Sebenda, D. *J. Macromol. Sci. (A)* 1972, **6**, 1145

10 Sittler, E. and Sebenda, J. *Collect. Czech. Chem. Commun.* 1976, **33**, 270

11 Fabri, G. and Talamini, G. *J. Polym. Sci. Polym. Lett.)* 1975, **13**, 469

12 Wittmer, P. and Gerens, G. *Makromol. Chem.* 1965, **89**, 27

13 Stehlicek, J., Gehrke, K. and Sebenda, J. *Collect. Czech. Chem. Commun.* 1967, **32**, 370

14 Falkenstein, G. and Dorfel, H. *Makromol. Chem.* 1969, **137**, 34