

# VISCOELASTICITY OF POLYMERIC SYSTEMS IN FLUID AND RUBBERY STATES IN UNIAXIAL EXTENSION AND SHEAR

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## ABSTRACT

Relaxation transition of linear polymers from fluid to rubbery state under the effect of deformation at temperatures far above  $T_g$  are considered. The transition is accompanied by loss of polymer fluidity that makes it impossible to obtain the rheological characteristics in simple shear experiments at shear stresses exceeding approximately  $(1-5) 10^6$  dyne/cm<sup>2</sup>. Based on shear experiments, predictions are made and some fundamental problems are stated concerning viscoelastic properties of polymers in uniaxial extension. Particular attention is drawn to the phenomenon of fracture and especially to durability—time to fracture of uncured polymers. The importance of dividing total deformation into reversible and irreversible components is demonstrated. The fast decrease of irreversible deformation, with tensile stresses and deformation rates exceeding the critical values, gives the best indication of loss of polymer fluidity. The master curves of dependence on temperature and molecular weight of tensile stress total deformation and its reversible and irreversible components for narrow distribution polyisoprenes in a very broad range of deformation rates have been obtained. It has been revealed experimentally that high-molecular narrow distribution polymers behave as linear bodies up to fracture. Fundamental peculiarities of the process of fracture of uncured polymers are established. Correlation of reversible deformation of broad distribution polymers in the rubbery state and their tensile strength in the frozen state is discussed.

## INTRODUCTION

The aim of the present paper is to consider the fundamental peculiarities of the viscoelastic properties of linear polymers over a very wide range of stresses and deformation rates at temperatures above their melting and glass transition points. Among the various physical states which can be assumed by polymers, we are primarily concerned with the fluid and rubbery states; we will also dwell briefly upon the glassy state.

It is common knowledge that the variation in the rate of an external mechanical effect may be equivalent to the temperature variation. Thus, an increase in deformation rate corresponds to a decrease in temperature, since in both cases the relaxation processes are inhibited. Therefore an increase in deformation rate may lead to a forced transition of a polymer

from the fluid to the rubbery state and then to the glassy state. It is the combination of the effects of the temperature and the increase in deformation rate that is important. When the polymer state is far enough from the glass transition point the most important role is played by the forced transition of the polymer from the fluid to the rubbery state. As the glass transition point is approached, the possibilities for forced transition of the polymer to the glassy state increase progressively.

It should be emphasized that the change in the physical state of polymers under the effect of variation in deformation rate is purely a relaxation phenomenon. To a first approximation, it is determined by the relationship between the deformation rate and a certain parameter having the dimensionality of time and approximately characterizing the relaxation properties of the polymer. This characteristic relaxation time depends on the temperature, nature, molecular weight and molecular-weight distribution (MWD) of the polymers.

Although the foregoing considerations are quite elementary, no proper conclusions had been drawn from them by anybody before our investigations<sup>1-9</sup> were carried out in recent years.

What are these conclusions and what is the main underlying conception? This conception is based on the fact that as a result of a forced transition of polymers from the fluid to the rubbery state under the effect of the increased deformation rate they begin to behave as quasi-cured ones, i.e. they become similar to structuralized—cured—systems with suppressed fluidity. With the appropriate combination of the temperature and deformation rate polymers can pass over from the fluid state to the glassy one, in which they can exhibit brittleness.

Transition of polymers from one physical state to another under the effect of variations in temperature and deformation rate manifests itself most pronouncedly in narrow-MWD polymers, in which, in addition, the molecular weight exceeds the critical value  $M_c$ , which corresponds to a change in the form of the dependence of the viscosity on the molecular weight<sup>10</sup> and to the appearance of a three-dimensional entanglement network, which simultaneously gives rise to large reversible deformations<sup>11</sup>. Therefore our papers in general, and this one in particular, give much attention to narrow-MWD high polymers. Besides, in the case of flexible-chain polymers with low glass transition points it is much easier to study their transition from the fluid to the rubbery state under the effect of increased deformation rates over a very wide temperature range.

### ON THE CRITICAL DEFORMATION REGIME IN SIMPLE SHEAR

Under shear deformation the transition of polymers to the rubbery—quasi-cured—state leads to a very complex set of phenomena associated with a decrease in or complete loss of adhesion of the polymer to the enclosing solid surfaces and to rupture of continuity due to the limited deformability of quasi-cured polymeric systems. The loss of adhesion of the polymer to the enclosing surfaces results in its separation from them. In capillary and rotational devices this enables one to determine the transition of the polymer from the fluid to the rubbery state on the basis of the

drastic change in the rate of its motion or on the basis of the fall in torque. In capillary devices, however, it is impossible to obtain any information on the properties of polymers in the rubbery state, and in rotational devices one can obtain only limited information in régimes of cyclic deformation with large amplitudes<sup>8</sup>.

In contrast to simple shear, uniaxial extension is not complicated by adhesion processes. Therefore under conditions of uniaxial extension it is possible not only to establish the transition of polymers from one physical state to another, but also to investigate their deformability in the forced rubbery and glassy states. Therefore, in this paper attention is focused on uniaxial extension. However, before we pass on to the results obtained under uniaxial extension we will recall the basic facts relating to simple shear.

In capillary viscometer experiments with narrow-MWD linear polymers whose molecular weights exceed  $(5-10) M_c$  at temperatures far above  $T_g$  the following was established. Over a very wide shear stress range these polymers behave, judging by the viscosity measurements, to a first approximation, as Newtonian fluids in which, however, large reversible deformations may accumulate (up to 100 per cent and more). Each polymer-homologous series is characterized by a definite critical value of the shear stress. At shear stresses equal to or higher than these critical values it is impossible to realize stationary flow. At near-critical shear stresses one can observe noticeable deviations from the Newtonian flow (usually beginning with stresses of 0.5 of the critical values). The critical stresses depend only slightly on the temperature, and within the high-molecular part of the polymer-homologous series are independent of the molecular weight. For all the polymer-homologous series of linear polymers known to us the critical stresses lie within the narrow range of  $(1-5) \times 10^6$  dyne/cm<sup>2</sup>. The critical values of deformation rates corresponding to the critical stresses are determined by the initial viscosity of the polymers and therefore strongly depend on the molecular weight and temperature.

For narrow-MWD linear polymers the critical deformation régimes can be predicted on the basis of the results of investigation by the method of small-amplitude sinusoidal deformation<sup>2-6</sup>. The dependence of the loss modulus on the frequency has a maximum, which separates, on the frequency scale, the terminal zone describing the fluidity region from the rubbery-state region. Supposing, on the one hand, that the circular frequency is numerically equal to the shear rate and, on the other, that in the polymers at hand the non-Newtonian behaviour is not manifested very strongly, we can assume equivalence of the loss modulus and the shear stress<sup>12, 13</sup>. Then the values of the shear stress and rates corresponding to the maximum of the loss modulus will be critical. This is due to the fact that it is impossible to realize a stationary flow if an increase in shear rate is associated with a decrease in stress.

In investigating the transition of polymers from the fluid to the rubbery state on rotational viscometers one of the most promising methods is the method of cyclic deformation with large amplitudes. This method has been applied by A. Isayev and E. Katsyutsevich, who demonstrated the following. At frequencies below the critical value corresponding to the maximum

of the loss modulus on the curve of its dependence on the circular frequency, an increase in deformation amplitude to values accessible to the measuring instruments (about 180 per cent) leads to a progressive increase in stress amplitude. Quite a different situation is observed in the process of deformation at above-critical frequencies (corresponding to the maximum of the loss modulus). In this case the stress amplitude increases with deformation amplitude only up to a certain critical value, and then drops abruptly. This is the manifestation of the decrease in adhesion of the polymer to the measuring surface in the rotational instrument under the effect of its transition to the rubbery state. The critical stress amplitude is slightly below the critical shear stress, which is recorded by the capillary viscometry method. It is practically independent of the temperature. Within each polymer-homologous series the critical stress amplitude is also independent of the molecular weight. In the frequency range corresponding to the rubbery state the critical deformation amplitude retains a constant value (which usually does not exceed 100 per cent). Accordingly, the critical deformation rate amplitudes, which are equal to the product of the amplitude by the frequency, increase proportionately to the frequency.

It should also be noted that the abrupt drop in torque and the separation of the polymer from the measuring surface (sometimes its fracture) in elastoviscometers, with the deformation rates assigned constant, occurs at stresses several times lower than the critical ones recorded in the capillary viscometry method. The cause for the lower critical stresses and critical stress amplitudes in rotational devices remains unexplored.

The above brief description of the results obtained under conditions of simple shear can be conveniently illustrated by the data of E. Borisenkova for a narrow-MWD high-molecular polyisoprene ( $M_w/M_n < 1.1$ ), all the more so since in subsequent discussion we give for this polymer a large body of data on its investigation under uniaxial extension. *Figure 1* gives an idea of the behaviour of the polyisoprene in the experiments on a constant-pressure capillary viscometer. The shear stresses on the capillary wall are laid off on the  $x$  axis, and the mean values of the rate gradient, on the  $y$  axis (in the region of vertical branches of the curves under consideration only volume outputs have a clear-cut physical meaning). Noticeable deviations from the Newtonian flow begin at a shear stress one and a half times less than critical. Attainment of the critical stress (temperature invariant) is associated with the spurt effect, i.e. a jumpwise increase in flowrate due to the loss of adhesion of the polymer to the capillary wall and to its slipping.

### SOME PREDICTIONS AND PROBLEMS CONCERNING THE CRITICAL AND ABOVE CRITICAL REGIMES UNDER UNIAXIAL EXTENSION

Proceeding from the results of experiments under simple shear one can make a number of important predictions and formulate some fundamental problems relating to uniaxial extension.

(1) Stationary flow under uniaxial extension can be achieved if the true stress does not exceed the critical value, which is a characteristic of the polymer-homologous series. This critical value, within each polymer-

## VISCOELASTICITY OF POLYMERIC SYSTEMS

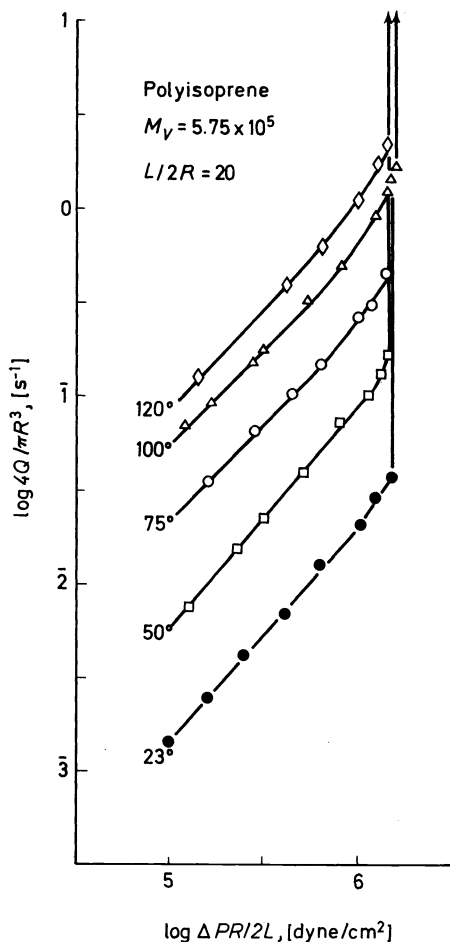


Figure 1. Flow curves and spurt effect in high-molecular polyisoprene ( $M_w/M_n$ ) < 1.1.

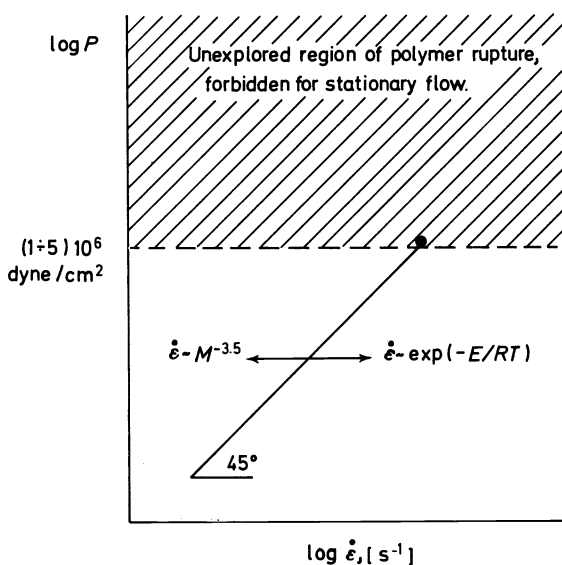
homologous series, must not depend on the molecular weight and must, to a first approximation, be constant at different temperatures. Just as in shear, the critical deformation rates must be determined by the initial value of longitudinal viscosity. In all cases the critical stresses must lie within a narrow range from  $1 \times 10^6$  to  $5 \times 10^6$  dyne/cm<sup>2</sup>.

(2) At stresses and deformation rates below critical (under isothermal conditions) the longitudinal viscosity must be constant, to a first approximation. This prediction is essential because it has been suggested in the past that the increase in viscosity with increasing deformation rate plays the determining role in ensuring the stability of the extension process.

(3) If the stresses and deformation rates exceed the critical values, under such deformation conditions the ability to accumulate irreversible deformation in polymers must be reduced, and since reversible deformations are

always limited in value, polymer fracture is always possible in the supercritical region.

The foregoing is illustrated schematically in *Figure 2*, where equal scale units along the coordinate axes are adopted.



*Figure 2.* Schematic representation of regions of stationary longitudinal flow and polymer fractures.

Let us define some problems of investigation into the process of uniaxial extension of linear polymers in the supercritical region, remembering that in such cases one cannot proceed from the results of experiments under simple shear.

(1) What is the rate of reduction in the ability of polymers to accumulate irreversible deformation before fracture with increasing stresses and deformation rates in the supercritical region, i.e. during their forced transition to the rubbery state? What are the possible reversible deformations in this state and how do they depend on the stresses and deformation rates?

(2) What is the durability of polymers in supercritical régimes of uniaxial extension, i.e. what is the relationship between the ultimate tensile strength and the time to deformation before fracture? If the polymers, in transition to the rubbery state, actually behave as cured elastomers, the form of the function describing the dependence of the durability on the ultimate tensile strength must be similar in the two cases.

(3) Is the fracture of polymer specimens passing over to the rubbery state a purely relaxation phenomenon, and is it then possible to establish a definite relationship between the tensile characteristics of polymers and their viscous properties? The affirmative answer to this question indicates in-

directly that in the fracture of polymers in a forced rubbery state mechanochemical effects do not play the determining role.

(4) Does the viscosity retain a constant value in prefracture régimes in the supercritical region of deformation (isothermal conditions)? The affirmative answer to this question emphasizes the insignificant role of the viscosity increase in ensuring the stability of the process of uniaxial extension.

(5) At temperatures closer to the glass transition point an increase in deformation rate may correspond to forced transition of polymers from the rubbery to the glassy state. In the rubbery state non-cured linear polymers behave as cured elastomers. Then the transition under consideration must obey the rules described by T. Smith<sup>14</sup> for cured elastomers. According to T. Smith, as the deformation rate increases the tensile deformation (reversible) passes a maximum. This maximum corresponds to a forced transition of polymers to the glassy state.

### ON EXPERIMENTAL TECHNIQUE

In the course of our investigations we used the four basic régimes of extensions and established their main features. These are the régimes of constant extension and deformation rates, constant forces, and true stresses. Preference is given to the régimes of constant deformation rates<sup>15</sup> and true stresses<sup>16</sup>. In contrast to most of the investigations known to us from the literature, in our work much attention is given to dividing the total deformation into its components, i.e. the reversible and irreversible constituents. The significance of this follows from the above-formulated problems.

The division of the total deformation into its components is based on the determination of elastic recoil in the specimens after deformation. On the elastic recoil of the polymers, however, is superimposed the effect of the surface tension, which can change the shape of the specimen<sup>17</sup>. In order to determine the elastic recoil with sufficient confidence, ignoring the surface tension effect, one has to use high-viscosity polymers. This condition is satisfied by high-molecular polymers.

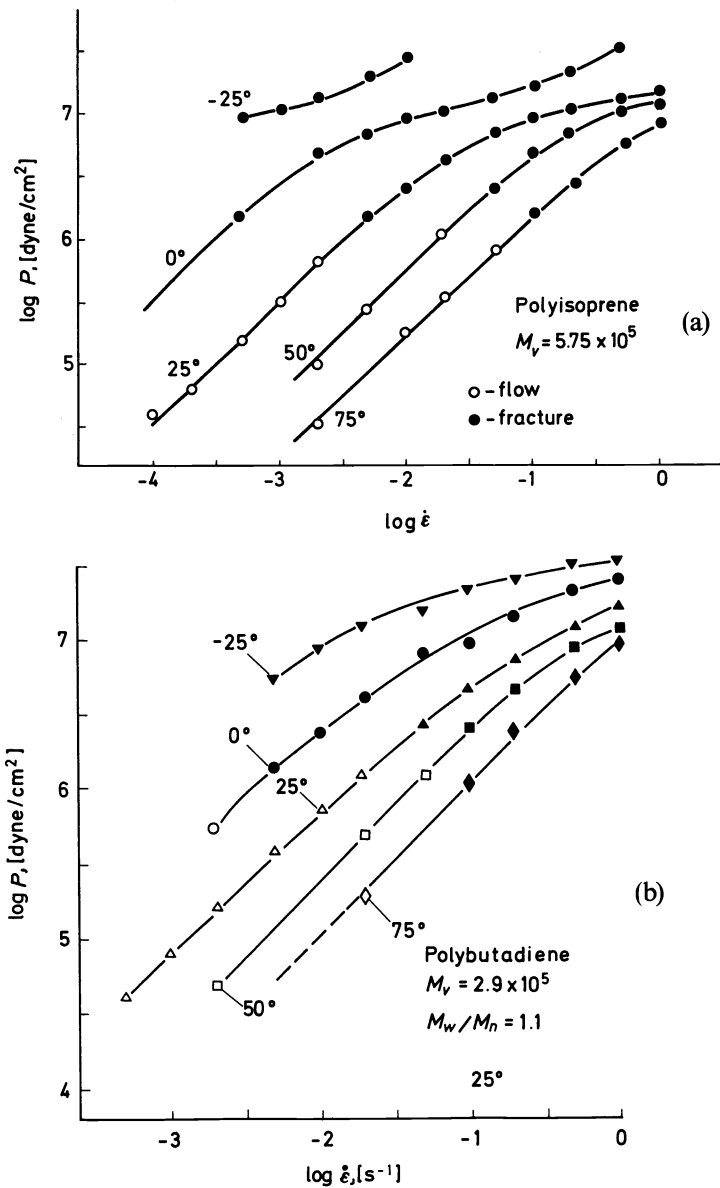
We begin the discussion of experimental results with cases where experiments are run at temperatures sufficiently remote from the glass transition point of the polymers. The results given below have been obtained by V. Volosevich in our laboratory in cooperation with S. Krashennikov, and with A. Malkin in an advisory capacity.

### VISCOELASTIC PROPERTIES OF NARROW DISTRIBUTION HIGH-MOLECULAR POLYMERS UNDER UNIAXIAL EXTENSION

We will now show how all the above predictions find proof in experiment, and will answer the questions just posed. Let us turn first to the dependence of the true stress on the deformation rate for a narrow-MWD polyisoprene. These data are presented in *Figure 3*. Here and in the subsequent figures the unshaded symbols relate to stationary flow conditions and the shaded ones correspond to deformation régimes in which specimen

fractures are observed. Henceforth we use the logarithmic measure of deformation after Hencky.

Inspection of *Figure 3* suggests the following important conclusions. In stationary flow régimes under isothermal conditions the true stress is directly



*Figure 3.* Dependence of true stress on total deformation rate for high-molecular polymers ( $M_w/M_n < 1.1$ ) at various temperatures, (a) polyisoprene; (b) polybutadiene.



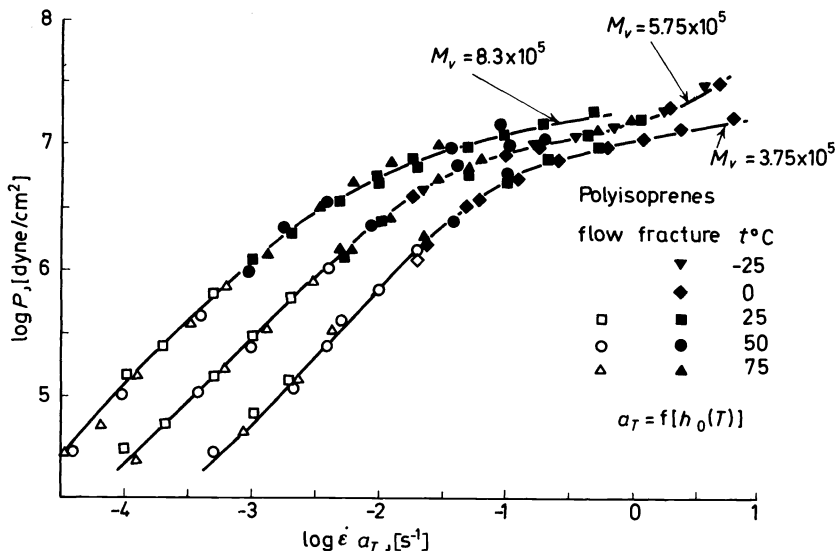
proportional to the deformation rate and, accordingly, the longitudinal viscosity is constant. This constancy of the viscosity is satisfied with an error not exceeding  $\pm 10$  per cent.

In accordance with the above predictions the critical stress corresponding to the appearance of fractures is about  $10^6$  dyne/cm<sup>2</sup> and is practically temperature independent. Non-stationary deformation régimes accompanied by fractures can be investigated over a very wide deformation rate range. In the supercritical region the rate of increase in stress with increasing deformation rate decreases considerably due to the reduction in specimen time to fracture (durability).

Later this problem will be considered in detail.

Of great importance is the possibility of applying temperature/rate reduction both in stationary régimes and in the far supercritical region of deformation. This is illustrated in *Figure 4* for three specimens of narrow-MWD polyisoprenes. The reduction coefficients are close to the universal values of the coefficients of the WLF equation<sup>18</sup>. From the figure it follows that in extension, as well as in shear, the critical stresses are independent of the molecular weight of the polymers.

The curves in *Figure 4* can be brought to coincidence by displacement along the rate axis. Accordingly, *Figure 5* exhibits the master curve for the



*Figure 4.* Temperature-invariant dependences of true stress on reduced rate of total deformation for high-molecular polyisoprenes ( $M_w/M_n < 1.1$  in all cases).

dependence of the stress on the reduced deformation rate. The possibility of this generalized representation of the data under consideration indicates that the polymer fracture process is of the nature of a relaxation.

For the understanding of what actually occurs on attainment of the

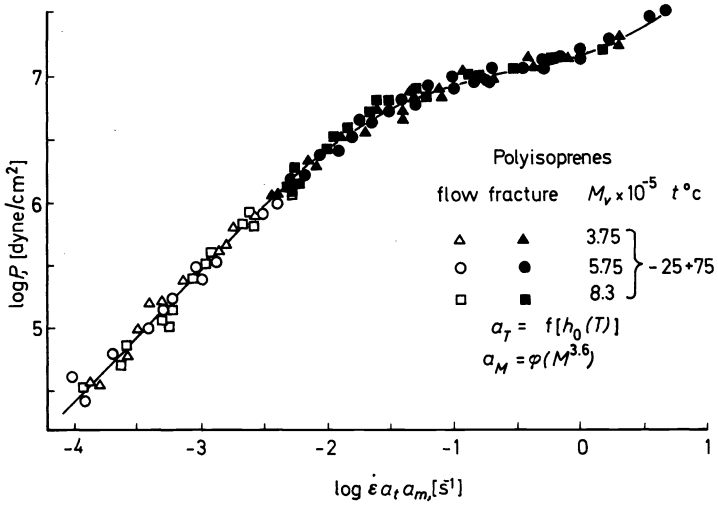


Figure 5. Master curve for dependence of true stress on reduced rate of total deformation for narrow-MWD polyisoprenes.

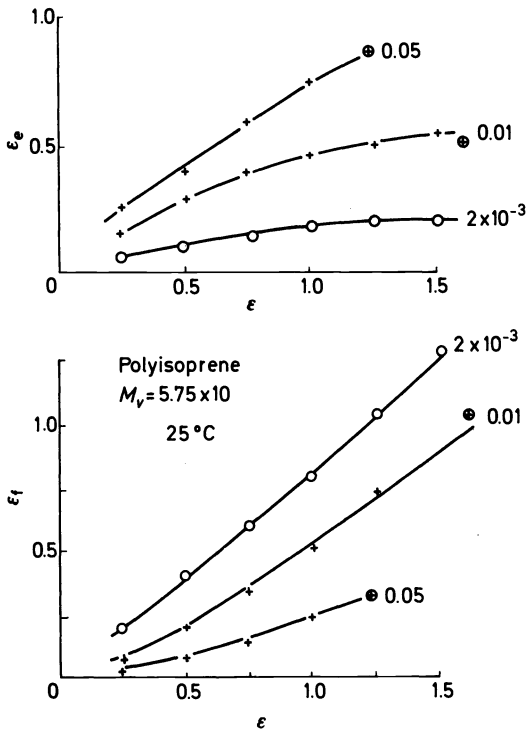
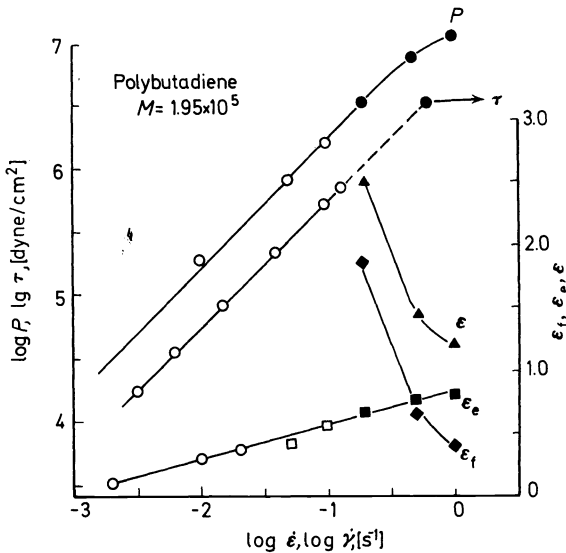


Figure 6. Dependence of reversible ( $\epsilon_e$ ) and irreversible ( $\epsilon_i$ ) deformations on total deformation ( $\epsilon$ ) at various rates of total deformation ( $\dot{\epsilon}$ ,  $s^{-1}$ ) for high-molecular polyisoprene ( $M_w/M_n < 1.1$ ).

critical deformation régime and of the behaviour of the polymers in the supercritical region it is very important to divide the total deformation into its reversible and irreversible components.

Let us now consider the accumulation of reversible and irreversible deformation with time in constant deformation rate régimes. The relevant data are presented in *Figure 6*. The abscissa values indicate the total deformation, which is proportional to time under conditions of a constant deformation rate. The upper graph shows the dependences of the reversible deformation and the lower graph, of the irreversible deformation on the total deformation. The deformation rates are given to the right of the curves.

A steady-state flow was achieved at the lowest of the rates used. At the other two deformation rates the polymer deformation ended in specimen fracture as shown by circles on the curves. At low deformation rates, when a steady-state flow is attained the rate of accumulation of irreversible deformation may exceed that of reversible deformation. The higher the deformation rate, the less irreversible deformation accumulates before fracture.



*Figure 7.* Dependence of true extension stress ( $P$ ), reversible ( $\epsilon_r$ ), irreversible ( $\epsilon_i$ ), and total ( $\epsilon$ ) deformation on total extension deformation rate ( $\dot{\epsilon}$ ); dependence of shear stress ( $\tau$ ) on shear rate ( $\dot{\gamma}$ ) for high-molecular polybutadiene ( $M_w/M_n < 1.1$ ).

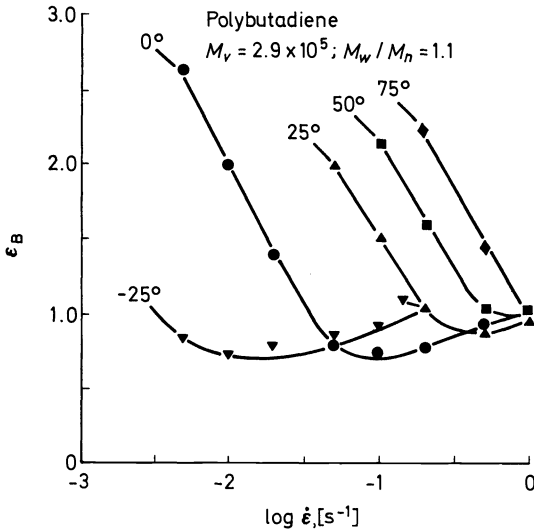
We will now answer the question, what actually happens in supercritical deformation régimes. To do this, we turn to *Figure 7*. In the upper left-hand part of the figure the longitudinal and shear flow curves are compared.

The spurt effect observed in capillary viscometers is shown by a horizontal arrow. The critical stresses corresponding to the spurt in shear and to the appearance of polymer specimen fracture in extension have closely similar values.

The lower curve shows that the reversible deformation increases particularly rapidly with increasing deformation rate in the supercritical deformation region. This is quite understandable, since in the rubbery state relaxation processes are weakened as compared with the fluid state.

The steeply falling curves show how the ability for accumulating irreversible and total deformation in the polymer is reduced in the initial part of the supercritical region.

Taking into account the indicated trends in the change of reversible and irreversible deformation with increasing deformation rate and stress it would be expected that the total deformation must pass through a minimum. To attain a minimum, more intensive development of reversible deformation is necessary, which is possible when the relaxation process slows down. This, in turn, requires a drop in temperature and the increase of molecular weight. Experiment confirms this assumption, which can be seen from the data presented in *Figure 8*. The figure exhibits the dependences of the total tensile deformation on the deformation rate.



*Figure 8.* Dependence of total tensile deformation at fracture on total deformation rate for high-molecular polybutadiene ( $M_w/M_n < 1.1$ ) at various temperatures.

Extensive information relating to the problems at hand has been obtained on polyisoprenes. Let us therefore turn to *Figure 9*.

The gradually rising curve in the upper left-hand part of the figure gives the dependence of the stress on the deformation rate in extension. If we refer the stresses in the supercritical region, not to the total rate of deformation, but to the rate of accumulation of irreversible deformation, the corresponding data will be represented by the unshaded dots, which are displaced to the left with respect to the curve under consideration. This displacement is shown by the arrows. Considering the difficulties involved in the measure-

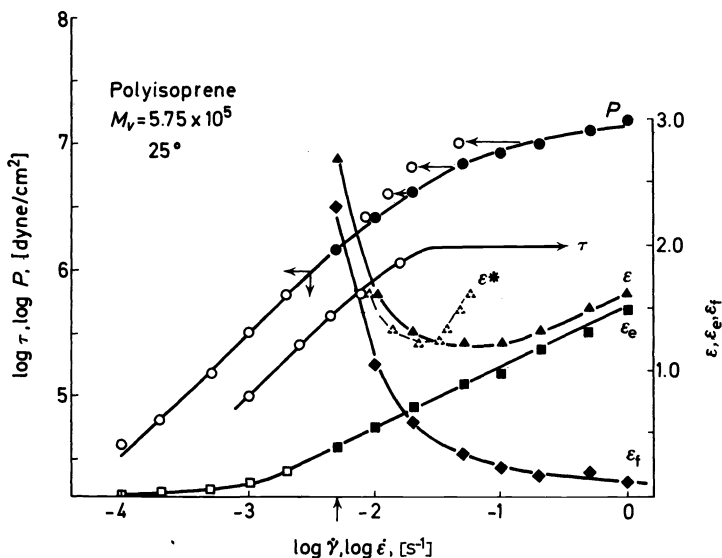


Figure 9. Dependence of true extension stress ( $P$ ), reversible ( $\epsilon_e$ ), irreversible ( $\epsilon_i$ ), and total ( $\epsilon$ ) deformation on extension deformation rate ( $\dot{\epsilon}$ ); dependence of shear stress ( $\tau$ ) on shear rate ( $\dot{\gamma}$ ) for high-molecular polyisoprene ( $M_w/M_n < 1.1$ ).

ment of irreversible deformation in régimes of deformation with low specimen durability, one can assume that the viscosity has a constant value, to a good approximation, not only in stationary flow régimes, but also in supercritical régimes. We will revert to this important question later on; meanwhile we will note that specially staged experiments showed the constancy of the viscosity in pre-stationary régimes of deformation until a stationary flow is attained.

The shear-flow curve runs parallel to the longitudinal-flow curve. The former ends in a horizontal section which corresponds to the spurt effect in capillary viscometers. As would be expected the stresses leading to the spurt and to specimen fracture in extension are of one and the same order of magnitude.

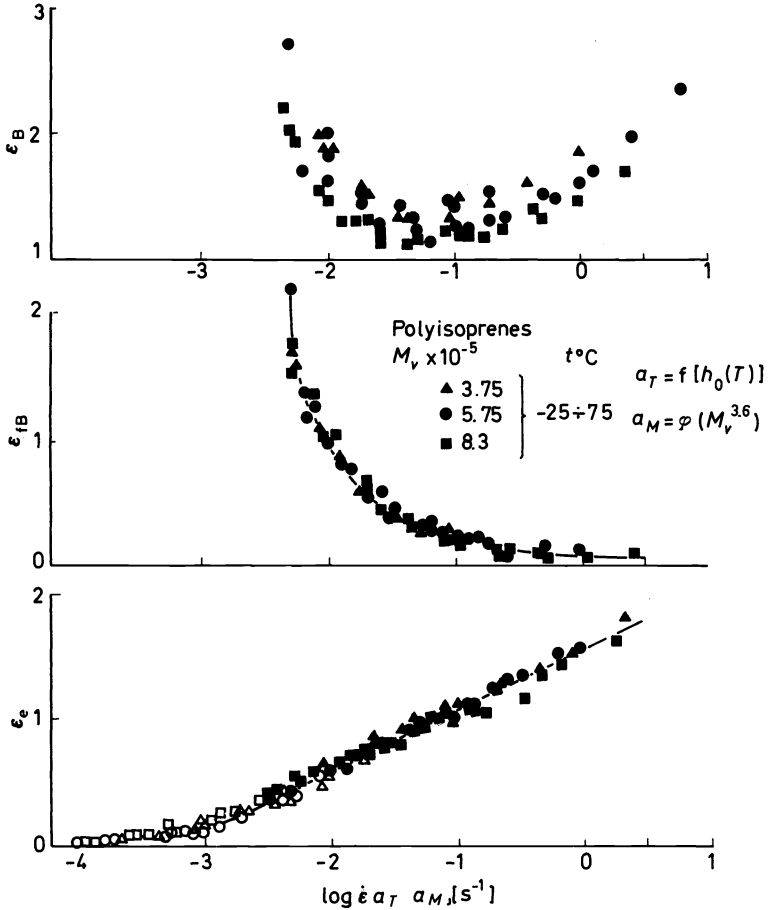
The steeply falling curve of irreversible deformation shows pictorially how the ability of polymers for accumulating irreversible deformation is reduced in the supercritical region. This is the manifestation of the loss of fluidity in polymers upon transition to the rubbery state. It should be stressed, however, that the fluidity is practically completely suppressed only in the far supercritical region. In the near-critical deformation region the analogy with cured polymers is by no means complete.

The reversible deformation increases rapidly in the supercritical region. In this case Young's modulus and the ultimate tensile strength are of the same order of magnitude.

The total tensile deformation passes through a clearly defined minimum. If we refer the total tensile deformation to the rate of irreversible deforma-

tion, assuming that precisely the latter is laid off on the abscissa, this minimum is defined still more sharply. This is shown by the curve with unshaded symbols marked with the letter  $\varepsilon^*$ .

The total tensile deformation and both its components—the reversible and irreversible amounts of deformation—are determined unambiguously by the relaxation characteristic of polymers. This enables one to obtain the master curves shown in *Figure 10*, where attention should be given to the greatest reversible deformations that can be realized in the supercritical region, i.e. in polymers in the forced rubbery state.



*Figure 10.* Master curves for dependence of total ( $\varepsilon$ ), irreversible ( $\varepsilon_i$ ) and reversible ( $\varepsilon_e$ ) deformation on reduced deformation rate for high-molecular polyisoprenes (in all cases  $M_w/M_n < 1.1$ ).

Above, attention was drawn to the fact that under isothermal conditions the viscosity retains a constant value not only in pre-stationary and stationary flow régimes, but also in pre-fracture régimes in the supercritical region.

## VISCOELASTICITY OF POLYMERIC SYSTEMS

This means that in all the extension régimes investigated the polymers under consideration behave as linear bodies, i.e. their behaviour must be described by the linear theory of viscoelasticity. The converse is also true, namely that if the polymers obey the theory of linear viscoelasticity both in the sub-critical and supercritical regions it will mean that they are actually linear bodies over the entire range of rates and stresses studied. Experiments completely confirm this.

According to the theory of linear viscoelasticity<sup>19</sup> the following relation must be satisfied.

$$P = 3\dot{\epsilon} \int_{-\infty}^{\infty} \theta H(1 - e^{-t/\theta}) dt \ln \theta$$

Here,  $P$  and  $\dot{\epsilon}$  are the true stress and the deformation rate, respectively,  $t$  is the time and  $\theta$  is the relaxation time in shear experiments.

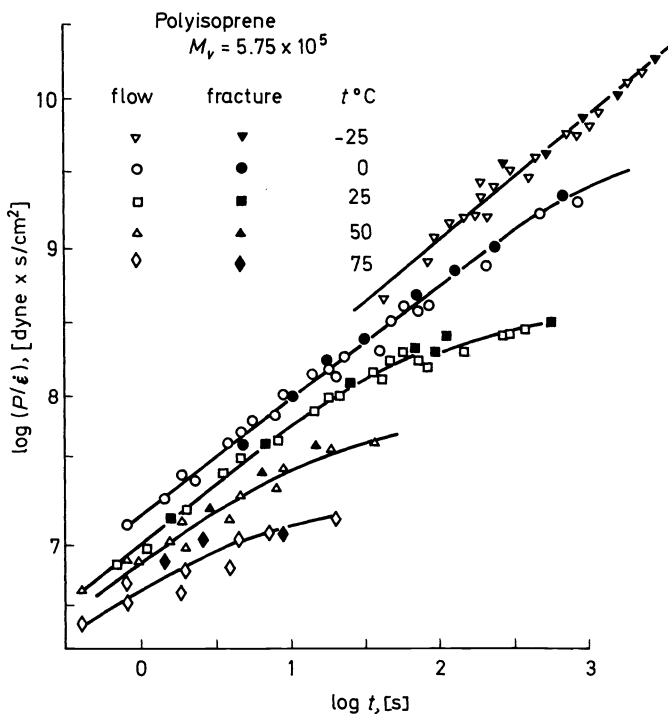


Figure 11. Time variation of ratio of true stress to total deformation rate for narrow-MWD high-molecular polyisoprene ( $M_w/M_n < 1.1$ ).

The curves in Figure 11 indicate that over a wide temperature range the data relating to deformation régimes which end both in a stationary flow and in specimen fracture are described in the same way. Moreover, if the stress is normalized, both in respect of the deformation rate and of the viscosity ( $\lambda$ ) measured in stationary flow régimes, we obtain the master curve shown in Figure 12. Here, the curve drawn among the points has been

computed by A. Malkin from the relaxation spectrum of the polymer in accordance with previously published results of shear experiments<sup>2</sup>.

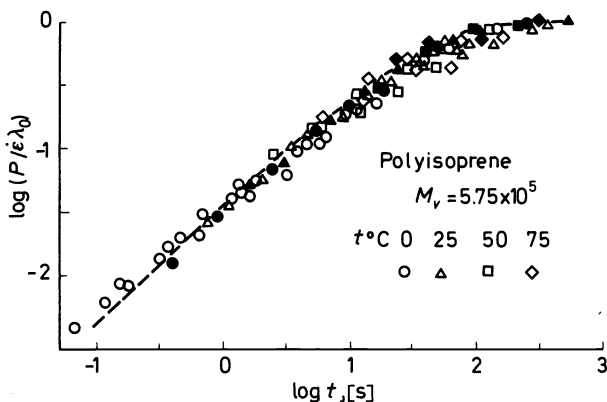


Figure 12. Temperature-invariant dependence of true stress normalized with respect to viscosity and total deformation rate on reduced extension time for high-molecular polyisoprene; extension time is normalized with respect to viscosity.

From the data presented in *Figures 11 and 12* it follows that over the entire range of draw ratios used (they reached 17-fold values) the polymer viscosity remained constant.

Therefore, in the general case, an increase in viscosity is by no means a necessary condition for the stability of the extension process. It should, however, be remarked that at very high degrees of extension a loss of stability of this process is observed. It is manifested in the appearance of non-homogeneity of the specimen cross section.

### TENSILE STRENGTH AND LONG-TERM DURABILITY OF NON-CURED POLYMERS

Let us now discuss the durability of polymers under conditions of a forced transition to the rubbery state. We will first consider a schematic generalization of data obtained in experiments in which a constant deformation rate was assigned in each case. They are shown in *Figure 13*. The time from the beginning of the experiment to specimen fracture is laid off on the ordinate, and the ultimate strength, on the abscissa. Equal units are adopted for the two logarithmic scales.

Under isothermal conditions durability is reduced according to the square law depending on the ultimate strength. For a given ultimate strength the durability increases rapidly with the molecular weight and decreases with increasing deformation rate; the ultimate strengths rise with a fall in temperature by the exponential law; the activation energy of the process is the same as for viscous flow. It may tentatively be assumed that for each



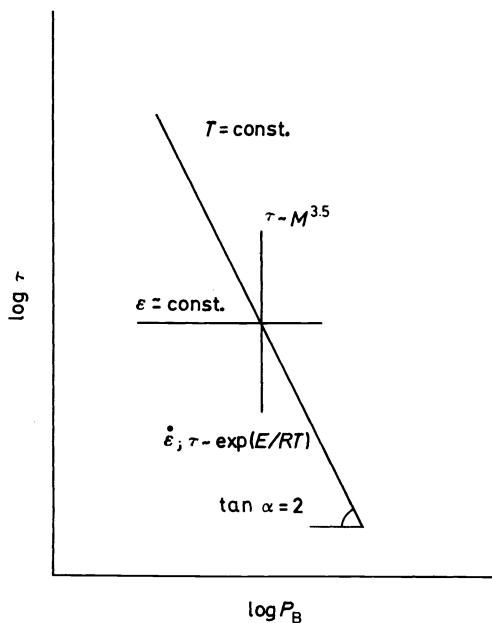


Figure 13. Schematic generalized representation of dependence of polymer durability ( $\tau$ ) on ultimate strength ( $P_B$ ) in testing narrow-MWD high-molecular polymers by the method of constant deformation rate.

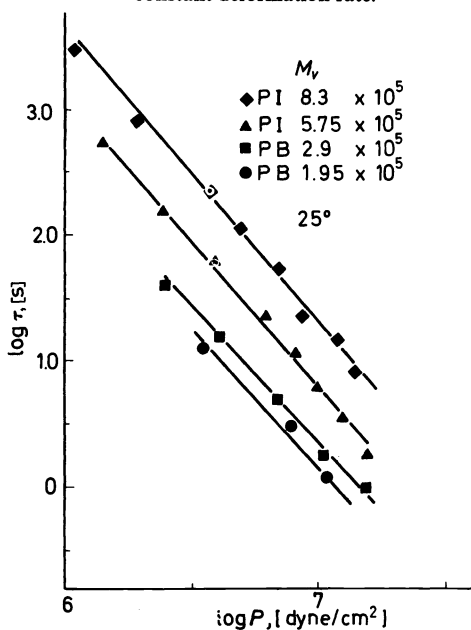


Figure 14. Dependences of durability ( $\tau$ ) on ultimate strength ( $P_B$ ) for narrow-MWD high-molecular polyisoprenes and polybutadienes (in all cases  $M_w/M_n < 1.2$ ); measurements by the method of constant deformation rate.

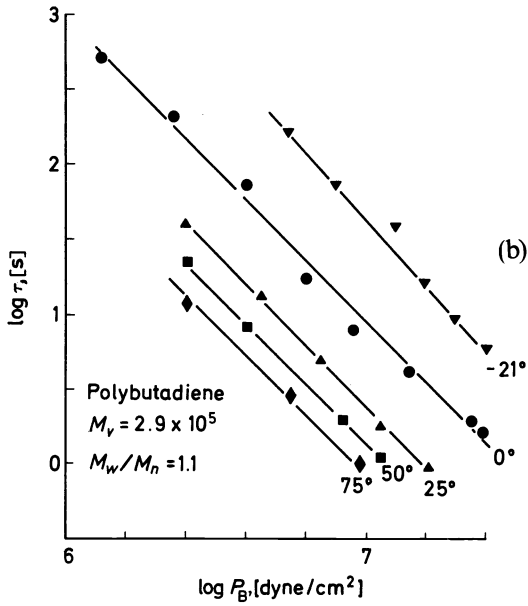
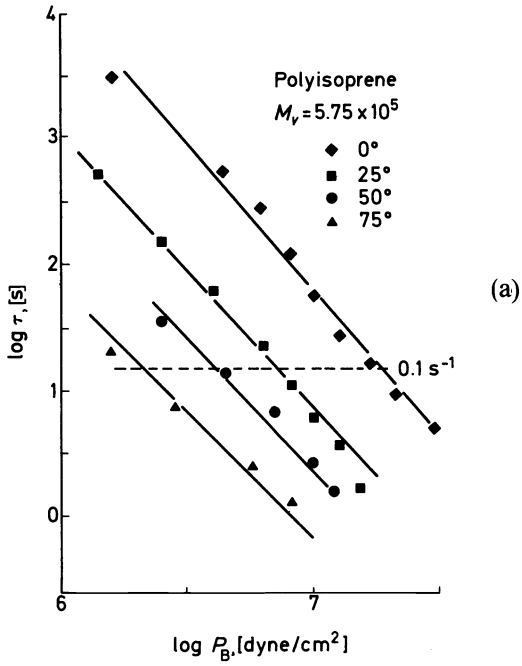
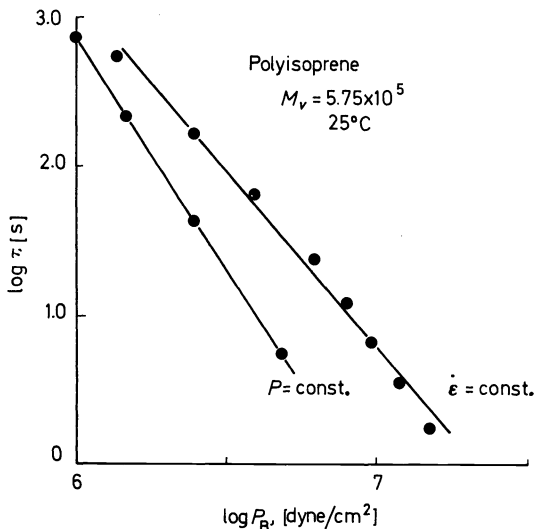


Figure 15. Dependence of durability ( $\tau$ ) on ultimate strength ( $P_B$ ) at various temperatures for narrow-MWD high-molecular polymers; measurements by the constant deformation rate method; (a) polyisoprene; (b) polybutadiene.

given value of the ultimate tensile strength the durability is directly proportional to the polymer viscosity. Thus, the durability of polymers in the forced rubbery state is determined by their relaxation characteristic. This opens up a possibility for generalizing the relaxation characteristics of non-cured polymers to the new region of the processes of their fracture and thereby predicting their durability in extension.

We will now show how general is the square law of decrease in durability with ultimate strength for different polymers and for each given polymer depending on the temperature. For this, let us inspect *Figures 14 and 15*.

We will now compare the determinations of the durability of polymers, on the one hand, by the method of assigning a constant deformation rate and, on the other, by the method of assigning a constant true stress. This comparison is given in *Figure 16*. It can be seen that in the constant-stress method the durability versus the ultimate tensile stress falls off more rapidly, by a cubic law as compared with the method of constant deformation rates.



*Figure 16.* Comparison of results of measurement of durability ( $\tau$ ) in relation to ultimate strength ( $P_B$ ) by constant deformation rate ( $\dot{\epsilon} = \text{const.}$ ) and constant true stress ( $P_B = \text{const.}$ ) methods.

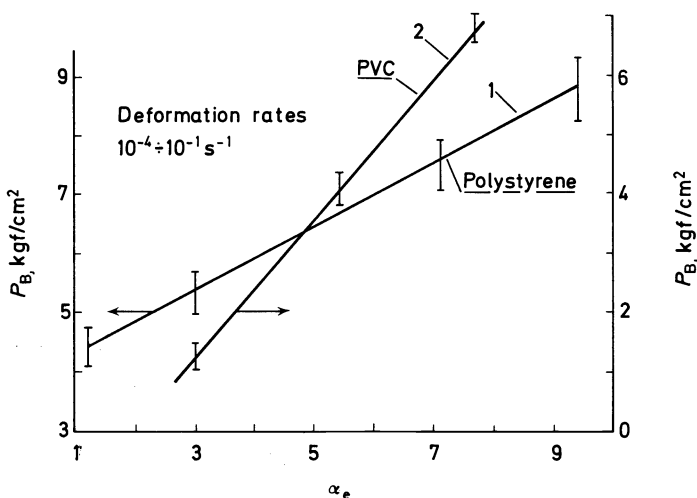
The slower rate of decrease in the durability of polymers when assigning constant deformation rates is easily explained. In this case the stress grows with time from the zero value at the initial moment of deformation, i.e. part of the time the polymer is under the effect of stresses below fractural. The influence of this factor is particularly strong at high ultimate strengths and low durabilities. Knowing the time variation of the stress at a constant deformation rate, one can estimate the durability of the polymer if it has been under a continuous effect of the stress that caused its fracture.

## ON THE QUALITATIVE CORRELATION OF A POLYMER'S REVERSIBLE DEFORMATION IN THE RUBBERY STATE WITH TENSILE STRENGTH AFTER TRANSITION TO THE GLASSY STATE

We will now dwell briefly on the experiments carried out by V. Fikhman and V. Alekseyeva<sup>21</sup> on polydisperse PVC and by B. Radushkevich on polydisperse polystyrene. The experiments were made under conditions of the polymers' forced transition to the glassy state.

The draw ratio due to the reversible deformation was determined, as usual, from the elastic recoil. As for the ultimate strength, it was estimated after a rapid fixation by cooling, of the reversible deformation. A correlation was established between the ultimate strength of frozen specimens and the reversible deformation. This is shown in *Figure 17*. The ultimate strengths are laid off on the ordinates, and the reversible draw ratio, on the abscissa.

The effect of the deformation rate on the reversible deformation of polymers in the region of their forced transition to the glassy state in extension is shown by the upper curve in *Figure 18*. The reversible draw ratio is laid off on the left ordinate and the deformation rate, on the abscissa.



*Figure 17.* Dependence of ultimate strength ( $P_B$ ) on reversible draw ratio ( $\alpha_e$ ) for polydisperse polymers rapidly vitrified by cooling.

As the deformation rate increases the reversible deformation passes a maximum just as has previously been described by T. Smith for cured elastomers<sup>14</sup>. The two lower curves show the strength characteristics of the polymers investigated. These characteristics were determined as follows. Polyvinyl chloride and polystyrene were deformed at given rates in the temperature range from 90° to 160°C, then they were quickly frozen and tested on a tensile machine in the glassy state. *Figure 18* indicates good corre-

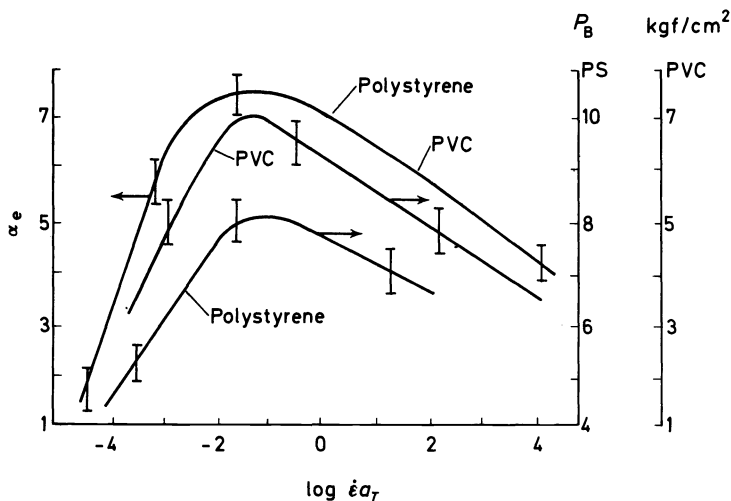


Figure 18. Dependence of reversible draw ratio ( $\alpha_e$ ) and of ultimate strength ( $P_B$ ) of polydisperse polymers on their reduced deformation rates at temperatures of 90° to 160°C; PVC/extension rates: 0.078, 0.77, 8.33 mm/s; deformation rate:  $0.002 \text{ s}^{-1}$ , PS/extension rate: 0.44 mm/s; deformation rates:  $5 \times 10^{-3} + 0.1 \text{ s}^{-1}$ .

lation between the reversible deformation (in the rubbery state) and the ultimate strength of the frozen polymers. This suggests an important conclusion that in order to ensure a high strength it is desirable to attain the highest extension rates in the region of the rubbery state (up to a forced transition to the glassy state) and the quickest possible fixation by cooling of the orientation effect obtained.

### CONCLUSION

Concluding the description of the results of investigation into the process of the extension of polymers in the fluid state and during their transition from this state to the rubbery state, we wish to note the following.

Proceeding from simple considerations it was possible to give a clear explanation and to suggest a system of conditions for the transition of polymers from the fluid to the forced rubbery state in shear. This, in turn, enabled us to predict the peculiarities of the behaviour of polymers in uniaxial extension and to study systematically a new domain of phenomena caused by limited deformability or durability of non-cured polymers at high stresses. It is particularly important that the entire set of the phenomena described for the first time in the present paper is unambiguously determined in a very simple way by their relaxation characteristic.

It is believed that this approach will be extremely promising in the study of the process of adhesional interaction of non-cured polymers with solid surfaces. In the case of adhesional interaction there must be critical conditions similar to those described above for shear and extension. The durability of the adhesional contact must obey the same laws as exist for the

process of uniaxial extension. In particular, this must explain the slightly lower values of the critical stresses in rotation devices (the longer continuous contact of each given portion of the polymer with the solid surface) as compared with capillary devices. The task to be faced in the near future is investigation into the critical and supercritical deformation régimes of non-cured polymers under conditions of their adhesional contact with solid bodies. In the first place there is a necessity of determining conditions when fracture of polymer occurs and when the loss of adhesion to solid bodies takes place.

In furtherance of the present work it is very important to cover, using one polymer with a low glass transition temperature, its transitions first to the rubbery and then to the glassy state. It is to be expected that with an appropriate combination of a decrease in temperature and an increase in deformation rate, when a forced transition of the polymer to a forced glassy state becomes possible, the reversible deformation will fall off after reaching a maximum. In a forced transition of a polymer to the glassy state its fracture mechanism must change: in particular, necking will occur. All this has been observed qualitatively by V. Volosevich. It is important to study these processes quantitatively, determining the pattern of regions of temperatures and deformation rates in which the change of the polymer fracture mechanism occurs, in particular the transition from the power law typical of cured elastomers to the exponential law governing the fracture of glassy polymers at temperatures below the glass transition point.

Of great interest is a systematic study of the conditions of loss of stability in the extension process at high extension draw ratios.

Of foremost significance is the generalization of the experience accumulated in the present work to the extension of wide-MWD systems: model mixtures and polydisperse polymers. This is important, in the first place, for the understanding of the mechanism of increase in viscosity at extension: first, in pre-stationary and pre-fracture deformation régimes, and secondly, upon increase in deformation rates in stationary-flow régimes<sup>20</sup>.

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