Translated from *Uspekhi Khimii*, 50, 137-160 (1981) U.D.C. 541.64:539.55

Changes in Rheological Properties during Formation and Transformation of of Polymers

A.Ya.Malkin

Published information on the changes in rheological properties of polymer melts and solutions accompanying various chemical processes—polymerisation, vulcanisation, hardening, gelation—is examined, and experimental methods for the rheological investigation of chemically unstable polymer systems are discussed in detail. Changes in rheological properties should be considered in relation to the chemical kinetics of the processes involved. Technical aspects of the problem are indicated. A list of 133 references is included.

CONTENTS

I. Introduction 76
II. Methods of investigation and their range of application 76
III. Polymerisation and polycondensation 77
IV. Vulcanisation of elastomers and hardening of thermosetting plastics 80
V. Gelation 84

I. INTRODUCTION

Polymers and compositions based on them provide a most interesting subject for the application of diverse physicochemical methods of investigation, largely because in this class of materials property indices can easily be changed by many powers of ten. Hence the measurement of particular characteristics is a sensitive method of physicochemical analysis of the material. A clear example is given by the rheological properties of polymers, which are highly sensitive to the length of the polymer chain, its structure, the molecular-mass distribution, and the content of the polymer in the system (solution or filled composition).

The general laws of the development of rheological properties by polymer systems as functions of the main determining factors have now been studied in some detail and have been summarised in several monographs[1-3]. Important achievements of the past decade have been measurements on specially synthesised series of monodisperse polymers and their model mixtures[4-10], and also the correlation of numerous and multifarious experimental results on the rheological properties of solutions of various polymers in different solvents throughout the possible composition range[11-18].

The many studies of the past decade have provided a reliable basis for a general quantitative description of the rheology of polymers. They had the common aim of investigating materials that were as pure as possible. Although such an approach is methodologically difficult, it is justified by the comparative ease and unambiguity with which experimental results can be interpreted. Yet this approach ignores several important classes of polymeric materials, among which polymers or polymer systems whose properties vary continuously with time should be specially distinguished. Two significant aspects are firstly that the time taken by these changes is comparable with the duration of observation and secondly that they are functionally inherent in certain polymeric materials, being responsible for their technical value. A fairly large number of cases correspond to these conditions, for time-variable systems are met in various branches of the chemical technology of polymers.

In principle two mechanisms—chemical reactions and physical phenomena—may cause the rheological properties of a material to vary with time. Below we shall consider only the occurrence on an experimental time scale of chemical reactions leading either to the formation of linear polymers or to the conversion of linear polymers (or oligomers) into three-dimensional networks. The process related to the latter case is gelation (gel formation), in which physical changes (primarily crystallisation) may be combined with chemical reactions.

II. METHODS OF INVESTIGATION AND THEIR RANGE OF APPLICATION

Study of the rheological properties of chemically unstable systems during the formation and transformation of polymers is a fairly new field of investigation, which has developed from the traditional rheology of polymers. It is therefore natural that this development has involved the widespread use of customary rheological methods with their appropriate experimental techniques and treatment of the results. However, the need for continuous monitoring of the state of the system has caused a gradual modification of the existing experimental apparatus.

The methodology of the rheology of polymers is based on steady-state and non-stationary measurements. The principles and experimental procedures related to non-stationary methods have been described in detail[19]. Among them only dynamic methods have been widely used for the study of rheologically unstable systems. They consist essentially in subjecting the test specimen to harmonic deformation of specified frequency ω and studying the response of the material in terms of the shear modulus of elasticity G and the mechanical loss angle $\tan\delta$, which depend on ω and, in the case of unstable systems, on the time t.

Relaxation methods have also found an extremely unusual application: it was proposed[20] to use them to monitor the

course of chemical reactions in rubbers subjected to an applied stress. However, this type of approach did not become widespread. Other non-stationary methods for studying viscoelastic properties of polymers were not applied to chemically unstable systems, apparently because of the fundamental difficulty of separating time effects due to relaxation phenomena from those due to chemical changes.

Non-stationary (dynamic) methods for studying chemical changes are used in the following cases—(i) to monitor the initial stage of polymerisation, primarily by means of vibration viscosimeters and procedures identical with those usual in viscosimetry[21]; (ii) to investigate the initial stages of the vulcanisation of rubber mixtures, usually by forced low-frequency vibrations, whose development led to commercial instruments and standardised methods; (iii) to study the hardening of thermosetting plastics and oligomers, especially in practical scientific research using the whole set of modern dynamic methods of measurement; and (iv) to assess the thermal stability of various polymers and to investigate high-temperature processes yielding infusible and insoluble resins.

A fair number of designs and measuring schemes are known that use various instruments operating under dynamic loading at the most diverse frequencies—from infrasonic to ultrasonic—for the above cases. Although various known designs can in principle be used for this purpose[19], the practical importance of thermostable polymers and the difficulties of preparing specimens for investigation led to the establishment of a special method—torsional braid analysis (the TBA method).[22-25]

In the TBA method a bundle of fibres (filaments) is impregnated with a solution of the test polymer. The solvent is then removed, and the usual measurements of modulus or elasticity and mechanical losses are made both on the filament with the deposited polymer and for comparison on a blank filament either under isothermal conditions or with temperature scanning. The properties of the polymer are found by difference, while the observed changes in measured indices enable the variation in state of the test material to be reliably monitored. The convenience of depositing the polymer, the small amount of polymer required, the ease of replacing the fibre braid, and the reliability with which specified temperature conditions are maintained, combined with the proposed[24] automated methods for processing the experimental data, constitute important advantages of this method in comparison with traditional dynamic methods of investigating polymers and give it promise in laboratory practice, especially for investigating newly synthesised polymers.

Steady-state methods of measurement are essentially viscosimetry[21,26] complicated by the fact that polymer systems are not viscous liquids but viscoelastic media[1]. Viscosimetric methods may be used when the test material is able to flow, and their application to the study of chemical processes is possible when the transition period preceding the establishment of steady-state flow and due both to viscoelastic and to thixotropic phenomena[27-31] is significantly shorter than the characteristic time of chemical reaction. In such case many traditional viscosimetric methods prove useful. However, the following substantial difficulties then arise: the deformation produced in any type of viscosimeter can itself have a definite effect on the course of a chemical reaction, and its intensity will depend on the rate of deformation; if the reaction is accompanied by considerable evolution of heat, special attention must be paid to maintaining controllable (e.g. isothermal) conditions of measurement; and in many cases chemical changes in polymers are accompanied by hundredfold and thousandfold changes in viscosity, so that the instrument should be able to measure viscosities of the test medium over a very wide range.

Viscosimetric methods are used industrially for two purposes—(i) to estimate the duration of retention of the fluid state by rubber mixtures (various types of Mooney viscosimeters are used[32]; certain methods of applying them have been standardised in several countries, in particular in the USA as ASTM D-1246, etc. and in the USSR we also have GOST 10 722 as a "method of determining the viscosity and the capacity for premature vulcanisation" of rubber mixtures), and (ii) to measure the "viability" of thermosetting plastics (the rotation viscosimeter developed in the USSR is used for this purpose[33,34]; an instrument of the same type is manufactured also in the Federal Republic of Germany by Gevaert; other suitable experimental methods have been reviewed[35]).

Viscosimetric methods have found very restricted use in the industrial production of polymers (isolated examples can be found[36,37]), despite the exceptionally high sensitivity of rheological indices to the composition of the polymer system and the structure of the macromolecular chain. Polymerisation processes are usually monitored by traditional viscosimetric methods and instruments. However, the problem of studying rapid polymerisation reactions, in particular of assessing the induction period and the intial stages in general, may require the development of scanning methods for monitoring viscosity[38].

The use of instruments combining viscosimetric and dynamic methods of measurement is extremely promising for the investigation of processes starting with a low-viscosity liquid and ending in separation of a solid product, for the whole process of hardening can be examined on a single small specimen. Instruments of this type are now manufactured in Great Britain (the Weissenberg rheogoniometer produced in several modifications by Sangamo Weston Ltd.), the USA (the dynamic spectrometer made by Rheometrix), and in the USSR.[39] An analogous instrument has been developed also for rubber mixtures[40].

III. POLYMERISATION AND POLYCONDENSATION

The change in viscosity and in the whole set of viscoelastic properties of a polymer system during chain growth is extremely striking, as a consequence of the very strong dependence of their governing parameters on the molecular mass and the concentration of the polymer in the solution[1-3], as well as the existence of critical points at which even the character of these relations changes[1,18,41,42]. Indeed, published qualitative results have shown that in actual cases the viscosity of the reaction mass changes by many powers of ten during polymerisation.

Measurements of the viscosity of polymers in the actual monomer are very significant in this connection. The proposed experimental technique makes it possible to follow the course of polymerisation by a dilatometric method with simultaneous measurement of viscosity[43,44]. Results for methyl methacrylate show[45] that the viscosity η is related to the extent of conversion β by the power formula

$$\eta = K\beta^n, \qquad (1)$$

where the constants K and n are determined by the composition of the reaction mass (the concentration of the initiator and the content of the molecular-weight regulator), but all cases show very high values of $n \cong 10$. The polymerisation of butyl methacrylate exhibits a similar $\eta-\beta$ relation, although the region of transition to concentrated solutions of macromolecular products at some critical value of β may be more sharply defined than with methyl methacrylate[46].

An extraordinarily rapid increase in viscosity has been observed also in the copolymerisation of butyl methacrylate with methacrylic acid, although for this sytem the effect is very strongly dependent on the composition of the copolymerising system, and an induction period of almost unchanged viscosity it observed intially[47]. However, evidence of an induction period depends to some extent on the way in which experimental results are presented, which is clearly shown by a comparison of the same data plotted on linear[48] and logarithmic[45] scales. Yet in all the above cases of radical polymerisation the $\eta-\beta$ relation, like the usual dependence of the viscosity of polymer solutions on molecular mass and concentration, undoubtedly consists of two parts—an initial segment with a relatively weak dependence of η on β, and the main segment, when at a considerable degree of conversion the dependence is extremely sharp, and the exponent n reaches very high values.

Extremely interesting experimental results illustrating the way in which viscosity changes during the polymerisation of acrylic monomers in the presence of fillers[49-53] also show change in the rate of increase of viscosity when a certain degree of conversion is reached. It was shown at the same time that the increase is accompanied by a sharp change in the whole complex of rheological properties of the polymerising system, with strengthening viscoelasticity of the solution, evidence of intense structure formation at a certain degree of conversion.

An initially slow and then extraordinarily rapid increase in viscosity of the reaction mass has been observed in the polymerisation of styrene in the actual monomer, which also has a radical mechanism[54] (it is especially interesting to compare these results with an investigation of the rheological properties of the model system formed by solutions of polystyrene of varying molecular mass in styrene[55], which will provide a physical basis for assessing the nature of the rheological transitions accompanying polymerisation). These experimental results[54] were represented by an exponential dependence of viscosity on extent of conversion, but the rheological results for solutions of polystyrene by power functions[55].

It is important to emphasise for the purposes of the present discussion that use of a single variable—extent of conversion—to describe the type of variation in viscosity has proved entirely valid for radical polymerisation under homogeneous conditions.

Unfortunately the above very interesting and significant results were not compared with the kinetics or the mechanism of polymerisation, which would have enabled sound judgments to be made on the relative roles of the main determining parameters—concentration of catalytic system, temperature, and change in the molecular mass of the product and its content in the reaction mass at various stages of polymerisation.

The monotonic character of the variation in viscosity during polymerisation is characteristic only of homogeneous processes. Various physicochemical effects, such as phase separation or inversion at a certain degree of conversion, formation of a heterogeneous system, substantially complicate the pattern of change in rheological properties. A very pertinent example is the formation of shock-resistant polystyrene. An important stage in this process is phase reversal, when at a certain degree of conversion of styrene in the polymer a transition takes place from a system in which the continuous phase is a solution of rubber in styrene to a system in which rubber is dispersed in another, newly formed continuous phase—a solution of polystyrene in styrene—the conditions at this point influencing significantly if not decisively the physicomechanical properties, i.e. the quality of the product.

A fundamental aspect of these problems is that phase reversal is accompanied by a jump in viscosity: the effective viscosity falls very rapidly at the instant of phase reversal (Fig.1 [56]). The drop in viscosity is very clearly evident, since until the critical moment the viscosity has been increasing owing to the polymerisation of styrene (but the polymer remains the dispersed component). The change in character of the variation in viscosity (from increase to decrease) is so marked that it may become an extremely reliable method for the technical monitoring of polymerisation. It should be noted that the viscoelastic properties of the composition change just as sharply at the point of phase reversal, which is evident e.g. in a decrease in the Weissenberg effect.

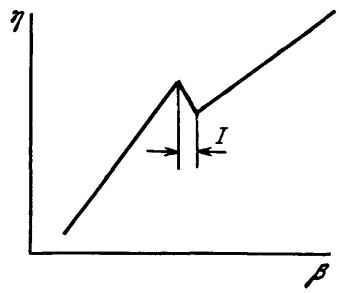


Figure 1. Variation in viscosity during polymerisation accompanied by phase reversal (in the range *I*).

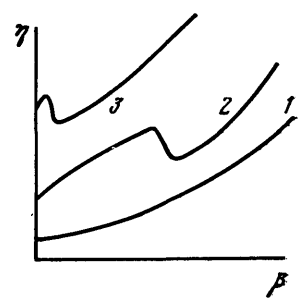


Figure 2. Variation in viscosity during: *1*) homogeneous polymerisation; *2*) phase transition during polymerisation; *3*) heterogeneous polymerisation.

The above example of an extremal change in viscosity at an instant of phase transition during polymerisation is apparently general in character. In this respect special interest attaches to viscosity measurements on methyl methacrylate polymerising in a solvent—precipitant mixture[57]. The composition of the medium was chosen to ensure that polymerisation took place under either homogeneous or transition conditions. Sharp differences were observed in the variation of viscosity (Fig.2 [57])—comparatively slow increase during homogeneous polymerisation (curve *1*), an extremal curve with change in phase state of the system (curve *2*), and a very sharp increase during heterogeneous polymerisation (curve *3*)—the continuance[57] of the relatively slow increase up to extremely high degrees of conversion being due to occurrence of the reaction in solution—not in the mass—so that the polymerising system was a not very concentrated solution.

Isolated qualitative observations show that the moment of phase reversal on formation of an insoluble polymer depends on the rate of mixing of the reaction mass. This is due to both physical causes (since the instant of phase separation depends on the rate of deformation[58,59]) and apparently to the influence of deformation on the rate of polymerisation. The latter is one of the most obscure and little studied aspects of the rheology of polymerising systems. Individual views on this aspect are extremely unconvincing, and there are hardly any "pure" researches in which this question would be studied.

The few investigations in which dependence of rate of polymerisation on deformation of the reaction mass has actually been observed include the discovery of the influence of rate of shear on rate of change of viscosity during the cross-linking of oligourethane[60]. However, the complexity of interpreting the results, consequent on the extremely specific character of the dependence of the effective viscosity of an oligomer on rate of shear, prevents their extension to other polymerising systems in general. Thus a region of dilatant behaviour—increase in effective viscosity with rate of shear—is often observed[60,61] with oligomers at low rates of shear. Significantly different flow curves are observed for concentrated solutions[1,6,13,18]. Therefore the type of dependence of viscosity on rate of shear changes as polymerisation proceeds, so that viscosity measurements with a constant rate of shear (as in Ref.60) may give points corresponding to different regions of the flow curve of the reaction mass, which makes their comparison ambiguous.

The character of the variation in viscosity depends on the mechanism of polymerisation, since the variation of the two principal factors—the mean molecular mass of the product and the polymer content of the reaction mass—is determined by this mechanism. The physical state of the specimen—whether it remains a solution during polymerisation or whether the system becomes heterogeneous, which very strongly influences the rheological properties—also depends on the nature of the reaction medium. Unfortunately, very little attention has been paid to these question: the few experimental results are qualitative in character and are in no way linked with the mechanism or the kinetics of polymerisation, although simple semi-quantitative considerations clearly indicate that the kinetics of polymerisation play a decisive part in the variation of the viscosity[62].

If polymerisation has a radical mechanism, the initial mean degree of polymerisation remains constant during a fairly lengthy initial stage[63], while the yield of polymer increases linearly with time. In terms of the governing parameters this implies that the initial stage consists in a temporally linear increase in concentration of polymer in solution. Hence the expected character of the variation in viscosity can be indicated, provided that the concentration dependence of the viscosity of solutions of specific composition is known. Experimental results make possible such an analysis, which has recently been made and has confirmed the validity of the suggested theoretical approach[64]. A more complete scheme of radical polymerisation must take into account the time variation of the mean molecular mass, which depends on the relation between reactions of chain growth and transfer. In any case, however, a detailed kinetic scheme of a specific radical polymerisation together with the constants of the elementary reactions provides sufficient basis for assessing the way in which the viscosity changes during polymerisation. Nevertheless, such an approach is valid as far as the gel point, which also can be detected by rheological methods and is associated with certain peculiarities in the viscosity properties of the reaction mass[65] or with change in the free volume as a factor determining the rheological properties of the polymerising system[66].

Another kinetic scheme, involving an ionic mechanism of polymerisation[67-69], is most simply represented by chain growth at a certain number of active centres, whose concentration A remains unchanged during the reaction, while chain termination is excluded. If the degree of conversion determined from the change in concentration of functional groups is β, the mean molecular mass of the resulting polymer is at some time proportional to the ratio β/A, while the concentration of polymer in solution is proportional to β. Thus both the molecular mass and the polymer content of the solution change, in contrast to the preceding case. This situation becomes substantially more complicated if the polymer separates from solution, which, of course, affects the rate of increase of viscosity[69].

Finally, in a specific kinetic scheme based on chain growth by a polycondensation mechanism all molecules are simultaneously involved in the increase in molecular mass, and the degree of conversion β corresponds to the mean degree of polymerisation $(1-\beta)^{-1}$, but the polymer concentration in solution during polycondensation is constant at unity. This implies that the course of changes in the governing parameters is significantly different during polycondensation than during radical or ionic polymerisation.

Dependence	Radical mechanism	Ionic mechanism	Polycondensation
$\bar{P}(\beta)$	1	β	$(1-\beta)^{-1}$
$c(\beta)$	β	β	1
$\eta(\beta)$	β^b	β^{a+b}	$(1-\beta)^a$

Thus the effects on variation in viscosity η of different types of dependence of mean degree of polymerisation $\bar{P}$ and concentration c on degree of conversion β is determined by the type of function $\eta(c,\bar{P})$. If it is assumed for illustration[1,18] that $\eta \propto \bar{P}^a c^b$ (where a and b are constants), the above effects of the mechanism of polymerisation on variation in viscosity can be summarised as in the Table. Although the degree of conversion β is the sole governing parameter in all cases, the character of the function $\eta(\beta)$ varies substantially depending on the mechanisms of formation of the polymer.

The above simple schemes of growth in viscosity during polymerisation apply to isothermal conditions. Non-isothermal phenomena during polymerisation exert a significant influence on changes in rheological properties, and may lead to completely novel non-trivial effects (a detailed survey of related problems has appeared[70,71]). Some of these cases, e.g. the changes in viscosity during adiabatic polymerisation, can be described quantitatively[62]. To obtain a more general description requires a very large body of calculations, which can be justified by the fundamental interest of the problem and for applied purposes. However, it is important that in all cases such calculations should be based on detailed knowledge of the kinetics of polymerisation, and also on establishment of the way in which viscosity depends on the molecular mass of the polymer and the content in the solution, for specific cases of theoretical or technical interest.

IV. VULCANISATION OF ELASTOMERS AND HARDENING OF THERMOSETTING PLASTICS

Elastomers and thermosetting plastics are both able to react to form a three-dimensional network of chemical bonds, with conversion from a liquid to a non-fluid and infusible material. It is this transition, in which all the rheological properties change within wide limits, that we shall discuss here. The most characteristic changes consist in an increase in viscosity to "infinitely" high values, an extremal change in hyperelastic properties at a stage preceding formation of a continuous three-dimensional network of chemical bonds[72,73], and ultimately the appearance of an equilibrium modulus characteristic of non-fluid systems. The components of the dynamic modulus of elasticity also change. Such changes are strongest at low frequencies, since the development of properties then involves movement of the macromolecular chain as a whole or of quite long segments. Formation of cross-links, however, hinders movement of the chain more strongly the larger the portion of it is involved in the elementary act of relaxation.

The great changes in rheological properties of oligomers during hardening or of rubbers during vulcanisation have formed the basis of various industrial methods for monitoring structural transformations by measuring the rheological (or mechanical) characteristics of the material. Among them the best known and quite widely used are methods for monitoring the vulcanisation of rubber mixtures using various designs of Vulcameter, Curometer, etc., as well as dozens of industrially produced and standardised, and also home-made, devices employing the most diverse types of loading. The initial stages of vulcanisation are usually monitored viscosimetrically, but the continuation of vulcanisation (hardening) after formation of the three-dimensional network of chemical bonds is recorded by dynamic methods. The chief experimental methods and modes of treatment of the results applied to rubbers and rubber mixtures for this purpose were summarised in a monograph[32].

The further efforts of investigators in this field are now directed at standardising test conditions and procedures as strictly as possible, achieving reproducible comparative results, and establishing correlations between characteristic points in relations obtained in different types of apparatus and technical indices of the moulded articles. In the immediate future we must even expect strengthening of the requirements for the standardisation of conditions of measurement together with automation of instruments used in industrial practice.

Study of the rheological changes accompanying the hardening of oligomers is in a somewhat different position. The specific nature of problems arising here is most conveniently illustrated by the example of epoxy-resins, whose hardening has been studied by means of the whole set of existing rheological methods. Hardeners of amine type have been used in most of this work.

Investigation of the initial stages of this process requires primarily the determination of viscosity—temperature—time ($\eta-T-t$) characteristics for multicomponent materials having various compositions[74-81]. A constant-temperature cross-section of such a characteristic can be represented schematically by the graph in Fig. 3. The greatest interest attaches to assessment of the positions of two points: the time t_0 defines the "viability" of the oligomer, i.e. the duration of the low-viscosity liquid state; and the time t^* corresponds to the attainment of a certain high viscosity, which in practice is defined as "gelation", i.e. the point at which fluidity is lost, although the polymer actually remains fluid for some time longer. The gelation point is determined by the accepted arbitrary technical methods and corresponds[74] to a very narrow viscosity range (~1200–1400 P). This result gives a quantitative basis for the technical estimates of t^* adopted in practice, which is important when considering non-isothermal hardening schedules for thermosetting resins. Nevertheless, this viscosity criterion is fairly arbitrary, for the mouldability of compositions based on epoxy resins is determined[75] by a viscosity of only 500 P, as was demonstrated for many systems differing in composition.

It is important to observe that in general there is no correlation between t_0 and t^*. Consequently the "viability" of a material is still an inadequate indication of its technical possibilities, and the ability to be moulded may be retained for a long time (between t_0 and t^*) if the increase in viscosity during this period is not very rapid. Therefore the complete time dependence of viscosity $\eta(t)$ must be used to assess the technical properties of compositions.

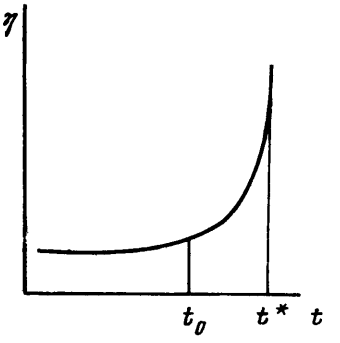


Figure 3. Assessment of critical points—"viability" and "gelation" times—in the hardening of oligomers.

The graph in Fig. 3 can be expressed analytically in various ways depending on the specific hardening reactions of actual oligomers. Often this relation is clearly described by means of an exponential function:

$$\eta=\eta_0\exp(kt), \qquad (2)$$

where η_0 is the initial viscosity and k the kinetic parameter of hardening, both of which depend on the temperature. An exponential time variation of viscosity usually "works" quite well in the initial range, but not as far as the gelation point, for the increase in viscosity accelerates as this point is approached. More complicated $\eta-t$ relations have also been suggested[78,79] which take into account the very sharp increase in viscosity in the hardening of epoxy resins.

The hardening of oligomers often takes place under non-isothermal conditions. It is therefore important to generalise formula (2), so that complete $\eta-T-t$ hardening characteristics can be obtained. For this purpose the temperature dependence of η_0 is expressed in the usual way:

$$\eta_0=\eta_\infty\exp(E_\eta/RT), \qquad (3)$$

where E_η is the activation energy of viscous flow and η_∞ a constant. The temperature dependence of the rate constant

k is described similarly, but with a different activation energy E_k, of hardening:

$$k=k_\infty \exp(E_k/RT). \quad (4)$$

Then

$$\ln\eta=\ln\eta_\infty+E_\eta/RT+tk_\infty\exp(E_k/RT). \quad (5)$$

Direct measurements have shown[74] that $E_k \approx 200$ kcal mole^{-1} for the hardening of epoxy resins with amine hardeners, while E_η varies with the composition of the materials from 22 to 41 kcal mole^{-1}. Both η_∞ and k_∞ are also strongly dependent on composition.

Formula (5) can be used to estimate the gelation time t^* under non-isothermal conditions. This is important technically, since actual hardening processes almost always take place under non-isothermal conditions and go to completion fairly rapidly, so that their direct observation is difficult. The appropriate generalisation is made by replacing kt in Eqn.(2) by the expression

$$\int_0^t k(T)\,dt = k_\infty \int_0^\infty \exp[E_k/RT(t)]\,dt. \quad (6)$$

Then

$$\ln\eta = \ln\eta_\infty + E_\eta/RT + k_\infty \int_0^t \exp[E_k/RT(t)]\,dt. \quad (7)$$

The integral on the right-hand side of (7) is evaluated (for a specified programme of temperature variation) by any numerical method†.

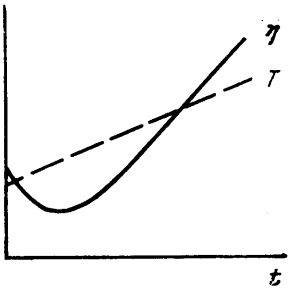


Figure 4. Variation in viscosity during non-isothermal hardening (linear time variation of temperature).

In practice a linear (or almost linear) time variation of temperature of a composition is often achieved. This gives a characteristic extremal variation in viscosity (Fig.4), due to competition, with rise in temperature, between softening (lowering of viscosity) and acceleration of the chemical reaction. Use of the generalised $\eta-T-t$ characteristic in formula (7) enables a correct estimate of the gelation time t^* to be made in this case, and an optimum hardening schedule to be selected by varying the rate of heating.

One factor restricting the possibility of increasing the rate of rise in temperature and thereby accelerating the technical process is the requirement that the temperature gradient across the mass must be lowered in the moulding of large or thick-walled articles. With external heating a uniform temperature field throughout the article cannot be guaranteed, so that hardening takes place non-uniformly, which leads to the appearance of considerable (or even unacceptably high) internal stresses. Therefore the choice of optimum rate of rise in temperature during the hardening of oligomers must take into account the heat-transfer conditions in an article of specific dimensions and the estimated internal stresses arising during heating, chemical reaction, and cooling.

The construction of $\eta-T-t$ characteristics has general value for analysing the non-isothermal hardening of thermosetting resins, compositions based on them, and other rheologically unstable materials undergoing particular chemical changes when heated. The fairly large number of studies of the changes occurring in the rheological properties of oligomers during hardening suggest a single type of behaviour governed by two characteristic indices—the duration of the initial ("induction") perod of slight increase in viscosity and the gelation time.

The possibility of the temperature—time superposition of chemorheological characteristics of polymer materials also has general value. It implies that the generalised time characteristic of the variation in viscosity can be constructed as a function of the product ta_T, where a_T is the temperature dependence of the rate of hardening. Direct measurements have shown[80] that a_T is described in terms of the same activation energy as that characterising the temperature dependence of the viscosity of the oligomer in the initial state. Apparently, however, this is not a universal rule, as has been emphasised above (the dependence of the activation energy of viscous flow on the composition of the hardened material with E_k unchanged during the hardening of epoxy resins by an amine type of hardener). Nevertheless, the possibility of applying temperature—time superposition in those specific cases in which it applies in practice provides an important method for constructing $\eta-T-t$ characteristics and enables technical parameters of a composition to be estimated at temperatures at which direct measurements cannot be made because of the high rates of hardening.

The relation between the activation energies of viscous flow and chemical reaction E_η and E_k is important in the consideration of changes in viscosity during non-isothermal hardening. In general these constants can be regarded as independent, and the general $\eta-T-t$ characteristic described by formula (7) can be used. The postulate that the change in viscosity due to hardening and the role of temperature as a factor controlling the rate of chemical reaction are far stronger than the actual temperature dependence of viscosity at a certain stage of structure formation is apparently legitimate and extremely useful in virtue of the equations it gives[81].

In essence this hypothesis is sufficient for the temperature—time superposition of $\eta-t$ relations obtained at different hardening temperatures. Hence follows in particular the possibility of estimating the activation energy (or the temperature dependence of the rate of chemical reaction in general) from the temperature dependence of the duration of reaction necessary to achieve a specified viscosity. Application of this approach to various thermosetting resins gave positive results. Thus the activation energy of the process characterised by the time variation of the viscosity of a resol agreed with the value found by an independent chemical method[82]. It was shown for epoxy resins that the activation energy of the process leading to the increase in viscosity was independent of the actual viscosity at which the corresponding duration of reaction was compared. The activation energy thus obtained from viscosimetric data was almost identical with the value found from a chemical study of the kinetics of hardening[81].

† The possibility of such an approach has recently been extended also to non-isothermal increase in viscosity of a polyester binder[113].

However, such a simple approach is restricted to the state of viscous flow: on the formation of non-fluid materials the possibility of temperature–time superposition becomes debatable. This is indicated by the differences observed between activation energies calculated from the induction period and from the gelation time[81]. Nevertheless, such differences may be fortuitous, in view of the ambiguity in the assessment of the instant at which fluidity is lost, since this point is actually determined from arbitrary indices.

The complexity involved in characterising the rheological properties of hardening polymer materials is due not only to the need to estimate changes in behaviour of the specimen with time but also to the fact that the test materials (except perhaps during the initial state) exhibit an anomalous viscosity effect, with the departure from Newtonian flow changing with the degree of structure formation. Therefore the problem of describing the flow of hardening polymers is of intrinsic value. The early papers[83,84] used the Bingham model of a viscoplastic medium to represent the viscosity properties of compositions based on phenol–formaldehyde resins. Actually, however, a true fluidity limit is most likely absent from such compositions until a three-dimensional network is formed[85,86], although a definite part may be played by the nature of the filler used, interaction of whose particles may lead to the appearance of solid properties in the compositions[87,88]. In such cases the appearance of a fluidity limit is not directly due to hardening of the oligomer, in contrast to what occurs during structure formation causing the gelation of polymer solutions[89]. Nevertheless, it is not always possible to draw a sharp boundary between these two phenomena.

A high filler content in hardening oligomers, even if it does not tend to form a stable structural network, leads to the boundary-layer slippage characteristic of highly filled compositions when they are forced through moulding channels[90,91]. In actual technical situations and in the laboratory investigations simulating them the dominant role in the hydrodynamic resistance of the channels is played by boundary-layer slippage until high degrees of structure formation are reached. The role of the filler is especially important in the flow of hardening compositions in the region of sharp changes in cross-section of the channel, e.g. in the entry portion of moulding channels[92], where a decisive part is played by the presence of the filler, not by hardening of the oligomer[92,93]. Boundary-layer slippage or rupture of the deformed composition occurs with various flows of highly filled oligomers[94], but this effect is not specific to hardening materials, since completely analogous phenomena are observed in the flow of various polymer materials[4,5,90,91].

The reliability of viscosimetric analysis for kinetic study of the hardening of oligomers largely depends on how far the change in properties of the specimen can be separated from thermal effects due to the exothermic character of hardening. The importance of this factor is clearly indicated by kinetic results for phenol–formaldehyde resins, which enabled their viscosity to be related to the extent of conversion[95,96]. Extrapolation of the results to "zero" specimen thickness proved that the induction period always observed in practice is not a true kinetic effect but is due to delay in the spread of temperature throughout the specimen. It has already been suggested above that the inevitable non-uniformity of the temperature field (and hence degree of conversion throughout the specimen) is a cause of internal stresses. Here another aspect of non-isothermal hardening is emphasised—as a factor complicating kinetic interpretation of the results—so that correct allowance for non-isothermal effects achieved by different methods[97–99] has general value for a whole range of problems associated with the changes in rheological properties of polymer materials undergoing structure formation.

Successive separation of thermal effects from the change in degree of hardening has shown that the increase in viscosity in the initial stages of structure formation in phenol–formaldehyde resins is described by the formula[90,91]

$$\eta=\eta_0(\beta)\exp(E/RT), \tag{8}$$

in which the pre-exponential factor $\eta_0(\beta)$ represents the effect of degree of conversion β on viscosity, while the activation energy $E = 8.22$ kcal mole^{-1} is almost independent of β until a considerable degree of conversion is attained. The maintenance of an unambiguous relation between degree of conversion and viscosity whatever the thermal history of the material is very important, since it enables a single main reaction to be regarded as causing the increase in viscosity. It is also responsible for the possibility of finding generalised $\eta-T-t$ characteristics in the form (7).

A similar approach to describing the degree of conversion attained as the sum of changes occurring with different laws of variation in the temperature of the material is valid also for rubber mixtures[100].

Another important aspect of the rheology of hardening compositions related to the non-isothermal character of flow is the influence of rate of deformation on kinetics of hardening. This problem has been very little studied, and existing data are unreliable just because effects due to the actual increase in rate of deformation and to the consequent evolution of heat (corresponding to the rise in temperature and in the rate of hardening) were not separated. Therefore the shortening of the time during which an oligomeric composition remains plastic, with increase in the flow rate of shear[101–103], may actually be due to non-equivalence of the temperature conditions of deformation. This is indicated also by the marked effect of initial temperature on the development of the effect, which may be associated with the viscosity of the oligomer: the higher the temperature the lower the initial viscosity of the reaction mass, and hence the smaller the evolution of heat at comparable rates of deformation and the weaker the influence of flow on the reaction kinetics. Therefore the influence of deformation on the course of the hardening of oligomers remains an open question.

It is very tempting to simplify the description of processes occurring in the initial stages of the hardening of oligomers by using a single parameter, e.g. the degree of conversion. This is possible if any leading mechanism of chemical changes in the reaction mass can be distinguished. Viscosity measurements during the formation of polyurethane are significant in this respect, when the precise meaning of the reaction mechanisms enabled the viscosity to be related to the molecular characteristics of the product at various stages of polycondensation[104].

Kinetic study of the hardening of oligomers by viscosimetry is mainly of value for the initial stages, which in practice correspond to preparation of the composition or decomposition of a hardening layer on a reinforcing material. Subsequent stages extending as far as the final article can conveniently and fruitfully be observed by a dynamic method, by measuring the time variation of the modulus of elasticity G and the mechanical loss angle $\tan\delta$.[105]

The most general picture of the variation in dynamic characteristics during hardening has been obtained with epoxy resins. It is shown diagrammatically in Fig. 5,[106] where the upper continuous curves represent the variation in the glass

point T_{gl} during vitrification, and t_{gl} is the length of the hardening period necessary to reach the region of vitrification. Analogous results (but not so complete) conforming to this pattern have been obtained by other workers[107,108]. In order to understand the results of rheological investigations on this process it is fundamentally important that we establish the relationship between three temperatures—that of the experiment T, the glass point of the unhardened composition T_{gl}, and the glass point of the final product $T_{gl,\infty}$—bearing in mind that achievement of maximum loss than δ corresponds to the relaxation transition point.

We may suppose, for example, that condtions of vitrification are attained before the gelation point (i.e. at $T < T_{gl}$). Maximum tan δ then corresponds to some degree of structure formation, and an already vitrified polymer will undergo only a slight decrease in tan δ as the process continues. Another case corresponds to the condition $T_{gl} < T < T_{gl,\infty}$, when two loss maxima are observed: the first occurs at the gelation point, i.e. on transtion from a fluid to a hyperelastic state, and the second at the glass point, i.e. the main relaxation transition. Finally, in the third case, with $T > T_{gl,\infty}$, gelation conditions are reached very rapidly (because of the high temperature), but vitrification does not take place: i.e. the material is in a hyperelastic state the whole time. This extremely informative view of the changes in dynamic properties of a composition is generally valid for the hardening of oligomeric resins. Important technical recommendations for two parameters—gelation time t_0 and vitrification time t_{gl}, the latter close to the time at which hardening is complete—can be obtained from this scheme. Taking Fig.5 to represent a model of the process, we can analyse the specific features of the hardening of various materials.

The fertility of applying a dynamic method to analyse the concluding stages in the formation of a rigid polymer has been demonstrated in estimating the degree of cyclisation when a polyester–amide film is heated to give a polyimide[109]. Measurements of the time dependence of the dynamic modulus of elasticity can usefully be employed for studying the induction period, the duration, and the completion of the linear and three-dimensional copolymerisation of organosiloxane monomers[110]. Interest attaches also to a recently developed method for analysing chemical changes in solid polymers by introducing a reactive component into the matrix of a heat-resistant rigid polymer: occurrence of a chemical reaction in the material, including intrachain processes, can be assessed from the variation in dynamic mechanical properties (loss angle and elastic modulus)[111,112].

The above results clearly show the possibility and the value of a dynamic method for investigating chemical processes in structure-forming oligomers and monomers. Therefore this method is readily used to monitor various real technical processes: for example, it has been proposed[113] to employ measurements of dynamic properties in the acoustic frequency range to monitor the completion of hardening in articles made from thermosetting resins and glassfibre-reinforced laminates based on them. A qualitative similarity was found[113] in the changes in acoustic (i.e. ultimately elastic) properties of binder and laminate. Although the type of time dependence of the measured signal varies, the positions of characteristic points corresponding to formation of a three-dimensional structure in the polymer and to completion of hardening almost coincide for polymer and composition based on it. Therefore use of a dynamic (e.g. acoustic) method will permit non-destructive monitoring of the concluding stage in the hardening of the polymeric binder in glass laminates. Such a method has been successfully used also to monitor foaming and subsequent hardening of polyurethane foam plastics[114].

A dynamic (or vibrational) method can also be used to monitor the vulcanisation of rubber mixtures, especially the hardening of liquid rubbers[115], when a complete change in modulus of elasticity can be observed, from low values corresponding to the liquid state right up to values in the region of the hyperelasticity plateau. However, a dynamic method will give entirely reliable results even for ordinary highly viscous rubber mixtures. This has permitted standardisation of a dynamic method for monitoring the vulcanisation of rubber mixtures (ASTM 2704–2706 in the USA), and a good correlation was shown[116] between values obtained by this method and by the customary but more inconvenient and less sensitive and reliable Mooney measurement of coefficients of viscosity.

Dynamic effects on the test material involved in non-destructive monitoring methods do not themselves in any way affect the kinetics. However, this does not limit the possibilities and prospects of applying dynamic (or vibrational) effects on structure-forming compositions, in particular thermosetting plastics. In fact, with increase in amplitude of deformation and transition to so called "large" amplitudes

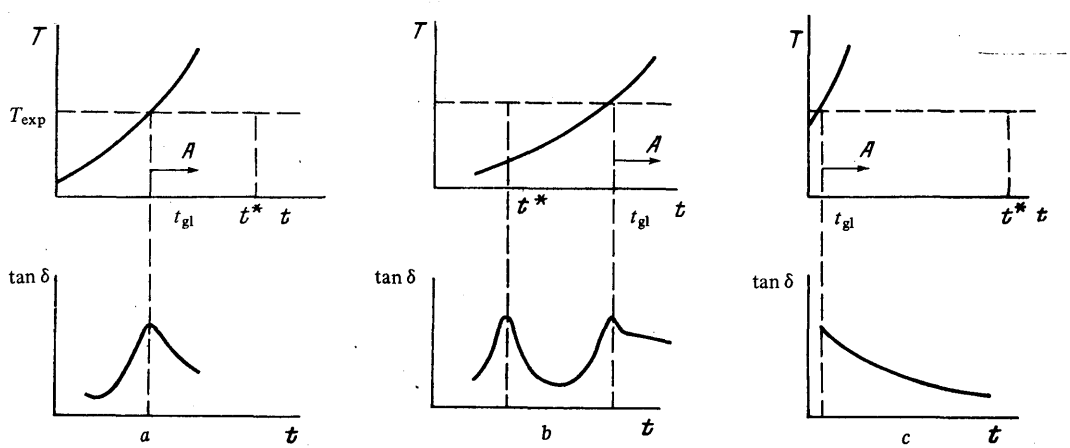


Figure 5. Variation in dynamic properties during hardening for different relations between experimental temperature and glass point: *a*) $T_{exp} < T_{gl}$; *b*) $T_{gl} < T_{exp} < T_{gl,\infty}$; *c*) $T_{exp} > T_{gl,\infty}$; *A*) the arrow indicates the region of the vitreous state of the material.

(in contrast to the "infinitesimal" amplitudes used for non-destructive measurements) vibrational effects become an efficient means of influencing the kinetics of chemical processes. This has been clearly demonstrated on the same epoxy resin[117]: increasing the amplitude of deformation led to a sharp fall in elastic modulus and to a delay in hardening, but the final state of the polymer subjected to vibration was characterised by a higher modulus. Cyclic deformation with large amplitudes presumably delays formation of a three-dimensional network of chemical bonds and intensified hardening.

Unfortunately the paper[117] gives only limited information on this interesting and promising aspect of the reality of structure-forming polymer systems. There is thus no basis at present for discussing how general is the significance of these facts. Undoubtedly, however, the use of large-amplitude dynamic effects can give important new information on the behaviour of polymer compositions during hardening and is of definite technical interest for controlling the rate of hardening and the properties of the end-products.

V. GELATION

Gelation is intermediate between polymerisation in solution and vulcanisation with respect to the accompanying change in rheological properties. The initial stages actually involve an increase in viscosity owing to chemical interactions of a limited number of macromolecules, which results in an increase in molecular mass of individual chain structures. Then a single three-dimensional network appears, which contains a considerable proportion of the initial chains, while the remaining solvent acts as a plasticiser of the rubberlike structure[118,119]. In the light of the above rheological approach, therefore, gelation involves conversion of a relatively low-viscosity liquid into a viscoelastic medium incapable of flow, regardless of the actual mechanism of gelation, which may be associated not only with chemical reactions but also with physical transitions (e.g. formation of microcrystalline regions).

The variation in viscosity during gelation has quite long been regarded as an extremely sensitive indication of the course of the process. Moreover, a rapid increase in viscosity with time has been interpreted as a criterion of conversion of the solution into a gel. Quite frequently, indeed, e.g. for ethanolic solutions the cellulose nitrate[120] or for aqueous polyacrylic acid[121], the variation in viscosity is extremely simple: a prolonged stable state or slight growth in viscosity is replaced by a very rapid fall in fluidity. The length of the induction period depends on the temperature, but the whole observed pattern of change in viscosity resembles so strikingly the kinetics of crystallisation of a polymer from solution that it can be regarded as indirect evidence of gel formation by a mechanism of crystallisation. More complicated cases of growth in viscosity with time are known, when the rate of change decreases[122].

However, known examples of increase in viscosity during gelation are partial in character, while possible ambiguity of results and interpretations based on viscosity measurements is due to ambiguity in the very concept of "viscosity" for non-Newtonian polymer solutions. The actual pattern of variation of viscosity properties during transition of a solution into a gel is substantially more complicated. As has been shown for gelling solutions of a polysulphonamide in dimethylacetamide[89], the way in which viscosity varies with time depends markedly on the conditions under which the measurements are made (Fig. 6): at high rates of shear the viscosity increases only slightly for a long time, and gives hardly any indication of the occurrence of gelation. Yet the possibility of gel formation may already have been established, if the clearest criterion of gelation—a yield point in a homogeneous system—has appeared. And then, if measurements are made at low rates of shear, a clear structure-formation effect is observed.

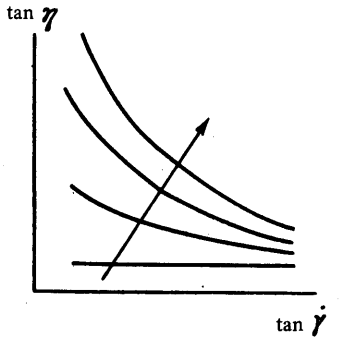


Figure 6. Variation in dependence of viscosity on rate of shear $\dot{\gamma}$ during gelation. The arrow shows the direction of increase in duration of the process.

Here we must emphasise the difference between the "state" and the "behaviour" of a material. In general this difference is well known for polymers: thus a polymer in a hyperelastic state may behave as a glass, but a melt as a rubber[2], which is a direct consequence of the relaxation mechanism of polymer deformation. The same applies to the solution—gel case. The existence of a yield point should in general be regarded as a criterion of a gel[89,119]. However, the appearance of a yield point (or a limiting shear stress) can have various causes. Thus in dispersions with a polymeric binder a solid filler may form a structure that undergoes brittle fracture at some critical stress[123]. A still closer approach to gels is made by liquid-crystalline polymer solutions, in which a well defined though not very high yield point is observed[124-126].

The borderline between jellies and other systems having a yield point is fairly arbitrary. But in any case the states of a system below and above the yield point must be distinguished. In this sense it is more correct to speak, not of the "state" of solution or gel, but of behaviour equivalent to "solution" or "gel" behaviour. However, even the transition between "fluid" and "non-fluid" states may be blurred if breakdown of the structural network formed by macromolecules takes time, i.e. if this network possesses durability[127].

From the rheological point of view transition to the gelatinous state is complete when the yield point, which increases during gelation, becomes equal to the tensile strength of the material, so that the possibility of transition to a fluid state has completely disappeared[89].

Gelation is characterised by the appearance not only of a yield point but also of a set of thixotropic properties, which in the early stages of gel formation are studied by the same rheological methods of rotational rheometry[128] as are thixotropic changes in polymer melts and solutions[129]. At the stage of formation of a three-dimensional structure the thixotropic properties of gels are observed by dynamic methods—from the time variation of the modulus of elasticity[130].

Furthermore, deformation may itself affect the rate of gelation[131], so that the introduction of shear in the measurement of viscosity is an active factor influencing the kinetics. Therefore viscosity measurements, especially if they are approached without sufficiently thorough analysis, are insufficient to assess the changes accompanying gelation. Additional information may, of course, be obtained by measuring the hyperelasticity or the viscoelastic properties of the material, which also change on formation of a jelly. But it is also relevant that in some cases rheological methods may be relatively insensitive to structural changes.

An investigation of gelation in gelatin solutions[132] has given results that are significant in this connection. Spectroscopic observation showed that, in the initial stage of structure formation, changes in intensity of several bands occured for ~6 h, indicating the occurrence of chemical reactions. These changes are entirely susceptible to the usual kinetic interpretation: they are described by a first-order equation with rate constant 0.01 min^{-1}. The viscosity, however, remains almost unchanged during this period, and increases significantly only after 9—10 h, a considerable time after completion of the chemical changes observed spectroscopically. Thus macroscopic changes (apparent in an increase in viscosity) do not necessarily follow all the microscopic processes. In the present case spectroscopic observations enable nucleation within individual molecules to be followed, whereas the viscosimetric method indicates the combined effects of intermolecular interactions—the formation of spiral multimolecular structures.

In concluding this discussion of jellies as systems undergoing changes in rheological properties during formation it must be emphasised that, despite the huge literature (a 1974 review[104] contains 399 references), very few systematic quantitative investigations of rheological changes in a system during gelation have been made, and available information is restricted to a number of particular examples.

---oOo---

This Review of published experimental facts and theoretical aspects of the changes in rheological properties accompanying polymerisation and the reactions of polymers and compositions based on them shows that the variation in all the rheological indices is regularly linked with the molecular characteristics of the polymer. This opens up wide possibilities for the use of rheological measurements for monitoring and controlling technical processes in the production of polymer materials and chemical stages in the moulding of articles (hardening, vulcanisation, etc.).

Until now this important and promising field has not received due development. The reasons are inadequate study of the relations between rheological characteristics and molecular parameters of specific and diverse materials, little attention paid to several fundamental problems, in particular the influence of rate of deformation on the kinetics of chemical processes, the absence or inadequacy of experimental technique, especially in controlling the technical process, and the absence of a general theoretical approach to the design of reaction vessels in which properties of the medium change significantly (in many cases even radically). Solving these problems will permit effective utilisation of rheological methods in the production and processing of polymer materials.

REFERENCES

1. G.V.Vinogradov and A.Ya.Malkin, "Reologiya Polimerov" (Rheology of Polymers), Khimiya, Moscow, 1977.
2. J.D.Ferry, "Viscoelastic Properties of Polymers", John Wiley, New York, 1974.
3. D.W.Van Krevelen, "Properties of Polymers—Correlation with Chemical Structure" (Translated into Russian), Khimiya, Moscow, 1976.
4. 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., 14A, 2425 (1972).
5. G.V.Vinogradov, A.Yu.Malkin, Yu.G.Yanovskii, E.K.Borisenkova, B.V.Varlykov, and G.V.Berezhnaya, J.Polym.Sci., A-2, 10, 1061 (1972).
6. A.Ya.Malkin, N.K.Blinova, G.V.Vinogradov, M.P.Zabugina, O.Yu.Sabsai, V.G.Shalganova, I.Yu.Kirchevskaya, and V.P.Shatalov, Eur.Polym. J., 10, 445 (1974).
7. A.Ya.Malkin, G.Zh.Zhangereeva, and M.P.Zabugina, Vysokomol Soed., 16A, 2360 (1974).
8. A.Ya.Malkin, O.Yu.Sabsai, G.Zh.Zhangereeva, M.P.Zabugina, and G.V.Vinogradov, Mekh.Polimerov, 519 (1977).
9. L.A.Holmes and J.D.Ferry, J.Polym.Sci., C-23, 291 (1968).
10. W.M.Prest Jr., J.Polym.Sci., A-2, 8, 1897 (1970).
11. V.E.Dreval', G.O.Botvinnik, A.Ya.Malkin, and A.A.Tager, Mekh.Polimerov, 1110 (1972).
12. A.Ya.Malkin, G.V.Berezhnaya, and G.V.Vinogradov, Mekh.Polimerov, 896 (1972).
13. N.K.Blinova, S.I.Sergeenkov, A.Ya.Malkin, Yu.G.Yanovskii, and G.V.Vinogradov, Mekh.Polimerov, 132 (1973).
14. V.E.Dreval', A.Ya.Malkin, G.V.Vinogradov, and A.A.Tager, Eur.Polym.J., 9, 85 (1973).
15. V.E.Dreval', A.Ya.Malkin, G.O.Botvinnik, J.Polym. Sci., Polym.Phys.Ed., 11, 1055 (1973).
16. V.E.Dreval', A.Ya.Malkin, A.A.Tager, and G.V.Vinogradov, Mekh.Polimerov, 729 (1973).
17. G.V.Vinogradov, A.Ya.Malkin, N.K.Blinova, S.J.Sergeenkov, M.P.Zabugina, L.V.Titkova, Yu.G.Yanovskii, and V.G.Shalganova, Eur.Polym.J., 9, 1231 (1973).
18. A.Ya.Malkin, Rheol.Acta, 12, 486 (1973).
19. A.Ya.Malkin, A.A.Askadskii, and V.V.Kovriga, "Metody Izmereniya Mekhanicheskikh Svoistv Polimerov" (Measurement of the Mechanical Properties of Polymers), Khimiya, Moscow, 1978.
20. A.V.Tobolsky, "Structure and Properties of Polymers" (Translated into Russian), Khimiya, Moscow, 1964, Chapter V.
21. A.Ya.Malkin, and A.E.Chalykh, "Diffuziya i Vyazkost' Polimerov.Metody Izmereniya" (Diffusion and Viscosity of Polymers—Methods of Measurement), Khimiya, Moscow, 1979.
22. J.K.Gillham, J.Macromol.Sci., Phys., B9, 209 (1974).
23. J.K.Gillham, Polym.Eng.Sci., 11, 295 (1971).
24. S.J.Stadnicki, J.K.Gillham, and Y.Hazony, Polymer Prep., 15, 556 (1974).
25. R.F.Boyer, J.Macromol.Sci., Phys., B9, 187 (1974).
26. I.M.Belkin, G.V.Vinogradov, and A.I.Leonov, "Rotatsionnye Progiby" (Rotational Flexings), Mashinostroenie, Moscow, 1968.
27. A.A.Trapeznikov and T.I.Korotina, Dokl.Akad.Nauk SSSR, 201, 1402 (1971).

28. A.A.Trapeznikov and A.T.Pylaeva, Vysokomol.Soed., 11A, 1294 (1970).
29. A.A.Trapeznikov, Zhur.Fiz.Khim., 41, 1247 (1967) [Russ.J.Phys.Chem., No.6 (1967)].
30. G.V.Vinogradov, I.M.Belkin, and V.A.Kargin, Dokl.Akad.Nauk SSSR, 148, 369 (1963).
31. A.I.Leonov and A.Ya.Malkin, Zhur.Prikl.Mekh. Tekh.Fiz., No.4, 107 (1965).
32. M.M.Reznikovskii and A.I.Lukomskaya, "Mekhanicheskie Ispytaniya Kauchuka i Reziny" (Mechanical Tests on Rubber), Khimiya, Moscow, 1968, p.54.
33. I.F.Kanavets, L.G.Batalova, and A.G.Romashova, Plast.Massy, No.1, 63 (1960).
34. V.I.Sviridov, A.D.Sokolov, N.N.Danilkin, and E.N.Mironov, Plast.Massy, No.6, 66 (1976).
35. M.S.Akutin, G.V.Vinogradov, B.V.Yarlykov, N.V.Afanas'ev, and I.K.Sanin, Uspekhi Khim., 44, 1517 (1975) [Russ.Chem.Rev., No.8 (1975)].
36. V.N.Fedoruk, N.I.Zolotukhin, L.D.Pertsov, G.A.Strunge, A.G.Chernova, and V.V.Sherbakov, Plast.Massy, No.7, 76 (1969).
37. I.S.Volchek and Yu.M.Lushkov, "Avtomatizatsiya Proizvodstv Polikondensatsionnykh Smol" (Automation of the Production of Polycondensation Resins), Khimiya, Moscow, 1976 p.42.
38. A.Ya.Malkin, B.V.Rendar, S.G.Kulichikhin, and L.I.Sherysheva, Vysokomol.Soed., 20A, 1913 (1978).
39. G.V.Vinogradov, A.Ya.Malkin, E.P.Plotnikova, A.A.Konstantinov, G.V.Krasheninnikov, A.K.Kulapov, V.M.Bogomolov, A.A.Shakhrai, and B.A.Rogov, Vysokomol.Soed., 20A, 226 (1978).
40. D.L.Fedyukin, N.V.Zakharenko, and Zh.S.Suzdal'nitskaya, Kauchuk Rezina, No.8, 46 (1971).
41. A.Ya.Malkin, G.V.Berezhnaya, and G.V.Vinogradov, Mekh.Polimerov, 896 (1972).
42. A.Ya.Malkin, G.V.Berezhnaya, and G.V.Vinogradov, J.Polym.Sci., Polym.Symp., No.42, 3, 1111 (1973).
43. A.V.Ryabov and D.N.Emel'yanov, Zavod.Lab., 30, 762 (1964).
44. A.A.Golubev, D.N.Emel'yanov, A.V.Ryabov, and E.L.Belyaeva, Trudy Khim.i Khim.Tekhnol., No.3, 92 (1975).
45. D.N.Emel'yanov, I.E.Kononova, A.V.Ryabov, and N.F.Simonova, Vysokomol.Soed., 17B, 163 (1975).
46. D.N.Emel'yanov, I.E.Kononova, and A.V.Ryabov, Trudy Khim.i Khim.Tekhnol., No.3, 88 (1975).
47. A.V.Ryabov, D.N.Emel'yanov, and V.M.Burova, Trudy Khim.i Khim.Tekhnol., No.2, 209 (1966).
48. A.V.Ryabov, D.N.Emel'yanov, and M.A.Chekushina, Trudy Khim.i Khim.Tekhnol., No.3, 122 (1965).
49. E.M.Morozova, A.S.Morozov, V.I.Eliseeva, and L.A.Travnikova, Lakokrasoch.Mater.Primenenie, No.3, 18 (1973).
50. E.M.Morozova, V.I.Eliseeva, A.S.Morozov, and L.A.Travnikova, in "Struktura i Svoistva Poverkhnostnykh Sloev Polimerov" (Structure and Properties of Surface Layers of Polymers), Naukova Dumka, Kiev, 1972, p.221.
51. E.M.Morozova, V.I.Eliseeva, and L.A.Travnikova, in "Termodinamicheskie i Strukturnye Svoistva Granichnykh Sloev Polimerov" (Thermodynamic and Structural Properties of Boundary Layers of Polymers), Naukova Dumka, Kiev, 1976, p.136.
52. E.M.Morozova, V.I.Eliseeva, Preprints, International Symposium on Macromolecules, Helsinki, 1972, Vol.2, Secto 1, p.651.
53. E.M.Morozova, V.I.Yelicejeva, and L.A.Travnikova, J.Polym Sci., Polym Symp., No.42, 73 (1973).
54. S.A.Gorodinskaya, N.V.Andriasyan, and Yu.I.Trokhin, Vestnik Kievsk.Politekh.Inst., Ser.Khim. Mashinostroeniya Tekhnol., (Izd.KGU, Kiev), No.11, 32 (1974).
55. Y.Ide and L.J.White, J.Appl.Polym.Sci., 18, 2997 (1974).
56. B.Berger, J.Appl.Polym.Sci., 9, 2887 (1965).
57. D.N.Emel'yanov, A.A.Golubev, A.V.Ryabov, and E.L.Belyaev, Vysokomol.Soed., 16A, 2426 (1974).
58. A.Ya.Malkin and S.G.Kulichikhin, Vysokomol.Soed., 19B, 701(1977).
59. A.Ya.Malkin and S.G.Kulichikhin, Kolloid.Zhur., 41, 141 (1979).
60. Yu.S.Lipatov and L.M.Sushko, Vysokomol.Soed., 13A, 2417 (1971).
61. A.A.Berlin, A.G.Kondrat'eva, N.N.Tvorogov, E.S.Pankova, and A.Ya.Malkin, Vysokomol.Soed., 15B, 740 (1973).
62. A.Ya.Malkin, in "Voprosy Techeniya Polimernykh Sistem" (Aspects of the Flow of Polymer Systems), Izd.Ural'sk.Nauch.Tsentra, Sverdlovsk, 1980.
63. Al.Al.Berlin, S.A.Vol'fson, and N.S.Enikolopov, "Kinetika Polimerizatsionnykh Protsessov" (Kinetics of Polymerisation Processes), Khimiya, Moscow, 1978.
64. S.G.Kulichikhin and A.Ya.Malkin, Vysokomol.Soed., 22A, 2093 (1980).
65. M.B.Lachinov, R.A.Simonian, T.G.Georgieva, V.P.Zubov, and V.A.Kabanov, J.Polym.Sci., Polym.Chem.Ed., 17, 613 (1979).
66. I.N.Cardenas and K.F.O'Driscoll, J.Polym.Sci., Polym.Chem.Ed., 14, 883 (1976).
67. A.Ya.Malkin, S.G.Kulichikhin, S.L.Ivanova, and M.A.Korchagina, Vysokomol.Soed., 22A, 165 (1980).
68. S.G.Kulichikhin, S.L.Ivanova, M.A.Korchagina, and A.Ya.Malkin, Dokl.Akad.Nauk SSSR, 243, 700 (1978),
69. A.Ya.Malkin, S.G.Kulichikhin, M.A.Korchagina, S.L.Ivanova, G.M.Talalaeva, L.I.Sherysheva, N.N.Avdeev, and A.E.Chalykh, Vysokomol.Soed., 21B, 444 (1979).
70. A.M.Stolin, A.Ya.Malkin, and A.G.Merzhanov, Uspekhi Khim., 48, 1492 (1979) [Russ.Chem.Rev., No.8 (1979)].
71. A.M.Stolin, A.G.Merzhanov, and A.Ya.Malkin, Polym.Eng.Sci., 19, 1061 (1979).
72. S.G.Kulichikhin, A.Ya.Malkin, and G.V.Vinogradov, Vysokomol.Soed., 12A, 129 (1970).
73. G.V.Vinogradov, A.Ya.Malkin, and V.G.Kulichikhin, in "Uspekhi Reologiya Polimerov" (Advances in the Rheology of Polymers), Khimiya, Moscow, 1970, p.181.
74. M.B.Roller, Polym.Eng.Sci., 15, 406 (1975).
75. S.Inoue, J.Soc.Mater.Sci.Japan, 22, 1064 (1973).
76. M.R.Kamal, Polym.Eng.Sci., 14, 231 (1974).
77. M.R.Kamal and S.Sourour, Polym.Eng.Sci., 14, 59 (1974).
78. H.-J.Boos and K.-R.Hauschildt, Angew.makromol. Chem., 62, 53 (1977).
79. H.-J.Boos and K.-R.Hauschildt, Angew.makromol. Chem., 79, 1 (1978).
80. R.P.White Jr., Polym.Eng.Sci., 14, 50 (1974).
81. F.G.Mussatti and C.W.Macosco, Polym.Eng.Sci., 13, 236 (1973).
82. Y.Tanaka and H.Kakiuchi, J.Appl.Polym.Sci., 7, 1063 (1963).
83. A.D.Sokolov and I.F.Kanavets, Plast.Massy, No.12, 61 (1963).

84. A.D.Sokolov and I.F.Kanavets, Plast.Massy, No.6, 23 (1964).
85. N.N.Danilkin and I.F.Kanavets, Plast.Massy. No.1, 29 (1970).
86. A.Rothenpieler, Kunststoffe, 59, 747 (1969).
87. M.S.Akutin, G.V.Vinogradov, N.V.Afanas'ev, B.V.Yarlykov, and I.K.Sanin, Plast.Massy, No.10, 39 (1973).
88. N.V.Afanase'ev, M.S.Akutin, B.V.Yarlykov, I.K.Sanin, L.V.Ryzhova, and T.I.Kamenskaya, Plast.Massy, No.3, 36 (1975).
89. A.Ya.Malkin, L.P.Braverman, E.P.Plotnikova, and V.G.Kulichikhin, Vysokomol.Soed., 18A, 2596 (1976).
90. N.I.Basov, V.A.Lyubartovich, V.A.Mironov, E.D.Paskhin, A.I.Leonov, and Yu.V.Kazankov, Mekh.Polimerov, 820 (1971).
91. N.I.Bassow, A.I.Leonow, Yu.W.Kasankow, W.A.Ljubartowitsch, V.A.Mironow, Plaste und Kautschuk, 19, 507 (1972).
92. G.G.Stankoi, E.B.Trostyanskaya, Yu.N.Kazanskii, V.V.Okorokov, and O.Ya.Mikhasenok, Plast.Massy, No.9, 49 (1968).
93. V.V.Okorokov, Yu.N.Kazanskii, and G.G.Stankoi, Plast.Massy, No.8, 27 (1969).
94. B.Schreiber, Kunststoffe, 59, 362 (1969).
95. G.M.Bartenev, V.V.Kuznechikova, Z.G.Povarova, and V.A.Kargin, Vysokomol.Soed., 11A, 2172 (1969).
96. A.Ya.Malkin and B.V.Yarlykov, Mekh.Polimerov, 930 (1968).
97. A.G.Merzhanov, V.G.Abramov, and L.T.Abramova, Dokl.Akad.Nauk SSSR, 171, 901 (1968).
98. A.G.Merzhanov and L..Smirnova, Fiz.Goreniya Vzryva, 12, 659 (1978).
99. A.Ya.Malkin, A.N.Ivanova, S.L.Ivanova, and Z.S.Andrianova, Inzh.-fiz.Zhur., 34, 636 (1978).
100. A.I.Leonov and A.I.Shvarts, Vysokomol.Soed., 14A, 695 (1972).
101. A.D.Sokolov and I.F.Kanavets, Plastmassy, No.2, 54 (1967).
102. N.N.Danilkin, I.F.Kanavets, and A.S.Perevertov, Plastmassy, No.11, 38 (1969).
103. A.D.Sokolov, No.7, 43 (1979).
104. S.D.Lipschitz and C.W.Macosko, Polym.Eng.Sci., 16, 803 (1976).
105. D.W.Sundstrom and M.F.English, Polym.Eng.Sci., 18, 728 (1978).
106. P.G.Babayevsky and J.K.Gillham, J.Appl.Polym. Sci., 17, 2067 (1973).
107. G.C.Papanicolaou, S.A.Paipetis, and P.S.Theocaris, J.Appl.Polym.Sci., 20, 903 (1976).
108. Yu.G.Yanovskii, E.I.Frenkin, M.G.Kharina, M.S.Murav'ev, and G.V.Vinogradov, Plastmassy, No.7, 10 (1977).
109. G.L.Slonimskii, A.A.Askadskii, F.N.Nurmukhametov, Ya.S.Vygodskii, Z.V.Gerashchenko, S.V.Vinogradova, and V.V.Korshak, Vysokomol.Soed., 18B, 824 (1976).
110. K.A.Andrianov, G.V.Vinogradov, Yu.G.Yanovskii, A.B.Zachernyuk, E.A.Burlova, and S.I.Sergeenkov, Dokl.Akad.Nauk SSSR, 232, 810 (1977).
111. A.A.Askadskii, Yu.I.Matveev, and G.L.Slonimskii, "Tezisy Soobshchenii.Mezhdunarodnyi Simpozium po Makromolekulyarnoi Khimii (Tashkent, 1978)" (Abstracts of Papers at International Symposium on Macromolecular Chemistry, Tashkent 1978), Nauka, Moscow, 1978, Vol.4, p.5.
112. Yu.S.Kochergin, A.P.Travnikova, A.A.Askadskii, E.S.Krongauz, G.L.Slonimskii, and V.V.Korshak, Vysokomol.Soed., 20A, 839 (1978).
113. B.N.Komarov and I.M.Al'shits, Plast.Massy, No.7, 61 (1974).
114. V.I.Shul'min and B.N.Komarov, Plast.Massy, No.9, 65 (1976).
115. E.I.Brailov and S.I.Shlol'nik, Kauchuk Rezina, No.8, 17 (1968).
116. C.W.Macosco and F.G.Mussatti, Polymer Preprints, 14, 103 (1973).
117. L.A.Faitel'son, V.D.Kiseleva, and V.I.Alksne, Mekh.Polimerov, 301 (1971).
118. S.P.Papkov, "Studneobraznoe Sostoyanie Polimerov" (Gel-like State of Polymers), Khimiya, Moscow, 1974.
119. L.Z.Rogovina and G.L.Slonimskii, Uspekhi Khim., 43, 1102 (1974) [Russ.Chem.Rev., No.6 (1974)].
120. S.Newman, W.R.Krigbaum, and D.K.Carpenter, J.Phys.Chem., 60, 648 (1956).
121. S.Crisp, B.G.Lewis, and A.D.Wilson, J.Dent.Res., 54, 1173 (1975).
122. A.G.de Castro, D.Bourgoin, and M.Joly, Rheol. Acta, 8, 295 (1969).
123. G.V.Vinogradov, A.Ya.Malkin, E.P.Plotnikova, O.Yu.Sabsai, and N.E.Nikolaeva, Int.J.Polym.Mater., Mater., 2, 1 (1972).
124. S.P.Papkov, V.G.Kulichikhin, A.Ya.Malkin, V.D.Kalmykova, A.V.Volokhina, and L.I.Gudim, Vysokomol.Soed., 14B, 244 (1972).
125. V.G.Kulichikhin, A.Ya.Malkin, S.P.Papkov, O.N.Korol'kova, V.D.Kalmykova, A.V.Volokhina, and O.B.Semenov, Vysokomol.Soed., 16A, 169 (1974).
126. S.P.Papkov, V.G.Kulichikhin, V.D.Kalmykova, A.Ya.Malkin, J.Polym.Sci., Polym.Phys.Ed., 12, 1753 (1974).
127. A.Ya.Malkin, O.Yu.Sabsai, E.A.Verebskaya, V.A.Zolotarev, and G.V.Vinogradov, Kolloid.Zhur., 38, 181 (1976).
128. O.C.C.Lin, J.Appl.Polym.Sci., 19, 199 (1975).
129. G.V.Vinogradov, A.Ya.Malkin, E.P.Plotnikova, and V.A.Kargin, Dokl.Akad.Nauk SSSR, 154, 1421 (1964).
130. J.Mewis and R.de Bleyser, J.Colloid Interface Sci., 40, 360 (1972).
131. K.Ono and K.Murakami, J.Polym.Sci., Polym. Letters Ed., 15, 507 (1977).
132. G.C.Finer, F.Franks, M.C.Phillips, and A.Suggett, Biopolymers, 14, 1995 (1975).
133. A.Ya.Malkin, A.M.Stolin, S.G.Kulichikhin, V.V.Maizeliya, G.M.Avdeeva, I.F.Pugachevskaya, and S.G.Chopornyak, Mekh.Kompozits, Mater., 362 (1980).

Plastmassy Plastics Scientific Research Institute, Moscow