

# FLOW AND RUBBER ELASTICITY OF POLYMERIC SYSTEMS

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## ABSTRACT

The rheological properties of linear high molecular weight compounds at temperatures above their glass transition region and melting point are considered. When the deformation rates at steady flow conditions are increased high-elastic deformations are first observed, then a viscosity anomaly develops. The interrelation of these phenomena depends greatly on molecular weight distribution.

Simple shear deformation processes at constant deformation rates are compared with those for uniaxial extension. The change in relaxation spectrum under continuous deformation of polymers is discussed. Attention is drawn to the presentation of rheological dependences in the form of master curves and it is shown that under simple shear the relaxation spectra of many polymeric systems change similarly.

The forced transition of polymers from the fluid to the high elastic state due to an increase in shear rate has been studied. The phenomenon is distinct for high molecular weight polymers with narrow molecular weight distribution. It is accompanied by transition of steady laminar flow to slippage of the polymer along the capillary wall alternating with relaxation and adhesion to the wall. Slippage accelerates the output of polymer from the capillary by decimal orders. The effect of temperature on the phenomenon is estimated.

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The purpose of this lecture is to review the latest experimental studies of the rheological properties of linear polymers at temperatures above their glass transition and melting temperatures, carried out at the Laboratory of Rheology of the Institute of Petrochemical Synthesis of the USSR Academy of Sciences in collaboration with a number of industrial laboratories.

The most important feature of rheological behaviour of polymeric systems is due to the combination of fluidity and high elasticity, i.e. to the ability to accumulate simultaneously unlimited irrecoverable and large recoverable deformations. However, while numerous papers have been devoted to measuring the viscosity of polymeric systems, information on their high elasticity, based on direct measurements, is very limited. The reason for this is that high-elastic deformations are estimated after unloading the samples, from their elastic recovery in time. This is much more difficult than measuring viscosity or normal stresses closely associated with high elasticity.

At low shear rates and stresses there is a simple relationship<sup>1,2</sup> between the first differential of normal stresses ( $P_{11}-P_{22}$ ), shear stresses ( $\tau$ ), high elasticity moduli ( $G_e$ ) and high-elastic deformations ( $\gamma_e$ ). However, at shear

stresses and rates ( $\dot{\gamma}$ ) differing substantially from zero theory gives no correct predictions of the type of this bond. It is therefore necessary to determine it experimentally at least, especially if it can describe the properties not only of polymers with different molecular weight distribution (MWD), but also of their solutions. Naturally, this requires extensive measurements of the high-elastic properties of polymers and their solutions, as well as systematization of published data.

Until recently most of the information on the rheological characteristics of polymeric systems pertained to simple shear and it will therefore be interesting to touch briefly on the peculiarities of behaviour of polymers during uniaxial extension.

When considering the high-elastic properties of polymeric systems in the fluid state one is naturally interested in the peculiarities of their behaviour on passing into the high elastic state under the action of increasing deformation rates: this pertains primarily to the change in fluidity of polymeric systems upon such forced transition to the high elastic state.

### DEVELOPMENT OF HIGH-ELASTIC AND IRRECOVERABLE DEFORMATIONS

Linear polymers display high elasticity simultaneously with a viscosity anomaly, when a continuous space network of macromolecular entanglements appears in them. This corresponds to the molecular weight reaching its critical value ( $M_{cr}$ ) and to sharp enhancement of the dependence of initial viscosity ( $\eta_{in} = \eta|_{\dot{\gamma} \rightarrow 0}$ ) on this quantity. It was shown in ref. 3 for a series of polydisperse polybutadienes, that with  $M \rightarrow M_{cr}$ ,  $\gamma_c \rightarrow 0$ . This immediately

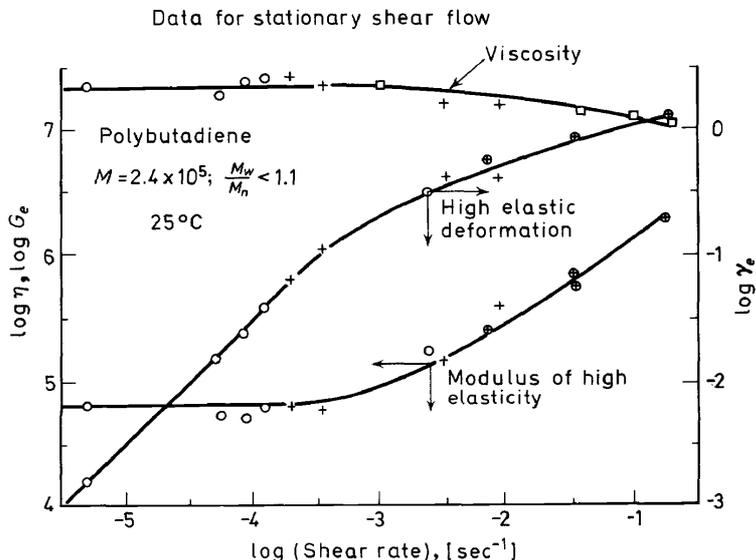


Figure 1. Change in viscosity, high-elastic deformation and high-elasticity modulus of mono-disperse polybutadiene as a function of shear rate.

raises the question of the relationship between the development of high-elastic deformations and viscosity anomalies under steady flow conditions.

In polymers with flexible chains, considerable high-elastic strains (dozens of per cent) are exhibited in the region of stresses and deformation rates where no viscosity anomaly can be registered to within about ten per cent. In this range of stresses and deformation rates the latter are related linearly to high-elastic deformations. Deviations from Hooke's and Newton's laws are detected to an accuracy not worse than that of the high-elastic strain measurement, at equal stresses and deformation rates. In the case of elongation the same applies to deviations from the constant values of the longitudinal viscosity and Young's modulus. At these stresses and deformation rates

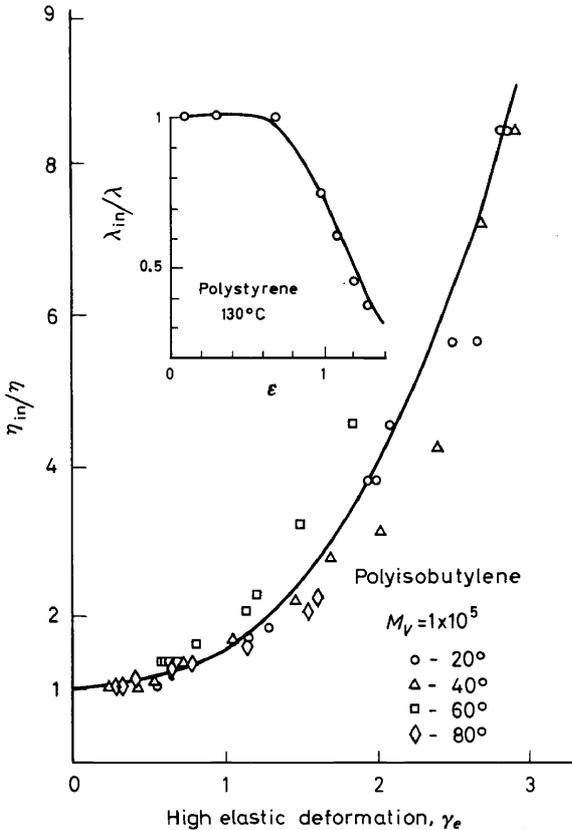


Figure 2. Interrelation of viscosity anomaly and high-elastic deformation for polyisobutylene under shear; the same for uniaxial extension of polystyrene.

high-elastic strains increase more slowly. This effect is enhanced on further increase of stresses and deformation rates. That is why it is found, when measurements can be made over a very wide range of stresses and shear rates, that viscosity changes of decimal order correspond to only a small change in high-elastic strain.

The feature common to both elongation and shear is that the high-elasticity

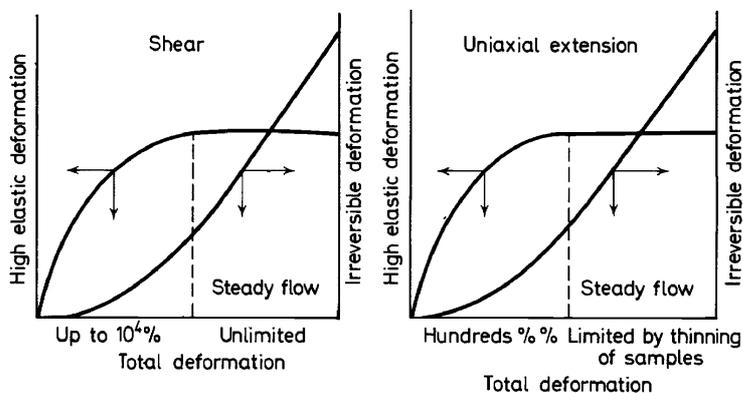
moduli increase with increasing stresses and deformation rates. The difference is that the viscosity increases upon elongation but decreases upon shear.

The ratio of changes of high-elastic moduli and viscosity is affected considerably by the fractional composition of polymer and its concentration in solution. Narrowing of MWD affects the viscosity anomaly most of all, sharply decreasing its development with increasing intensity of deformation. This is illustrated for the case of shear by the data of O. Sabsai, shown in *Figure 1*. They pertain to an investigation of polybutadiene (PB) at room temperature.

Polydispersed polymers exhibit a viscosity anomaly very sharply both on simple shear and on uniaxial extension. In these cases with increasing  $\tau$  and  $\dot{\gamma}$  the change in  $\eta$  quickly overtakes the growth of  $\gamma_t$ , though even here high-elastic deformations develop more intensively than the viscosity anomaly at low  $\dot{\gamma}$ . This is explained by *Figure 2*, which sets out the data of M. Zabugina for shear deformation of polyisobutylene (PIB,  $M_v = 1 \times 10^5$ ) and of B. Radushkevich for uniaxial extension of polystyrene ( $M_v = 3 \times 10^5$ ). In the latter case the longitudinal viscosity and the high-elastic strain are denoted by  $\lambda$  and  $\epsilon$ , respectively.

Now let us make a brief summary of how molecular weight and MWD of polymers affect their viscous and high-elastic characteristics. At  $M > M_{cr}$  the viscosity is very greatly dependent on  $M$ ; in solutions it may increase considerably as the solvent deteriorates. The viscosity anomaly depends greatly on MWD and solvent quality. On the other hand, the initial moduli of high elasticity ( $G_{in}$ ) depend weakly on  $M$ , and vary little with varying solvent quality in polymer solutions. It follows from this that both during

Middle values of constant deformation rate



*Figure 3.* Development of high-elastic and irrecoverable deformations in fluid polymeric systems on passing from rest to steady flow.

elongation and shear narrowing MWD under a prescribed deformation schedule should increase the ratio  $\eta/G$ , which can be regarded as a certain characteristic relaxation time ( $\theta_c$ ). It rises abruptly with increasing molecular weight of polymer. This makes it possible to extend to the case of simple shear the idea developed for uniaxial extension<sup>4</sup> concerning the existence of a

critical product of  $\theta_c$  by deformation rate, above which steady flow cannot be realized, since exceeding this critical product causes discontinuity in the deforming polymer. At high  $M$  and narrow MWD this may occur not only upon elongation, but upon shear as well.

Now let us examine the development of high-elastic and irrecoverable deformations in passing from a state of rest to steady flow at constant deformation rate when  $\eta \ll \eta_{in}$ .

The rate of accumulation of high-elastic and irrecoverable deformation changes on passing from the state of rest to steady flow. This is shown schematically by Figure 3, which generalizes experimental data obtained by us using the constant deformation rate method. It is also important that at constant deformation rate high-elastic strains develop more slowly than the stress.

In application to accumulation of irrecoverable deformation and to its characteristic parameter, viscosity, the corresponding data are illustrated by Figure 4.

Middle values of constant deformation rate

$$\text{Viscosity} = \frac{\text{Stress}}{\text{Rate of irreversible deformation}}$$

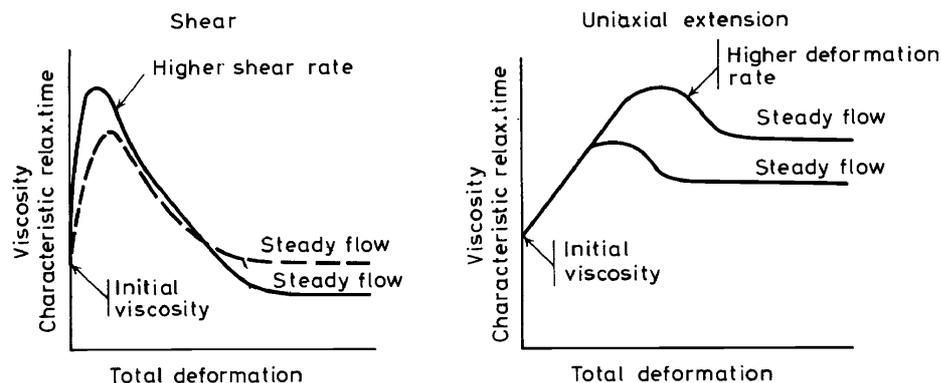


Figure 4. Change in viscosity of fluid polymeric systems on passing from rest to steady flow.

When highly viscous polymers are elongated at increased rates only the ascending branch of the total strain versus viscosity curve is observed. This corresponds to a high rate of stress increase, which overtakes the increase in strain and involves rapid growth of the high-elasticity modulus. The simultaneous increase not only of the high-elasticity modulus, but especially of the viscosity, results in considerable growth of the characteristic relaxation time and then in failure of the samples before steady state flow is reached. This has already been mentioned above.

To account qualitatively for the data considered above it seems useful to advance the hypothesis that in condensed and highly concentrated polymeric systems capable of displaying unlimited irrecoverable deformations, high-elastic deformations are accompanied by an orientation effect,

which, as in solid amorphous polymers, may increase intermolecular interaction.

Indeed, the relative role of high-elastic deformation is the greatest at the initial stage of deformation at constant deformation rate. Here the orientation effect should be the most intensive. Accordingly, antithixotropy is displayed at this stage of deformation both in shear and in extension. However, on further development of the deformation, when the rate of accumulation of irrecoverable deformation increases, these two kinds of deformations begin to differ. In shear, rotation of the elements of the deforming medium plays a relatively large role. It should suppress the orientation effect and favour a decrease in density of the fluctuational space network of entanglements in the polymeric system. This accounts for the long time it takes to reach steady state flow conditions in shear.

Competitive influence of the orientation effect and of breakdown of the supermolecular structure (network of entanglements) is exhibited in elongational flow too. This causes maxima to appear on the longitudinal viscosity versus deformation dependence curves. But here it is less pronounced than in shear, and therefore at steady flow conditions longitudinal viscosity increases with increasing rate of deformation.

An important problem is the direct estimation of the orientation effect and the role it plays in the deformation of condensed polymeric systems in the fluid state. Evidently, the most effective technique may be to deform amorphous polymers at temperatures above the glass transition region and subsequently to freeze the samples quickly and estimate the orientation effect in the solid sample.

### **RELAXATION SPECTRA AND CHANGES CAUSED IN THEM BY DEFORMATION OF POLYMERS**

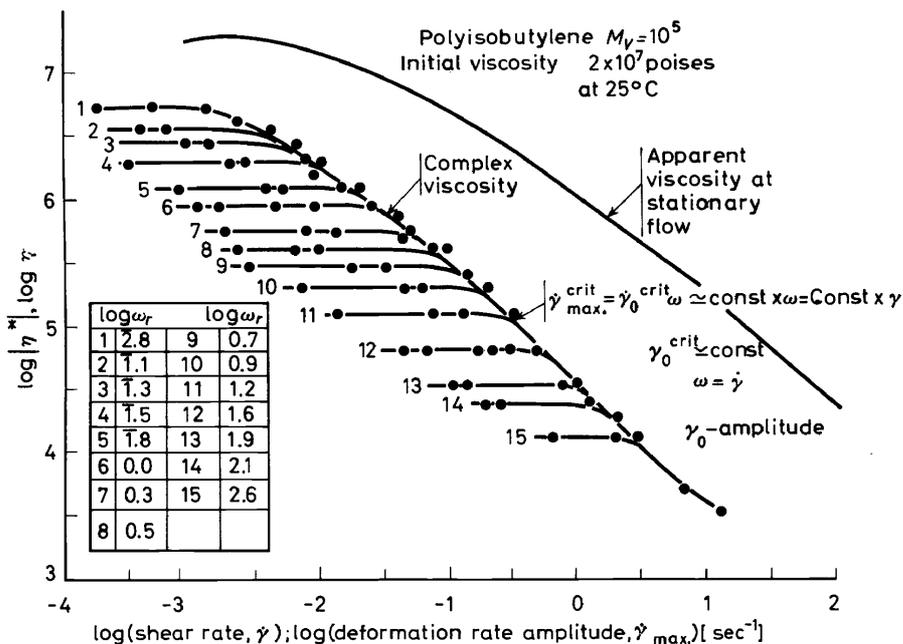
It is natural to associate the change in structure of polymers during shear deformation with those of their structural elements that suppress attainment of steady state flow. For steady state flow to develop the most long lived, i.e. slowly relaxing, structural elements must be destroyed. From the point of view of examining relaxation spectra this means that their long-time part should change, namely, should be truncated. This idea was formulated quantitatively in refs 5 and 6. The problem is to estimate these changes, and this makes it necessary to determine the relaxation spectrum in the non-linear region of deformation.

There are a number of studies<sup>7-11</sup>, in which small-amplitude vibrational deformation régimes were superimposed on non-linear steady-state régimes. Though it has been pointed out that such superposition may perturb stationary flow<sup>12</sup>, this effect is evidently of a secondary nature, and superposition makes it possible to estimate fairly reliably changes in the relaxation spectrum during the flow of polymeric systems. It was shown recently<sup>13, 14</sup> that by using large-amplitude vibrational régimes the spectrum truncation corresponding to a definite shear rate at steady flow can be determined directly, provided the vibrations remain sinusoidal.

The approach to this problem was as follows. Both low and large cyclic deformation amplitudes were employed, the low ones being such that the

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storage and loss moduli were independent of amplitude. There is a definite critical amplitude value for each given frequency. If it is exceeded, the parameters characterizing the viscoelastic properties of the polymeric system become dependent on amplitude. The critical values of the parameter form a single monotonic dependence on deformation rate amplitude  $\dot{\gamma}_{\max} = \gamma_0 \omega$ , where  $\gamma_0$  is the amplitude and  $\omega$  is the circular frequency. All this is illustrated by the data in *Figure 5*. It shows the dependence of the absolute value of complex viscosity on the deformation rate amplitude. The amplitude



*Figure 5.* Complex viscosity versus deformation rate amplitude and apparent viscosity versus shear rate for polyisobutylene.

dependences of complex viscosity over a wide range of frequencies at amplitudes corresponding to their critical values, form an envelope representing the uniform dependence of complex viscosity on the deformation rate amplitude. This dependence describes the properties of the polymer at cyclic deformation régimes similar to continuous deformation under steady flow conditions. Indeed, the experimentally found apparent viscosity versus shear rate dependence at steady flow can be obtained by shifting the envelope of curves representing the dependence of complex viscosity on deformation rate amplitude in the direction of the abscissa axis. The critical values of deformation rate amplitude corresponding to the envelope are proportional to the critical amplitude and circular frequency values. But since the critical amplitude is practically independent of frequency, the critical deformation rate amplitudes are directly proportional to frequency, and therefore also to shear rate. The proportionality coefficient depending

on the nature of the polymeric chain and the molecular weight, increases with the latter. This means that vibratory action at critical amplitude is equivalent to steady flow conditions. On the other hand, since there is a correlation between the apparent and complex viscosity measured at low amplitudes, this means that in the critical amplitude range the effect of amplitude is equivalent to the effect of frequency.

On the basis of measurements of the parameters determining the viscoelastic properties of polymeric systems at low and large amplitudes, and making use of the theory of linear viscoelasticity, we obtain the relaxation spectra.

The spectrum of a polymeric system, unaltered by deformation, can be called an initial spectrum, and the truncated one, an effective spectrum. These definitions of relaxation spectrum types are essentially nothing but an extension of the viscosity and elasticity modulus concepts to deformation régimes that cannot be described by the laws of Newton or Hooke and Young with constant viscosity, shear or elongation moduli.

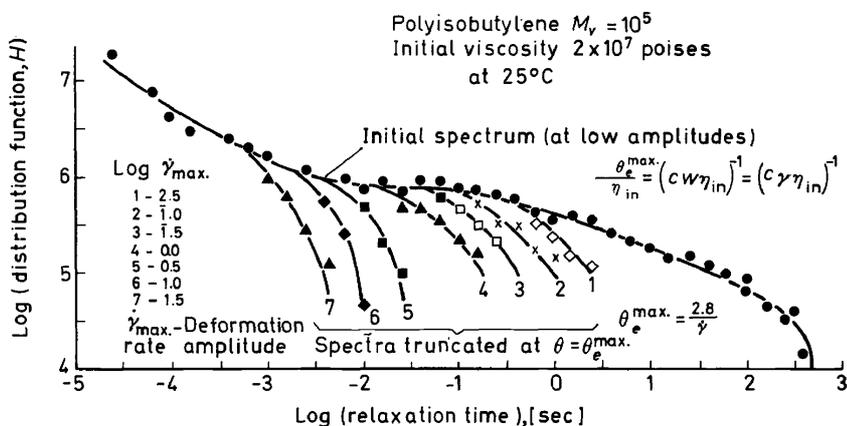


Figure 6. Initial and effective relaxation spectra of polyisobutylene.

Important concepts are those of the maximum initial and effective relaxation times ( $\theta_{in}^{max.}$  and  $\theta_e^{max.}$ ). They determine the long-time boundaries of the initial and effective spectra. Their values are selected to correspond to the experimentally determined initial and effective values of viscosity and normal stress coefficients

$$\xi = (P_{11} - P_{22})/2\dot{\gamma}^2.$$

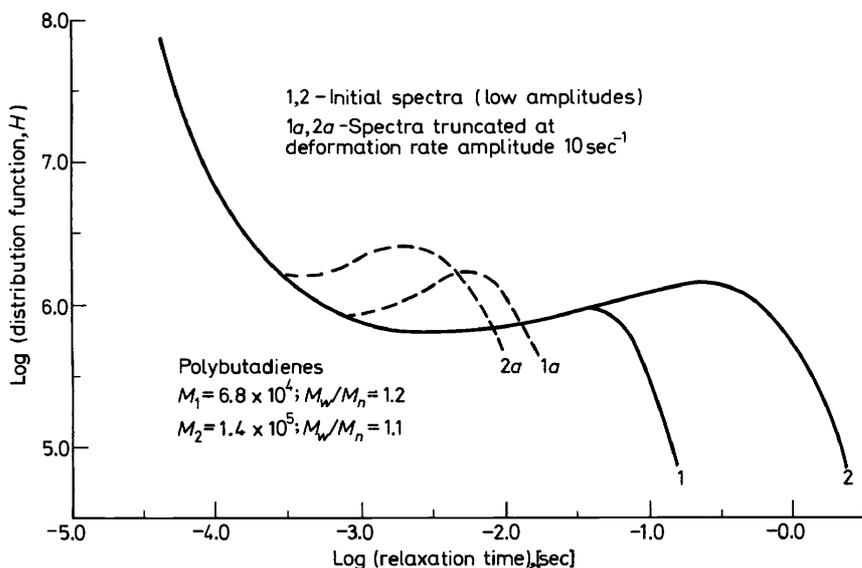
Upon shear deformations the long-relaxation-time sides of the effective relaxation spectra are truncated. In the case of polydispersed low-molecular PIB ( $M_v = 1 \times 10^5$ ,  $\eta = 2 \times 10^7$  poises at  $25^\circ\text{C}$ ) this is illustrated by Figure 6. Here  $H$  is the distribution function of relaxation times  $\theta$ ;  $\theta_e^{max.}$  corresponds to various deformation rate amplitudes.

In ref. 14 it is shown that there is a simple unambiguous relation between  $\dot{\gamma}_{max.}$  at the vibrational régimes under consideration and  $\dot{\gamma}$  at steady-state

flow of polymeric systems. Hence, each of the effective spectra in *Figure 5* describes a state of PIB, which can be realized if steady-state conditions can be reached. Hence,  $\theta_e^{\max.}$  values correspond unambiguously to steady-state shear rate, and in the case of the effective spectra shown in *Figure 6*,  $\theta_e^{\max.} = 2.8 \dot{\gamma}^{-1}$ .

And as is usual with polymers above the glass-transition and melting temperatures, the initial relaxation spectrum (*Figure 6*) includes a fluidity branch (RHS of the spectrum), a high-elasticity plateau (middle part, weakly developed in this case) and a transition to the glassy region (left-hand ascending branch).

The character of spectrum shown in *Figure 6* is typical of polydispersed polymers with a short and inclined plateau. In this case at vibrational régimes with large  $\gamma_0$  not only the entire fluidity branch may be truncated from the initial spectrum, but the high-elasticity plateau as well. Limiting truncation of the initial spectrum is described by the extreme left effective spectrum and is determined by the impossibility of testing the polymer under vibrational régimes at higher  $\dot{\gamma}_{\max.}$  because it then tears off the measuring surfaces.



*Figure 7.* Initial and effective relaxation spectra of monodisperse polybutadienes.

Reference 15 examines the specific features of truncation of the spectra of monodispersed polymers. It occurs as shown in *Figure 7* for two PB samples. The fluidity branch of the spectrum for polymers with narrow MWD is a steeply declining one, covering a narrow range of large  $\theta$ . The transition to the region of relaxation times describing the high-elastic state is very abrupt. This transition occurs through a maximum, which shifts towards larger  $\theta$  with increasing  $M$ , and, what is especially important, is more pronounced,

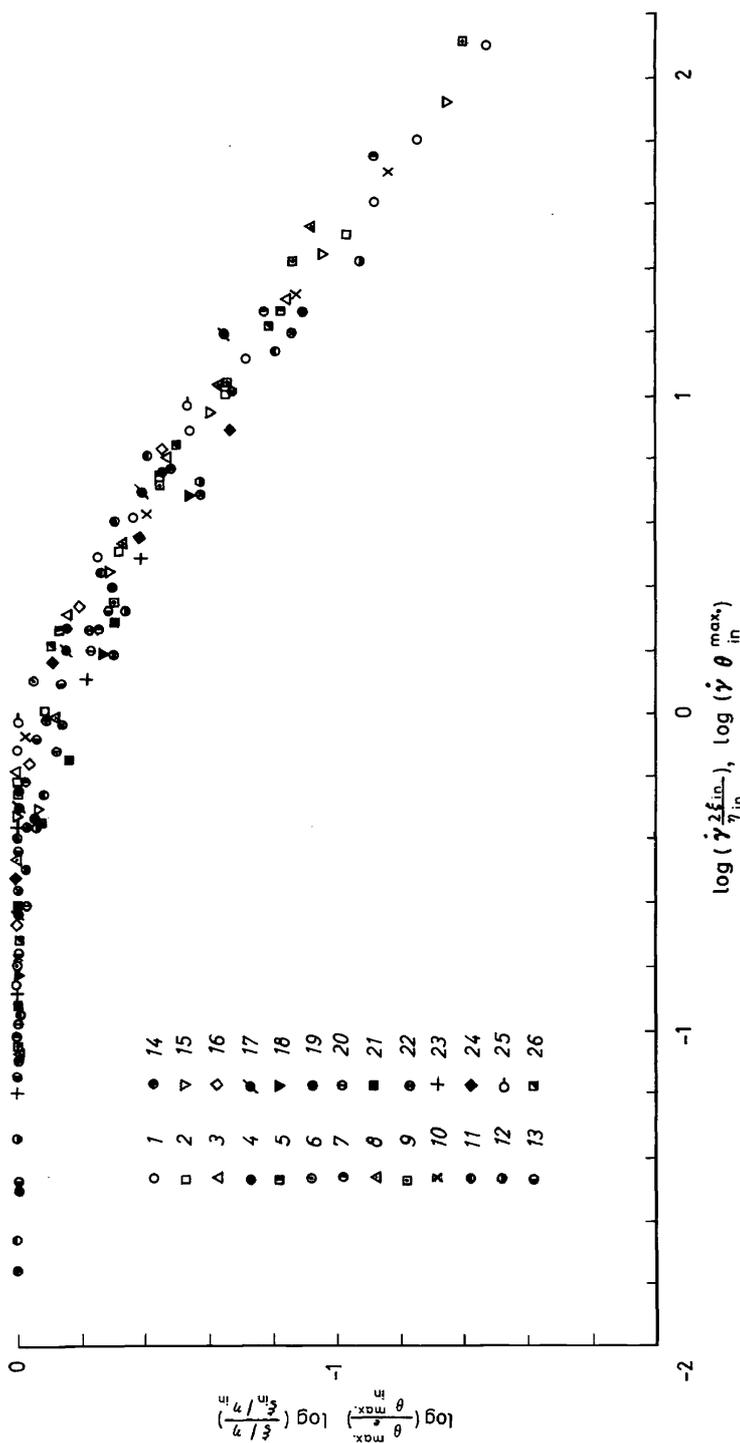


Figure 8. The master curve for the relaxation characteristic of polymeric systems at steady flow régimes. Polyisobutylene<sup>18</sup>: 1—22; 2—40; 3—60; 4—80; 5—100°C. Polystyrene ( $M_v = 2.2 \times 10^5$ ) in decalin: 25°C: 6—18.4; 7—29; 8—38; 9—46.6; 10—57.3 per cent by weight (data of G. Berezhnaya, Institute of Petrochemical Synthetics). Polybutadiene: 11— $M = 1.5 \times 10^5$ ;  $M_w/M_n = 1.1$ ; 22°C (data of G.B.). Polybutadiene— $M = 2.4 \times 10^5$ ;  $M_w/M_n = 1.1$  in  $\alpha$ -methyl-naphthalene, 22°C: 12—10; 13—30; 14—50 per cent by weight (data of G.B.). Polymethylmethacrylate in diethylphthalate<sup>19</sup>; 30°C: 15—5 per cent by weight. Polyisobutylene in tetralin<sup>20</sup>; 25°C: 16—12 per cent by weight. Polystyrene in decalin: 19, 21, 30°C: 17—9.34; 18—15; 19—20.1 per cent by weight. Polystyrene in chlorinated diphenyl<sup>22</sup>; 27°C: 20—13; 21—16 per cent by weight. Polydimethylsiloxane<sup>23</sup>; 20°C: 22— $M = 4.7 \times 10^5$ ;  $M_w/M_n = 1.29$ ; 23— $M = 9.7 \times 10^4$ ;  $M_w/M_n = 1.18$ . Polyethylene<sup>11</sup>; 150°C: 25— $8 \times 10^4$ ; 26— $2.5 \times 10^6$ .  $\eta_{in}$  poises: 24— $1.4 \times 10^4$ ; 25— $8 \times 10^4$ ; 26— $2.5 \times 10^6$ .

i.e. the transition from the fluidity to the high-elasticity region is more abrupt.

Note that curve 2a for the higher-molecular PB sample runs fairly distant from the left-hand, steeply ascending branch of forced glass transition of the polymers. It is important to draw attention to the fact that at large-amplitude vibrational régimes the scaling factor for recalculating deformation rate amplitude to steady shear rate may be very high in value (it depends on the molecular weight and nature of polymer). Accordingly, the limiting truncations at vibrational régimes correspond to high steady-state shear rates. Experiment shows, and this will be discussed additionally below, that in the case of the PB samples under consideration steady-state flow cannot be accomplished even at much lower shear rates.

The above is connected with essential circumstances. First of all, at vibrational deformation régimes of polymers acceleration may have a strong effect on their rheological characteristics. Secondly, the greater the deformation, e.g. the amplitude, the lower the intensity of deformation at which tests can be carried out at vibration régimes. The limiting case is that of constant deformation rate—steady-state flow realized at minimum deformation rates. Thirdly, in polymers with narrow MWD and fairly high  $M$  no spectrum truncation covering any considerable part of the high elasticity region can be accomplished.

The dimensionless ratio  $\theta_e^{\max.}/\theta_{in}^{\max.}$  can be accepted as the simplest measure of spectrum truncation. This ratio should be determined unambiguously by the intensity of deformation action on the polymeric system. A. Isayev showed that important results can be obtained by examining this ratio as a function of the dimensionless parameter  $\dot{\gamma}\theta_{in}^{\max.}$ . His approach to this problem consists of using A. Tobolsky's conception of the determinative importance of maximum relaxation times<sup>16</sup> for polymeric systems in the fluid state; on the other hand, it is based on ref. 17, which deals with a generalized characteristic of the viscous behaviour of these systems.

For the function  $\theta_e^{\max.}/\theta_{in}^{\max.}$  versus  $\dot{\gamma}\theta_{in}^{\max.}$  one gets the master curve shown in Figure 8, which describes universally the behaviour of polydispersed and monodispersed polymers and concentrated polymer solutions at different temperatures. This means that the relaxation spectrum truncation of the polymeric systems shown in Figure 8 is independent of the shape of the spectra.

Proceeding from what has been said above, A. Isayev came to substantial conclusions. If, applying the linear theory of viscoelasticity to effective spectra, as is done for initial spectra, we write the expressions for the effective values  $\xi$  and  $\eta$  in terms of the function  $H$  and then determine the derivative  $d\xi/d\eta$ , we find

$$\xi = \int_0^{\theta_e^{\max.}} H_d(\theta)\theta \, d\theta; \eta = \int_0^{\theta_e^{\max.}} H_d(\theta) \, d\theta; \frac{d\xi}{d\eta} = \theta_e^{\max.}(\dot{\gamma})$$

Above we pointed out the experimental fact that the spectrum truncation, determined by the value of  $\dot{\gamma}$ , is independent of the form of spectrum. It follows therefore that

$$2(\xi/\eta) = \theta_e^{\max.}$$

It is also obvious that

$$2(\xi_{in}/\eta_{in}) = \theta_{in}^{\max.} = (\eta_{in}/G_{in})$$

This means that the values  $\theta_e^{\max.}$  and  $\theta_{in}^{\max.}$  can easily be found by measuring the shear and normal stresses. No less interesting is the reverse problem, namely, to get an approximate estimate of  $\xi$  and  $G_e$  or  $\gamma_e$  from the master curve in Figure 8 in the non-linear deformation region, knowing  $\eta_{in}$  and  $\xi_{in}$  and making use of  $\eta$  measurements.

An important particular case of the dependence shown in Figure 8 is presentation of the results of viscosity measurements in temperature-invariant form.

The temperature dependence of  $G_{in}$  for the more common commercial polymers is weak; there is no need to know  $G_{in}$  and to find  $\theta_{in}^{\max.}$  for their temperature invariant characterization. Satisfactory results are obtained<sup>17</sup> for the dependence  $\eta/\eta_{in}$  versus  $\dot{\gamma}\eta_{in}$ . The situation is different if the viscosity characteristics of different polymers (especially poly- and mono-dispersed

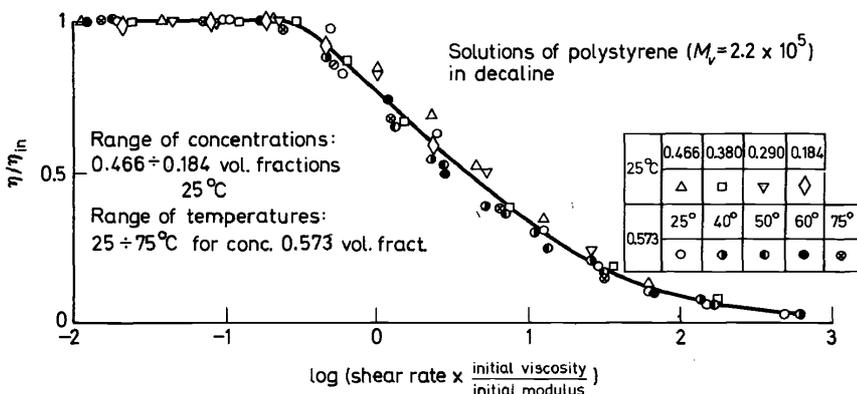


Figure 9. Concentration-temperature-invariant characteristic of viscosity of decalin solutions of polystyrene.

ones) are to be compared or a temperature-concentration-invariant characteristic is to be obtained for polymer solutions when the polymer concentration varies over a wide range. Considerable differences of  $G_{in}$  and  $\theta_{in}^{\max.}$  at the same value of  $\dot{\gamma}\eta_{in}$  may correspond to all these cases. This was demonstrated for polystyrene solutions by A. Malkin and G. Berezhnaya. Taking into account the concentration dependence of  $G_{in}$  one easily obtains the concentration-temperature-invariant characteristic of  $\eta/\eta_{in}$  (Figure 9). This means that taking into account the concentration dependence of  $\dot{\gamma}\eta_{in}$  after F. Bueche<sup>44</sup> is insufficient for concentration-invariant characterization of the viscous behaviour of polymer solutions; allowance must also be made for the concentration dependence of  $G_{in}$ .

From the relation between  $\eta$ ,  $\xi$  and  $G_e$  discussed above it follows that

$$(P_{11} - P_{22})/G_e = 2(\tau/G_e)^2$$

Quadratic dependence of normal on shear stressed makes a good fit in the non-linear deformation region<sup>18, 26</sup>. The importance of the above notation of this dependence demonstrates the fact that when written thus it describes experimental data in the temperature-concentration-invariant form. This is essential for polymer solutions, whose high-elasticity modulus is strongly dependent on concentration. It will be useful to note that in a narrow shear stress interval either the values of  $G_e$  or those of  $G_{in}$  may be used. This is illustrated by the data of A. Malkin and G. Berezhnaya (Figure 10).

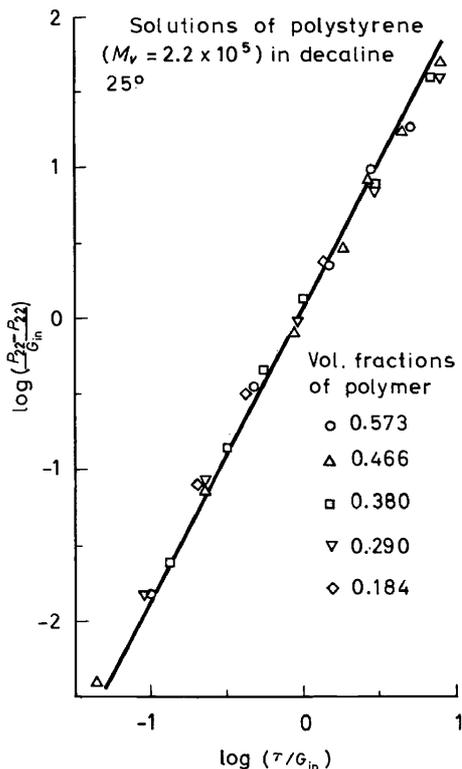


Figure 10. First differential of normal stresses versus shear stresses, normalized by initial shear modulus for solutions of polystyrene in decalin.

Since  $\theta_e^{\max.}$  is a function only of  $\dot{\gamma}$  and  $\theta_{in}^{\max.}$ , and taking dimensions into account, it follows from the above relation  $\theta_e^{\max.} = (\gamma_e/\dot{\gamma})$  that there should exist a universal dependence of  $\gamma_e$  on  $\dot{\gamma}\theta_{in}^{\max.}$  for the polymeric systems shown in Figure 8. This is confirmed by Figure 11.

The dependences shown in Figures 8 and 11 immediately give the answer to the interesting question of how high-elastic deformation varies with truncation of the relaxation spectrum. This can be seen in Figure 12.

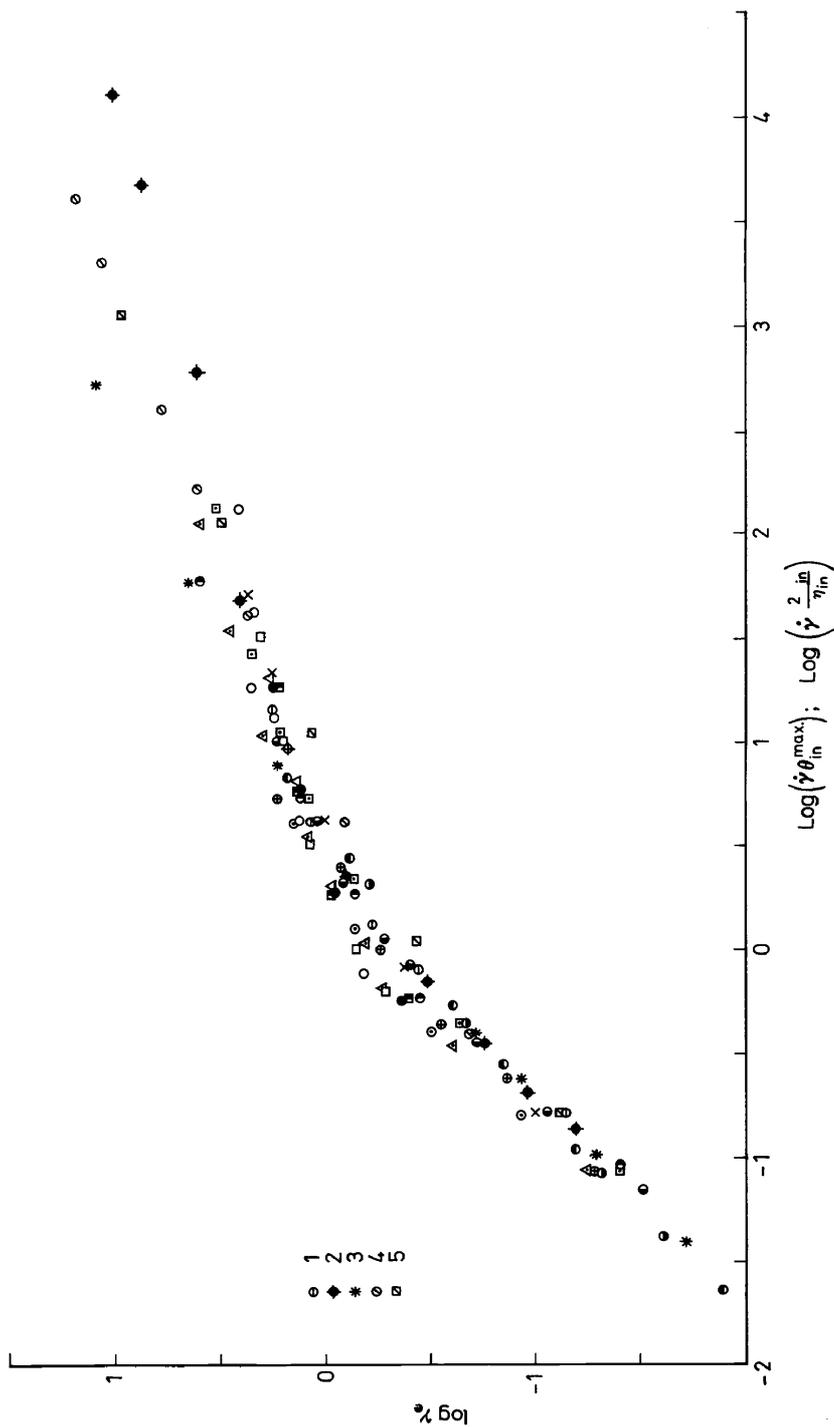


Figure 11. Master curve for high-elastic deformation of polymeric systems. Polybutadiene: 1— $M = 2 \times 10^5$ ;  $M_w/M_n = 1.1$ ; 22°C (data of G.B.). Polystyrene in diethylphthalate<sup>24</sup>; 2—22°C; 60 per cent by volume. Polyisobutylene in vaseline oil<sup>25</sup>; 25°C, 3— $M_w = 1.4 \times 10^6$ ; 4.15 per cent by volume; 4— $M_w = 1.5 \times 10^7$ ; two per cent by volume; 5— $M_w = 2.8 \times 10^6$ ; three per cent by volume, see symbols 1, 3, 5 in the caption to Figure 8.

It has already been pointed above that at constant deformation rate high-elastic deformations lag behind the shear stress, since the long-time part of the relaxation spectrum is responsible for the development of the former. In the region of relaxation times close to  $\theta_{in}^{max}$ , truncation of these times has little effect on  $\eta$ , but influences  $\gamma_e$  greatly. Further truncation of

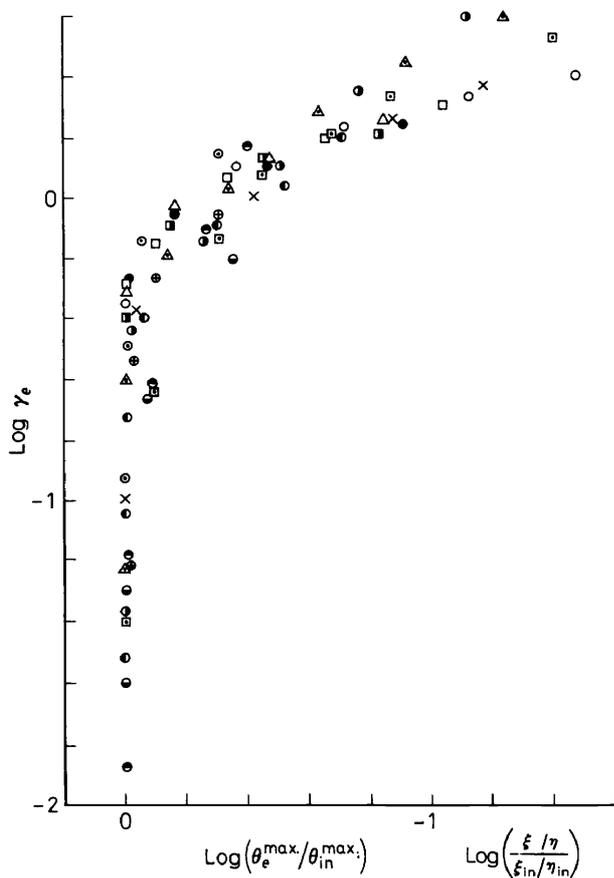


Figure 12. Effect of relaxation spectrum truncation on high elasticity of polymeric systems (symbols as for Figure 8).

large relaxation times enhances the change of  $\eta$ , while the development of  $\gamma_e$  is retarded. This is easily understood, because high-elastic deformations depend on the entanglement network, which is broken down more and more with increasing deformation rate.

Thus, the set of simple dependences suggested by A. Isayev enables an approximate estimate to be made of normal stresses, high-elasticity moduli, and high-elastic deformations in the non-linear deformation region from  $\eta_{in}$  and  $\xi_{in}$ , by making use of the flow curve.

## TRANSITION TO THE HIGH-ELASTIC STATE AND LOSS OF FLUIDITY OF POLYMERIC SYSTEMS WITH INCREASING DEFORMATION RATE

It has long since been established<sup>27</sup> that viscous low-molecular liquids display brittleness at very high deformation rates, being incapable of flowing and behaving like glassy solids. Qualitatively this is determined by the interrelation between the deformation rate and a certain characteristic relaxation time of the liquid. In macromolecular compounds the fluid state is separated from the glassy by the high-elastic state, a typical feature of which is the presence of a space network of macromolecular entanglements. The formation of this network increases viscosity and the characteristic relaxation time of the system. Accordingly, this should lower the critical deformation rate at which the polymeric system stops displaying fluidity. Does this occur only at deformation rates corresponding to transition of the macromolecular system to the glassy state or will the system lose its fluidity even in the high-elastic region? There are grounds to suppose that macromolecular compounds of high macromolecular entanglement density should lose their fluidity with increasing deformation rates, when the transition from the fluid to the high-elastic state occurs, but without displaying the brittleness typical of the glassy state. However, it is impossible to say beforehand what form this loss of fluidity will take, i.e. what specific phenomena it may incur.

When studying the effect of high deformation rates on the behaviour of polymeric systems in the fluid state attention was concentrated mainly on disturbance of their steady flow. The latter has been investigated in greatest detail in application to extrusion of polymer melts, and is exhibited as various distortions in shape of extrudate. The pertinent experimental facts and their explanations can be found in the reviews<sup>28, 29</sup>.

When the shear stress is increased to a definite critical value some linear polymers display a jumpwise increase in rate of extrusion. The extrusion rate may increase by a decimal order or more, so that this phenomenon acquires the nature of a spurt of extrudate, and is incompatible with the usual behaviour of liquids. This phenomenon has been given most attention for the case of linear polyethylenes<sup>30-35</sup>.

The specific behaviour of melts of linear polyethylenes (PE) at high  $\tau$  has never been associated with their transition to the high-elastic state under the influence of high  $\dot{\gamma}$ . However, there is every reason to do so, because in linear PE the molecular weight of the network chain between entanglements ( $M_e$ ) is small<sup>37</sup>. It follows therefore that the entanglement density of linear PE is high even at comparatively low  $M$ .

It was pointed out in ref. 35 that spurting is more pronounced and occurs at lower deformation rates with PE of narrow MWD. This is quite natural, because at a given  $M$  the entanglement density of a polymer with a narrow MWD is higher than that of one with a wide MWD. It was indicated above that polymers with narrow MWD display an especially sharp transition from the fluid to the high-elastic state.

When studying the nature of spurting it is useful to deal with linear polymers of narrow MWD. This is essential not only because spurting should be more distinct in them, but also because this may facilitate establishment

régimes on molecular characteristics.

As is known, polymers of narrowest MWD are produced by anionic polymerization. PB are convenient for studying critical deformation régimes, because they have low  $M_{cr}$  values and therefore a high entanglement network density is attained in them at not very high  $M$ . According to ref. 38 for PB the molecular weight ( $M_e$ ) of the network chain is equal to 2800.

The results of a study of the critical deformation régimes of PB, discussed below, were obtained for a series of polymers specially prepared for this purpose by anionic polymerization on secondary butyllithium by V. Shatalov and V. Shalганova (Synthetic Rubber Institute, Voronezh Branch). The polymers are briefly characterized in *Table 1*.

*Table 1.* Brief characteristics of polybutadienes obtained by anionic polymerization on secondary butyllithium

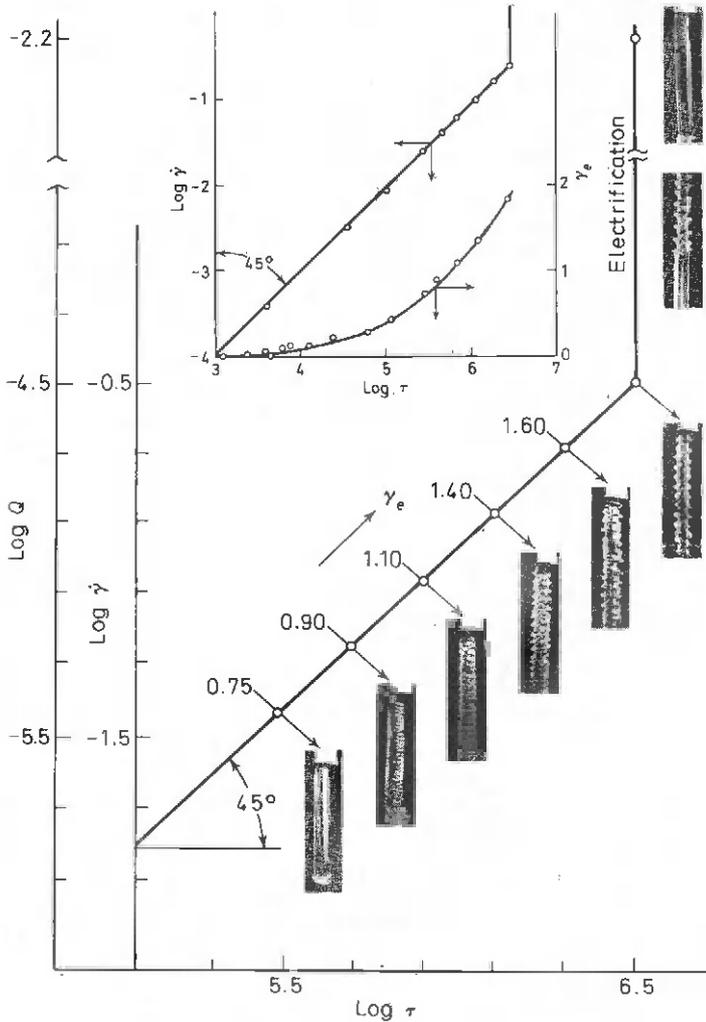
N	$M_v$	$M_w/M_n$	Microstructure, %%		
			cis/1,4	trans/1,4	1,2
1	$3.8 \times 10^4$	1.22	45	45	10
2	$6.8 \times 10^4$	1.2	44	42	14
3	$1.0 \times 10^5$	1.1	44	42	14
4	$1.5 \times 10^5$	1.1	47	44	9
5	$2.0 \times 10^5$	1.1	45	46	9
6	$2.4 \times 10^5$	1.1	45	46	9
7	$5.8 \times 10^5$	—	51	39	10

First let us consider the data obtained by E. Borisankova (*Figure 13*) at room temperature with a constant pressure capillary viscometer (CPCV) for PB of molecular weight  $2.4 \times 10^4$  ( $M_w/M_n = 1.1$ ). Viscosity measurements were made with capillary 1 mm in diameter ( $D$ ) and 25 mm in length ( $L$ ). The same figure shows the dependence  $\gamma_e$  versus  $\tau$  after the data of O. Sabsai.

The values of  $\gamma_e$  are shown at the points through which the flow curve is drawn and photographs are given showing the appearance of the polymer extrudate at the capillary outlet. The appearance of roughness on the extrudate surface and the development of shape distortions (elastic turbulence) is observed at considerably lower  $\gamma_e$  than was thought earlier<sup>36</sup>, and, which is no less essential, at flow régimes close to Newtonian. When the critical stress ( $\tau_c$ ) and shear rate ( $\dot{\gamma}_c$ ) corresponding to spurting are reached, the polymer discharge increases jumpwise. At these régimes the extrudate begins to issue in screw form, then follows a cylindrical section, the diameter and length of which are close to the diameter and length of the capillary. This cylindrical section is followed by an uneven extrudate. At spurting régimes the polymer extrudate issuing from the capillary carries a positive charge. Electrification increases if the metallic capillary is earthed. Electrification

of the polymer extrudate may serve as an indication of slippage in the capillary.

The intensity of spurting depends on the capillary length. This was demonstrated by E. Borisenkova for a PB sample at room temperature in CPCV tests. The results are shown in *Figure 14*, from which it is evident that the



*Figure 13.* Flow curve and dependence of high-elastic deformation on shear strain for a mono-disperse polybutadiene.

length of the vertical branch of the flow curve is considerable only at fairly high  $L/D$  ratios. Hence, for pronounced spurting to occur the polymer must be deformed considerably in the capillary. It should also be noted that at  $\tau = \tau_s$  an extrudate of diameter close to  $D$  is obtained only from capillaries

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of sufficiently great length. The effect of capillary length on spurting of a PB extrudate is similar to what was described for linear polyethylene<sup>32</sup>.

B. Yarlykov studied a PB of molecular weight  $2.4 \times 10^5$  on a constant discharge capillary viscometer. In this case when  $\dot{\gamma} = \dot{\gamma}_s$  the pressure begins to fluctuate. At the spurting régime the PB extrudate acquires a characteristic shape. It consists of three regularly alternating sections: a smooth one of length of the same order as the capillary, and an uneven one and a screw-shaped one of considerably greater length. With increasing rate of emergence

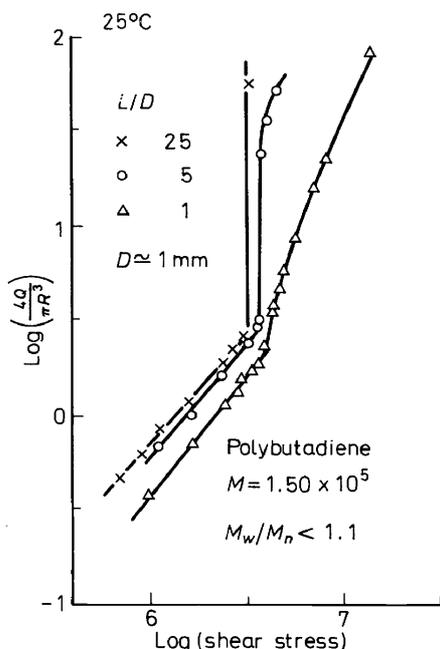


Figure 14. Flow curves of a monodisperse polybutadiene, obtained for capillaries of diameter 1 mm with length-to-diameter ratio:  $\Delta$  1;  $\circ$  5;  $\times$  25.

of the extrudate from the capillary the frequency of pressure fluctuation increases and at fairly high rates it cannot be registered with an instrument of low time resolving power. These phenomena are similar to those described for polyethylenes<sup>30-35</sup>.

In the constant pressure and constant discharge methods the values of  $\tau_s$  and  $\dot{\gamma}_s$  coincide within the error of measurement. Thus,  $\tau_s$  and  $\dot{\gamma}_s$  determined in capillary viscometers are independent of the method of measurement, though certain phenomena accompanying extrudate spurting show up differently in these methods.

O. Steinwartz (Tyre Institute) made tests with a PB sample on a RV-2 rotational viscometer<sup>39</sup> at atmospheric and elevated hydrostatic pressures. Her data are shown in Figure 15. At atmospheric pressure and shear rates exceeding incipient elastic turbulence during flow of the polymers through the capillaries the friction torque was observed to fluctuate. The shear

stresses estimated from the average torque value were lower than found by capillary viscometry. When the speed of the measuring surface was increased the fluctuations of the torque became stronger, and its average value decreased rapidly, so that increasing speeds resulted in a considerable decrease of the torque. Further increase of the speed resulted in heating of the polymer and increase of the torque. At hydrostatic pressure above

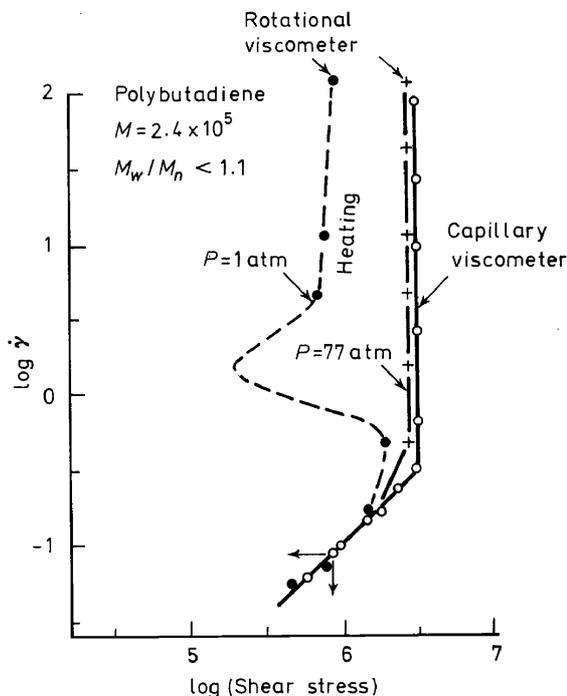


Figure 15. Effect of hydrostatic pressure on results of viscosity measurements in rotational viscometer.

70 or 80 atm the data of rotational and capillary viscometry differed insignificantly. Hence, it follows that the extreme left-hand dashed line in Figure 15 gives a fictitious shear rate versus shear stress dependence, because in experiments like those described the usual calculation of shear rate is senseless. This is due to the fact that the decrease in stress with increasing speed of the working surface is caused by polymer slippage.

The agreement between the data of rotational and capillary viscometry in experiments conducted under comparable conditions is important evidence of the fact that the occurrence of spurting during shear is independent of the kind of stressed state, being determined by the level of the latter and the properties of polymer.

Now let us examine the data for a series of PB of different molecular weight, obtained by E. Borisenkova on a CPCV at room temperature (using the same capillary as in the experiments shown in Figure 13). They are given in

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Figure 16, the arrows indicating the points where elastic turbulence sets in. It is evident from this figure that  $\tau_s$  is independent of  $M$  when  $M > 6 \times 10^5$ . The ratio of  $\tau_s$  to the stress at which elastic turbulence appears is constant and equals approximately 4.7. In PB with a narrow MWD spurting is

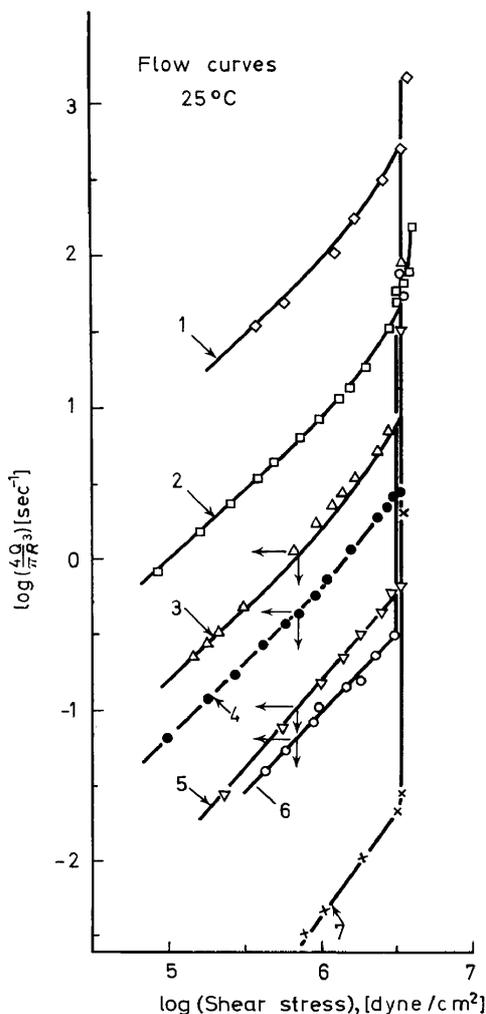
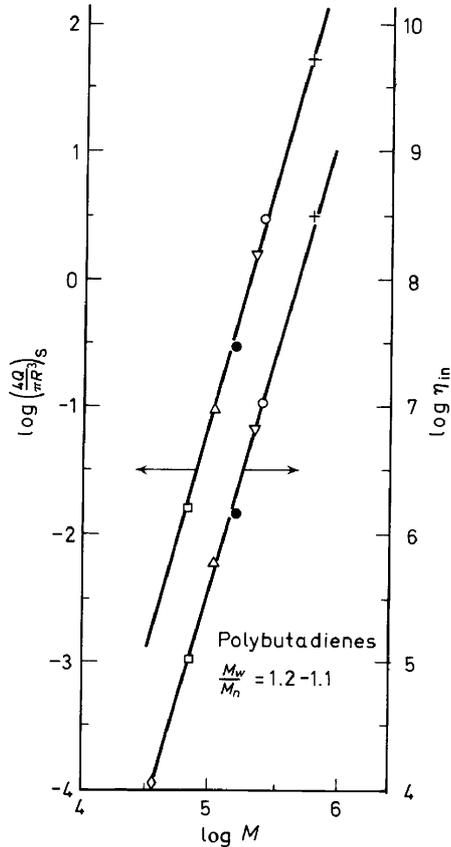


Figure 16. Flow curves of monodisperse polybutadienes at 25°C. Values of  $M$  and  $M_w/M_n$  respectively: 1— $3.8 \times 10^4$ ; 1.22. 2— $6.75 \times 10^4$ ; 1.20. 3— $1 \times 10^5$ ; 1.1. 4— $1.5 \times 10^5$ ; 1.1. 5— $2 \times 10^5$ ; 1.1. 6— $2.4 \times 10^5$ ; 1.1. 7— $5.8 \times 10^5$ .

observed in all cases at a weakly pronounced anomaly. At  $\tau = \tau_s$  the discharges of high-molecular PB may increase by decimal orders. In addition to that  $\tau > \tau_s$  is observed in the high discharge region (not shown in the figure).

It follows from *Figure 16* that  $\dot{\gamma}_s$  is strongly dependent on  $M$ . It is inverse to the dependence of  $\eta_{in}$  on  $M$ , as is shown in *Figure 17*.

Important results were obtained by B. Radushkevich (Synthetic Fibre Institute) in uniaxial extension tests at room temperature using PB samples



*Figure 17.* Dependences of critical shear rate of spurting and initial viscosity on molecular weight of polybutadienes.

with molecular weights over  $2.4 \times 10^5$ . As during shear, steady flow of these samples could be accomplished only at constant viscosity régimes or with a weakly pronounced anomaly. Moreover, the critical stress corresponding to the highest deformation rates at which the steady flow is still observed (which were nevertheless very low in absolute value), is independent of  $M$ . The critical elongation rates are in the same dependence on  $M$ , as in shear. The significance of these experiments is determined by the fact that they demonstrate the direct relation between critical spurting régimes during shear and tensile rupture of the sample.

It is known from studies of spurting in PE that  $\tau_s$  depends very little on temperature. According to E. Borisenkova's data the same is observed for

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PB (Figure 18). It is important that the dependence  $\dot{\gamma}_s$  versus  $t^0$  corresponds to that of  $\eta_{in}$  versus  $t^0$ .

The results obtained for PB described above were compared with data for polyisoprenes (PI) with narrow MWD, prepared specially for this purpose using anionic polymerization by V. P. Shatalov and V. P. Yudin (Synthetic Rubber Institute, Voronezh Branch). E. Borisenkova's CPCV tests showed that similar data are obtained for PB and PI. It was found that  $\tau_s$  for PI is about 1.5 times smaller than that for PB. The  $\tau_s/\tau_t$  ratios for both polymer homologous series are the same.

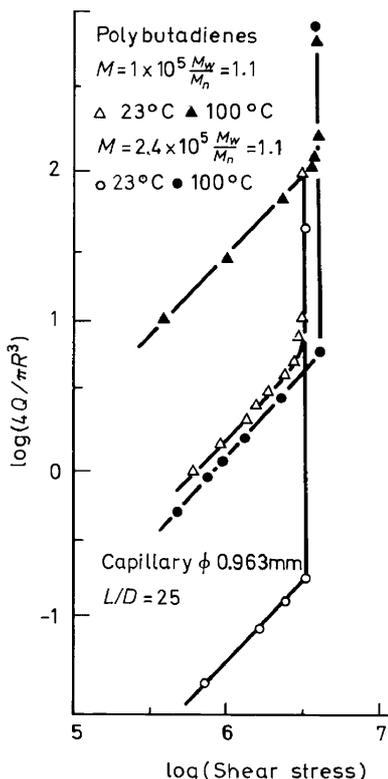


Figure 18. Effect of temperature on flow curves of monodisperse polybutadienes.

The experimental data discussed above raise a number of questions. Why are the critical spurting régimes the most pronounced in monodisperse polymers? Why is this phenomenon observed only at  $M > M_{cr}$ ? What is responsible for the constancy of  $\tau_s$  at different temperatures within a polymer homologous series and for the weak dependence of  $\tau_s$  on the nature of the polymer chain? What is the explanation for the nevertheless strong dependence  $\dot{\gamma}_s$  on temperature,  $M$  and nature of polymer chain? At what states on the temperature scale do the critical deformation parameters of polymers of different polymer homologous series correspond?

Answering these questions involves an examination of relaxation spectra and viscoelastic characteristics of the polymers for which these spectra are determined. As a matter of fact, the deformation régimes at which spurling occurs correspond to the high-elasticity region on the relaxation spectrum. At these deformation régimes steady flow may be impossible in uncross-linked polymers. The conditions limiting the generality of this proposition are as follows. The high-elasticity region should be clear-cut and of considerable extent on the relaxation time scale so that the deformation régime corresponding to spurling be sufficiently remote from the region of the relaxation spectrum describing the fluid state of the polymer. These limitations are easily realized with monodispersed polymers of high  $M$ , because their high-elasticity regions are strongly developed, as a rule, and their fluidity regions are limited to a narrow range of large  $\theta$ .

E. Dzyura showed that this problem can be examined more vividly by making use of the frequency dependences of the complex modulus components compared with the characteristic of steady state flow régimes. Since the function  $\dot{\gamma}$  versus  $\tau$  for PB is linear to a sufficiently close approximation up to spurling a quantitative correlation<sup>40</sup> of the dependences  $\tau$  versus  $\dot{\gamma}$  and  $G''$  versus  $\omega$  can be used,  $G''$  being the loss modulus and  $\omega$ , the circular frequency. This is explained by Figure 19.

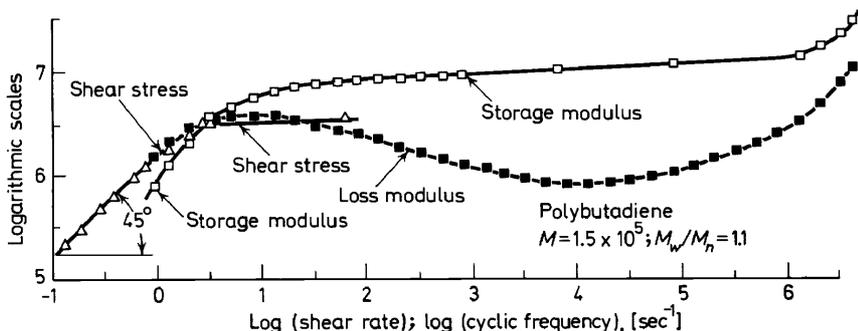


Figure 19. Frequency dependences of complex modulus components and shear stress versus deformation rate for a monodisperse polybutadiene.

In analysing the problem it is essential to make use of the theory of H. Oser and R. Marvin<sup>45</sup> and the work of V. Pokrovsky, reported to the Fifth Rheology Symposium (Institute of Petrochemical Synthesis, 19–23 May 1970). These authors accept the relation  $M/M_{cr} = M/2M_e$  as the determining parameter.

A maximum appears on the  $G''$  versus  $\omega$  curve when the high-elasticity plateau, estimated from  $G'$  versus  $\omega$ , is well pronounced, which is determined by sufficiently high entanglement density. This corresponds to  $M/M_e$  values of the order of 10 to 20, which in the case of PB corresponds to  $M > 6 \times 10^4$ . Indeed, spurling appears in PB at precisely these  $M$ .

In the case of polymers whose molecular weights are in accord with the condition mentioned above, the level of the high-elasticity plateau and the

height of the maximum on the  $G''$  versus  $\omega$  curve are constant within the same polymer homologous series. The latter accounts for the constancy of the  $\tau_s$  at which spurting occurs in PB and PI of different molecular weights. On the other hand, with increasing  $M$  the maximum shifts towards lower  $\omega$ , and this shift should be proportional to  $\eta_{in}$ . This is fully in accord with experimental data on  $\dot{\gamma}_s$  versus  $\eta_{in}$  and  $\dot{\gamma}_s$  versus  $M$ .

The shift of the maximum along the  $\omega$  scale due to changes in temperature is determined by the dependence  $\eta_{in}$  versus  $t^0$ . Indeed, it was shown above (Figure 18) that  $\dot{\gamma}_s$  versus  $t^0$  does not differ from  $\eta_{in}$  versus  $t^0$ . On the other hand, the influence of temperature on the height of the maximum is determined by the change this causes in entanglement density. Since the activation energy of entanglement formation is low<sup>37</sup>, temperature has little effect on the height of the maximum. This accounts for the weak temperature dependence of  $\tau_s$ .

The relation of  $M_e$  of different linear polymers is discussed in ref. 41 on the examples of PB and PS. Extending this approach to include PI, we find that the values of  $M_e$  for PB, PI and PS are in a ratio of 1:(2.5 to 3):(8 to 10). This at least qualitatively accounts for the fact that spurting is observed in monodisperse PB at much lower  $M$  than in PI, and that no spurting was observed in a rather large number of published studies of the viscous behaviour of PS. It appears in PS in a fairly pronounced form at  $M > 10^6$ , to which correspond very high viscosities at the usual temperature conditions at which PS is studied.

When examining the critical deformation régimes of polymers of different homologous series their corresponding states should pertain to the transition from the fluid to the high-elastic state. The question of corresponding states determined by the temperature scale is discussed in ref. 41, where it is shown that this is estimated by the remoteness from the glass transition temperature region. In this way corresponding critical deformation régimes can be found in different homologous series.

The approach to the study of the critical deformation régimes of polymers, discussed above, is the first purposeful attempt of this kind. It seems promising, and immediately gives rise to a number of question which must be elucidated. What is the connection between critical spurting régimes and the appearance of elastic turbulence? What effect does spectrum truncation exert on the critical deformation régimes? What is the quantitative relationship between  $\dot{\gamma}_s$  and the corresponding  $\theta_e^{max}$  and  $\gamma_e$ ? How does MWD affect the critical régimes in PB and PI etc., etc? It is very important to compare the conditions of spurting in PE with their relaxation characteristics.

In concluding the discussion of the deformation of fluid polymers at increased shear rates mention should be made of polymer crystallization induced by orientation of macromolecules in the stream<sup>42-45</sup>. This process enhances the resistance of the polymers to flow and can stop it completely. On the other hand, as was shown above, under the same conditions movement of non-crystallizable polymers may be greatly accelerated. The cause for the difference in behaviour of the polymers considered depends on the ability of non-crystallizable polymers not only to pass from the fluid to the high-elastic state, but to relax readily as well. This is the determining factor when slippage of polymers occurs along a solid boundary.

## CONCLUSIONS

Depending on molecular weight and molecular weight distribution, steady flow of polymeric systems is possible at deformation rates not exceeding the critical values corresponding to attainment of the regions of forced glass transition or of the forced high-elastic state.

In the fluid state region the main parameters characterizing the rheological properties of polymeric systems (coefficient of viscosity and normal stresses and high-elasticity moduli) are not only mutually related, but their values are determined unambiguously by the relation between the deformation rate and the maximum initial relaxation time, namely, by the dimensionless parameter equal to their product.

The development of high-elastic deformations is determined by the long-time part of the relaxation spectrum, occurring most intensively when deformation causes very small changes in the relaxation spectrum.

The main difference between shear and elongation is the difference in the way the relaxation spectrum of the polymer varies due to deformation. As a result, the viscosity changes in different directions for elongation and shear, whereas the high-elasticity modulus increases in both cases. Considerable narrowing of the molecular weight distribution substantially decreases the differences in deformation behaviour of polymers on shear and on elongation.

## ACKNOWLEDGEMENT

An important contribution to the entire complex of the studies discussed above concerning the effect of MWD on the rheological characteristics of polymers was made by the laboratory of Professor I. Poddubny (Synthetic Rubber Institute) and primarily by Dr V. Grechanovsky. A major contribution in characterizing the polymeric systems used in the work was made by Dr L. Titkova.

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