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Problems of Non-isothermal Character in Polymerisation Processes

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The results of the study of the radical polymerisation of vinyl monomers taking place under non-isothermal conditions, namely under purely adiabatic conditions, with transfer of heat to the surrounding medium, under the conditions of propagation of the polymer front, and the influence of hydrodynamics on the kinetics of polymerisation, have been reviewed. Various data on the ionic polymerisation of lactams, where the spontaneous heat production in the reaction is determined not only by the chemical source of heat release but also by the crystallisation of the resulting polymer, have been analysed. The results of the study of the condensation of epoxide compounds under the influence of amines under adiabatic conditions and under conditions of propagation of the polymer front have been discussed briefly.
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I. INTRODUCTION

Many processes in the synthesis of polymeric materials are characterised by highly exothermic reactions and low values of the coefficient of thermal conductivity of the monomer–polymer mixture. This combination of thermophysical characteristics of the polymerisation medium together with the reaction rates actually observed in practice often leads to superheating of the reaction mass and the appearance of a non-uniform space–time distribution of the temperature and the extent of the reaction. A consequence of the formation of these non-uniform fields is the difficulty of controlling the process and in a number of cases a deterioration in the properties of tne polymeric materials formed.

Spontaneous heat production in a polymerising system may lead to a change in the thermal conditions such as a change from bulk polymerisation to a self-propagating polymerisation front, or may influence the concentration of macroradicals and the intensity of the manifestation of the gel effect, or may lead to "burn-out" of the initiator long before the consumption of the monomer, and to the start of polymerisation by thermal initiation. Effects of this kind lead to a significant change in the regular kinetic features and properties of the materials formed. The development of new energetically rational processes, and the intensification of existing processes, must involve the analysis of the kinetic characteristics of non-isothermal polymerisation.

The traditional approach to the study of the kinetics of polymerisation processes involves an analysis under isothermal conditions. At the same time, in practical technological problems, it is usually necessary to deal with non-isothermal conditions as such or with departure of the reaction from isothermal conditions as a result of the influence of various factors.

In the last ten years, at least two factors have led to an increased interest in polymerisation reactions under non-isothermal conditions. The first of these is the deeper knowledge of the inter-relationship between the conditions of synthesis and the structure and properties of polymers, which has led, in particular, to a sharp increase in the number of studies of the control of the molecular-mass distribution (MMD) and the influence of the MMD on the properties of polymers. The second factor is the trend towards the use of non-isothermal conditions to intensify industrial polymerisation processes in reactors of different type, and also to harden oligomeric systems and to obtain cross-linked structures directly in articles.

The present review examines and summarises for the most part work carried out in recent years by Enikolopov and co-workers.

II. FREE-RADICAL POLYMERISATION

Polymerisation by a radical mechanism, which is the simplest and has been studied in most detail, has become the principal object of study in the investigation of non-isothermal effects. This process can be carried out in practically all known thermal conditions, and the analysis of the consequent problems is important for practical applications.

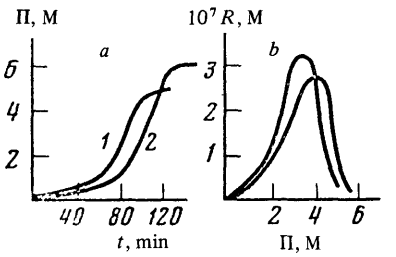


Figure 1. Change in the yield of polymer (П) (*a*) and the concentration of macro-radicals *R* (*b*) during adiabatic polymerisation[1]: *1*) quasi-stationary solution, *2*) exact solution; $I_0 = 10^{-3}$ M, $T_0 = 350$ K.

1. The Kinetics of Polymerisation Under Adiabatic Conditions

In the adiabatic polymerisation of vinyl monomers, depending on the difference between the activation energies for the decomposition of the initiator and for the termination of the chains, an adiabatic increase in the temperature of the polymerisation medium should mainly be reflected in the increased rate of decomposition of the initiator. Thus at sufficiently high rates of change of temperature, the use

of the principle of quasi-stationary concentrations (QSC) in the classical sense may become incorrect. In fact, numerical computer analysis of a kinetic scheme including initiation, propagation, and bimolecular termination shows[1] that there is a fairly marked difference between the quasi-stationary and the true solutions (Fig. 1), the discrepancy between which depends chiefly on the magnitude of the heat of polymerisation (Q), the activation energies (E_i, E_t), and the pre-exponential factors (k_{i0}, k_{t0}) of the rate constants for initiation (k_i) and termination (k_t).

If in the equation for the concentration of macroradicals (R)

$$\frac{dR}{dt} = k_i(t)\,I(t) - k_t(t)\,R^2 \qquad (1)$$

the relative deviation of the true concentration of macroradicals from the quasi-stationary concentration ($\bar{R}$) is denoted by the quantity $\Delta = R/\bar{R} - 1$, then[2]:

$$\frac{d\Delta}{dt} = -\Delta(1+y)\,a(t) + \frac{1+\Delta}{2}\,\Psi(t) \qquad (2)$$

where

$$a(t) = \sqrt{k_i(t)\,k_t(t)\,I(t)};\quad \Psi(t) = \frac{1}{RT^2}(E_t - E_i)\frac{dT}{dt} + k_i(t);\quad y = R/\bar{R}$$

$I(t)$ is the concentration of the initiator, and T the temperature.

Analysis of Eqns. (1) and (2) shows that if $ta(t) \gg 1$ and $k_i(t)/a(t) \ll 1$, then $\Delta \to 0$, that is under non-isothermal conditions it is possible to use the QSC principle. In fact, the numerical solution of the system of kinetic equations for the adiabatic polymerisation of styrene, methyl methacrylate, and n-butyl methacrylate shows that for $ta(t) \geq 10^2$ and $k_i(t)/a(t) \leq 10^{-3}$ the QSC method can be used with sufficiently high accuracy.

Subsequently, the QSC principle was developed for cases in which it is possible to have the gel effect during adiabatic polymerisation; the conditions for the use of the QSC principle for the theoretical study of molecular masses and the MMD for the formation of the polymer were also studied[3].

The kinetics of radical polymerisation under adiabatic conditions when the QSC method is applicable have been studied theoretically[1,4,5]. The influence of various methods of initiation—photo- or radiation (W_i = const), thermal ($W_i = k_M M^2$), material ($W_i = k_i I$), complex ($W_i = k_{i1} I_1 + k_{i2} I_2$), and mixed ($W_i = k_i I + k_M M^2$) on the kinetics of formation and yield of the polymer were studied; here, W_i is the rate of initiation, and M the monomer concentration.

For the first three cases of initiation, the original kinetic equations can be solved in analytical form; the graphical representation of these solutions is given in Fig. 2, which shows that for radiation (curve 2) or thermal (curve 3) initiation, the polymerisation gives 100% conversion, whereas for material initiation (curve 1) the conversion is much lower. The reason for the low yields for material initiation is that during the adiabatic increase in the temperature of the reaction mixture, complete "burn-out" of the initiator takes place long before the monomer is used up. The experimental study[6-11] of the kinetics of the radical polymerisation of styrene, methyl methacrylate, and n-butyl methacrylate under the influence of various peroxide initiators has shown that in accordance with theory, the yield of polymer formed does not exceed 40–50% of the original monomer concentration. Under specially selected conditions during the initiated adiabatic polymerisation of methyl methacrylate and n-butyl methacrylate, there is a gel effect[12], and in spite of the "burn-out" of the initiator, the yield of polymer may correspond to the practically complete consumption of the monomer. Since the realisation of this situation depends on the nature of the monomer, from the practical viewpoint, increasing the yield of polymer with material initiation is of considerable interest. For this purpose, a theoretical study was made[1] of the dependence of the yield of polymer on the initial conditions, the kinetic parameters, and the thermophysical characteristics of the monomer–polymer mixture. A significant increase in the yield can be achieved by using mixtures of initiators with different activation energies of decomposition.

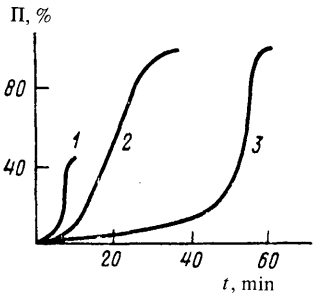


Figure 2. Kinetics of the adiabatic polymerisation of styrene for material (*1*), radiation (*2*), and thermal (*3*) initiation[1].

The influence of mixtures of different initiators on the kinetics of the polymerisation of styrene and methyl methacrylate using dicyclohexyl peroxydicarbonate (CPC), benzoyl peroxide (BP), t-butyl peroxide (tBP), cumyl peroxide (CP), and isobutyrodinitrile as initiators has been studied experimentally[13].

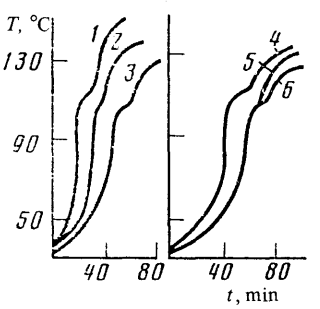


Figure 3. Kinetic curves for the polymerisation of methyl methacrylate under the influence of a mixture of initiators[13]: *1*) M_0 = 5.7, [CPC] = 0.22, [tBP] = 0.5; *2*) M_0 = 5.1, [CPC] = 0.2, [tBP] = 0.5; *3*) M_0 = 4.7, [CPC] = 0.22, [tBP] = 0.2; *4*) M_0 = 4.7, [CPC] = 0.1, [tBP] = 0.09; *5*) M_0 = 4.7, [CPC] = 0.05, [tBP] = 0.15; *6*) M_0 = 4.7, [CPC] = 0.05, [tBP] = 0.21 M.

The kinetics of the change in temperature during the reaction for initiation by a mixture of CPC and tBP are shown in Fig. 3. The addition to the polymerisation system

of a second initiator (tBP) characterised by a higher activation energy leads to a change in the nature of the kinetic curves. A noteworthy feature is that the kinetic curves, in agreement with the theoretical results, show two inflections, indicating separate initiation in this system.

Comparison of the yields of polymethyl methacrylate and polystyrene obtained for initiation by a mixture of CPC with tBP or with CP with the yields for initiation by these initiators separately shows that in the first case the conversion increases by 60%, whereas the use of BP with other initiators is not effective, because of induced decomposition[14].

Under the conditions of adiabatic polymerisation, because of the continuous increase in temperature, the role of thermal initiation increases. For high degrees of transformation and high initial concentrations of monomer, thermal initiation may become the principal source of primary radicals. In fact, when the polymerisation of n-butyl methacrylate is carried out[11] without a solvent at higher temperatures (curve *1* in Fig.4*a*), the kinetic curves show a second abrupt change in temperature, due to thermal initiation. Dilution levels out the thermal polymerisation (curve *2* in Fig.4*a*), because of the low residual concentration of the monomer.

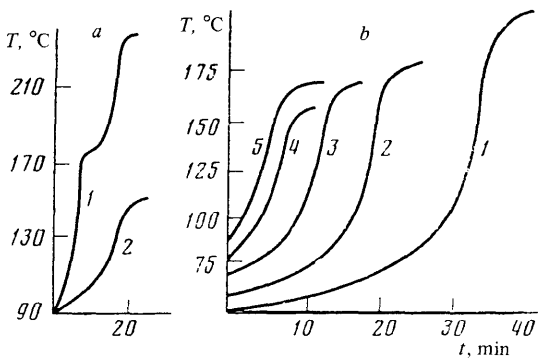


Figure 4. Kinetic curves for the adiabatic polymerisation of n-butyl methacrylate in the block (*a*, curve *1*; *b*, curves *1–5*) and in solution (*a*, curve *2*) for different initial temperatures[11,12].

The kinetics of the thermal polymerisation of styrene under adiabatic conditions was the subject of a special study[15] involving variation of the initial temperature and concentration of the monomer. To obtain a quantitative description of the kinetic curves, the authors cited carried out kinetic calculations assuming unimolecular, bimolecular, and termolecular mechanisms of initiation, and good agreement with experiment was obtained only for second-order kinetics.

In polymerisation under adiabatic conditions, complete decomposition of the monomer may be observed not only for thermal polymerisation but also when there is a gel effect. In fact, in a study of the polymerisation of n-butyl methacrylate in the bulk at an initial temperature of 50 °C,[12] an adiabatic increase in temperature was observed, corresponding to the practically complete consumption of the monomer (curve *1* in Fig.4*b*). With increase in the initial temperature of the reaction, there is a decrease in both the yield of polymer (at temperatures of 50, 70, 80, and 90 °C, the yields of polymer are 6.3, 4.5, 3.25, and 2.9 M respectively) and the final temperature of the system. The observed complete consumption of n-butyl methacrylate at 50 °C can in principle be attributed to an additional source of radicals, capable of bringing about thermal polymerisation. In this case, however, increase in the initial temperature of the reaction should lead to an increase in the rate of the thermal polymerisation itself, and hence to the complete consumption of the monomer, irrespective of the initial temperature of the reaction.

Thus this behaviour of the kinetic curves can be explained only by the gel effect in the reaction mixture. Comparison of experiment with calculations based on a kinetic model of the process makes it possible in this case to study the dependence of the rate constant of chain termination on the extent and temperature of the reaction.

The alternation of initiation and thermal polymerisation under adiabatic conditions is of methodological interest for the study of the mechanism of thermal initiation. In these cases, in the initial stage of the reaction, "burn-out" of peroxide impurities takes place, and all the subsequent information contained in the kinetic curves relates only to thermal polymerisation. Thus more reliable information on the mechanism of thermal initiation can be obtained by studying the polymerisation of vinyl monomers under adiabatic conditions, as was done for n-butyl methacrylate and styrene[12,15].

From the viewpoint of the determination of the elementary rate constants, a fact of considerable methodological interest is that at the moment of burn-out of the initiator, the quasi-stationary character with respect to the macroradicals breaks down, and post-polymerisation takes place; the latter can be studied using ordinary non-isothermal methods for determining elementary constants[16–21].

2. Nature of the Change in the Molecular Masses and the MMD in Adiabatic Polymerisation

The use of familiar methods (Laplace transformation, generating function method, etc.) for calculating the MMD function for radical polymerisation processes under adiabatic conditions involves considerable mathematical difficulties, because of the change in the rate constants with increase in the reaction temperature. Another limiting factor in the use of ordinary methods is that in adiabatic polymerisation, at the moment of "burn-out" of the initiator, the quasi-stationary character with respect to the macroradicals breaks down, so that to take detailed account of the characteristic kinetic features determined by the MMD of the final product, it is necessary to study the polymerisation without using the QSC method.

The nature of the change in the molecular masses and the MMD of the resulting polymer during the polymerisation under conditions when the QSC method is applicable or when this method is not applicable has been studied[1] in relation to the method of initiation.

For a constant rate of initiation up to high degrees of transformation, the mass-average ($\bar{P}_w$) and number-average ($\bar{P}_n$) molecular masses increase linearly with increase in the degree of transformation, but at the end of the reaction they decrease slightly, because of the consumption of the monomer. There is an analogous change in the ratio $\bar{P}_w/\bar{P}_n$, which is a measure of the polydisperse character of the resulting polymer. For thermal initiation, the ratios $\bar{P}_w/\bar{P}_n$ and $\bar{P}_z/\bar{P}_n$ ($\bar{P}_z$ is the *z*-average molecular mass) increase before the end of polymerisation.

For initiation by a material initiator, the values of $\bar{P}_w/\bar{P}_n$ and $\bar{P}_n$ decrease during the reaction as a result of an increase in the rate of decomposition of the initiator and a decrease in the lifetime of the macroradicals. In the initial stages of the reaction, $\bar{P}_n$ and $\bar{P}_w$ change in the same sense,

but subsequently, $\bar{P}_n$ decreases more rapidly than $\bar{P}_w$, since the formation of the low-molecular-weight polymer makes a more significant contribution to the first moment of the MMD function. For the same reason there is a slight broadening of the MMD of the resulting polymer.

For complex initiation (two initiators, initiator + thermal initiation), the curve giving the change in the instantaneous number-average molecular mass has several extremal points, due to the successive "burn-out" of the initiators or an increase in the role of thermal initiation with increase in the temperature of the system.

The moment of "burn-out" of the initiator has a fairly strong influence on the nature of the change in the MMD and the molecular masses, since the lifetime of the growing "live" chains may increase without limit. In this case, for a quantitative description of the adiabatic polymerisation, it is obviously necessary to analyse the MMD without using the QSC principle. For this purpose, the system of differential equations for the moments of the distribution of the "live" and "dead" polymers was solved numerically using a computer[1]. Analysis of the results shows that at low degrees of polymerisation, where the rate of bimolecular termination by a disproportionation mechanism is low because of the low concentration of macroradicals, the number-average molecular masses of the "live" and "dead" polymers increase and then decrease, and at the end of the polymerisation a new moderate increase in $\bar{P}_n$ for the "dead" polymer and a fairly intense increase for the "live" chains are again observed. For the "live" polymer, almost up to the end of the polymerisation, the ratio $\bar{P}_w/\bar{P}_n = 2$, after which, as the initiator is used up, it decreases to 1, due to the increase in the lifetime of the growing macromolecules, that is a change to "live" polymerisation.

The ratio $\bar{P}_w/\bar{P}_n$ for the "dead" polymer is close to 1.5 practically up to the end of the polymerisation, and it increases sharply only after the initiator has been used up. The increase in the polydisperse character of the "dead" polymer is also due to the "burn-out" of the initiator, so that the decrease in the rate of termination at the end of polymerisation leads to an increase in the length of the "live" chains by several orders of magnitude, and this has a stronger influence on the value of $\bar{P}_w$.

The results of the experimental study of the nature of the change in the MMD and the molecular masses in the adiabatic polymerisation of n-butyl methacrylate show complete agreement with these regular features[11].

As already noted, the determination of the MMD function using a Laplace transformation or a generating function involves considerable mathematical difficulties, and these methods can be used successfully only in those cases where the MMD function can be found analytically.

A method of finding the MMD function which eliminates these difficulties and is particularly effective in the analysis of non-isothermal polymerisation is therefore of interest[22,23]. The method involves essentially the reduction of the original system of differential equations for the "live" macromolecules to one equation in partial derivatives

$$\frac{\partial R(x,t)}{\partial t} + \frac{\varphi_2(t)}{N}\frac{\partial R(x,t)}{\partial x} = \varphi_1(t)R(x,t) \qquad (3)$$

where $x = j/N$; the number N is related to the chosen scale with respect to x, $\phi_1(t) = k_p(t)M$, $\phi_2(t) = \phi_1(t) + k_t(t) + k_t'(t)$, and k_t and k_t' are the rate constants for termination by recombination and disproportionation respectively. Eqn.(3) is solved by the method of characteristics.

The mass-average molecular mass and the ratio $\bar{P}_w/\bar{P}_n$ calculated by this method on a computer for the adiabatic polymerisation of styrene are given in Fig.5, where the points give the experimental data. The theoretical calculations show good agreement with experiment.

It should be noted that the maximum rate of polymerisation, corresponding to the maximum concentration of macroradicals, and the minimum value of $\bar{P}_n$, are reached for the same degree of polymerisation. The subsequent decrease in the concentration of macroradicals and increase in their lifetime leads to an increase in the molecular mass and a decrease in the rate of the process.

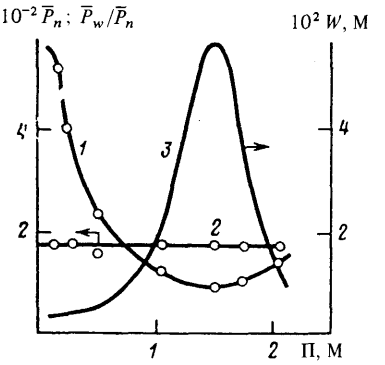


Figure 5. Change in the number-average molecular mass of polymerisation ($\bar{P}_n$, curve *1*), the width of the MMD ($\bar{P}_w/\bar{P}_n$, curve *2*), and the rate of polymerisation (W, curve *3*) during the adiabatic polymerisation of styrene[22]; $M_0 = 4.36$ M, $T_0 = 36$ °C; continuous curves—theory; points—experiment.

3. The Influence of Heat Removal on the Kinetics of the MMD

A periodic-action ideal-mixing reactor can be considered[24]. By changing the conditions of heat exchange at the walls of the reactor, it is possible to change the polymerisation conditions from isothermal to adiabatic. An indication of the non-isothermal character of the polymerisation process is provided by the Semenov parameter κ. For reactions with a high exothermicity and a high activation energy there is a sharp distinction, according to the Semenov parameter, between low-temperature (quasi-isothermal heating not more than 15–20 °C) and high-temperature (quasi-adiabatic, heating to 60–200 °C) polymerisation conditions. The intermediate zone is extremely narrow, and it is possible to speak of a critical value of the parameter κ. The intermediate zone becomes broader only for a low exothermicity and low activation energy of the process.

The change from one set of conditions to another is effectively illustrated by the dependence of the instantaneous number-average degree of polymerisation γ_n of the "live" polymer on the degree of transformation (α) (Fig.6).

For isothermal polymerisation, the quantity γ_n usually decreases monotonically with the degree of transformation (curve *1* in Fig.6). The appearance of heat production leads to a sharp decrease in the degree of polymerisation, since the activation energy of initiation is generally much greater than the effective activation energy of polymerisation. The change in γ_n may then be non-monotonic, and under low-temperature conditions, for example, the increase

in γ_n for the "live" polymer in the central phase of the process takes place as a result of cooling of the reacting mass (curve *2* in Fig.6).

The physical reason for the increase in the number-average chain length under high-temperature conditions is different. The rapid progressive increase in heating leads to the complete "burn-out" of the initiator, as a result of which the rate of initiation tends to zero, and $\bar{P}_n$ tends to infinity. Only macroradicals remain in the system, and very long polymer chains are formed (curve *3* in Fig.6).

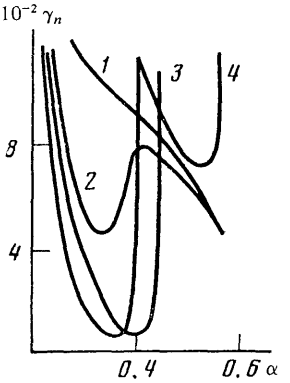


Figure 6. Dependence of the degree of polymerisation on the degree of transformation with heat removal under isothermal (*1*), low-temperature (*2*), and high-temperature (*3*) conditions and with thermal initiation (*4*).[24]

The qualitatively different changes in the degree of polymerisation during the reaction are responsible for the fundamentally different MMD under low-temperature and high-temperature conditions. Under the first conditions for degrees of conversion up to 0.5, the chain length is long and close to the initial quasi-stationary value, the distribution is narrow, and the heating increases the width of the MMD by not more than 5–20%. Under high-temperature conditions, the number-average molecular mass of the final polymer is much smaller (by factors of 3–10) than the quasi-stationary value, and the distribution is 2–3 times broader than the isothermal distribution (Fig.7). It should be emphasised that the narrow intermediate zone becomes broader only in the case of thermal "degeneration" of the process, that is for a small exothermicity of polymerisation or for a weak increase in the reaction rate with temperature.

Study of the detailed polymerisation kinetic scheme shows that allowance for chain transfer smooths out the differences in the polydisperse character between the quasi-isothermal and quasi-adiabatic conditions. With decrease in the degree of polymerisation under both sets of conditions, a marked decrease in the width of the distribution under high-temperature conditions is observed (curve *2* in Fig.7).

The existence of thermal initiation leads to separation of the process under high-temperature conditions into two quite distinct stages. At first, the initiator "burns-out" completely, and the heating of the system "includes" the thermal polymerisation mechanism. An interesting feature is that 100% conversion of the monomer is achieved only in the adiabatic case, and even with slight heat exchange, the consumption of the monomer leads to cooling of the reagents, and the reaction stops at $\alpha < 1$.

By itself, heat production in the reaction only broadens the MMD, but produces no qualitative changes in the nature of the distribution. A bimodal MMD may be produced, however, even in the simplest polymerisation kinetic scheme, if the heat exchange of the reactor is separated into two stages, and the temperature of the surrounding medium in the second stage is 30–40 K higher than that in the first.

In a continuous-acting ideal-mixing reactor, the constant supply of fresh reagents is responsible for a number of characteristic physical features of the processes[5], the most important of which is the possible existence of several stationary states of the reactor for the same values of the parameters. As in a periodic-action reactor, in this case also there are low-temperature and high-temperature conditions with corresponding types of MMD, determined by the kinetic scheme of the reaction.

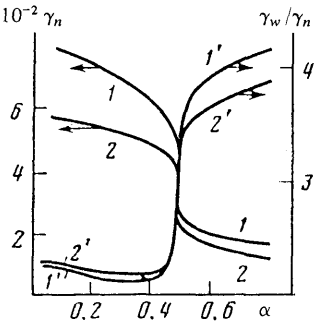


Figure 7. Influence of chain transfer on the degree of polymerisation (*1*, *2*) and the width of the MMD (*1'*, *2'*);[24] the curves were calculated without (*1*) and with (*2*) allowance for chain transfer.

4. Polymerisation During Propagation of the Thermal Wave

A classical example of the propagation of the front of an exothermic chemical reaction is provided by the burning of a flame in gaseous media. The comprehensive experimental and theoretical examination of this phenomenon is much in advance of the study of processes of this kind in condensed media. The analogy existing between the propagation of the front of exothermic reactions in gases and condensed media makes it possible to apply the results of classical theory to condensed systems.

The problem of the stationary velocity of the front of a chemical reaction was first examined in the theory of the combustion of gases by Zel'dovich and Frank-Kamenetskii[25–28]. The essential feature of this theory, namely the assumption that the coefficients of diffusion and temperature conductivity are equal, establishes a relationship between temperature and concentration, and makes it possible to reduce the system of two equations for diffusion and thermal conductivity to one equation, which unambiguously relates the rate of heat liberation to temperature. Because of the temperature dependence of the kinetic constants, the solution of the boundary problem requires additional assumptions, one of which is the assumption that the reaction zone is narrow and the chemical reaction takes place chiefly at temperatures close to those of the adiabatic

heating. In this case the boundary problem breaks down into two Cauchy problems: one in the range in which the reaction rate can be neglected, and the other in the range where the convective term in the thermal conductivity equation is neglected. The "joining" of the solutions for the two ranges makes it possible to obtain an analytical expression for the stationary velocity of the reaction front.

For the propagation of the front of a chemical reaction in a condensed medium, it is obviously impossible to assume that the coefficients of diffusion and thermal conductivity are equal, since they may differ by several orders of magnitude, and in most cases diffusion can be neglected.

The propagation of the front of an exothermic reaction in a condensed medium has been examined in a different formulation of the problem by a number of authors[29-37]. The conditions of existence and the unique character of the solution were studied, and various approximate methods for calculating the stationary velocity of the front were proposed. The method proposed in Ref.30 is based on the assumption that the reaction zone is narrow. It can be readily seen that for the general form of the dependence of the rate of heat liberation on the degree of transformation and temperature, the system of kinetic and thermal conductivity equations has a solution.

The approximation of a narrow reaction zone is based on the fact that, because of the high activation energy of the chemical reaction, most of the transformation takes place in a narrow range at temperatures close to the adiabatic heating of the reaction mixture. This makes it possible to replace the temperature by its maximum value in the equation for the temperature gradient in the reaction zone.

The approximation of a narrow reaction zone is not always applicable, however, even for high values of the activation energy of the chemical reaction. An important factor which restricts the applicability of this assumption in a number of cases is the nature of the dependence of the reaction rate on the degree of transformation. It has been shown[32,33], in particular, that for orders of reaction greater than unity, the assumption that the reaction zone is narrow is not correct. When there is retardation of the reaction, this approximation is unjustified even for high values of the activation energy.

An interesting characteristic feature of exothermic polymerisation reactions is the possible development of the process by a mechanism analogous to the propagation of a flame in a gas mixture. This was first pointed out in Ref.38. In subsequent studies[39-42] of the polymerisation of methyl methacrylate and triethylene glycol γ,ω-dimethacrylate under the influence of BP at a pressure of up to 5000 atm, propagation of the front of the polymerisation wave was established experimentally. Estimation of the velocity of the front showed that this phenomenon cannot be attributed to diffusion of active centres from the reaction zone into neighbouring layers with subsequent initiation of the reaction in these layers, since in this case the values of the velocity of the front should have been much lower than the experimental values. This gives grounds for assuming that the propagation of the polymerisation front in a cold mixture is thermal in character, that is it is similar to the normal propagation of a flame.

Special measurements[41] showed that there is no temperature gradient in the central part of the transverse cross-section of the reaction mixture. This means that under the conditions of the experiment, adiabatic propagation takes place, that is the front of the polymerisation wave is planar; the measured rate of displacement of the front is normal to this plane. The measured values of the rate of propagation of the thermal wave lie in the range 1–3 cm min^{-1}, depending on various parameters of the polymerisation mass. The structure of the front of the polymerisation wave, the influence of the concentration and nature of the initiator on the process of polymerisation propagation, and the role of pressure and the initial temperature have been studied[41,42]. It has been shown, in particular, that the stationary rate of propagation of the front of the polymerisation wave (u) increases with increase in the initial concentration of the initiator according to the law $u \sim I_0^{0.38}$.

Analysis of the thermodynamic characteristics shows that at atmospheric pressure, the boiling point of the monomer is reached for many monomers even at low degrees of transformation ($\leq$30%). Thus the propagation of the polymerisation reaction in this case must be accompanied by foaming of the polymerisation mixture[42]. Thus there exists a limiting pressure, below which stationary propagation of the polymerisation front is impossible.

When polymerisation is carried out under the conditions of propagation of the thermal wave with the reactor in a horizontal position and with mixtures having a low viscosity, convection is generally produced as a result of the existence of the heating zone. Convection cannot be eliminated even by using high pressures (up to 4000 atm). When the polymerisation reaction is carried out from above downwards in a column of liquid, convection is produced by the dropwise descent of the polymer formed. The experimental data show that in this case, for example with methyl methacrylate, breakdown of the front is not observed when a pressure above 1500 atm is used. Thus the prevention of convective breakdown of the front and boiling of the polymerisation mass is an important consequence of the use of high pressure in the propagation of the radical polymerisation reaction.

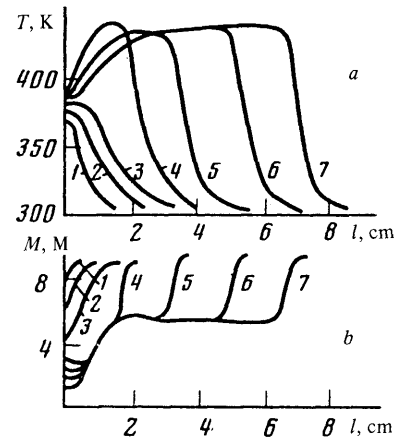


Figure 8. Profiles of the change in temperature (a) and the monomer concentration (b) along the direction of the reaction front after different times (s): *1*) 200, *2*) 800, *3*) 1600, *4*) 2400, *5*) 3000, *6*) 3600, *7*) 4200.[48]

The stationary propagation of the planar front of radical polymerisation with allowance for the specific characteristic features of the kinetics of the process has been studied theoretically by a number of authors[43-49]. The results of a numerical analysis[48], carried out without using the QSC method, show (Fig.8) that for material initiation in the presence or absence of the gel effect, the main mass of the

monomer reacts in a narrow temperature range at temperatures close to adiabatic heating. This result subsequently made it possible to use the approximation of a narrow reaction zone to find the stationary velocity of the front in analytical form.

The kinetic equations can obviously be simplified using the method of QSC with respect to the macroradicals. The study of this possibility for processes taking place under polymerisation wave propagation conditions[50,46] showed that with material initiation and assuming a narrow reaction zone, the conditions for quasi-stationary character have the form

$$\frac{k_t}{k_p} \gg 1; \quad \left(\frac{I_0 k_t}{k_i}\right)^{\frac{1}{2}} \gg 1$$

where the reaction rate constants are taken at the temperature of adiabatic heating.

The approximation of a narrow reaction zone made it possible to obtain analytical expressions for the stationary velocity of the polymerisation front with consumption of the initiator[46,47] and also for conditions under which its concencentration is constant[43]. In the first case, the analytical dependence of the limiting degree of transformation on the initial concentration of the initiator was obtained, and the width of the reaction zone estimated. The stationary rate of propagation of the polymerisation front is proportional to the initial concentration of the initiator to the power 0.4, which shows complete agreement with the experimental data. Comparison of the theoretical and experimental values of the stationary rate of propagation of the front and the limiting degree of transformation α_{lim} shows marked lack of agreement, however (Fig. 9). Thus experiment showed practically complete consumption of the monomer, whereas the theoretically predicted degree of transformation is 0.6—0.7 (curve *1* in Fig. 9*b*).

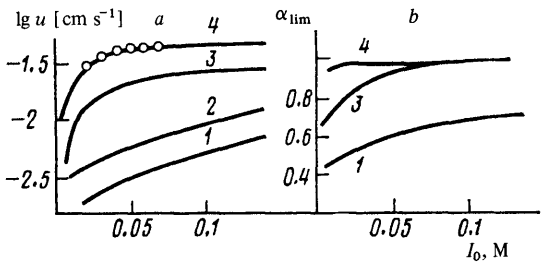


Figure 9. Dependence of the stationary velocity of the wave propagation front (u, cm s^{-1}) (*a*) and the limiting degree of conversion (*b*) on the initiator concentration; *1*) without allowance for pressure and the gel effect[44], *2*) with allowance for pressure, *3*) with allowance for the gel effect, *4*) with allowance for pressure and the gel effect[49]; points—experiment[41].

This lack of agreement between the experimental[39-42] and theoretical[43-46] results can be attributed to the existence of thermal polymerisation or the effect of high pressures and an extremely marked gel effect, not taken into account in the theory.

Allowance for polymerisation by thermal initiation should obviously lead to complete conversion. Published data[51] show, however, that the contribution of thermal polymerisation to the stationary velocity of the front is small (up to 3.5×10^{-3} cm s^{-1}). Thus a necessary step forward in the understanding of the nature of the discrepancy between theory and experiment was the study of the influence of pressure and the gel effect on the stationary velocity of the polymerisation front and the yield of polymer formed[49]. Fig. 9*a* (curve *2*) shows that allowance for pressure leads to an increase in the magnitude of the stationary rate, but it still remains appreciably lower than the experimental value, and the limiting degree of transformation (curve *3* in Fig. 9*b*) corresponds to complete consumption of the monomer only at values of I_0 equal to 0.1—0.15 M. The theoretical data show good agreement with experiment only when simultaneous account is taken of pressure and the gel effect (curves *4* in Fig. 9*a* and 9*b*), and estimates for these conditions give a reaction zone width of 0.2 cm, which also shows good agreement with experiment.

As already noted, at high temperatures, thermal initiation may become the main source of radicals. At the same time, there have been practically no studies of its role in processes of radical polymerisation taking place under conditions of polymerisation wave front propagation, apart from a theoretical analysis of the influence of thermal initiation on the stationary rate of polymerisation, which shows that when there is no gel effect, for a reaction of first order with respect to the monomer, more acceptable values of the stationary rate are obtained in the approximation of a narrow reaction zone (curves *1* and *2* in Fig. 10). When there is a gel effect, this approximation can also be used for higher orders of the reaction (curves *3* and *4* in Fig. 10).

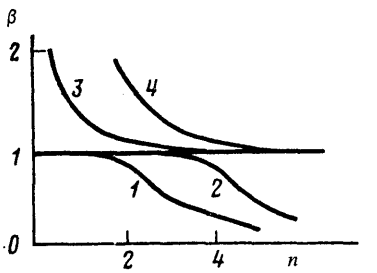


Figure 10. Ratio of the rates obtained from the results of analytical and numerical calculations of the rate of propagation of the front ($\beta = u_{anal}/u_{num}$) as a function of the kinetic order of the reaction (n);[51] the curves were calculated in the approximation of Ref. 30 (*1*, *2*) and without it (*3*, *4*).

The kinetics of non-isothermal radical polymerisation in a periodic reactor without mixing have been studied theoretically and experimentally[52-54]. The results of numerical calculations and the analytical solution of the problem indicate that in these systems, for definite values of the parameters, values analogous to those for frontal polymerisation are observed. In fact, in the radical polymerisation of MTF-9 acrylate polyester, which has a high viscosity ensuring throughout the entire process heat transfer takes place by a purely conductive mechanism, the authors cited observed "layer" polymerisation conditions at atmospheric pressure[54].

There have been practically no experimental studies of the molecular masses and MMD in radical polymerisation under conditions of reaction front propagation. A theoretical analysis of the change in the molecular masses,

polydisperse character, and MMD of the resulting polymer has been carried out[47,51]. The calculations show that the average molecular masses decrease sharply behind the front of the thermal wave, but at the same time the decrease in the values of $\bar{P}_w$ and $\bar{P}_n$ is not the same, so that the polydisperse character of the resulting polymer at first increases because of the "burn-out" of the initiator (Fig. 11*b*), but remains practically constant behind the wave front.

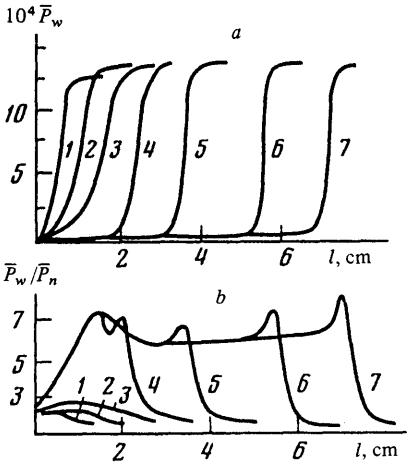


Figure 11. Change in $\bar{P}_w$ (*a*) and the width of the MMD (*b*) under front propagation conditions during the polymerisation of styrene[48]; $I_0 = 10^{-2}$ M, $T_0 = 300$ K, starting temperature 380 K; the numbering of the curves is the same as in Fig. 8.

A broad MMD is a characteristic feature of polymerisation under reaction front propagation conditions. It should be remembered that for polymerisation under adiabatic conditions, the ratio $\bar{P}_w/\bar{P}_n$ for the final polymer is always appreciably greater than two, but for adiabatic polymerisation a narrow MMD may be preserved by stopping the polymerisation at the moment when the initiator "burns-out". This procedure is obviously impossible in principle for polymerisation under reaction front propagation conditions.

Chain transfer to the monomer or the solvent for frontal polymerisation leads to a decrease in the width of the MMD, and when this reaction is sufficiently intense, the MMD remains the most probable until the end of polymerisation.

5. Non-Isothermal Polymerisation in Tubular Reaction Vessels

The most important macrokinetic feature of polymerisation—the increase in the viscosity by several orders of magnitude—has a particularly marked influence on the course of the process in a tubular reactor. This influence is two-fold: firstly, there is appreciable distortion of the reagent flow rate profile, and secondly, there is a qualitative change in the integral characteristics of the process, primarily the pressure–flow rate characteristic, that is the dependence of the pressure drop (Δp) on the flow rate (q). The study of the process in the simplest one-dimensional version makes it possible to study the pressure drop–flow rate relationship, the longitudinal temperature profiles, and the influence of these parameters on the kinetics of polymerisation and the MMD of the products.

Polymerisation can take place under low-temperature or high-temperature conditions. In the absence of heat sources other than chemical sources, and when thermal conductance is negligible, increase in the consumption of the reagents leads to a proportionate displacement of all the points of the longitudinal profiles of temperature and concentration along the axis of the reactor. The temperature peak under high-temperature conditions ("hot spot"), with increase in the consumption, moves to the outlet from the reactor and may even leave the reactor[55]. There is then a unique relationship between the value of the flow rate of the reagents and the longitudinal temperature profile.

If the thermal conductivity in the axial direction is high (high thermal flux along the metal walls of the reactor), the relationship between the stationary states of the reactor and the flow rate become ambiguous. There exists a range of change in the flow rate within which one set of parameters corresponds to three different states of the reactor: low-temperature, high-temperature, and an intermediate unstable state. The arrival at specific reactor operating conditions depends on the initial conditions. In this case there is a complete analogy between the process of polymerisation in a tubular reactor and the process of combustion. With change in the consumption, flare-up or quenching of the process is observed, that is there is a change from low-temperature to high-temperature conditions and vice versa, and these changes show hysteresis. The range of non-unique solutions may consist of two separate regions of change in the flow rate, and there exists a range of values of the flow rate in which only high-temperature conditions are realised[56].

Heat liberation as a result of internal viscosity (dissipation of energy) may also lead to a non-linear change in the longitudinal temperature profiles. The mechanical source of heat increases in proportion to the square of the flow rate and to the viscosity of the liquid. Its contribution may naturally be particularly marked in polymerising systems. Studies have shown[57] that mechanical heat liberation plays the role of "trigger" for the change from low-temperature to high-temperature conditions, if the conditions of the process are close to the critical conditions for this change. Otherwise, the dissipation of mechanical energy has no qualitative influence on the operation of the reactor.

An important characteristic of a tubular reactor is the relationship $\Delta p(q)$, called the pressure–flow rate characteristic of the reactor. The form of this relationship is determined by the change in the distribution of the average (with respect to cross-section) viscosity along the length of the reactor with increase in the flow rate. The pressure–flow rate characteristic itself determines a number of regular features of the operation of the reactor, including qualitative features. For a polymerisation reactor, the $\Delta p(q)$ relationship is particularly complex. In the first place, the viscosity of the reacting mixture increases sharply during the reaction, and also changes with change in temperature. In the second place, as noted above, with change in the flow rate, non-linear changes take place in the longitudinal temperature profiles, and hence in the degree of transformation of the monomer. The viscosity undoubtedly depends on the molecular mass of the resulting polymer, but essentially no analysis of the effect of this factor has been published.

These characteristic features define the form of the $\Delta p(q)$ relationship. The marked increase in the viscosity is the reason for the basically non-monotonic character of this relationship. For very low values of the flow rate, the whole reactor is filled with very viscous polymerisation

products. Increase in the flow rate leads to the removal of products and to filling of a part of the reactor with less viscous reagents. The average viscosity in the reactor decreases rapidly, and the pressure drop $\Delta p \sim q \int_0^{\alpha} \mu(x)dx$ decreases. As a result, the $\Delta p(q)$ relationship at very low flow rates shows a clearly defined maximum[58], which is more marked, the greater the increase in the viscosity during the polymerisation. The flow rates corresponding to the maximum pressure drop also correspond to the almost complete transformation of the monomer at the outlet from the reactor ($\alpha \sim 0.95$).

A non-monotonic $\Delta p(q)$ relationship is also observed for the non-isothermal flow of an inert liquid, whose viscosity decreases rapidly with temperature. The decrease in the pressure drop with increase in the flow rate may take place as a result of the displacement of colder liquid, which has been able to cool during flow, by hotter and consequently less viscous liquid[59], or as a result of an increase in the dissipative heating[60]. Both of these effects, however, take place at extremely high values of the flow rate, much greater than those which can be realised in technological polymerisation processes.

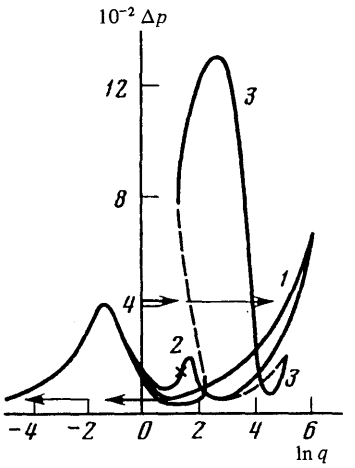


Figure 12. Pressure–flow rate characteristics of a tubular polymerisation reaction[60]: *1*) low-temperature conditions (the arrows indicate the hysteresis changes with change in the pressure drop); *2*) change from a dissipative source for the process to high-temperature conditions (the asterisk marks the point of change); *3*) high axial thermal conductivity (the broken lines are the branches of the curve for the unstable intermediate solution).

The above-mentioned change from low-temperature to high-temperature conditions for the process as a result of a mechanical source of heat may take place at comparatively low values of the flow rate. The form of the pressure–flow rate curve changes qualitatively, and new extremal points appear on it (curve *2* in Fig.12), since a complete rearrangement of the temperature and concentration profiles takes place. There is a sharp increase in both the heat production and the degree of transformation, so that there is competition between the temperature and concentration dependence of the viscosity, and either the former (in the case of solutions) or the latter (for bulk polymerisation) may predominate. The specific form of the $\Delta p(q)$ relationship may be extremely complex.

The situation is even more complicated when a decisive role is played by axial thermal conductivity. In addition to the maximum under low-temperature conditions (low values of the consumption), the pressure–flow rate characteristic shows a much larger peak under high-temperature "combustion" conditions, determined by the movement of the "front" along the reactor (curve *3* in Fig.12). In addition, branches of the $\Delta p(q)$ curve corresponding to stationary unstable states of the reactor exist.

In the experimental realisation of the process, it is possible to keep the flow rate or the pressure drop constant. In either case, several different stationary reactor operating conditions are possible, corresponding to the same value of the fixed parameter. With change in the parameter (for example the pressure drop in Fig.12), abrupt changes from one branch of the solution to another are possible. The points of the changes do not coincide, that is hysteresis is observed, and for $\Delta p = \text{const}$ it is not thermal (as in combustion processes) but purely hydrodynamic.

The study of the flow rate profiles is possible only for a two-dimensional arrangement. The process has been studied for low-temperature conditions (or for the isothermal case).[61–63] As a result of the adhesion of the liquid to the walls of the reactor for an initial parabolic flow rate profile, the layers of liquid next to the wall are in the reactor for an extremely long time. The reaction in these layers takes place to a high degree of transformation, that is very viscous polymerisation products are formed, and the rate of flow at the wall decreases. Since the consumption is constant, there is a corresponding increase in the flow rate in the axial zone. The residence time of the reagents close to the axis decreases, so that there is a decrease in the degree of transformation of the monomer and the viscosity of the liquid, leading to an even greater increase in the rate of flow in the axial zone, etc.

This leads to the production of two quite distinct flow zones: a layer of very viscous slow-moving reaction products next to the wall, and a stream of reagents with low viscosity in the axial zone of the reactor, penetrating through the products (Fig.13). The ratio of these two zones depends on the flow rate, that is on the rate of supply of the reagents. To obtain uniform products at the outlet, it is necessary to have flow rates which are sufficiently low, so that the stream of unreacted liquid does not move out of the reactor. As a result of the "extension" of the flow rate profiles (Fig.13), the flow rate at the axis may be several tens of times greater than the average rate. As a result, there is a decrease in the flow rate (or an increase in the length of the reactor) necessary for complete polymerisation, compared with that calculated from the average residence time.

A study of the influence of the deformation of the flow rate profile on the MMD for "live" polymerisation[64] showed that the existence of two flow zones (essentially two fractions with markedly different molecular weights) may lead to the formation of a bimodal MMD at the outlet from the reactor.

An analysis of high-temperature polymerisation conditions in a tubular reactor with allowance for the distribution with respect to the cross-section of the velocity, temperature, and concentrations indicates that these conditions are unstable[65–67]. Within a definite range of change in the flow rates in the reactor, a polymerisation front is formed.

There exists a front stabilisation stage in which the rate of supply of the reagents is equal to the rate of "combustion". In the experiment, the duration of the stabilisation stage reached several tens of minutes. In this time interval, accumulation of viscous reaction products takes place ahead of the front, primarily with an increase in their viscosity, leading to an increase in the rate of flow in the axial zone. The rate of supply of the reagents becomes greater than the rate of "combustion", the front is deformed, and its central part is displaced towards the outlet from the reactor. The flow rate in the axial zone increases, with an increase in the rate of supply of the colder products to the less hot (as a result of curvature) front. The front cools and leaves the reactor.

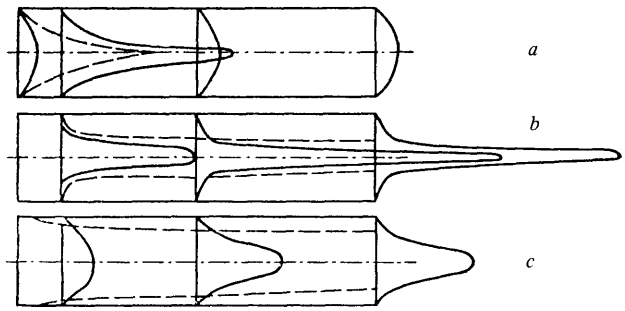


Figure 13. Profiles of the axial rates of flow in a tubular polymerisation reactor for different values of the flow rate: *a*) $q = 1$, *b*) $q = 10$, *c*) $q = 50$;[63] the broken line indicates the boundary of the layer of viscous products.

III. VARIOUS OTHER POLYMERISATION PROCESSES UNDER NON-ISOTHERMAL CONDITIONS

Many chemical reactions, although having smaller thermal effects and activation energies, are capable of taking place with spontaneous thermal acceleration under certain conditions. These reactions include various processes of ionic polymerisation, polycondensation, and vulcanisation (cross-linking).

Fairly reliable data on non-isothermal kinetics have been published for the anionic activated polymerisation of lactams and the polycondensation of epoxide compounds under the influence of amines, and these are examined in the present section. The non-isothermal kinetics of these processes make it possible to separate the common and distinctive features for various types of reaction taking place under non-isothermal conditions.

1. Anionic Activated Polymerisation of ε-Caprolactam

The anionic activated polymerisation of lactams (AAPL) opens up extensive possibilities for preparing constructional materials by "chemical" forming, that is directly from the monomers. The simplicity of the "monomer–article" technological scheme realised in the case of AAPL, however, hides major problems. These difficulties are related on the one hand to the complexity of the process itself and on the other hand to the spontaneous heat production in the reaction mixture. In spite of the fact that the exothermicity of the polymerisation of ε-caprolactam, for example, is only 3.2 kcal mole^{-1}, the adiabatic heating of the monomer–polymer mixtures may reach 70–90 K. In addition, the polymerisation of the lactam is accompanied by the simultaneous crystallisation of the resulting polyamide with a heat release of 6 kcal mole^{-1}, which also contributes to the increase in temperature. The spontaneous heating in AAPL is due not to high thermal effects of the chemical and physical processes taking place but to the high rate of the chemical reaction and the low values of the coefficients of thermal conductivity of the polymerising mixture.

The non-isothermal AAP of ε-caprolactam has been reported by a number of authors[68–73], who established that under adiabatic AAPL conditions for an initial polymerisation temperature of 150 °C and above, the polymerisation and crystallisation take place separately, whereas below 150 °C a combined process is observed. To exclude the influence of crystallisation on the kinetics of polymerisation, the process was studied either in the initial stages[74] or at temperatures above 150 °C.[75]

The development of experimental methods for separating information on the separate processes of polymerisation and crystallisation from the overall kinetics of the increase in temperature is obviously of interest.

A number of almost simultaneous papers[73,76,77] pointed out this new direction in the study of the kinetics of the AAP of lactams, chiefly ε-caprolactam. These papers described methods for the separate study of the kinetics of polymerisation and crystallisation taking place in parallel. Of these methods, the simplest and most reliable is the method[73] based only on experimental data. The results of this work can be examined briefly.

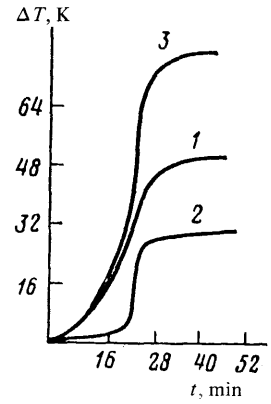


Figure 14. Kinetics of the change in temperature in the activated anionic polymerisation of ε-caprolactam;[73] *1*) polymerisation, *2*) crystallisation of the polymer, *3*) overall curve.

Independent experiments carried out at initial temperatures of 150 °C and 125 °C show that the actual temperature (T) of a reaction satisfies the respective equations:

$$T - T_0 = M_0 \frac{\Delta H_p}{c\rho} \alpha$$

$$\frac{T - T_0}{\alpha} = M_0 \frac{\Delta H_p}{c\rho} + \frac{\Delta H_{cr}}{c\rho} \eta$$

Here, M_0 is the initial concentration of the monomer, α and η are the extents of the polymerisation and crystallisation, ΔH_p and ΔH_{cr} the heats of polymerisation and crystallisation, c the heat capacity, and ρ the density.

Gravimetric determination of the yield of polymer during the polymerisation and use of the known value $M_0\Delta H_p/c\rho = 52$ made it possible to separate from the overall kinetic curve (curve *1* in Fig.14) the increase in temperature due only to polymerisation (curve *2* in Fig.14), and from the difference between curves *1* and *2* the change in temperature as a result of crystallisation (curve *3*). The limiting heating due to crystallisation obtained in this way agrees with the degree of crystallinity determined experimentally from the density[78].

A series of kinetic curves for polymerisation and crystallisation during the AAP of ε-caprolactam, obtained by this method, is given in Figs.15*a* and 15*b*.[79]

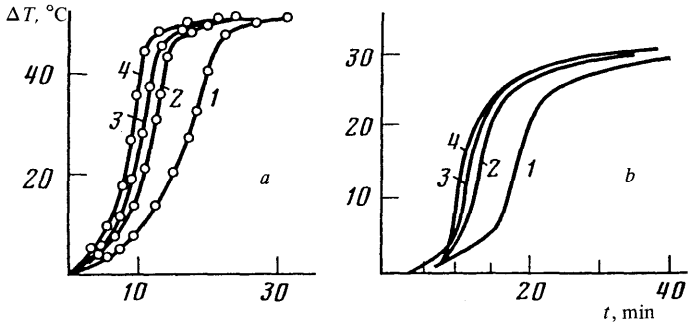


Figure 15. Kinetic curves for the polymerisation of ε-caprolactam (*a*) and the crystallisation of the polyamide (*b*) at different activator concentrations, M: *1*) 3.35×10^{-2}; *2*) 4.78×10^{-2}; *3*) 5.74×10^{-2}; *4*) 6.70×10^{-2}; $T = 125$ °C, concentration 3.35×10^{-2} M.[79]

The kinetic curves for the crystallisation of the resulting polyamide show three regions of increase in temperature: a slow increase, a range corresponding to a high rate of change in temperature, and the stage corresponding to the slow completion of the crystallisation process. The existence of three regions on the crystallisation kinetic curves, confirmed by the form of the dependence of η on α, is due to the sequence of stages involving nucleation, crystal growth, and secondary crystallisation, as confirmed by microscope studies of the morphology of the resulting polymers[80,81].

The methods developed for separating the kinetics of polymerisation and crystallisation make it possible not only to carry out a qualitative analysis of the kinetics of polymerisation and crystallisation but also to obtain a quantitative description of the kinetics of these complex processes[78,82-85].

Adiabatic thermometry is also of interest in the study of composition in combined polymerisation. The method is more valuable for copolymers having restricted solubility. A thermometric method has been proposed[86] for determining the composition of copolymers for the case of the anionic activated copolymerisation of ε-caprolactam with ω-dodecalactam.

Using published data[87] and assuming that in the adiabatic copolymerisation of ε-caprolactam with ω-dodecalactam the product $c\rho$ remains constant (the increase in the heat capacity is compensated by the decrease in the density), the authors cited obtained the equation

$$\Delta T_{cop} = \Delta T_{cl} N_1 + \Delta T_{dl} N_2 \qquad (4)$$

where ΔT_{cop} is the total increase in temperature due to adiabatic copolymerisation, ΔT_{cl} and ΔT_{dl} the adiabatic heating due to the polymerisation of caprolactam and dodecalactam, and N_1 and N_2 the mole fractions of the monomers in the copolymer.

By taking account of the fact that the values of the adiabatic heating for ε-caprolactam and ω-dodecalactam are 52 K and 20 K respectively and measuring the degree of transformation, it is possible, from the kinetic curves for the increase in temperature and a modification of Eqn.(4), to determine the composition of the copolymers formed for different initial ratios of the monomers.

Fig.16 gives the change in the composition of the copolymer during the reaction, together with data on the composition, obtained by ^{1}H NMR and elemental analysis. The good agreement of the values obtained indicates that the approach developed for the determination of the composition of the copolymers from adiabatic thermometric data is correct.

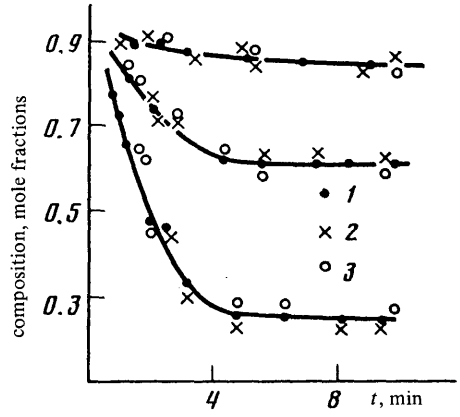


Figure 16. Kinetics of the change in the composition of the copolymer during the adiabatic copolymerisation of ε-caprolactam and ω-dodecalactam from data obtained by thermometry (*1*), ^{1}H NMR (*2*), and elemental analysis (*3*).[86]

There are no published experimental data on AAPL under the conditions of the propagation of a polymerisation wave. Studies of this kind may be of practical interest, in relation to the development of new methods for obtaining thick-walled monolithic articles based on polyamides.

A number of theoretical studies[88,89] showed the existence of a single thermal wave for combined processes of polymerisation and crystallisation. These results make it possible to formulate the conditions for carrying out frontal polymerisation experimentally for AAPL processes.

2. The Polycondensation of Epoxide Oligomers With Amines

The kinetics of the hardening of epoxide oligomers with different molecular masses under the influence of *m*-phenylenediamine (*m*PDA) under adiabatic conditions have been studied[90,91]. For the same initial reaction conditions,

increase in the molecular mass of the original oligomer leads to an increase in the rate of hardening. The authors cited attribute this to the catalytic effect of the hydroxyl groups, whose concentration increases with increase in the molecular mass of the oligomer. A quantitative description of the kinetic data was proposed.

Subsequently, on the basis of this approach, it was shown possible to harden epoxide oligomers under conditions of reaction front propagation[92].

Characteristic profiles of the change in temperature with time in the reactions of the epoxide oligomer ED-20 with *m*PDA and of ED-20 with polyethylenepolyamine are given in Figs.17*a* and 17*b* respectively. After the thermal wave reaches stationary conditions, both the current reaction rate and the limiting temperature are the same in different layers. This means that the same quantity of epoxide groups reacts in each layer.

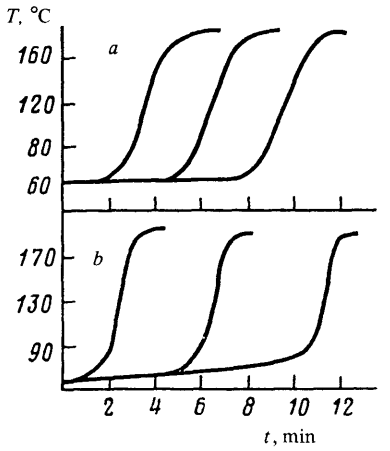


Figure 17. Temperature–time profiles for the hardening of epoxide resins in the presence of amines under thermal wave conditions[92]; temperature 60 °C (*a*) and 30 °C (*b*).

Special measurements showed that the temperatures at the surface of the thermal wave are the same, that is adiabatic propagation of the reaction front takes place in the experiment. Studies of the influence of the initial concentrations of the amine (A_0) and the epoxide groups (E_0) on the stationary rate of propagation of the wave show that $u \sim A_0^{0.63} E_0^{0.73}$. Increase in the initial temperature of the reaction mixture leads to an increase in both the maximum rate and the stationary rate, but since the maximum reaction rate increases more rapidly than the stationary rate, degeneration of the hardening front was observed at temperatures greater than 40 °C for PEPA and 80 °C for *m*PDA. This degeneration of the thermal wave, that is the change from frontal hardening conditions into volume hardening conditions is generally due to low values of the activation energy of the reactions taking place (8–10 kcal mole^{-1}).

The dynamics of the hardening of epoxide compounds by amines under conditions of thermal wave propagation have been studied by numerical methods[93].

Analysis of the solutions obtained shows that there are two reaction front propagation zones. The first corresponds to non-established conditions, and the second to established conditions, that is to stationary propagation of the hardening front.

An important conclusion from the comparison of the temperature and conversion profiles is that under stationary conditions the temperature profile is considerably in advance of the conversion profile. This means that the main mass of the product under conditions of stationary propagation of the thermal wave is formed in a narrow temperature range close to the adiabatic heating of the reaction mass. The influence of the initial concentrations of epoxide groups (E_0) and amine (A_0) and the kinetic and thermophysical parameters on the rate of propagation of the wave has also been analysed. The observed relationship, $u \sim A_0^{0.65} E_0^{0.8}$ is confirmed experimentally[92].

The approximation of a narrow reaction zone has been used[94] to find an analytical expression for the stationary velocity of the hardening front, and this again shows good agreement with experimental data.

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The material examined in the present review on polymerisation processes of different type taking place under non-isothermal conditions shows that the interpretation is complicated by the need to take account of the thermophysical characteristics of the system, the temperature dependence of the parameters, and a number of other factors.

The development of the theory of processes of this kind is making it possible, however, to use these complications to achieve a marked increase in the amount of kinetic information extracted from the kinetics of the process being studied.

A most important aspect of the study of non-isothermal kinetics is the rational allowance for the dynamics and distribution of the heat of reaction; this is necessary when planning polymerisation processes in large systems, for example in the chemical forming of large models. The approaches described in the present review provide a basis for developing new energetically rational processes, and also for intensifying existing technological processes.

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