Translated from *Uspekhi Khimii*, 48, 1492 - 1517 (1979) U.D.C. 541.11:547.9

Non-isothermal Processes and Methods of Investigation in the Chemistry and Mechanics of Polymers

A.M.Stolin, A.Ya.Malkin, and A.G.Merzhanov

We shall discuss kinetic processes relevant to the chemistry and the mechanics of polymers in which the internal evolution of heat (due to exothermic reactions or to dissipative deformation) exceeds the ability of the system to transfer heat to its surroundings, so that the chemical reaction or the mechanical process occurs under non-isothermal conditions at a rate which is dependent on temperature. Processes of this type include: non-isothermal polymerisation (in a batch or a flow reactor), thermal phenomena during the cyclic deformation, extension, and external friction of polymers, and flow under conditions of dissipative heating. We shall describe the common features of all these phenomena, their characteristics, and their most important consequences from the standpoint of research and technology. 164 references.

CONTENTS

I. Introduction 798
II. General theory of non-isothermal processes 798
III. Non-isothermal polymerisation 800
IV. Non-isothermal deformation of solid polymers 803
V. Non-isothermal flow 806
VI. Conclusions 808

I. INTRODUCTION

Many processes in the chemistry and mechanics of polymers are accompanied by evolution of heat. The resulting increase in temperature can affect the process very substantially if the relevant rate constants are strongly temperature dependent. Non-isothermal effects have many interesting and important consequences, and their study is an unusual and very revealing (though indirect) method of highlighting the basic features of the phenomenon under study.

The aim of this review is to discuss the non-isothermal processes of relevance to the chemistry and mechanics of polymers. The direct analogy which exists between these two topics justifies a common approach. Thus the analogue of the evolution of heat during polymerisation is the dissipative nature of deformation processes in all polymers. The analogue of the increased rate of a chemical reaction at elevated temperatures is the increased rate of the relaxation processes. In both cases the temperature rise is opposed by the transfer of heat to the surroundings, but the finite thermal conductivity of the reaction medium or of the polymer undergoing deformation gives rise to non-isothermal conditions. These analogies are by no means trivial, because the phenomena being compared are different in nature, and each phenomenon has its own specific features (such as the gradual disappearance of the monomer during chemical reaction and the formation of a new phase during polymerisation, or the relaxation into different physical states during deformation). Heat evolution during deformation is a well-known phenomenon for polymers in any physical (relaxation) state, and is due to internal friction or to the visco-elastic properties of most polymeric materials[1-4].

Thus the basic feature common to the whole of our discussion will be the dissipative nature of the polymerisation and mechanical deformation processes, which gives rise to an increase in the temperature of the reacting mass (deformation) and hence to an increase in the rate of the chemical reaction (relaxation).

II. GENERAL THEORY OF NON-ISOTHERMAL PROCESSES

The development of the theory of non-isothermal processes is closely associated with the theory of combustion. The work on combustion by Semenov, Zel'dovich, Frank-Kamenetskii, and others[5-7] laid the foundations of our understanding of chemical reactions under non-isothermal conditions. More recently the theory of non-isothermal processes has been further developed in connection with various problems in chemical technology[8,9] and in thermal analysis[10-12].

Non-isothermal processes can be classified in different ways, but the most rational classification relies on the origin of the non-isothermal behaviour. From this point of view we can distinguish two important classes of non-isothermal phenomena: internally non-isothermal and externally non-isothermal. Processes of the first class are characterised by constant external conditions, for example an invariant temperature at the surface of the reacting system. Non-isothermicity is produced by an internal source of heat, such as an exothermic or endothermic reaction, energy dissipation by viscous flow, etc. The power output of the source is usually strongly temperature-dependent, and therefore we can expect positive or negative feedback loops. Processes of this type are considered in detail in the theory of combustion.

The second class of phenomena includes processes with weak heat evolution. In this case the non-isothermicity arises mainly from changes in external conditions. Non-isothermal processes preceding the establishment of thermal equilibrium under constant external conditions are sometimes of interest. In both cases the thermal field in the system is not substantially affected by the internal source of heat, and the feedback is not marked. This situation often arises in the thermal analysis of reacting systems, and occasionally in chemical technology[9].

Exothermic processes of the first class are the most interesting. Their strong positive feedback produces specific non-isothermal phenomena which can only be

explained by combined heat evolution and heat transfer effects. These processes include thermal explosions, ignition phenomena, and the propagation of a thermal wave.

1. Thermal Explosion[13-16]

Consider a system including a source of heat with a high and strongly temperature dependent energy output (for example, an exothermic reaction with a large exoergicity and a high activation energy). The heat evolved by the reaction is partly transferred to the surroundings and partly retained in the system, leading to self-heating. The resulting temperature rise accelerates the evolution of heat by a positive feedback mechanism. Under suitable conditions the process can become self-accelerating and produce a thermal explosion if some well-defined critical (or limiting) conditions are met. Below the thermal explosion limit the exothermic reaction proceeds "quietly", with a small amount of self-heating in a stationary (or quasi-stationary) regime. Feedback effects are not very marked in this case.

The simplest form of the thermal explosion equations for condensed systems is

$$C\rho\frac{\partial T}{\partial t}=\lambda\left(\frac{\partial^2 T}{\partial x^2}+\frac{n}{x}\frac{\partial T}{\partial x}\right)+Q\rho k_0 e^{-E/RT}\varphi(\eta), \quad (1)$$

$$\frac{\partial\eta}{\partial t}=k_0 e^{-E/RT}\varphi(\eta), \quad (2)$$

$$\left.\begin{array}{l} t=0 \quad T=T_0, \quad \eta=0; \\ x=0 \quad \partial T/\partial x=0; \quad x=r: \ -\lambda\partial T/\partial x=\alpha(T-T_0) \end{array}\right\}, \quad (3)$$

In these equations T is the temperature of the system, T_0 is the temperature of the surroundings, x is the spatial coordinate, r is the characteristic dimension of the reactor, η is the extent of conversion of the reactant, t is time, C, ρ, and λ are the specific heat, density, and thermal conductivity of the system, Q is the thermal effect (exoergicity) of the reaction (per unit volume), k_0 is the pre-exponential factor, E is the activation energy, α is the thermal emission coefficient, n is a geometric coefficient ($n = 0$ for a plane-parallel plate, $n = 1$ for an infinite cylinder, $n = 2$ for a sphere), and $\varphi(\eta)$ is the kinetic function. The problem consists in defining the critical phenomena: the critical condition (i.e. the relationship between the parameters which distinguish the two regimes, $F(T_0, r, \alpha\ldots) = 0$), and the induction period (the duration of the period of gradual temperature rise preceding the explosion, $t_{ind} = t_{ind}(T_0, r, \alpha\ldots)$).

The structure of the thermal field plays a very important role in the theory of non-isothermal processes. Both the amount of self-heating and the temperature gradients are usually small in the non-explosive regimes. Often Eqn. (1) is replaced by the simpler heat balance equation, ignoring spatial non-isothermality:

$$C\rho\frac{dT}{dt}=Q\rho k_0 e^{-E/RT}\varphi(\eta)-\alpha\frac{S}{V}(T-T_0), \quad (4)$$

where S is the heat transfer surface and V is the reaction volume. Eqn. (4) is physically justified when the Biot number is small ($Bi = \alpha r/\lambda \ll 1$),[17-19] and also under conditions of forced or free convective mixing[20,21]. A more general treatment of Eqn. (4) can be developed by introducing two new parameters: the average temperature and the effective heat transfer coefficient. The error introduced by using Eqn. (4) in general is small, because the temperature rise preceding the explosion is usually small.

2. Ignition[22,23]

During a thermal explosion the self-accelerating reaction occurs throughout the volume of the system, whereas during ignition it is localised (usually on the surface layer, under the influence of a powerful flow of heat from an external source). The mechanism and the rate of supply of heat are always important in ignition processes, and also the non-stationary thermal field in the system. The kinetic features of the source of heat are less important, because ignition occurs in the initial stages of the process. Ignition is often described by a single equation based on the model of a zero-order reaction:

$$C\rho\partial T/\partial t=Q\rho k_0 e^{-E/RT}+\lambda\partial^2 T/\partial x^2,$$

$t = 0 \quad T = T_{init}$;

$x = 0$ 1) $T = T_0$ (heated plate),

2) $-\lambda\partial T/\partial x = q_0$ (radiant flux of intensity q_0),

3) $-\lambda\partial T/\partial x = \alpha(T - T_0)$ (convective flow),

where T_{init} is the initial temperature.

We are sometimes interested in pulsed regimes, when the external source of heat acts for a limited time only. The commonest problems in ignition theory are to calculate the delay time of the ignition and the critical conditions (as in the case of the thermal explosion).

3. Propagation of a Thermal Wave[24-28]

This is the most interesting of the phenomena considered in the theory of non-isothermal processes. It is well known that a thermal wave cannot exist in an inert system: any injected heat pulse immediately decays. However, in systems including a non-linear source of heat which is strongly temperature dependent non-isothermal processes can become self-propagating, giving rise to a wave of temperature rise moving at constant speed through the "cold" substrate.

Thermal waves are described by the system of equations

$$C\rho\partial T/\partial t=Q\rho k_0 e^{-E/RT}\varphi(\eta)+\lambda\partial^2 T/\partial x^2, \quad (5)$$

$$\partial\eta/\partial t=k_0 e^{-E/RT}\varphi(\eta), \quad (6)$$

$$\left.\begin{array}{l} t=0 \quad T=T_{init}, \quad \eta=0; \\ x=0 \quad T=T_{ign}>T_{init}, x=\infty, \quad \partial T/\partial x=0 \end{array}\right\} \quad (7)$$

and the solution is expressed in the form

$$T=T(x-ut), \ \eta=\eta(x-ut); \quad (8)$$

where u is the velocity of propagation of the wave and T_{ign} is the ignition temperature.

The sytem (5)–(7) also describes the ignition process which precedes the stationary propagation of the wave. The velocity of the wave is often determined from steady-state equations in a coordinate system for which the wave front is stationary and the reactants are moving towards the front:

$$\lambda\frac{d^2T}{dx^2}-C\rho u\frac{dT}{dx}+Q\rho k_0 e^{-E/RT}\varphi(\eta)=0, \quad (9)$$

$$u\frac{d\eta}{dx}=k_0 e^{-E/RT}\varphi(\eta), \quad (10)$$

$$\left.\begin{array}{l} x=-\infty \quad T=T_0, \quad \eta=0, \quad dT/dx=0, \\ x=+\infty \quad T=T_0+Q/C\rho, \quad \eta=1, \quad dT/dx=0. \end{array}\right\}. \quad (11)$$

The existence of thermal waves and their velocity usually depend on the total emission of energy from the heat source: in other words regimes with $\varphi(1) = 0$ are usually considered.

All these phenomena are critical, and they occur only if

$$\beta = \frac{RT_*}{E} \ll 1, \quad \gamma = \frac{C\rho}{Q} \cdot \frac{RT_*^2}{E} \ll 1, \tag{12}$$

where T_* is a scaling temperature which characterises the process. They are studied in the theory of combustion—the most important topic in the theory of non-isothermal processes. If the inequalities (12) are not extreme the phenomena tend to degenerate, and their boundaries become more diffuse.

In the case of endothermic processes the feedback loop is negative, and this simplifies the problem and leads to stable stationary regimes with varying degrees of non-isothermality.

Externally non-isothermal processes are very interesting in chemical kinetics because they offer the possibility of non-isothermal methods of investigation[10-12]. The course of a chemical reaction in these systems is almost entirely determined by the external conditions and by heat transfer, and the reciprocal effect of the reaction on the heat transfer process is unimportant. Under heat exchange conditions such that the temperature gradients in the reacting volume are small, and the system is able to "absorb" the small temperature changes produced by the heat of reaction, we can calculate the reaction rates and their dependence on temperature and on the extent of reaction, i.e. we can study the chemical kinetics of the system. This is usually done by imposing a linear temperature rise on the surrounding medium.

Non-isothermal processes are widespread in chemistry, physics, energetics, chemical industry, and other branches of science and technology. They are typical of oxidation reactions, thermal decomposition, synthesis from the elements, polymerisation, etc. Many physical processes such as nuclear reactions, phase transitions, viscous flow, the interaction of matter with high-frequency electromagnetic fields, etc. also occur in a non-isothermal regime[29]. The theory of non-isothermal processes and the ideas which have been developed from it are independent of the specific nature of the processes considered, and are based on the general phenomenological laws of heat evolution and heat transfer. Not surprisingly, therefore, we can legitimately rely on analogies and transfer results from one system to another when discussing specific non-isothermal processes.

III. NON-ISOTHERMAL POLYMERISATION

1. General Description

Polymerisation usually occurs under conditions of self-heating, produced by the exothermicity of the chain growth reaction. If the thermal effect of this reaction is small, the reaction rate is only weakly temperature dependent, and the viscosity of the reacting mass in the initial stages of polymerisation is low, then we can maintain approximately isothermal conditions and keep the temperature constant by vigorous stirring and by thermostatting the walls of the apparatus. On the other hand the temperature of the system will tend to increase continuously during polymerisation if the viscosity is high, the thermal conductivity of the mixture is low, and the thermal acceleration resulting from the temperature dependence of the reaction rate is large. Under the latter set of conditions polymerisation processes must be classified as non-isothermal.

Heat evolution effects have recently been recognised as a favourable feature in polymerisation reactions, often responsible for the practical success of a proposed reaction. Typical examples are adiabatic and frontal[30,31] polymerisation reactions, thermal initiation[32], etc. These methods allow us to impose "extreme" conditions on the reaction and thus to accelerate the polymerisation process.

The study of non-isothermal polymerisation is concerned with two basic problems. The first (or direct) problem consists in obtaining information on the process itself from data on the properties of the mass undergoing polymerisation (physical, rheological, and chemical). A macro-kinetic approach is used, and a model of the process is developed from the transport equations, the equations of chemical kinetics, and the equations of state. By solving this problem we arrive at the temperature distribution, the extent of reaction, and the structural characteristics (molecular weight distribution) of the product in space and in time.

The second (or inverse) problem consists in obtaining the characteristics of the chemical reaction (rate constants and activation energies) from information on the process itself, for example from the experimentally determined time dependence of the heat evolution or of the temperature at one point or at a small number of points. The solution of this problem usually involves the use of macro-kinetic relationships previously obtained by solving the direct problem.

Polymerisation processes can also be classified in terms of the complexity of the chemical reaction involved. The kinetically simplest polymerisation processes are those strongly dominated by a single reaction. A number of polycondensation and vulcanisation reactions[33,34] are of this type. Radical polymerisation reactions involve a more complex kinetic scheme which must, in general, allow for the initiation, growth, and breaking of chains[35].

We shall discuss the results of studies of the thermal regimes of polycondensation and radical polymerisation processes in chemical reactors of simple design. Some results on the macro-kinetics of ionic polymerisation are examined in Refs. 36 and 37, and will not be considered here. There are no published data on the macro-kinetics of emulsion, suspension, and other types of polymerisation under non-isothermal conditions.

2. Simple Kinetic Scheme

The thermal regimes of reactions of this type are generally similar to those of true or degenerate thermal explosion reactions. We can therefore describe the macro-kinetics of these polymerisation processes by applying the methods of the classical theory of thermal explosions (see above) in a static reactor. However due allowance must be made for some specific features of polymerisation processes, such as the lower values and the greater range of the heats of reaction (Q) and of the activation energies (E) of polymerisation processes as compared with explosive systems.

Temperature and concentration gradients cannot exist in an ideally stirred reactor. This model is described by the heat balance equation (4) and the kinetic equation (2). The system of equations (2)–(4) has been analysed[38,39] with special reference to polymerisation processes involving a wide range of the parameters Q and E. It was

found that three characteristic regions of thermal regimes are possible.

1) A region of non-degenerate thermal self-acceleration. Depending on the relative magnitude of the heat evolution and of the heat extraction, described by the Semenov criterion $\kappa = QE\rho k_0 \exp(-E/RT_0)/[\alpha(S/V)\cdot RT_0^2]$, the self-heating during polymerisation can be small (if $\kappa < \kappa_{cr}$) or large and rapidly increasing (if $\kappa > \kappa_{cr}$). The critical value κ_{cr} is very sharply defined. The extent of reaction during the development of the maximum heating rate is negligible, and therefore regimes corresponding to $\kappa > \kappa_{cr}$ are undesirable in polymer technology.

2) A region of degenerate thermal self-acceleration. In this case we have a sub-critical regime in which the rate of growth of the temperature is decreasing continuously, and a super-critical regime corresponding to thermal self-acceleration. However the transition between these two regimes is gradual (degeneracy of the critical conditions). The degree to which the polymerisation can be accelerated is limited by the availability of the monomer, and the extent of reaction during the development of the maximum temperature is considerable.

3) A region of thermal regimes without self-acceleration. In this region the rate of self-heating decreases with time, and the monomer has almost completely disappeared when the maximum temperature is reached.

The boundaries between these three regions are not sharp: they are determined by the values of the two dimensionless parameters $\gamma = C\rho RT_*^2/(QE)$ and $\beta = RT_*/E$, which describe the thermal effect and the activation energy of the reaction. The last two regions are technologically important.

Three thermal regimes exist also in the case of polymerisation in a batch reactor without stirring[40-42], to which the heat balance equation for conductive heat transfer (1) applies. Different boundary conditions for the temperature are possible. The heat dissipation conditions are usually defined in terms of the Biot criterion. Since the thermal field is not uniform over the cross-section of the reactor the extent of reaction is also, in general, not uniform. The degree of non-uniformity increases with the Frank-Kamenetskii criterion $\delta = Qk_0Er^2/(\lambda RT_0^2 e^{E/RT_0})$, which characterises the ratio of the rates of heat evolution and heat relaxation by conductive heat transfer. At low values of δ the polymerisation occurs fairly uniformly over the volume of the reactor (volume polymerisation). At large values of δ the reaction goes to completion first in the outer layers of the reaction volume, after which the polymerisation front moves towards the centre of the reactor (frontal polymerisation)[40,41].

The quantity η is the only kinetic characteristic in the initial equations (1), (2), and (4) on which the present discussion is based. This characteristic could be, for example, the concentration of monomer in the reaction mixture. However the structure and the properties of the product depend on a whole range of reactions of the growing chain, which yield polymers with different molecular weight distributions (MWD) and, in general, different amounts of chain branching. In non-isothermal polymerisation (which includes the vast majority of technological processes) the rate constants of the various steps of the polymerisation reaction have different temperature coefficients, and as a result the MWD can be very different from the distribution expected for isothermal polymerisation. This is a serious problem, which can radically alter the properties of the product (see, for example, Refs. 43 and 44).

A quantitative estimate of the effect of non-isothermicity on the MWD of the resulting polymer cannot be made in general, because the solution of the problem is sensitively dependent on the special kinetic features of the process. However we can develop a general approach to this problem by introducing the "generalised" time τ, defined by the pattern of the previous temperature changes. Thus in the case of anionic polymerisation with very fast initiation, when only the rate constant for chain growth (K) is relevant to the overall kinetics, the generalised time τ is given by[45]

$$\tau = \int_0^t K[T(t)]\,M(t)\,\mathrm{d}t, \qquad (13)$$

where M is the concentration of monomer in the reaction mixture (depending on time t), and K depends on temperature (which also varies with time). This approach allows us to calculate the MWD of the resulting polymer by postulating quasi-isothermal conditions with respect to the variable τ. Some technological aspects of the effect of non-isothermal polymerisation on the MWD of the resulting polymer are discussed in Refs. 46 and 47.

We must stress that a very similar approach, relying on the use of a "generalised" time, had been developed previously[48] to describe non-stationary processes during visco-elastic relaxation. The approach can be applied to any non-isothermal deformation or relaxation phenomenon, making the system quasi-isothermal. The most detailed studies in this area have been on problems of polymer creep[49,50].

3. Radical Polymerisation

The macro-kinetics of radical polymerisation under non-isothermal conditions were first investigated by Maksimov[31,51-53], who combined the kinetic equations for chain growth and initiator decomposition with the heat balance equation (1) on the assumption of constant concentration of free radicals during the polymerisation (quasi-stationary hypothesis).

Because of the kinetic peculiarities of radical polymerisation, new and interesting types of behaviour are possible. The basic kinetic feature, associated with the consumption of the initiator, is that high levels of self-heating are not reached in the "explosion" regime (because of the rapid "burning up" of the initiator). Another characteristic feature of radical polymerisation is the gel effect, which consists in an increased rate of polymerisation as a result of the increase in viscosity (and decrease in the rate of chain breaking) as the extent of reaction increases. Corrections for the gel effect in macroscopic treatments are usually applied by various empirical formulae[53-55]. Under non-isothermal conditions the increase in temperature assists the motion of macrochains, and the gel effect is displaced towards higher extents of reaction (or is eliminated).

The gel effect during radical polymerisation produces a new thermal regime, called the intermediate regime[53]. In this regime the self-heating is small during the initial stages of polymerisation, but in the later stages the reaction rate increases rapidly and the mixture reaches high temperatures.

4. Propagation of the Polymerisation Front

The polymerisation reaction can occur in layers, with a propagating polymerisation front, the heat evolved in the reaction zone being taken away by the colder layers in which the reaction had started. This "frontal" polymerisation regime has considerable practical importance because it offers lower working temperature and lower polymerisation (shrinkage) stresses.

Enikolopyan and coworkers[56-59] describe the macrokinetics of this regime by starting from steady-state equations of type (8)–(10). The problem consists in determining the linear velocity of polymerisation, the width and structure of the front, the temperature distribution, and the extent of reaction: this can be done by using the concepts and methods of the theory of thermal waves[25-29]. The basic assumption needed to arrive at an analytic solution of the system (9)–(11) is that the reaction is confined to a narrow region where the temperature T_m is a maximum. Allowance should also be made for the difference in thermal and physical properties between the initial mixture and the polymerised product, i.e. for the dependence of the thermo-physical properties of the system on the extent of reaction. This is not possible with existing methods of calculation.

In radical polymerisation under frontal conditions it is important to consider the presence of the gel effect. An attempt to allow for the gel effect by using empirical formulae is described in Ref. 60.

5. Optimisation of Technological Processes

Optimisation problems can be formulated from a macrokinetic description of the polymerisation process. Various optimisation criteria are possible: the only requirement is that the criterion should be consistent with well validated methods of calculating and predicting the behaviour of polymerisation reactors. To solve the optimisation problem we must allow for the changes in structural parameters and in physical and mechanical characteristics resulting from the polymerisation, because these characteristics determine the properties of the finished item of interest to the consumer. Work on these problems has only just begun. Thus some recently reported investigations[61-63] of the optimisation problem aimed to minimise the reaction time while maintaining externally controllable temperature gradients, extents of reaction, and radical temperature differences at all extents of reaction.

6. Determination of the Kinetic Characteristics

Failure to allow for the exothermic effects of the reaction, which give rise to variations in temperature, reaction rate, and extent of reaction over the reacting volume, can lead to serious errors in the kinetic description of the non-isothermal polymerisation process. The problem of the kinetics of setting of a phenol–formaldehyde resin, which has been discussed in the literature for many years, is a particularly good example: different workers arrive at contradictory conclusions on the main kinetic features of this reaction. Most of them assume the presence of a significant induction period, because the time dependence of the measured kinetic factor is S-shaped. However Basov and coworkers[64] studied the dependence of the observed induction period t_{ind} on the size of the reaction vessel in a series of experiments with flat vessels of variable thickness d. They observed a square-law dependence of t_{ind} on d, and the induction period vanished on extrapolation to $d = 0$. This means that the induction period is an apparent "non-isothermal" effect. When the experimental results are extrapolated to isothermal conditions the rate of poly-condensation becomes constant, and the induction period disappears.

One consequence of the development of the theory of non-isothermal polymerisation was the appearance of new methods of determining the kinetic model of the process and of calculating the kinetic parameters. The most rigorous solution of this (inverse) problem relies on continuous measurement of self-heating against time. This is often done under conditions of uniform heating, when temperature distributions within the reaction volume can be ignored.

For polymerisation under adiabatic conditions we can write[65,66]

$$C\rho \mathrm{d}T/\mathrm{d}t = -Q\mathrm{d}M/\mathrm{d}t, \tag{14}$$

where M is the concentration of monomer. If the ratio $Q/C\rho$ is constant this simplifies to

$$M_0 - M = (T - T_0)C\rho/Q, \tag{15}$$

where M_0 and T_0 are the initial concentration and temperature respectively. When the reaction is complete we have

$$\Delta T = T_\infty - T_0 = M_0 Q/C\rho. \tag{16}$$

Thus the fact that the self-heating $\Delta T = T_\infty - T_0$ is independent of T_0 and is proportional to the initial monomer concentration M_0 confirms on the one hand that polymerisation is proceeding under truly adiabatic conditions and on the other hand that the ratio $Q/(C\rho)$ is constant.

The extent of reaction can be expressed in terms of the dimensionless parameter $\eta = (M_0 - M)/M_0$, or

$$\eta = (T - T_0)/(T_\infty - T_0). \tag{17}$$

For a reaction of the n-th kinetic order we have

$$-\mathrm{d}M/\mathrm{d}t = k_0 M^n \exp(-E/RT). \tag{18}$$

In this case Eqns. (14)–(18) allow us to express the rate of change of temperature as

$$(T_\infty - T)^{-n}\frac{\mathrm{d}T}{\mathrm{d}t} = k_0 (T_\infty - T_0)^{1-n}\exp(-E/RT). \tag{19}$$

Thus a plot of $\lg[(T_\infty - T)^{-n}dT/dt]$ against $1/T$ should be a straight line from which the kinetic constants k_0, E, and n can be evaluated (in the case of n, by trial and error). This method has been used by several workers[63-73].

This simple procedure has been extended to more complex kinetic schemes[74-76]. We shall consider its application to radical polymerisation with full allowance for the three basic steps (initiation, chain growth, and chain breaking). The reaction is usually assumed to be quasi-stationary (rate of change of the concentration of macroradicals much smaller than their rate of formation and of disappearance, and rate of initiation equal to the rate of chain breaking). With this assumption the kinetics of radical polymerisation can be described by the expressions

$$-\mathrm{d}M/\mathrm{d}t = k_{\mathrm{eff}} I^{1/2} M \exp(-E_{\mathrm{eff}}/RT), \tag{20}$$

$$-\mathrm{d}I/\mathrm{d}t = k_{i0} I \exp(-E_i/RT), \tag{21}$$

where M and I are the time-dependent concentrations of monomer and of initiator, k_{eff} and E_{eff} are the effective kinetic constants of the polymerisation reaction ($k_{\mathrm{eff}} = k_{p0}(k_{i0}/k_{t0})^{1/2}$; $E_{\mathrm{eff}} = E_p + \frac{1}{2}(E_i - E_t)$; k_{i0}, k_{t0}, k_{p0}, E_i,

E_t, and E_p are the pre-exponential factors and the activation energies for the initiation, chain breaking, and chain growth reactions respectively).

If the reaction occurs under adiabatic conditions we can write

$$-Qm\mathrm{d}M=(C_1m_1+C_2m_2+C_3m_3)\,\mathrm{d}T \tag{22}$$

or

$$\mathrm{d}M/\mathrm{d}T=-C/Q, \tag{23}$$

where $C = C_1 + C_2m_2/m_1 + C_3m_3/m_1$, Q is the heat of the chain growth reaction, C_1, C_2, C_3 and m_1, m_2, m_3 are the specific heats and the masses of the reaction medium, the solvent, and the bulb respectively. In Eqn. (22) the thermal contributions of the initiation and chain breaking reactions are ignored because these reactions are weakly exothermic in comparison with the chain growth reaction.

Replacing M by the dimensionless parameter $\eta = (M_0 - M)/M_0$ we can re-write Eqn. (20) in the form

$$\mathrm{d}\eta/\mathrm{d}t = k_{\mathrm{eff}}\,(1-\eta)\,I^{1/2}\exp(-E_{\mathrm{eff}}/RT). \tag{24}$$

By introducing the simplifying assumption that the concentration of initiator remains constant ($I = I_0 = \mathrm{const}$) we can write $k' = k_{\mathrm{eff}}I_0^{1/2}$, and the problem reduces to the vase of adiabatic polymerisation with a simple kinetic scheme. Tonoyan and coworkers[74] proposed a formula for the concentration of initiator which allows for its variation with temperature and time:

$$I=I_0\exp\{-k_{i0}t\exp(-E_i/RT)\}. \tag{25}$$

In this case Eqn. (24) becomes

$$\lg\left(\frac{\varepsilon_1}{T_\infty-T}\frac{\mathrm{d}T}{\mathrm{d}t}\right)+\frac{k_it}{4.6}\exp\left(-\frac{E_i}{RT}\right)=\lg k_0+\frac{1}{2}\lg I_0-\frac{E}{RT}. \tag{26}$$

Truly adiabatic conditions are not usually possible, and the solution of the inverse problem should take account of the transfer of heat to the surroundings. A thermographic method[77,78] has been proposed to evaluate the function $\varphi(\eta)$ in the case of simple kinetics. The same method is used in Ref. 37.

If temperature distribution over the volume of the reactor can be ignored the thermal regime of the reaction is given by the heat balance equation

$$C\rho\frac{\mathrm{d}T}{\mathrm{d}t}=Q\rho\frac{\mathrm{d}\eta}{\mathrm{d}t}-\alpha\frac{S}{V}(T-T_0) \tag{27}$$

with the initial conditions

$$t=0\quad T=T_{\mathrm{init}},\ T_0=T_{0\,\mathrm{init}},\ \eta=0. \tag{28}$$

From Eqn. (27) the rate of the non-isothermal reaction and the extent of reaction are found to be

$$\frac{\mathrm{d}\eta}{\mathrm{d}t}=\frac{C}{Q}\frac{\mathrm{d}T}{\mathrm{d}t}+\frac{\alpha(S/V)}{Q\rho}(T-T_0),\quad \eta=\frac{C}{Q}(T-T_{\mathrm{H}})+\frac{\alpha(S/V)}{Q\rho}\int_0^t(T-T_0)\,\mathrm{d}t. \tag{29}$$

Eliminating time as a parameter in Eqn. (29) we can evaluate the kinetic function $d\eta/dt = \varphi(\eta)$. If the semi-logarithmic plot of reaction rate against reciprocal temperature for a fixed η is linear we can determine the pre-exponential term and the activation energy. It is sometimes found that the activation energy varies with the extent of reaction. This effect may be associated with the increase in viscosity of the reaction medium. By carrying out non-isothermal polymerisation without temperature gradients we can convert the non-isothermal kinetic curves into isothermal curves, and thus simplify the treatment of the experimental results. Hence the kinetics of non-isothermal polymerisation are most conveniently investigated with special experimental arrangements to ensure this condition. The solution of the inverse problem outlined above in the presence of temperature distributions requires experimental measurement of the distribution and calculations on a computer.

IV. NON-ISOTHERMAL DEFORMATION OF SOLID POLYMERS

1. Cyclic Deformation

During the cyclic deformation of solid polymers heat is evolved as a result of the non-ideality of the elastic deformations, which causes some of the mechanical work done in the cycle to be irreversibly dissipated and converted into heat. If the properties of the material do not change within the cycle this work is given by the formula

$$A_\tau=\pi\varepsilon_0\sigma_0\sin\delta, \tag{30}$$

where ε_0 and σ_0 are the amplitude of the deformation and the stress respectively for a frequency ω, and δ is a characteristic of the material called the mechanical loss angle. It is important to note that δ is a function of temperature and frequency, and it can vary quite sharply within some ranges of these parameters. From the point of view of the present discussion we should also note the steep fall in elasticity and the increase in mechanical losses of polymers in the region of relaxation transitions (the most important of which is the glass transition). Sharp changes in mechanical properties and in δ are observed also as a result of phase transitions if the temperature rise produced by the deformation is sufficient to exceed the phase transition temperature.

Since the number of vibrations per unit time is $\omega/(2\pi)$, the energy A evolved per unit time during the cyclic deformation of polymeric materials is

$$A=\frac{\omega}{2\pi}A_\tau=\frac{\varepsilon_0\sigma_0}{2}\omega\sin\delta=\frac{\varepsilon_0^2\omega}{2}G'', \tag{31}$$

where G'' is a characteristic of the mechanical properties of visco-elastic materials called the loss modulus.

The values of δ and G'' for various polymeric materials in different physical states are listed in standard tabulations (see, for example, Refs. 2 and 79). We should stress that in every case $G'' > 0$, i.e. the deformation process is invariably dissipative. Formulae (30) and (31) apply both to solid and to rubbery substances. As in the cases considered above the rise in temperature is controlled by the transfer of heat to the surroundings, and the material constants which characterise the level of heat evolution are strongly temperature dependent, at least in some critical regions of temperature. Therefore, as has already been pointed out[80-83], this mechanical phenomenon is analogous to non-isothermal chemical reactions. The similarity extends to the critical effects: thermal explosion in the case of a chemical reaction and a similarly sharp and uncontrollable increase in temperature during cyclic deformation (leading to the destruction of the item or to the loss of its ability to withstand changes in shape.

Different regimes of temperature change are possible during cyclic deformation[80,84]. In the case of efficient heat exchange and moderate stresses we observe self-heating up to some equilibrium temperature which depends on the amplitude of the stresses[85] (since this amplitude

determines the intensity of the heat evolution). This is the "stationary" case, the most favourable mode of operation of plastics components, and is the mechanical analogue of a non-isothermal reaction proceeding under conditions far removed from the "thermal explosion" regime (for example, a polymerisation with a relatively small heat of reaction). The analogy can be extended to the manner in which the process comes to an end: the reaction stops by the depletion of reactants (in the absence of "topping up"), and the component is destroyed by the exhaustion of its mechanical durability.

The analogy between the thermal effects associated with cyclic deformation and those produced by a chemical reaction applies also under non-stationary self-heating conditions, resulting in an avalanche-like temperature rise followed by destruction of the sample (or component). The increase in temperature causes an increase not only in the heat transferred to the surroundings (as a result of the increased temperature difference) but also in the heat evolution within the sample, since the mechanical losses are greatest at softening (or relaxation transition) temperatures. If the temperature dependence of the heat evolution (dQ_+/dT) is more marked than that of the heat losses (dQ_-/dT) the temperature continues to rise up to the critical region where the material softens and resistance to deformation is lost.

These general cosiderations define the conditions of the transition from the non-stationary regime of temperature growth during cyclic loading to the stationary regime of isothermal deformation (though at a temperature higher than the initial temperature). The conditions are given[80-83] by the simultaneous solution of the two equations

$$Q_+ = Q_-; \quad dQ_+/dT = dQ_-/dT. \tag{32}$$

The solution of this system depends on the temperature (and frequency) dependence of the mechanical losses accompanying the cyclic loading of the particular polymeric material, on the size and shape of the sample, on the way in which the load is applied (since this determines the non-uniformity of the stress distribution, and therefore the rate of heat evolution), and on the heat exchange conditions. Some typical calculations of the critical parameters (i.e. some solutions of Eqns. (32) for various assumed types of loading) are given in the literature[84,86].

Thus studies of the non-isothermal cyclic loading of solid polymers indicate the existence of two basic non-isothermal deformation regimes: a "stationary" regime, leading to a "new" isothermal state in which the stable temperature level depends on the amplitude of the applied stresses, and non-stationary regime characterised by the onset of a critical self-heating ΔT_K at a well-defined amplitude of the applied stresses. It is important to note that the value of ΔT_K is almost independent of the external conditions (loading regime and heat exchange conditions), and in this sense it is a characteristic constant of the material. Critical values of the self-heating (ΔT_K) and of the stresses for many constructional polymers have been tabulated[84].

The stationary and the non-stationary heating regimes described above for samples undergoing cyclic deformation can be interpreted as "pure" manifestations of the heating effects arising from specific combinations of a dissipative factor and a heat transfer factor. At very high levels of applied stress the self-heating can be small if the sample is destroyed before reaching very high temperatures. Another important non-extreme case is a continuous slow rise in temperature—or even a rise followed by a fall in temperature—without reaching a stationary regime. This behaviour is usually associated with changes in the mechanical (visco-elastic) properties of the material during deformation as a result of concomitant physical or chemical structural processes[87-91].

2. Uniaxial Strain

The evolution of heat during the non-cyclic deformation of solid polymers in the uniaxial strain regime reflects the specific features of the molecular mechanism responsible for the structural changes accompanying the deformation. These changes are invariably accompanied by heating effects[92-99] which are a measure of the deviation of the material under study (under the particular deformation conditions) from the "ideal elastic body" or "ideal rubber" models which describe the purely energetic or entropic mechanisms of reversible deformation. In extreme cases the structural changes can lead to oriented crystallisation, with its accompanying thermal effect[100].

Heat evolution of this type has relatively little effect on the way in which the polymer deforms, because the temperature dependence of the mechanical properties of the material in a single physical (or relaxation) state is relatively weak: in other words, the "feedback" effect which plays a crucial role in most non-isothermal processes is absent in this case. Large effects can be expected if the rise in temperature produced by the heat evolved during deformation is sufficient to bring the sample to a transition region where the properties of the polymer are changing rapidly, thus affecting the subsequent deformation. This behaviour is most clearly seen when the temperature of the glassy sample rises to the glass transition temperature T_g. The mechanism of the stretching process changes radially above T_g. The most important aspect of this "devitrification" effect is the necking down of the sample, i.e. the sudden transition from a non-oriented to an oriented state[102], which occurs whether the devitrification takes place under isothermal conditions by an increase in the free volume[101] or whether it is due to a rise in temperature above T_g. The rapid increase in molecular mobility above T_g contributes to the relaxation processes and produces a sudden decrease in the rate of heat evolution.

The way in which this process develops depends on a number of factors: the ratio of the intensity of heat evolution by the mechanical deformation of the rigid polymer to the rate of heat transfer to the surroundings, the compliance (ability to store elastic energy) of the neck or of the yielding sections of the test piece, and also the strength of the polymer. In the simplest and most obvious case the local heating in the necking region, which can be as high as several tens of degrees, leads to a stationary necking down regime[98,103,104].

We shall not attempt to compare alternative mechanisms of the necking down effect, or to discuss the possibility of neck formation under strictly isothermal conditions (which is well established, and suggests that the mechanism of this phenomenon is not necessarily thermal[102,105]). For our present purpose we only need to mention the relevance to the set of phenomena considered here of a non-isothermal mechanism of neck formation (more strictly, the quasi-isothermal mechanism, analogous to the stationary cyclic loading process discussed in the previous section). This mechanism depends on intense, local heat evolution, temperature rise, and a sudden increase in molecular mobility before reaching devitrification conditions (and therefore before reaching the possibility of changes in

physical state, which tend to suppress the mobility by assisting molecular orientation of the polymer). This thermal mechanism of neck formation causes stationary propagation of the neck over the sample at a rate equal to the rate of deformation until the whole of the sample is included in the neck.

These are not the only non-isothermal phenomena during uniaxial stretching. Under certain conditions[106,107] the stationary neck propagation mechanism (which can be likened to a stationary chemical reaction) is replaced by an oscillatory stretching mechanism which has no analogues among the polymerisation processes but is similar to the oscillatory regimes observed in chemical reactions[108].

The critical condition for the appearance of self-oscillations during stretching under non-isothermal conditions is a particular combination of mechanical properties (which determine the elastic and the dissipative properties of the specimen being deformed) and heat-transfer properties (which determine whether the temperature of the polymer can rise above T_g). In these circumstances the stored elastic energy is suddenly released, leading (after a period of elastic deformation up to the critical strain) to an explosive growth in the rate of deformation when the local temperature in the necking region reaches T_g, and to a very sharp increase in the compliance of the polymer in this region. The increase in temperature causes a decrease in stress and an equally sharp decrease in the rate of heat evolution. The length of the high-temperature region of the sample is limited by the low thermal conductivity. Therefore, after the stress has collapsed and the cold zone has been reached we expect a new stage of slow stretch in the elastic region with accumulation of elastic energy in the easily deformed parts of the kinematic circuit and with a slow increase in stress until a new "collapse" is produced by the strong non-isothermal effect. The repetition of these phenomena produces a periodic (oscillatory) mechanism of non-isothermal stretching, and the resulting neck develops a clearly defined "banded" structure.

The direct link between the peaks in the local rate of deformation, the changes in stress during elongation, and the surges in heat evolution (with corresponding sharp changes in temperature) has been confirmed by direct observations[98,99,109]. This is a convincing illustration of the non-isothermal nature of the effect, involving all the aspects of the phenomena with which the present review is concerned: the role of heat evolution as an internal property of the system, the strong temperature dependence of the parameters which determine the rate of heat evolution (feedback effect), and the crucial importance of heat transfer to the surroundings.

These experimental facts on the oscillatory regime of neck formation during the stretching of polymers, and their physical treatment in terms of the general model of non-isothermal deformation processes, have been discussed in the literature[106,107] and formulated mathematically[110].

3. External Friction

External friction is a typical dissipative effect, limited by the transfer of heat to a solid support or to the surrounding atmosphere, and originating from heat evolution by surface friction. The system usually reaches an equilibrium temperature (corresponding to equality of heat evolution and heat extraction) which can be much higher than the initial temperature. This phenomenon is well understood, including the extreme temperature increases (similar to the "thermal explosion" in chemical reactions) which lead to the melting of metal bearings under excessive load. Equally catastrophic results can be produced in bearings made of polymeric materials by heat evolution and uncontrolled temperature rise, especially since the poor thermal conductivity of polymers allows the temperature of the friction surface to increase by a large amount. This can lead to true melting of the surface layer or to substantial softening (loss of hardness and strength) if the polymer cannot melt.

The critical self-heating is analogous to the uncontrolled temperature rise during cyclic deformation, and it involves essentially the same mechanism, since the frictional resistance to slip is due in part to periodic visco-elastic deformations of the polymeric material. The combined measure of the resistance to deformation and of heat evolution by friction is the coefficient of friction, which depends on the slip velocity, to some extent on the load, and on the temperature, and which is found to increase very rapidly near the melting (or softening) temperature of the polymer, leading in extreme cases to a transition from external slip to viscous flow in a layer of very high viscosity[111-115]. A mathematical theory of this phenomenon has been developed[116].

Melting effects as a result of heat evolution by external friction in polymers are not always unfavourable in polymer technology. In the initial stages of polymer treatment processes, when the material must be converted into a state capable of flowing, heat evolution by strong external friction can contribute very significantly to the temperature rise of the charge. This effect is especially marked in extrusion, because the conversion of the solid polymer into a flowing state in the first few turns of the worm conveyor occurs mainly by the heat of external friction.

The reverse transition—from a flowing to a rigid state—occurs in parallel with the flow of the polymer, and it plays an important role in the feed channels of moulding machines and during the filling of the mould. In this case the flowing material is cooled at the walls of the channel, forming a solid layer of increasing thickness. However the continuing flow causes dissipation in the layer, maintaining the flow properties and hindering the growth of the solid layer. Thus we have a complicated interaction between the increase in viscosity due to heat transfer to the cold walls of the channel and the resulting increase in dissipation, which limits the increase in viscosity. This technologically important and complex problem—the growth of solid layers under non-isothermal conditions—has been discussed by many workers[117-121]. The most convincing results were obtained in a recent study[122] of a material with well characterised thermo-physical properties (polyethylene), which clearly established the basic features of the phenomenon. In particular it was shown that under certain conditions the boundaries of the solid layers in a plane-parallel channel remain almost parallel as a result of the interplay of these effects. On the whole, the thickness of the solid layer increases with t^m (where t is time). The exponent is $m \simeq 0.4$, but its exact value depends on the properties of the material. The method of calculation used in Ref. 122 can be applied to other materials of technological interest.

The transition of the melt from a flowing to a rigid state occurs under non-isothermal conditions, and is due to crystallisation of the polymer. Therefore it should not be confused with the basically different transition from a flowing to a rigid state discussed in Refs. 123–126, which

occurs primarily under isothermal conditions and is due to relaxation phenomena. We note that crystallisation during flow can occur under isothermal conditions under the influence of orientation effects, which cause a shift in the temperature of the phase transition[127-131]. This mechanism can also produce a transition from a flowing to a rigid state, but in contrast to the non-isothermal mechanism discussed above it does not involve the two features common to the whole groups of mechanical phenomena discussed in this review: heat transfer and heat evolution by deformation.

V. NON-ISOTHERMAL FLOW

1. Dissipative Flow and Non-isothermal Viscometry

One of the most important aspects of the deformation of flowing systems is the evolution of heat. The deformation is non-isothermal for a number of reasons. The most important is the viscous or dissipative evolution of heat at high rates of deformation in highly viscous systems. In rheologically complex systems the thermal effects are accompanied by structural changes at various levels. In the deformation of reactive media additional heat can be evolved by chemical reaction (for example, polymerisation).

In the non-isothermal flow of liquids the resistance to deformation does not vary monotonically with flow rate. This is easily explained, for example, in the simple case of the shear flow of a Newtonian liquid, for which

$$\tau = \mu(T)\dot{\gamma}, \tag{33}$$

where τ is the stress, $\dot{\gamma}$ is the shear rate, and $\mu(T)$ is the temperature-dependent viscosity. The viscosity coefficients of many polymer systems (both solutions and melts) are accurately known and have been tabulated systematically[2,79,132-135].

In the isothermal case τ increases with $\dot{\gamma}$ according to formula (33). However in the non-isothermal case the resistance to deformation increases only as long as the self-heating is small. At higher strain rates the intensity of the dissipative evolution of heat increases, the self-heating becomes more pronounced, and the viscosity decreases. When the temperature dependence of the viscosity is non-linear this factor becomes even more important, and τ begins to decrease. The variation of the dissipative heat evolution $q(T)$ with temperature depends on the flow conditions[136]. Since

$$q(T) = \tau\dot{\gamma}, \tag{34}$$

it follows that for a constant kinematic parameter $\dot{\gamma}$ (flow rate under forced flow conditions, or velocity of the moving boundary under Couette flow) we can write

$$q(T) = \dot{\gamma}^2\mu(T). \tag{35}$$

In this case $q(T)$ decreases with increase of temperature.

On the other hand if we keep constant the dynamic parameter τ (the drop in pressure, or the driving force at the moving boundary) we have

$$q(T) = \tau^2/\mu(T). \tag{36}$$

In this case the evolution of heat increases with temperature, and the temperature of the liquid rises continuously as a result of thermal feedback[136]. This is the essential analogy between the progress of a chemical reaction in a viscous liquid and the non-isothermal flow of that liquid.

These features are observed in a number of dissipative phenomena[136-139]. The most fully investigated is the hydrodynamic thermal explosion[136], which can be realised experimentally in a rotating viscometer[140]. This is essentially a thermally unstable flow situation, in which the heat generated by internal friction cannot be extracted through the walls of the vessel. This produces a gradual increase in temperature and in the angular velocity of the rotor (for a constant applied torque).

Specific dissipative phenomena are possible during the forced flow of polymers in a tube of finite length. The convective flow of heat through the outlet cross-section and the limited residence time of the liquid in the tube are analogous to the consumption of reactant in a chemical reaction. However the non-linearity of the dissipative (heat evolution) function does not lead to a hydrodynamic thermal explosion in this case: it produces a sharp, discontinuous transition from a low-temperature and low-flow stationary regime to a high-temperature regime, and *vice-versa*, as the pressure drop is gradually changed. The critical conditions for the forward and the reverse transition are not identical (hysteresis effect). This phenomenon has been called hydrodynamic thermal ignition and extinction[138].

Interesting effects are observed from the interaction of dissipative heat evolution and elastic deformation. Self-oscillating flow regimes are possible for some combinations of the characteristic times of heat evolution, heat transfer, and elastic deformation, leading to relaxation fluctuations in stress, temperature, and heat evolution function. A wide variety of different flow regimes can be induced by different ratios of the characteristic times[139].

An important practical application of the theory of non-isothermal flow in viscous liquids has been the development of the non-isothermal method of studying rheological properties[141-143], which relies on the self-heating of the liquid in order to measure viscosity at different temperatures. The non-isothermal method consists in analysing the experimentally measured time-dependent changes in the temperature of the liquid $T(t)$ and in the speed of the rotor of a rotating viscometer $n(t)$ for a constant applied torque M = const, or by measuring $M(t)$ for n = const. This procedure ensures uniform heating of the liquid over the entire volume and minimises heat transfer to the surroundings. Under quasi-stationary hydrodynamic conditions, which exist for relatively high values of the Prandtl criterion $\mathrm{Pr} = \mu/(\rho a) \gg 1$ (where μ is the viscosity, ρ is the density, and a is the thermal diffusivity coefficient) we can determine the variation of the effective viscosity with temperature and with shear stress from experimental plots of $T = T(t, M)$ and $n = n(t, M)$.

This approach is specially useful for determining the variation of viscosity with temperature T and with the extent of reaction of the polymerising mass η, whose value (together with the rate of polymerisation $d\eta/dt$) can be obtained from the heat balance equation[77,78].

2. Non-isothermal Polymerisation in Flow Reactors

Macro-kinetic studies of flow reactors have progressed slowly in recent years. The special features of these reactors (outflow of the reaction products and limited residence time in the reactor) do not allow direct application of the theory of thermal explosions, as was done for batch reactors. Nevertheless the methods of this theory can be applied successfully to an analysis of the thermal

regimes. Typical of this approach are a number of studies[8,144,145] of the course of exothermic reactions in reactors assumed to have ideal mixing, ideal displacement, or displacement with longitudinal transport. The system of equations which describes the thermal regime in these reactors differs from the equations for batch reactors only in having additional terms for the rate of removal of heat and of the reaction products of the flow. In the simplest case of a single exothermic reaction in an ideally mixed flow reactor the equations can be expressed in the dimensionless form[145]

$$\gamma\, d\theta/dt = \exp[\theta/(1+\beta\theta)]\varphi(\eta) - \theta/\varkappa, \qquad (37)$$

$$d\eta/dt = \exp[\theta/(1+\beta\theta)]\varphi(\eta) - \eta/Da,$$

$$\theta = \frac{E}{RT_*^2}(T-T_*), \quad \tau = k_0 e^{-E/RT_*}t, \quad \eta = \frac{M_0 - M}{M_0}, \quad \beta = \frac{RT_*}{E},$$

$$\gamma = \frac{C}{Q}\frac{RT_*^2}{E}, \quad \varkappa = \frac{Q\rho}{\alpha_*(S/V)}\frac{E}{RT_*^2}M_0 e^{-E/RT_*},$$

$$Da = \frac{V}{\omega}k_0 e^{-E/RT_*}, \quad \alpha_* = \alpha + \frac{C\rho}{S}\omega. \qquad (38)$$

In these equations T_* is a scaled temperature defined as

$$T_* = (\alpha S T_0 + C\rho\omega T_{in})/(\alpha S + C\rho\omega), \qquad (39)$$

where T, T_0, and T_{in} are the temperatures of the material, of the surroundings, and of the incoming flow respectively, α_* is the effective heat transfer coefficient (allowing for all the heat losses), ω is the volume flow rate, $\varkappa$ is the Semenov criterion, and Da is the Damkeler criterion.

The most important parameters are the Semenov criterion (which expresses the ratio of the characteristic times for the removal and the production of heat) and the Damkeler criterion (which expresses the ratio of the residence time to the reaction time).

In the case of ideal displacement reactors the convective flows of heat and of matter in the longitudinal direction are important, and they give rise to a boundary condition at the inlet of the reactor. In displacement reactors with longitudinal transport we must introduce additional second-order terms for the effect of the diffusional flows of heat and of matter in the flow direction, and these give rise to a boundary condition at the outlet of the reactor.

A unique feature of polymerisation in flow reactors is the possibility of several stationary states. Zel'dovich[146,147], and, later, van Heerden[148], showed that the stable low-temperature and high-temperature regimes of an ideally mixed reactor depend on the ratio of the Semenov and the Damkeler parameter. The transition from the low-temperature to the high-temperature regime (ignition and extinction), and *vice-versa*, shows hysteresis: the critical conditions for the forward and the reverse transition are not usually identical. Similar features are observed in an adiabatic displacement reactor of finite length[149-151]. In the presence of lateral heat exchange the number of possible stationary states increases to five[152,153].

The existence of a low-temperature (quasi-isothermal) and a high-temperature (quasi-adiabatic) regime is demonstrated in Ref. 154 for an ideally mixed reactor and in Ref. 149 for a displacement reactor. In both these papers the sharp change from one regime to the other is ascribed to changes in the criteria describing the external conditions of the process. Beskov and coworkers[155] also point out the possibility of two regimes in a displacement reactor, but they ascribe it to changes in the internal criterion γ, i.e. to degeneracy of the critical conditions[38,39].

The general formulation of the non-stationary problem with allowance for longitudinal transport is discussed in Refs. 156 and 144. The results obtained are highly relevant to our understanding of the validity of our current models of flow reactors (ideally mixed, or displacement).

The thermal regimes of flow reactor operation have so far been treated as the displacement of an elementary volume in space. Maksimov and coworkers[156] attempted to allow for a radical velocity distribution in the liquid in the form of a Poiseuille profile, which causes a marked spread of residence times. The result is a "saddle-shaped" temperature and extent of reaction profile, and also the extension of the high-temperature (quasi-adiabatic) regime to include conditions in which the mean residence time is smaller than the induction period of the adiabatic thermal explosion.

Numerical solutions[157,158] of the equations describing polymerisation in a tube reactor have shown that the initial parabolic velocity profile becomes "stretched" in the axial direction if allowance is made for the variation of viscosity with temperature and concentration.

The residence time of the charge in the reactor depends on the viscosity. As the viscosity increases (due to the formation of products) the dissipative self-heating of the charge becomes increasingly important. This factor determines the conditions for changes in regime, and it can produce novel hydrodynamic effects. Even in the absence of chemical heat evolution we can find critical hysteresis effects due to the non-linearity of the variation of viscosity with temperature[138] or with extent of reaction[159]. These phenomena are reflected by discontinuous changes in flow rate with applied pressure. The increase of viscosity under forced flow can also result in blocking of the channel[159].

The interaction of dissipative and chemical heat evolutions is discussed in Refs. 160–164. Various "hydrodynamic", "chemical", and "intermediate" regimes have been demonstrated, and the number of possible stationary states of the system has continued to increase.

A full mathematical analysis of polymerisation in a flowing medium is given in Ref. 164, where the problem is treated as a one-dimensional case of the viscometric flow between two rotating cylinders separated by a narrow gap. Of course, this simple model can only reveal the principal effects produced by non-isothermal flow during the polymerisation of a liquid. In this model formulation it is assumed that the variation of the viscosity μ with reciprocal temperature and with extent of reaction is experimentally known:

$$\mu = \mu_0 \exp(U/RT + B\eta), \qquad (40)$$

where U is the activation energy for viscous flow, R is the gas constant, and B is a constant which allows for the effect of the reaction on the viscosity of the charge, and hence on the intensity of the dissipative processes. It is assumed that U is independent of η.

A full formulation of the problem includes the kinematic equation for the distribution of velocity in the gap, the equation for the temperature distribution with allowance for the dissipative factors and for the heat transfer conditions at the walls of both cylinders, and the kinetic equation for η, allowing for the strong temperature dependence of the reaction rate. We note that η occurs in formula (40) as well as in formula (4), i.e. there is a complex interaction between the basic factors (temperature, flow rate, and rate of reaction), which is typical of the class of non-isothermal problems considered in this review.

A study[164] of several variants of the solution of this model problem has shown that the presence of dissipative heat sources (associated with the flow of the charge) assists the transition to a flow regime similar to the

hydraulic thermal explosion, i.e. to a sudden, uncontrolled decrease in viscosity and increase in the speed of rotation (if the torque applied to the rotating cylinder is kept constant) or decrease in torque (if the speed of rotation is kept constant). However it is important to note that if we fix the angular velocity of the rotating cylinder and we ignore the heat of the chemical reaction we always arrive at a stationary flow regime[160]. The role of the parameter B in formula (40), which allows for the effect of the reaction on the dissipation by viscous flow, is most important in flow regimes which fall short of the thermal explosion conditions. In this case the parameter B (i.e. the effect of the extent of reaction on the viscosity of the system) determines the maximum self-heating and the change in extent of reaction with time.

In spite of the great practical importance of a combined study of non-isothermal flow and chemical reaction the number of publications in this area is relatively small. Studies of this type are only just beginning, and existing results are limited to a few special model systems. These results show that the effects are far from trivial, but they cannot be applied directly to real technological situations or even to laboratory experiments.

---o0o---

The number of non-isothermal effects in the chemistry and mechanics of polymers is vast. Their basic qualitative features in various regimes of polymerisation and deformation are now well recognised, and the most important effects produced by non-isothermal regimes have been described. However the work so far has been confined to observations in the laboratory. Yet, most industrial processes in polymer technology occur under essentially non-isothermal conditions. The need is quite obvious, but so far it has had very little effect on the general approach to non-isothermal processes because of the great complexity of an adequate quantitative treatment of the interplay of dissipation, deformation, and heat transfer phenomena. Only recently, with the development of appropriate theoretical models and computational techniques, have solutions of the model problems been obtained. Further developments in this direction must remain the main objective of quantitative studies of non-isothermal industrial processes for the production and application of polymeric materials.

REFERENCES

1. J.D. Ferry, "Viscoelastic Properties of Polymers" (Translated into Russian), Inostr. Lit., Moscow, 1963.
2. G.V. Vinogradov and A.Ya. Malkin, "Reologiya Polimerov" (Rheology of Polymers), Izd. Khimiya, Moscow, 1977.
3. M. Shen (Editor), "Visco-elastic Relaxation in Polymers" (Translated into Russian), Izd. Mir, Moscow, 1974.
4. S. Gilham, Rubber Chem. Techn., 30, 1202 (1957).
5. N.N. Semenov, Uspekhi Fiz. Nauk, 23, 251 (1940); 24, 433 (1940).
6. D.A. Frank-Kamenetskii, "Diffuziya i Teploperedacha v Khimicheskoi Kinetike" (Diffusion and Heat Transfer in Chemical Kinetics), Izd. Nauka, Moscow, 1967.
7. Ya.B. Zel'dovich, "Teoriya Goreniya i Detonatsii Gazov" (Theory of Detonation and Combustion in Gases), Izd. Akad. Nauk SSSR, Moscow–Leningrad, 1944.
8. A.G. Merzhanov, Symposium "Protsessy Goreniya v Khimicheskoi Tekhnologii i Metallurgii" (Combustion Processes in Chemical Technology and Metallurgy), Izd. Nauka, Moscow, 1975, p. 5.
9. A.G. Merzhanov, "Proceedings of the Fifth CHISA Congress on Combustion Processes in Chemical Reaction Engineering", Prague, K4.20, 1975, p. 33.
10. J. Sestak, V. Satava, and W.W. Wenla, Termochim. Acta, 7, 333 (1973).
11. A.G. Merzhanov, Fiz. Goreniya i Vzryva, 9, 4 (1973).
12. A.G. Merzhanov, V.V. Barzykin, A.S. Shteinberg, and V.T. Gontkovskaya, Thermochim. Acta, 21, 301 (1977).
13. N.N. Semenov, Zhur. Russ. Fiz.-Khim. Obshch., Fizika, 60, 247 (1928).
14. O.M. Todes, Zhur. Fiz. Khim., 4, 71 (1933); 13, 868 (1939).
15. D.A. Frank-Kamenetskii, Zhur. Fiz. Khim., 13, 738 (1939); 20, 139 (1946).
16. A.G. Merzhanov and F.I. Dubovitskii, Uspekhi Khim., 35, 656 (1966) [Russ. Chem. Rev., No. 4 (1966)].
17. V.V. Barzykin and A.G. Merzhanov, Dokl. Akad. Nauk SSSR, 120, 1271 (1958).
18. P.H. Thomas, Trans. Faraday Soc., 54, 60 (1968); 56, 833 (1960).
19. V.V. Barzykin and A.G. Merzhanov, Zhur. Fiz. Khim., 38, 2640 (1964) [Russ. J. Phys. Chem., No. 11 (1964)].
20. A.G. Merzhanov, V.V. Barzykin, V.G. Abramov, and F.I. Dubovitskii, Zhur. Fiz. Khim., 35, 2083 (1961) [Russ. J. Phys. Chem., No. 9 (1961)].
21. A.G. Merzhanov and E.A. Shtessel, Astronautica Acta, 18, 191 (1973).
22. Ya.B. Zel'dovich, Zhur. Eksper. Teor. Fiz., 9, 1530 (1939).
23. A.G. Merzhanov and A.E. Averson, Combustion and Flame, 16, 89 (1971).
24. Ya.B. Zel'dovich and D.A. Frank-Kamenetskii, Dokl. Akad. Nauk SSSR, 19, 693 (1938).
25. B.V. Novozhilov, Dokl. Akad. Nauk SSSR, 141, 151 (1961).
26. A.G. Merzhanov, Combustion and Flame, 14, 143 (1969).
27. A.G. Merzhanov, Archiwum Procesow Spalania, 5, 17 (1974).
28. A.G. Merzhanov, V.V. Barelko, I.I. Kurochka, and K.G. Shkadinskii, Dokl. Akad. Nauk SSSR, 221, 1114 (1975).
29. A.G. Merzhanov and E.N. Rumanov, Symposium "Gorenie i Vzryv. Materialy Chetvertogo Vsesoyuznogo Simpoziuma po Goreniyu i Vzryvu" (Combustion and Explosion. Proceedings of the Fourth All-Union Symposium on Combustion and Explosion), Izd. Nauka, Moscow, 1977, p. 149.
30. A.A. Berlin, S.A. Vol'fson, and N.S. Enikolopyan, "Kineticheskii Metod v Sinteze Polimerov" (The Kinetic Method in Polymer Synthesis), Izd. Khimiya, Moscow, 1977.
31. E.I. Maksimov, Teor. Osnovy Khim. Tekhnol., 7, 380 (1973); 8, 618 (1974).
32. Kh.S. Bagdasar'yan, "Teoriya Radikal'noi Polimerizatsii" (Theory of Radical Polymerisation), Izd. Nauka, Moscow, 1966.

33. F. W. Billmeyer, "Introduction to the Chemistry and Technology of Polymers" (Translated into Russian), Inostr. Lit., Moscow, 1958.
34. A. I. Lukomskaya, P. F. Badenkov, and L. M. Kepersha, "Teplovye Osnovy Vulkanizatsii Rezinovykh Izdelii" (Thermal Foundations of the Vulcanisation of Rubber Articles), Izd. Khimiya, Moscow, 1972.
35. C. H. Bamford, W. G. Barb, A. D. Jenkins, and P. F. Onyon, "Kinetics of Vinyl Polymerisation by Radical Mechnisms" (Translated into Russian), Inostr. Lit., Moscow, 1961.
36. A. Ya. Malkin, S. L. Ivanova, and M. A. Korchagina, Vysokomol. Soed., A19, 2224 (1977).
37. A. Ya. Malkin, A. N. Ivanova, S. L. Ivanova, and Z. S. Andrianova, Inzh.-Fiz. Zhur., 4, 636 (1978).
38. A. G. Merzhanov, E. G. Zelikman, and V. G. Abramov, Dokl. Akad. Nauk SSSR, 180, 639 (1968).
39. E. G. Zelikman, Zhur. Fiz. Khim., 43, 236 (1969) [Russ. J. Phys. Chem., No. 2 (1969)].
40. A. G. Merzhanov, V. G. Abramov, and V. T. Gontkovskaya, Dokl. Akad. Nauk SSSR, 148, 156 (1963).
41. G. B. Manelis and L. P. Smirnov, Fiz. Goreniya i Vzryva, 12, 354 (1976).
42. A. G. Merzhanov and L. P. Smirnov, Fiz. Goreniya, i Vzryva, 12, 659 (1976).
43. A. Ya. Malkin, N. K. Blinova, G. V. Vinogradov, M. P. Zabugina, O. Yu. Sabsai, V. C. Shalganova, I. Yu. Kurchevskaya, and V. P. Shatalov, Europ. Polymer J., 10, 445 (1974).
44. J. R. Martin, J. F. Johnson, and A. R. Cooper, J. Macromol. Sci.—Rev. Macromol. Chem., C8, 57 (1972).
45. W. H. Ray, J. Macromol. Sci.—Rev. Macromol. Chem., C8, 1 (1972).
46. S. A. Vol'fson, G. G. Aleksanyan, and E. I. Maksimov, Symposium "Uspekhi Khimii i Fiziki Polimerov" (Advances in Polymer Chemistry and Physics), Izd. Khimiya, Moscow, 1973, p. 329.
47. G. G. Aleksanyan, Thesis, Moscow, 1975.
48. J. Hopkins, J. Polymer Sci., 29, 63 (1958).
49. A. Ya. Malkin, O. Yu. Sabsai, and N. G. Gromakovskaya, Mekh. Polimerov, 755 (1974).
50. A. A. Askadskii, "Fiziko-khimiya Poliarilatov" (Physical Chemistry of Polyarylates), Izd. Khimiya, Moscow, 1968, p. 96.
51. A. G. Merzhanov, E. I. Maksimov, I. R. Chernyi, and Z. B. Maiofiz, "Makrokineticheskoe Issledovanie Polimerizatsii Etilena pri Vysokom Davlenii" (Macrokinetic Investigation of the Polymerisation of Ethylene at High Pressure), Izd. OIKhF Akad. Nauk SSSR, Moscow, 1970.
52. E. I. Maksimov, Dokl. Akad. Nauk SSSR, 191, 1091 (1970).
53. E. I. Maksimov and L. P. Smirnov, Symposium "Gorenie i Vzryv. Materialy Chetvertogo Vsesoyuznogo Simpoziuma po Goreniyu i Vzryvu" (Combustion and Explosion. Proceedings of the Fourth All-Union Symposium on Combustion and Explosion), Izd. Nauka, Moscow, 1977, p. 164.
54. A. A. Berlin, T. Ya. Kefeli, and G. V. Korolev, "Poliefirakrilaty" (Polyacrylates), Izd. Nauka, Moscow, 1976.
55. O. A. Edel'shtein, B. R. Smirnov, V. P. Grachev, and G. V. Korolev, Symposium "Khimiya Aromaticheskikh i Nepredel'nykh Soedinenii" (Chemistry of Aromatic and Unsaturated Compounds), Izd. Irkutsk. Univ., 1971.
56. N. M. Chechilo, R. Ya. Khvilivitskii, and N. S. Enikolopyan, Dokl. Akad. Nauk SSSR, 204, 1180 (1972).
57. B. B. Khanukaev, M. A. Kozhushner, and N. S. Enikolopyan, Dokl. Akad. Nauk SSSR, 214, 625 (1974).
58. G. G. Aleksanyan, Kh. A. Arutyunyan, V. L. Bodneva, S. P. Davtyan, E. V. Prut, B. A. Rozenberg, K. G. Shkadinskii, and N. S. Enikolopyan, Vysokomol. Soed., A17, 913 (1975).
59. N. F. Surkov, S. P. Davtyan, B. A. Rozenberg, and N. S. Enikolopyan, Dokl. Akad. Nauk SSSR, 228, 141 (1976).
60. S. P. Davtyan, N. F. Surkov, B. A. Rozenberg, and N. S. Enikolopyan, Dokl. Akad. Nauk SSSR, 232, 379 (1977).
61. S. P. Davtyan, Kh. A. Arutyunyan, A. O. Tonoyan, B. A. Rozenberg, and N. S. Enikolopyan, Symposium "Protsessy i Apparaty Proizvodstva Polimernykh Materialov, Metody i Oborudovanie dlya Pererabotki Ikh v Izdelie" (Processes and Apparatus for the Production of Polymeric Materials, Methods and Equipment for Treating Finished Articles), No. 2, Izd. MIKhM, Moscow, 1977, p. 18.
62. N. S. Enikolopyan and S. A. Vol'fson, Vestnik Akad. Nauk SSSR, No. 8, 62 (1976).
63. R. G. Gleizer, G. I. Faidel', and F. A. Shatkhan, Plastmassy, 7, 15 (1976).
64. N. I. Basov, V. A. Lyubartovich, V. A. Mironov, A. I. Leonov, and Yu. V. Kazankov, Mekh. Polimerov, 619 (1971).
65. Ya. B. Zel'dovich and V. V. Voevodskii, "Teplovoi Vzryv i Rasprostranenie Plameni v Gazakh" (Thermal Explosion and Flame Propagation in Gases), Izd. Moskov. Mekhan. Inst., 1947, p. 103.
66. P. Wittmer and H. Gerrens, Makromol. Chem., 89, 27 (1965).
67. M. A. El-Azmirly and O. A. Abuzeid, Plaste und Kautschuk, 20, 335 (1973).
68. M. A. El-Azmirly and M. M. Ammar, Indian J. Techn., 10, 103 (1972).
69. G. M. Chil'-Gevorgyan, A. K. Bonetskaya, and S. M. Skuratov, Zhur. Fiz. Khim., 39, 1794 (1965) [Russ. J. Phys. Chem., No. 7 (1965)].
70. B. A. Arutyunov, V. V. Vlasov, O. A. Gerashchenko, S. V. Mishchenko, and N. P. Puchkov, Inzh.-Fiz. Zhur., 29, 1080 (1975).
71. V. D. Moiseev, N. G. Avetisyan, A. G. Cherkova, and A. A. Atrushkevich, Plastmassy, 3, 12 (1971).
72. V. V. Korshak, T. M. Frunze, V. V. Kurashov, and V. I. Zaitsev, Dep. VINITI, No. 6197-73 (1973).
73. A. Kh. Arutyunyan, S. P. Davtyan, B. A. Rozenberg, and N. S. Enikolopyan, Vysokomol. Soed., A16, 2115 (1974).
74. A. O. Tonoyan, A. D. Leikin, S. P. Davtyan, B. A. Rozenberg, and N. S. Enikolopyan, Vysokomol. Soed., A15, 1847 (1973).
75. A. O. Tonoyan, S. P. Davtyan, B. A. Rozenberg, and N. S. Enikolopyan, Vysokomol. Soed., A16, 611 (1974).
76. N. M. Kuvarina, A. O. Tonoyan, G. G. Aleksanyan, E. V. Prut, S. P. Davtyan, A. A. Zharov, B. A. Rozenberg, and N. S. Enikolopyan, Vysokomol. Soed., A16, 1005 (1974).
77. A. G. Merzhanov, V. G. Abramov, and L. T. Abramova, Zhur. Fiz. Khim., 41, 179 (1967) [Russ. J. Phys. Chem., No. 1 (1967)].
78. A. G. Merzhanov, V. G. Abramov, and L. T. Abramova, Dokl. Akad. Nauk SSSR, 171, 901 (1966).

79. D. V. van Krevelen, "Properties and Chemical Structure of Polymers" (Translated into Russian), Izd. Khimiya, Moscow, 1976.
80. S. B. Ratner and V. I. Korobov, Dokl. Akad. Nauk SSSR, **161**, 824 (1965).
81. S. B. Ratner and V. I. Korobov, Mekh. Polimerov, 93 (1965).
82. V. I. Korobov, Thesis, Moscow, 1966.
83. S. B. Ratner, S. G. Agamalyan, S. T. Buglo, and A. V. Stinskas, Dokl. Akad. Nauk SSSR, **204**, 335 (1972).
84. S. B. Ratner and S. G. Agamalyan, Obzory NIITEKhim, **6**, 56, Moscow (1974).
85. S. B. Ratner and A. V. Stinskas, Mekh. Polimerov, 179 (1967).
86. S. B. Ratner and S. T. Buglo, Mekh. Polimerov, 465 (1969).
87. R. A. Shaperi and D. E. Kenti, Raketnaya Tekh. i Kosmonavtika, No. 2, 84 (1966).
88. P. P. Oldyrev, Mekh. Polimerov, 111 (1967).
89. P. P. Oldyrev and V. P. Tamuzh, Mekh. Polimerov, 864 (1967).
90. V. G. Savkin, V. A. Belyi, T. I. Sogolova, and V. A. Kargin, Mekh. Polimerov, 803 (1966).
91. O. F. Kireenko, A. M. Leksovskii, and V. P. Regel', Mekh. Polimerov, No. 3, 483 (1968).
92. F. H. Müller and A. Engelter, Kolloid-Z., **152**, 15 (1957).
93. F. H. Müller, Kunststoffe, **49**, 67 (1959).
94. F. H. Müller, in "Rheology, Theory and Applications" (F. Firich, Editor), Vol. 5, Academic Press, New York, 1972.
95. Yu. K. Godovskii, G. L. Slonimskii, V. S. Papkov, and T. A. Dikareva, Mekh. Polimerov, 785 (1970).
96. G. L. Slonimskii, Yu. K. Godovskii, V. S. Papkov, and T. A. Dikareva, Vysokomol. Soed., **B10**, 798 (1968).
97. Yu. K. Godovskii, Thesis, Moscow, 1972.
98. G. P. Andrianova, B. A. Arutyunov, and Yu. V. Popov, J. Polymer Sci., Polymer Phys. Ed., in press.
99. G. P. Andrianova, Yu. V. Popov, and B. A. Arutyunov, Vysokomol. Soed., **A18**, 2311 (1976).
100. G. P. Andrianova, Yu. V. Popov, and S. D. Artamonova, Vysokomol. Soed., **B17**, 876 (1975).
101. G. P. Andrianova and V. A. Kargin, Vysokomol. Soed., **A12**, 3 (1970).
102. G. P. Andrianova, Symposium "Uspekhi Khimii i Fiziki Polimerov" (Advances in Polymer Chemistry and Physics), Izd. Khimiya, Moscow, 1973, p.162.
103. Yu. V. Popov, Thesis, Moscow, 1974.
104. S. W. Allison and I. M. Ward, Brit. J. Appl. Phys., **18**, 1151 (1967).
105. Yu. S. Lazurkin, Thesis, Moscow, 1954.
106. A. S. Kechek'yan, G. P. Andrianova, and V. A. Kargin, Vysokomol. Soed., **A12**, 2424 (1970).
107. G. P. Andrianova, A. S. Kechekyan, and A. V. Kargin, J. Polymer Sci., A-2, **9**, 1919 (1971).
108. A. M. Zhabotinskii, "Kontsentratsionnye Avtokolebaniya" (Concentration Fluctuations), Izd. Nauka, Moscow, 1974.
109. R. Roseen, J. Materials Sci., **9**, 929 (1974).
110. G. I. Barenblatt, Rheol. Acta, **14**, 924 (1974).
111. G. A. Preis and P. F. Pavlik, Vestnik Mashinostr., No. 2, 39 (1960).
112. Sh. M. Bilik, Symposium "Trenie i Iznos Metallov i Plastmass" (Friction and Wear of Metals and Plastics), Izd. Nauka, Moscow, 1964, p. 87.
113. M. D. Bezborod'ko and L. I. Shabarov, Plastmassy, **9**, 26 (1964).
114. G. V. Vinogradov, V. A. Mustafaev, Yu. Ya. Podol'skii, and Yu. M. Malinskii, Dokl. Akad. Nauk SSSR, **163**, 1419 (1965).
115. V. A. Mustafaev, Yu. Ya. Podol'skii, and G. V. Vinogradov, Mekh. Polimerov, No. 5, 95 (1965).
116. A. I. Leonov and V. A. Mustafaev, Symposium "Temperaturnaya Zadacha Treniya" (The Temperature Problem in Friction), Izd. Nauka, Moscow, 1965.
117. L. F. Toor, R. C. Ballman, and L. Cooper, Modern Plastics, **12**, 38 (1960).
118. D. H. Harry and R. C. Parrot, Polymer Eng. Sci., 10, 209 (1970).
119. J. L. Berger and C. G. Godos, Polymer Eng. Sci., **13**, 102 (1973).
120. M. R. Kamal and S. Kenig, Polymer Eng. Sci., **12**, 294 (1972).
121. M. R. Kamal and S. Kenig, Polymer Eng. Sci., **12**, 302 (1972).
122. C. Gutfinger, E. Broyer, and Z. Tadmor, Polymer Eng. Sci., **15**, 515 (1975).
123. G. V. Vinogradov, A. Ya. Malkin, Yu. G. Yanovskii, E. K. Borisenkova, B. V. Yarlykov, G. V. Berezhnaya, V. P. Shatalov, V. G. Shalganova, and V. P. Yudin, Vysokomol. Soed., **A14**, 2425 (1972).
124. G. V. Vinogradov, A. Ya. Malkin, Yu. G. Yanovskii, E. K. Borisenkova, B. V. Yarlykov, and G. V. Berezhnaya, J. Polymer Sci., Polymer Phys. Ed., 10, 1061 (1972).
125. G. V. Vinogradov, A. Ya. Malkin, V. V. Volosevich, Appl. Polymer. Symp., No. 27, 45 (1975).
126. G. V. Vinogradov, A. Ya. Malkin, B. W. Jarlykow, B. W. Raduschkewitch, and W. D. Fichman, Plaste und Kautschuk, **17**, 241 (1970).
127. G. V. Vinogradov, A. Ya. Malkin, E. K. Borisenkova, B. V. Yarlykov, and V. A. Kargin, Dokl. Akad. Nauk SSSR, **179**, 1366 (1968).
128. A. K. van der Vegt and P. P. A. Smith, Adv. Polymer. Sci. Techn. Ind. Soc. Chem. Ind. Monograph, **26**, 313 (1967).
129. V. L. Folt, R. W. Smith, and C. E. Wilkes, Rubber Chem. Techn., **44**, 1 (1971).
130. T. Kawai, T. Matsumoto, M. Kato, and H. Maeda, Kolloid-Z. und Z. Polymere, **222**, 1 (1968).
131. S. Torza, J. Polymer Sci., Polymer Phys., Ed., 13, 43 (1975).
132. V. E. Dreval, A. Ya. Malkin, and G. O. Botvinnik, J. Polymer Sci., Polymer Phys. Ed., 11, 1055 (1973).
133. A. Ya. Malkin, Rheol. Acta, **12**, 486 (1973).
134. V. E. Dreval, A. Ya. Malkin, G. V. Vinogradov, and A. A. Tager, Europ. Polymer J., **9**, 85 (1973).
135. D. W. van Krevelen and P. J. Hoftyzer, Angew. Makromol. Chem., **52**, 101 (1976).
136. A. G. Merzhanov and A. M. Stolin, Dokl. Akad. Nauk SSSR, **198**, 1291 (1971).
137. S. A. Bostandzhiyan, A. G. Merzhanov, and S. I. Khudyaev, Dokl. Akad. Nauk SSSR, **163**, 133 (1965).
138. A. G. Merzhanov and A. M. Stolin, Zhur. Prikl. Mekh. Tekh. Fiz., No. 1, 65 (1974).
139. A. M. Stolin and S. I. Khudyaev, Dokl. Akad. Nauk SSSR, **207**, 60 (1972).
140. A. G. Merzhanov, A. P. Posetsel'skii, A. M. Stolin, and A. S. Shteinberg, Dokl. Akad. Nauk SSSR, **310**, 52 (1973).
141. A. G. Merzhanov, A. M. Stolin, and B. N. Shatalov, Symposium "Teplo- i Massoperenos" (Heat and Mass Transfer), No. 7, Minsk, 1976, p. 18.

142. B. I. Shatalov, A. M. Stolin, V. I. Kukushkin, and A. G. Merzhanov, Symposium "Teplo- i Massoperenos" (Heat and Mass Transfer), No. 3, 1972, p. 417.
143. Zh. A. Zinenko, A. M. Stolin, and F. A. Khrisotomov, Zhur. Prikl. Mekh. Tekh. Fiz., No. 3, 103 (1977).
144. V. G. Abramov and A. G. Merzhanov, Fiz. Goreniya i Vzryva, 4, 548 (1968).
145. A. G. Merzhanov and V. G. Abramov, Chem. Eng. Sci., 32, 475 (1974).
146. Ya. B. Zel'dovich, Zhur. Tekh. Fiz., 11, 49 (1941).
147. Ya. B. Zel'dovich and Yu. A. Zysin, Zhur. Tekh. Fiz., 11, 501 (1941).
148. C. van Heerden, Ind. Eng. Chem., 45, 1242 (1953).
149. A. A. Butakov and E. I. Maksimov, Dokl. Akad. Nauk SSSR, 209, 643 (1973).
150. E. A. Ivanov, V. S. Beskov, and M. G. Slin'ko, Teor. Osnovy Khim. Tekhnol., 1, 488 (1967).
151. V. Hlavacek and H. Hofmann, Chem. Eng. Sci., 25, 173 (1970).
152. V. Hlavacek, H. Hofmann, and M. Kybicek, Chem. Eng. Sci., 26, 1629 (1971).
153. A. Varma and N. Amundson, Canad. J. Chem. Eng., 51, 2 (1973).
154. E. I. Maksimov and V. B. Solomonov, Fiz. Goreniya i Vzryva, No. 3 (1977).
155. V. S. Beskov, V. P. Kuzin, and M. G. Slin'ko, Khim. Prom., 1, 4 (1965).
156. E. I. Maksimov, N. I. Peregudov, and A. A. Butakov, Fiz. Goreniya i Vzryva, 568 (1975).
157. S. Lynn and J. E. Huff, Amer. Inst. Chem. Engineers J., 17, 475 (1971).
158. R. Sala, F. Valz-Gris, and L. Zanderighi, Chem. Eng. Sci., 29, 2205 (1974).
159. D. A. Vaganov, Zhur. Prikl. Mekh. Tekh. Fiz., No. 2, 168 (1975); No. 1, 114 (1977).
160. S. A. Bostandzhiyan, A. G. Merzhanov, and N. M. Pruchkina, Zhur. Prikl. Mekh. Tekh. Fiz., No. 5, 38 (1968).
161. A. M. Stolin and A. G. Merzhanov, Fiz. Goreniya i Vzryva, 7, 502 (1971).
162. A. M. Stolin, Fiz. Goreniya i Vzryva, 11, 425 (1975).
163. I. G. Dik, Fiz. Goreniya i Vzryva, 12, 81 (1976).
164. P. V. Zhirkov, S. A. Bostandzhiyan, V. I. Boyarchenko, and Zh. A. Zinenko, Symposium "Teplomassy 5, Trudy Pyatoi Vsesoyuznoi Konferentsii po Massoobmenu" (Heatmass 5, Proceedings of the Fifth All-Union Conference on Mass Exchange), Vol. 2, Minsk, 1976, p. 50.

Chernogolovka Section of the Institute
of Chemical Physics of the USSR
Academy of Sciences

"Plastmassy" Plastics Research
Institute, Moscow