# The exothermal effects of superimposed processes of activated anionic polymerization of ε-caprolactam and crystallization of the polymer formed

**A. Ya. Malkin**
*Research Institute of Plastics, USSR*, 111112, *Moscow E*-112, *Perovsky proezd* 35, *USSR*

**and V. P. Beghishev and S. A. Bolgov**
*Institute of Continuum Mechanics of the Urals Research Centre of the USSR Academy of Sciences, Perm'*, 614013, *USSR*

(*Received* 11 *August* 1980; *revised* 3 *June* 1981)

We have carried out a calorimetric investigation of the anionic polymerization of ε-caprolactam and of the crystallization of the polymer produced. Measurements were made at 160°–190°C under isothermal conditions with the use of activators of various chemical types and functionality. We have obtained the kinetic constants of the polymerization reaction which agree with the values found earlier in a non-isothermal experiment. The autocatalytic nature of this reaction has also been confirmed. The kinetics of the crystallization of poly-ε-caproamide have been studied and the values of the kinetic constants found. It has been shown that an increase in the functionality of the activator slows down the crystallization and increases the degree of crystallinity of the end product. A method is proposed for the calculation of the overall exothermal effect for the temperature range within which the polymerization and crystallization proceed simultaneously. This method is based on the assumption that only the polymerized portion of the reaction mass can be crystallized. The method has been verified by the experimental data obtained.

**Keywords** Polymerization; crystallization; exothermal effects; ε-caprolactam; calorimetry; kinetics

## INTRODUCTION

In polymer chemistry and technology there are many cases where the polymerization (or polycondensation) and crystallization of the product occur simultaneously. In fact, this situation is encountered at all times when the formation of macromolecules takes place at a temperature below the melting temperature of the polymer. An analysis of such processes calls for a joint consideration of the kinetics of the polymerization and crystallization. Such a combined treatment becomes especially important when the course of the process is judged by the exothermal effect, which reflects both phenomena, i.e. polymerization and crystallization. As far as we know, no general approach has been described in the literature to the solution of the problem of separation of the enthalpy effects attending the simultaneous occurrence of such processes. At the same time, the necessity of a search for such a solution is dictated by the difficulties that actually exist in the analysis of the kinetics of different concurrent processes. The aim of the present work is to consider problems of this kind for the case of the anionic activated polymerization of ε-caprolactam (AAPC), which takes place at a temperature below the melting temperature of the polymer produced.

The kinetics of AAPC have been studied by the method of solution of the inverse non-isothermal problem[1]. This is an indirect method. It has demonstrated, however, the main specific features of AAPC and it has primarily shown that AAPC proceeds with auto-acceleration. The macrokinetics of this reaction can be described by an equation of the autocatalytic type:

$$\frac{d\beta}{dt}=k\frac{[C][A]}{[M_0]}(1-\beta)\left(1+\frac{m\beta}{([A][C])^{1/2}}\right)\exp\left(-\frac{U}{RT}\right) \quad (1)$$

where [A] and [C] are the concentrations of the activator and catalyst, respectively; $[M_0]$ is the initial concentration of the monomer, which is introduced into equation (1) for dimensional reasons; $U$ is the activation energy of the AAPC process; $R$ is the gas constant; $T$ is the absolute temperature; $k$ is the pre-exponential factor; $m$ is a constant characterizing the intensity of auto-acceleration of the reaction; and $\beta(t)$ is the degree of conversion, which depends on time $t$.

At $\beta \ll 1$ this equation reduces to a kinetic equation which is first order with respect to the monomer. An essential restriction of this equation is that it has been derived for the special case $f[A]=[C]$, where $f$ is the functionality of the activator used. In the derivation of this equation, just as in the subsequent treatment, it is assumed that the degree of conversion $\beta$ is directly proportional to the enthalpy removal before crystallization:

$$q_1(t)=\frac{Q_1}{C\rho}\beta(t) \quad (2)$$

where $Q_1$ is the enthalpy of the AAPC reaction; $C$ is the

0032-3861/82/030385-06$03.00

***Table 1*** Activators used for the AAPC reaction

| | Chemical name | Abbreviation | Functionality | $T_b$, (°C/mm Hg) | $n$ |
|---|---|---|---|---|---|
| 1 | Acetyl caprolactam | AcCl | 1 | | |
| 2 | Phenyl isocyanate | PhIC | 1 | 48/10 | 1.5362 (20°) |
| 3 | 2,4-Toluylene diisocyanate | TDI | 2 | 120/10 | 1.5669 (25°) |
| 4 | 4,4′-Diphenylmethane diisocyanate | MDI | 2 | 157/0.19 | 1.5907 (50°) |
| 5 | 4,4′,4″-Triphenylmethane triisocyanate | TTI | 3 | 90.5 ($T_m$) | 1.6148 (80°) |
| 6 | Trimer of 2,4; 2,6-toluylene diisocyanate related as 65:35 respectively | TTDI | 3 | 89 | – |

$T_b$ = boiling temperature
$T_m$ = melting temperature

heat capacity; and $\rho$ is the density of the reaction mass. The linearity of the relationship between $q_1$ and $\beta$ signifies that the change in density upon polymerization is practically compensated for by the change in the heat capacity of the reaction mass, so that $C\rho = \text{constant}$. Therefore, the quantities $q_1$ and $\beta$ are interchangeable (within a constant factor).

The kinetics of AAPC have, in fact, been investigated in earlier work. Two problems remain open: the establishment of the law of summation of the enthalpy of polymerization ($q_1$) and crystallization ($q_2$), which would enable one to resolve the overall enthalpy observed into $q_1$ and $q_2$; and of the regularities governing the crystallization of poly-ε-caproamide produced by the AAPC method with the use of various activators. The aim of the present paper is to provide answers to these questions.

## EXPERIMENTAL

For our investigation we used ε-caprolactam, which was subjected to polymerization in an inert atmosphere by the conventional two-reactor scheme; appropriate quantities of the catalysing and activating systems were prepared at 120°C prior to each experiment. The catalyst used is Na-caprolactam prepared from metallic Na and ε-caprolactam, and compounds of various chemical structure were used as activators (*Table 1*). The vacuum-distilled ε-caprolactam was dried in a vacuum cabinet at a residual pressure of 5–10 mm Hg and at a temperature of 50°–55°C for 20 h and was then stored before use in a vacuum desiccator at a residual pressure of 2–3 mm Hg.

Acetyl caprolactam, phenyl isocyanate and diisocyanates were prepared by distillation in a vacuum, 4,4′,4″-Triphenylmethane triisocyanate (TTI) was purified by repeated recrystallization from heptane.

The catalyst concentrations studied, [C], ranged from $3.2 \times 10^{-1}$ to $8.97 \times 10^{-2}$ mol $\mathrm{l}^{-1}$ (or from 0.35 to 1.0 mol%). The activator concentration [A] was chosen so as to satusfy the following relation:

$$f\,[\mathrm{A}] = [\mathrm{C}] \qquad (3)$$

Solutions of the activator and catalyst in the monomer were placed separately in the calorimetric cell, which was thermostatically controlled to the temperature of the experiment. The polymerization was started after the reaction mixture had been prepared and rapidly stirred. The experiments were conducted under isothermal conditions at a temperature 160°–200°C at which the AAPC reaction takes place with a yield of no less than 98%. The upper limit of this temperature range was determined by the tendency to approach the melting temperature of the polymer ($T = 220$°C), which lowered the yield of the polymer and slowed down the crystallization sharply. The lower limit was dictated by the fact that at $T < 160$°C the rate of polymerization was slowed down considerably and the polymer yield was reduced, which introduced undesirable complications into the treatment of the results obtained.

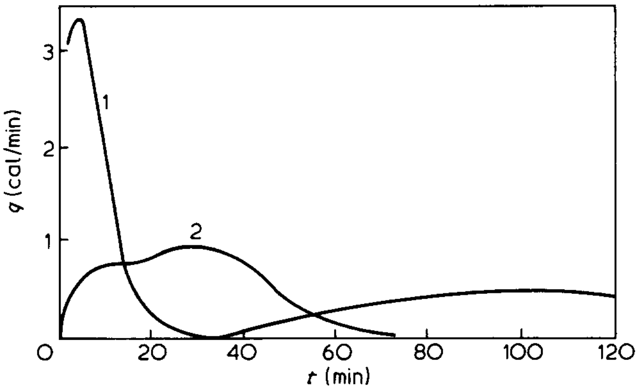

***Figure 1*** Typical examples of the intensity of heat flux observed in the course of the polymerization and crystallization processes. 1—$T$ = 200°C, the polymerization and crystallization are separated in time; 2—$T$ = 160°C, the crystallization is superimposed on polymerization

The overall enthalpy $q(t)$ of the polymerization and crystallization were estimated with the aid of an automatic differential calorimeter, the operating principle of which is based on the measurement of the integral heat flux from the sample with an error of measurement not exceeding 2% and with the specified temperature being maintained constant to within ±0.5°C. The time constant of the instrument was no more than 150 s.

The spread of the experimental data (especially in the region of polymerization) was at least ±8% of the mean value with respect to the intensity of exothermal effect $q$ at each moment of time. Therefore, each experiment was repeated 6 times at least, which is why the results obtained may be considered reliable with an error of up to ±3.3%.

## RESULTS AND DISCUSSION

The primary experimental results were in the form of the dependence of the enthalpy $q$ on time $t$. They were of two types, as can be clearly seen from the example given in *Figure 1*. This figure shows the dependences of $\dot{q}$ obtained near the upper and lower limits of the temperature range studied. In the first case, the process clearly resolves into

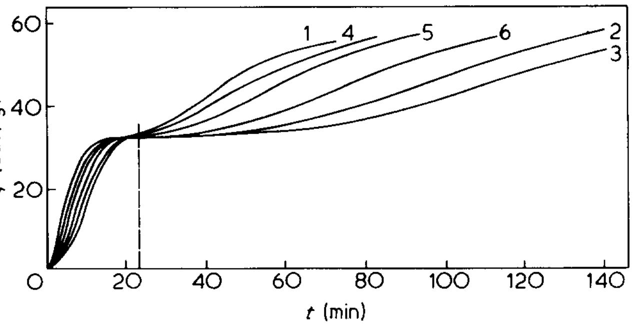

*Figure 2* Exothermal effects of polymerization and crystallization. The conditions under which the processes were carried out: $T = 190°C$; $[C] = 4.49 \times 10^{-2}$ mol l$^{-1}$. The activators used: AcCl (1), TTDI (2), TTI (3), PhIC (4), TDI (5), MDI (6)

two components and the functions $q_1(t)$ and $q_2(t)$ can easily be found. In the second case, the quantities $q_1$ and $q_2$ are almost completely superimposed and the occurrence of the two processes can be deduced only from the presence of a point of inflection on the experimental curves and the resolution of $q$ into $q_1$ and $q_2$ cannot be made on the basis of the initial data alone. In an earlier work[2] we proposed a general analytical method of resolution of $q$ into $q_1$ and $q_2$, which will be described and used here.

The principal methodological procedure, which makes possible the separation of the enthalpy attending the polymerization and crystallization, is the determination of the constants of the corresponding kinetic processes in the temperature range within which the separation of the overall exothermal effect $q(t)$ into the components $q_1(q)$ and $q_2(t)$ is carried out in an unambiguous manner, this being followed by the extrapolation of the values of these constants with respect to their temperature dependences to the region of low temperatures, where the processes under discussion are superimposed.

A comparison of the theoretically calculated overall exothermal effects $q(t)$ with experimental data furnishes a criterion of the validity of the approach proposed.

The most critical point for the method of resolving the superimposed exothermal effects is the assumption concerning the nature of the summation of $q_1$ and $q_2$. Considering that only the polymerized portion of the material participates in the crystallization process up to a given moment of time, we can suggest the following form of the law for the summation of the enthalpies:

$$\dot{q}(t)=Q_1 \cdot \dot{\beta}(t)+Q_2 \cdot \dot{\alpha}(t) \cdot \beta(t) \tag{4}$$

where $Q_1$ and $Q_2$ are the overall enthalpies of the polymerization and crystallization processes, respectively; $\beta(t)$ is the degree of conversion in the polymerization reaction; and $\alpha(t)$ is the degree of conversion in the crystallization process. The inclusion of the quantity $\beta(t)$ in the second term reflects the mutual effect of the polymerization and crystallization processes and has a clearcut physical meaning: only the polymerized portion of the sample mass undergoes crystallization.

Direct determination of the kinetic $\beta(t)$ curves is possible over the temperature range in which the exothermal effects of the polymerization and crystallization processes are separated in time. Typical experimental data referring to this case are presented in *Figure 2* for activators of various functionalities at a temperature of 190°C and the concentration [C] being equal to 0.5 mol%. In this case we obtain curves for the isothermal polymerization. These curves were treated, according to equation (1), using the following forumla:

$$\dot{\beta}(t)=k_0(1-\beta)(1+m_0\beta)e^{-U/RT} \tag{5}$$

where $k_0$ and $m_0$ are constants.

The results obtained by the treatment of the experimental data with the aid of this equation (after the constants $k_0$ and $m_0$ have been chosen for each concentration of the catalytic system) have shown that this equation enables one to calculate the dependence $q_1(t)$ correctly.

The maximum deviations of the calculated values of $q_1(t)$ from the experimental data do not exceed $\pm 3\%$, i.e. they lie within the measurement error. This proves the validity of the conclusion drawn earlier[1] that the AAPC proceeds with auto-acceleration and that the macrokinetics of this reaction can be described by an equation of the autocatalytic type[1].

The isothermal measurements carried out in this work have also made it possible to confirm the results obtained earlier[1] on the nature of the dependences of $k_0$ and $m_0$ on the concentration of the catalytic system provided that $[C]=[A]{\cdot}f$, which was fulfilled in all the experiments carried out, as was observed earlier[1]. In actual fact, it has been found that $k_0$ and $m_0$ may be given in the form

$$k_0=k\frac{[C][A]}{[M_0]} \quad \text{and} \quad m_0=\frac{m}{\sqrt{[C][A]}} \tag{6}$$

where the constants $k$ and $m$ depend on the nature of the catalytic system.

At the initial stage of AAPC (at $\beta \ll 1$) the reaction is first order with respect to the product ([A][C]) (at $[A]=[C]/f$), and when the auto-acceleration of the reaction becomes effective, an increase in the concentration of the catalytic system leads to the weakening of the self-acceleration effect. All this makes it possible to reliably estimate the constants $k$, $m$, and $U$, which enter into equation (1) and also the enthalpy of polymerization. The values of these quantities are presented in *Table 2*, which also gives (in parentheses) the corresponding data obtained earlier[1]. A comparison reveals a satisfactory agreement between the two series of measurements carried out by independent and basically different methods, except for AAPC which is activated by 2,4-toluylene diisocyanate (TDI). The causes of the discrepancy between the results of measurements of the kinetic constants, which have been carried out by means of the isothermal and non-isothermal methods, have not

*Table 2* Kinetic constants of polymerization obtained with the use of various activators for AAPC

| Activator | $k \cdot 10^{-10}$ (l mol$^{-1}$ min$^{-1}$) | $m$ (mols l$^{-1}$) | $U$ (kcal mol$^{-1}$) | $Q_1$ (cal/g) |
|---|---|---|---|---|
| AcCL | 0.8 (0.77) | 0.98 (0.93) | 17 (16.8) | 32 (30.5) |
| PhIC | 2.2 (2.22) | 0.36 (0.30) | 17 (20.0) | 32 (31.5) |
| TDI | 4.8 (2.7) | 0.24 (0.7) | 17 (15.6) | 32 (31.5) |
| MDI | 6.8 (6.7) | 0.17 (0.16) | 17 (17.3) | 32 (31.5) |
| TTI | 3.5 | 0.39 | 17 | 32 |
| TTDI | 2.8 | 0.5 | 17 | 32 |

been clarified; this discrepancy may be due either to a certain difference in the quality of the materials used or to the specific features of the calorimetric method.

On the whole, an independent test carried out by the isothermal method has confirmed the results of the analysis, which has been checked by a more complicated and indirect non-isothermal method.

In order to describe the kinetics of crystallization, we used the Avrami equation given here in the form:

$$\alpha(t) = 1 - \exp[-(t/t_0)^n] \qquad (7)$$

where $\alpha(t)$ is the degree of crystallinity at time $t$, which is proportional to the exothermal effect of crystallization $q_2(t)$; $t_0$ is the characteristic time of the process; $n$ is a constant.

The temperature dependence of the characteristic time $t_0$ is used in the form proposed by Mandelkern[3], namely:

$$t_0 = C \cdot \exp\left[\frac{E}{RT} + \frac{T_m^{\gamma} \cdot \psi}{T(T_m - T)^{\gamma}}\right] \qquad (8)$$

where $\psi$ and $C$ are constants; $E$ is the activation energy of the process of transport of the material across the melt-crystal interface; $T_m$ is the equilibrium melting temperature; $\gamma$ is a constant determined by the geometry of the growth of crystals.

As seen from equation (8), the temperature dependence of the rate of crystallization is made up to two components. With low degrees of supercooling, characteristic of the experiments carried out, the first term in equation (8) remains constant and, hence, can be included in the pre-exponential factor. There remains only the high-temperature term associated with the critical size of the nucleus; therefore, assuming that $\gamma = 1$, we can write the dependence $t_0(T)$ in the form

$$t_0 = C \cdot \exp\left[\frac{\psi T_m}{T(T_m - T)}\right] \qquad (9)$$

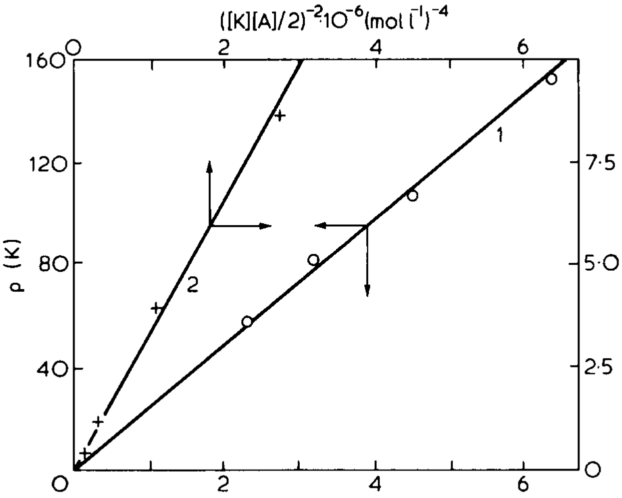

*Figure 3* Dependences of the constants $\psi$ (1) and $C$ (2) on the product of the concentrations ([C] [A]) for 2,4-toluylene diisocyanate as activator ([C] = 2[A])

It should be noted that the overall enthalpy of crystallization varies somewhat, depending on the choice of the activator. Evidently, this is associated with the fact that the final degree of crystallinity attained depends on the nature of the activator since the extent of completeness of the crystallization depends on the spatial structure of macromolecules of the same type. Therefore, when treating the experimental data according to equation (7), $\alpha = 1$ was taken to mean the quantities corresponding to the overall enthalpy observed for a given activator.

The treatment of the experimental data in the coordinates of the Avrami equation has shown that in all the cases the same value the exponent $n$ equal to 3 may be used. This facilitates the comparison of the role of the activator, which can be conveniently made by using the values of the constant $t_0$. The construction of the dependence $t_0(T)$ in the coordinates of equation (9), ln $t_0$ vs. $1/T(T_m - T)$, has made it possible to determine the values of the constants of the temperature dependence of the characteristic time of the crystallization process. All these quantities depend on the concentration of the catalytic system. An example of the dependences of $C$ and $\psi$ on the product ([A][C]) with 2,4-toluylene diisocyanate used as the activator and with the condition [C] = 2[A] is shown in *Figure 3*. Analogous data have been obtained for other activators. The results of the estimation of the kinetic constants of the crystallization process of poly-ε-caproamide produced by the AAPC reaction through the use of activators of various functionalities are given in *Table 3*; the analytical treatment of the results of measurements presented in *Figure 3* has shown that the dependence of the constants $C$ and $\psi$ on ([A][C]) can be expressed as follows:

$$C = C_1([A][C])^{-2} \quad \text{and} \quad \psi = \psi_1([A][C])^{1/2} \qquad (10)$$

The values of the kinetic constants $C_1$ and $\psi_1$ are also listed in *Table 3*.

Thus, the overall results of the investigation of the isothermal kinetics of the crystallization of poly-ε-caproamide produced by the APPC reaction can be described by the Avrami equation (7) in which the dependence of the time constant $t_0$ on temperature and

*Table 3* Constants of the temperature dependence of the characteristic time of crystallization for various activators

| Activator | $n$ | $t_0$ (min at $T_0$ = 190°C) | $C$ (min at [C] = 4.49 x 10$^{-2}$ mol l$^{-1}$) | $\psi$ (K at [C] = 4.49 x 10$^{-2}$ mol l$^{-1}$) | $C_1 \times 10^6$ (min mol$^4$ l$^{-4}$) | $\psi_1 \times 10^{-3}$ (K. l mol$^{-1}$) |
|---|---|---|---|---|---|---|
| AcCL | 2.8 | 50 | 0.20 | 155 | 0.81 | 3.45 |
| PhIC | 2.9 | 56 | 0.79 | 120 | 3.21 | 2.67 |
| TDI | 3.0 | 65 | 3.75 | 80 | 3.68 | 2.54 |
| MDI | 2.8 | 87 | 9.30 | 62 | 9.10 | 1.97 |
| TTI | 3.2 | 112 | 16.50 | 54 | 7.46 | 2.09 |
| TTDI | 3.1 | 126 | 21.40 | 50 | 9.68 | 1.93 |

*Table 4* Content of the insoluble gel-fraction in polycaproamide produced by the AAPC reaction through the use of the trimer of 2,4-toluylene diisocyanate as activator

| [C] (mol %) | Percentage gel-fraction |
|---|---|
| 0.15 | 72 |
| 0.2 | 68 |
| 0.3 | 50.6 |
| 0.6 | 50 |
| 1.0 | 42 |

the concentration of the catalytic system at ($[A]=[C]/f$) is given by

$$t_0=\frac{C_1}{([A][C])^2}\exp\left[\frac{\psi_1([A][C])^{1/2}T_m}{T(T_m-T)}\right] \qquad (11)$$

In this connection it should be emphasized that the duration of the process required to complete the crystallization, or the characteristic time of crystallization, $t_0$, depends substantially on the functionality of the activator, i.e. in the final run on the degree of branching and degree of crosslinking of macromolecules.

To check this, the samples of poly-ε-caproamide prepared by using polyfunctional activators were tested for the content of the insoluble gel-fraction. The results obtained are given in *Table 4*. As can be seen from this table, the content of the gel-fraction depends on the catalyst concentration, but in all cases it remains rather high (more than 40%). The appearance of side branches and even of crosslinks slows the crystallization down considerably. But the overall (final) degree of crystallinity increases (as can be seen from a comparison of the magnitude of the maximum thermal effect $Q_2$). Evidently, the sluggishness of the process of crystallization makes it easier for the degree of order to increase since at the high temperature at which the crystallization was carried out ($T \gg T_g$) the mobility of macromolecules is fully retained.

The quantitative kinetic data obtained above give grounds for testing equation (4), which corresponds to a case where the polymerization and crystallization proceed in a single time interval and the corresponding exothermal effects are not separated in time. Extrapolating the kinetic relationships obtained to the region of up to 160°C and calculating $q(t)$ by means of equation (4), we derived the dependences that are compared in *Figure 4* with the experimental data. The broken lines in this figure represent the results of calculations carried out in accordance with the following simple additive scheme:

$$q(t)=Q_1\beta(t)+Q_2\alpha(t)$$

and the crosses represent the experimental data. Obviously, the use of the simple additive scheme does not provide satisfactory results, which in this case is due to the inadequacy of such a scheme. As regards the results of calculations made by using equation (4), they lead to a quite satisfactory agreement with the experimental findings. In particular, such an approach describes sufficiently accurately the gradual changeover from the extreme case, where the polymerization and crystallization processes are clearly separated by the

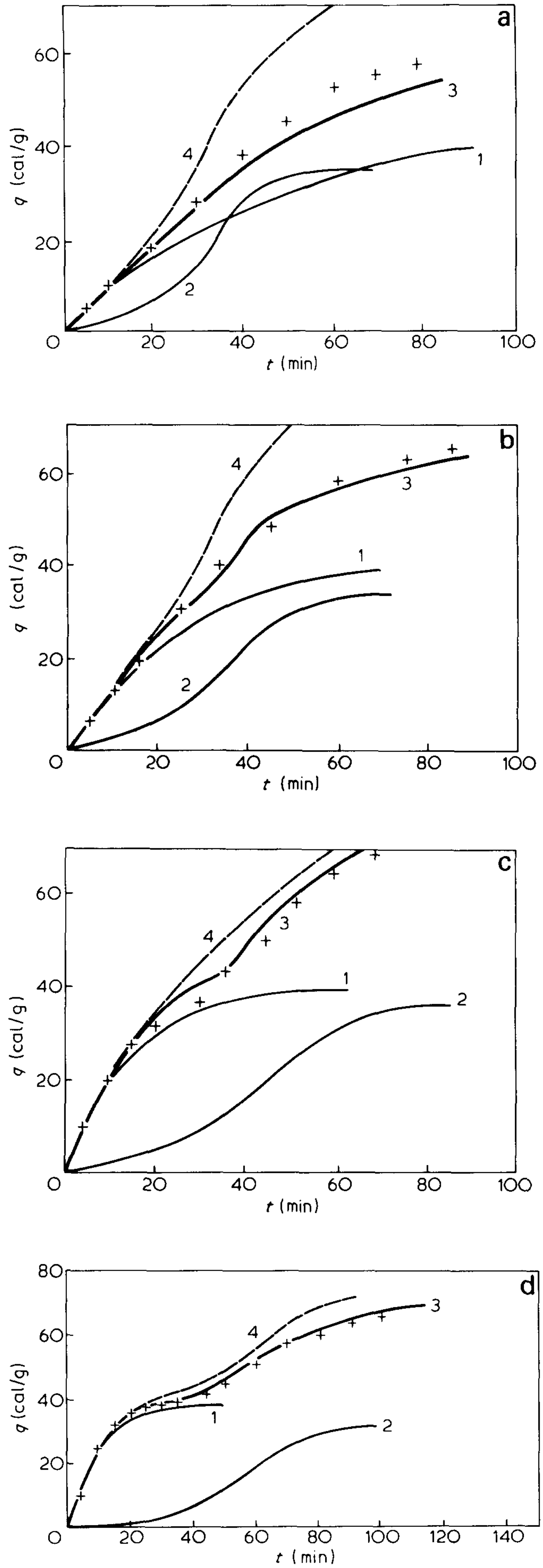

*Figure 4* Enthalpy observed at $T$ = 160°C (a), 170°C (b), 180°C (c), 190°C (d). 1, $q_1$ and 2, $q_2$

temperature region where such a separation is gradually degenerated.

## CONCLUSIONS

A calorimetric investigation of the AAPC reaction and the crystallization of the poly-ε-caproamide produced, which occur under isothermal conditions, has enabled us to determine the constants of the kinetic equations of polymerization and crystallization. The kinetic data obtained for the AAPC reaction have confirmed the conclusion made earlier on the basis of non-isothermal measurements as to the auto-accelerating character of this reaction. These findings have also confirmed the numerical values of the constants that refer to activators of various nature and functionalities. The functionality of the activator used has an effect on the degree of branching of the resulting macromolecules and on the content of the gel-fraction, which strongly effect the rate of crystallization of the polymer produced. For the temperature region, where the polymerization and crystallization processes are superimposed, we have proposed the rule of summation of the exothermal effects of both processes based on the assumption that only the polymerized portion of the reacting mass can be crystallized. The rule of summation proposed here is confirmed by the experimental data obtained.

## REFERENCES

1 Malkin, A. Ya., Ivanova, S. L., Frolov, V. G., Ivanova, A. N. and Andrianova, Z. S. *Polymer*, in press
2 Beghishev, V. P., Bolgov, S. A., Malkin, A. Ya., Subbotina, N. I. and Frolov, V. G. *Vysokomol. Soedin.* (*B*) 1979, **21**, 714
3 Mandelkern, L. 'Crystallization of Polymers', McGraw-Hill Co., New York, 1964