

FUNDAMENTAL PROBLEMS CONCERNING THE INTERRELATION OF THE STRUCTURE OF POLYMERS AND THEIR RHEOLOGICAL PROPERTIES IN THE FLUID STATE

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ABSTRACT

The viscoelastic properties of linear polymers with $M > 5M_c$ (M_c corresponds to the formation of a spatial network of entanglements), their mixtures and concentrated solutions are discussed. Under the influence of deformation there may take place a transition of polymers to the high-elastic state, which thus determines the limits of their fluidity. This transition is observed not only for high-molecular-weight polymers of narrow distribution but also for their mixtures and concentrated solutions. The relative simplicity of the rheological properties of high linear polymers and their mixtures is provided by the sharpness of their transition into the high-elastic state. In the case of mixtures of high polymers the mechanism of anomalous viscosity due to the reduction of dissipation losses upon transition of high-molecular-weight components to the high-elastic state is of predominant importance. In a wider range of molecular weights ($M > M_c$) and also in the case of polymer solutions it is the decrease of the network density under the influence of deformation that becomes important.

The separate effects of high-molecular-weight components on the viscoelastic properties of their mixtures are in contradiction to the conception of a random network of macromolecular chains. Consideration is given to the temperature dependence of the viscosity of polymers of narrow MWD and of the dynamic properties of their mixtures, in a wide temperature range.

The problems associated with the specificity of the rheological properties of polymeric systems at high rates of deformation are formulated; these problems are of interest from the theoretical point of view and for the processing of polymers.

INTRODUCTION

First let us define certain problems.

In considering the properties of polymeric systems in the fluid state one is first of all confronted with the question of the boundaries of this state. The upper temperature limit is determined by thermo-oxidative degradation. We shall not dwell on this point. The lower limit is governed by crystalliza-

tion and glass transition. At temperatures above the melting and glass-transition points the physical state of a polymeric system depends on the ratio of the rate of deformation to the rate of relaxation processes occurring in it, which is occasionally estimated by using a certain characteristic relaxation time. This problem is of paramount importance to the understanding of the peculiarities of the viscoelastic properties of polymeric systems depending on their nature, deformation rate and temperature. It is important both for the understanding of structural specificity and for the estimation of the processability of polymer systems. In those cases where steady flow is realized and also in transient processes it is essential for the peculiarities of the rheological properties of polymeric systems to be estimated as a function of stress.

At present we have most complete information on the viscoelastic properties of nonpolar or weakly polar linear homopolymers. Special attention should be paid to the properties of narrow fractions and the model systems prepared from them. It is with this topic that the present communication is primarily concerned.

It is generally known that over a narrow range of molecular weights there is observed an abrupt change of the rate of the dependence of viscosity on molecular weight. When this critical molecular weight, M_c , is attained, the polymer becomes capable of large reversible, high-elastic deformations, which are related to the formation of a spatial network of macromolecules¹. It is just this critical molecular weight that leads one to speak of polymers and its value can conveniently be used to standardize the molecular weights of polymers. It is sometimes more preferable to make use of the number of atoms, forming the main chain of polymer, rather than molecular weights. But the approach to the problem remains in principle the same.

It is generally believed that at molecular weights exceeding the critical value the application of a shear stress to the polymer may change the density of nodes of the macromolecular network, which results in an inproportionately rapid increase of deformation rate—anomalous viscosity is observed. Anomalous viscosity becomes more prominent with increasing length of macromolecular chains and hence with increasing density of the network of entanglements. At the same time, as the density of the network of entanglements increases, anomalous viscosity undergoes a change at an ever increasing shear stress. This accounts for the well known fact that for linear polymers of narrow molecular-weight distribution and molecular weight much exceeding the critical value, Newtonian flow behaviour is observed up to very high stress values. Until recently no attention has been paid to the following two circumstances: the existence of a sharply pronounced critical stress, below which the viscosity of polymer remains approximately constant with decreasing temperature, and the existence of anomalous viscosity even for monodisperse polymers of high molecular weight.

The theories²⁻⁵ based upon the concept of the network structure of polymers, or on mechanical models equivalent to this concept, indicate that at molecular weights exceeding approximately five critical values, the increase of the rate of deformation (frequency) must lead to the transition of a polymeric system to the high-elastic (rubber-like) state. To this transition

there corresponds the cessation of relative displacements of the centre of gravity of macromolecules and the associated decrease of the dissipation loss, which causes the appearance of a maximum on the plot of the loss modulus against frequency. The magnitude of maximum loss cannot depend on molecular weight; it can only change very slightly with temperature (increase proportionately to the absolute temperature). The frequency corresponding to the maximum of the loss must vary in inverse proportion to initial viscosity, which thereby determines its dependence on molecular weight and temperature.

For monodisperse high-molecular-weight linear polymers the transition from the fluid to the high-elastic state is sharply pronounced. It takes place in a narrow range of deformation rates (frequencies).

The existing theories treat the transition of polymers from one physical state to another for the case of harmonic régimes of low-amplitude deformation. It is impossible to predict *a priori* the criteria for the transition of polymers to the high-elastic state and the manner in which this transition will proceed when unlimitedly large deformations are specified. Another question which is of no less importance arises in connection with this fundamental problem: Is it possible to realize a steady flow, an accumulation of unlimitedly large deformations, if the uncrosslinked polymer undergoes a transition to the high-elastic state?

The studies carried out in our laboratory^{6,7} have shown that the simplest situation exists for polymers of narrow molecular-weight distribution, whose molecular weight exceeds ten critical values. They are noted for high density of entanglement nodes and hence for high uniformity of segmental distribution between the entanglements. It is for this reason that the network of macromolecules can withstand high stresses without any significant change of the density of entanglement nodes and that Newtonian flow is suddenly replaced by the transition of polymer to the high-elastic state. Since the critical rates of deformation and shear stress determine a state that borders upon Newtonian flow behaviour, they are simply related to what is predicted by the theory of linear viscoelasticity which considers the viscoelastic characteristics of polymeric systems upon their low-amplitude deformation at various frequencies. What is unexpected is the fact that the accumulation of a rather large deformation (of the order of 100–200 per cent) has no significant effect on the transition in question.

In shear, the adhesion of the polymer to the surface of a solid body relative to which it is being deformed is of importance. When the polymer is in the fluid state, one may always assume that the polymer displays perfect adhesion to the solid surface. But in the high-elastic state the polymer behaves as a quasi-cured body. It is on the basis of this conception that one may speak of the loss of fluidity by polymers upon their transition to the high-elastic state.

When the polymer is brought to the high-elastic state, its adhesion to the surface of solid bodies is impaired. In extrusion, this results in wall slippage of the polymer in the duct, which increases the output by hundreds and thousands of times. In rotational devices the detachment of polymer from the working surface is accompanied by the decrease of the torque to zero. It is thus the impairment of the adhesion of polymer to solid surfaces that

enables the clear-cut identification of the transition of polymer from the fluid to the high-elastic state—from the discontinuous variation of the parameters characterizing the behaviour of polymer upon deformation. This is schematically shown in *Figure 1*. Emphasis is here placed on the correlation of the conditions of the estimation of the transition of polymer to the high-elastic state when it is tested at low amplitudes and loses its adhesion to the bounding surfaces with large deformations being specified.

A number of problems arise in connection with what has been said above: (1) By what methods can one estimate the deformability of uncrosslinked polymers in the high-elastic state? That it is impossible to achieve this under the conditions of shearing experiments is now obvious. Whether it can be realized on uniaxial extension has been unknown up to now. (2) Can the wall slippage be prevented and the adhesion of polymers to solid surfaces be provided under the conditions of shearing experiments by increasing the pressure? (3) How can the reduction of the adhesion of polymers to solid surfaces be used to accelerate the conditions of their motion?

The next question refers to the relation between the conditions in which anomalous viscosity is exhibited by polymers of narrow distribution and their transition to the high-elastic state. The transition of polymers to this state under the conditions of non-Newtonian flow should be expected in the case of polymers with molecular weights of the order of five critical values when a high uniformity of segmental density has not yet been achieved. Can the decrease of the effective density of entanglements due to deformation shift the transition of polymer into the high-elastic state to higher rates of deformation? What actually happens in this practically very important region of molecular weights still remains obscure.

The fall of temperature must retard the formation of a network of entanglements. The change of its density under the influence of polymer deformation and hence the anomalous viscosity must therefore become progressively more strongly pronounced with decreasing temperature. Consequently, at lower temperatures the high-elastic state may border upon the non-Newtonian flow régime. The activation energy of the formation of a network of entanglements is very low. Therefore, for the transition from the Newtonian flow régime to non-Newtonian behaviour at high shear stresses it is necessary that the temperature be decreased very considerably. This point will be discussed in more detail later.

Polydispersity has a great effect on the entire range of viscoelastic properties of polymeric systems.

Let us consider a polymeric system which contains components having a molecular weight higher than the critical. In this case, a deformation rate at which the highest-molecular-weight component changes to the high-elastic state can easily be attained. Its contribution to the dissipation loss of the system is lowered and it will pass to the state of a high-elastic filler. The decrease of dissipation losses at shear rates corresponding to the transition of the high-molecular-weight component to the high-elastic state means a decrease of apparent viscosity. This is the manifestation of the second mechanism of non-Newtonian behaviour for linear homopolymers (the first mechanism, as pointed out above, is caused by the change of the density of entanglement nodes). Naturally, the effect of high-molecular-weight com-

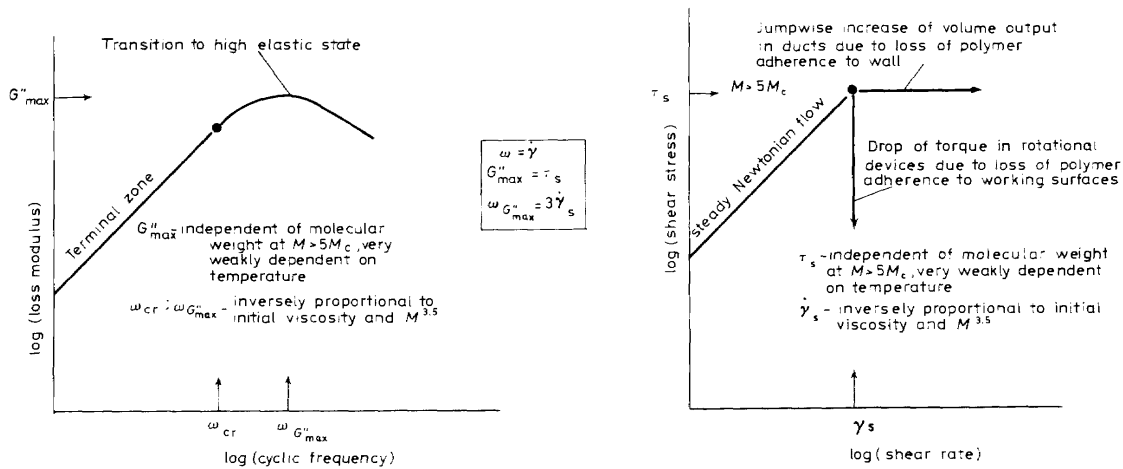


Figure 1. The correlation between the conditions of transition of high-molecular-weight polymers of narrow MWD into the high-elastic state according to data of dynamic tests at low amplitudes and the results of experiments on capillary viscometers.

ponents on the conditions of flow of a polymeric system depends on molecular weight distribution.

Let us assume that a polymeric system contains high-molecular-weight components. Then, on approach to the critical value of shear stress, which is characteristic of a given polymer-homologous series and corresponds to the transition into the high-elastic state, there is observed a sharp increase of the rate of deformation. In the case of polydisperse polymers, however, no jumpwise transition from the fluid to the high-elastic state is observed, the transition typical of high-molecular-weight samples of narrow distribution.

The presence of low-molecular-weight components can provide the adhesion of the system to the surface of solid bodies when high-molecular components have already acquired the high-elastic state. Under these conditions, no wall slippage takes place. At a high content of high-molecular-weight components, however, there will occur a break of continuity within the medium being deformed. This is due, as will be shown below, to the fact that no unlimitedly large deformations develop in polymers being in the high-elastic state. They either undergo a break of continuity or are detached from the measuring surface with which they are in contact during deformation under the subcritical régimes.

When the content of high-molecular-weight components is not great, the compliance of the system is very much increased. In this case, of paramount importance is the entire range of phenomena caused by large reversible deformations—large entry effects, the formation of whirls and pulsations in the entry zone of ducts in extrusion, the secondary flow in rotational apparatuses, and others.

Thus, within a single polymer-homologous series, with increasing shear rate and stress, there may take place quite different phenomena, depending on the composition of polymeric systems, phenomena ranging from the loss of fluidity for high-molecular-weight samples of narrow distribution to phenomena caused by the development of large reversible deformations for polydisperse systems of wide MWD, with a low content of very high-molecular-weight components.

Of great importance is the determination of boundary conditions under which, depending on the composition of polymeric systems, one type of behaviour of a polymeric system is replaced by another. Very little work has so far been done along this line.

The conditions of the transition of polymer from the fluid to the high-elastic and glassy states may be most rigorously characterized on the basis of measurements of their viscoelastic properties under the conditions of harmonic vibrations of low amplitude. Let us now consider the results of these measurements and compare them with data obtained on capillary and rotational viscometers and also in cyclic deformation of high amplitude. The case of uniaxial extension will also be discussed.

THE DYNAMIC CHARACTERISTIC AND STEADY FLOW OF LINEAR POLYMERS OF NARROW MWD OVER A WIDE RANGE OF TEMPERATURES, FREQUENCIES AND SHEAR RATES

Among linear polymers, polybutadienes obtained by anionic polymeriza-

tion are very convenient objects for investigations. They are available in the form of narrow fractions and are noted for their low glass-transition temperatures. They can be studied over a wide range of temperatures, up to $(T/T_g) = 2.5$. The critical molecular weight of polybutadienes is as low as 5600^8 . One can therefore investigate samples of polybutadiene for which the value of (M/M_c) reaches and even exceeds 100.

The dependence of the viscoelastic properties of polybutadienes on the molecular weight has been discussed earlier⁷. It has been shown that at $(M/M_c) \geq 10$ the maximal value of loss modulus (G''_{\max}) is independent of molecular weight. With an error not exceeding 10 per cent the loss moduli are proportional to the frequency up to its value $\omega_{cr} = 0.1\omega_{G''_{\max}}$, where $\omega_{G''_{\max}}$ is the frequency corresponding to the maximum of loss modulus. The frequencies ω_{cr} and $\omega_{G''_{\max}}$ vary in inverse proportion to the initial viscosity (η_0), which determines unambiguously the dependence of these quantities on molecular weight and temperature. The region of unproportional variation of G'' and ω covers the range of three-fold change of G'' . A very slightly pronounced unproportionality of the variation of G'' and ω , observed over a narrow range of these values renders the correlation between the dynamic characteristics and the parameters governing the steady flow conditions quite reliable.

Steady flow in the ducts of round and rectangular cross-sections can be attained only up to shear stresses numerically equal to G''_{\max} . When this critical value of shear stress is reached, there is observed the phenomenon of spurt—the volume output increases in a jumpwise manner. The longer the duct, the stronger is the change of the output. An explanation for this is simple. When the critical régime of deformation is attained, the adhesion of the polymer to the duct wall is sharply reduced and the polymer is thrown from the wall with a velocity which is greater the higher the pressure acting at the duct entry.

In full conformity with what has been found for the dependence of the viscoelastic properties of polymers on the frequency at low amplitudes, the critical shear stress, at which the spurt occurs, is independent of the molecular weight, and the critical shear rate varies in inverse proportion to the initial viscosity. Here the critical shear rate is always somewhat lower than the circular frequency $\omega_{G''_{\max}}$, corresponding to the values of G''_{\max} . This may be due to one of the following factors: the perturbation effect in the zone of entry of the polymer into the duct and that of its exit from the duct or the effect of the accumulation of large reversible deformations on the transition of polymer from the fluid to the high-elastic state.

To a first approximation, it may be assumed that for linear high polymers of narrow MWD the spurt is replaced in a jumpwise manner by Newtonian flow. A more thorough examination of the régimes of steady flow shows, however, that even in the case of polymers of very narrow MWD there is always observed anomalous viscosity on approach to the spurt. In this case the non-proportionality of shear stresses and rates is of the same magnitude as for the dependence $G''(\omega)$.

Now let us turn to the discussion of new data obtained by Ulyanov, Barancheva and Yanovsky for the temperature dependence of the viscoelastic properties of polybutadienes. *Figure 2* shows how, over a very wide

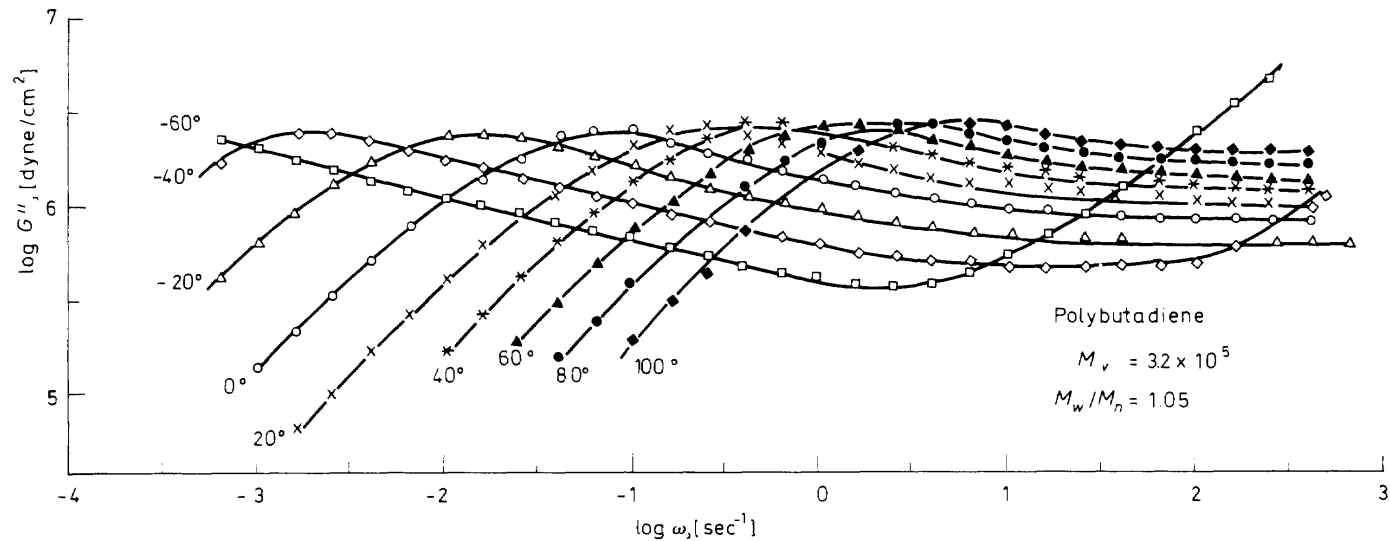


Figure 2. The frequency dependence of loss modulus for high-molecular-weight polybutadiene.

INTERRELATION OF THE STRUCTURE OF POLYMERS

temperature range, the loss modulus varies as a function of frequency. The lower portions of the terminal zones correspond to the condition $G'' \sim \omega$, i.e. to the constant values of dynamic viscosity. The extent of the zones of transition from the proportionality between G'' and ω to maxima depends only slightly on temperature. The extent of these zones is small. It is one decimal order with respect to frequency and corresponds approximately to the three-fold change of G'' .

The maxima separate distinctly the regions of fluidity (terminal zones) and high-elasticity. The height of the maxima falls with decreasing temperature somewhat less than the absolute temperature. In strict agreement with theory the shift of the maxima along the frequency axis is determined by the variation, with temperature, of the initial viscosity or (which is the same thing) of the dynamic viscosity in the region of its values where it is independent of frequency. This is illustrated by the data of *Figure 3*, from which it is seen that

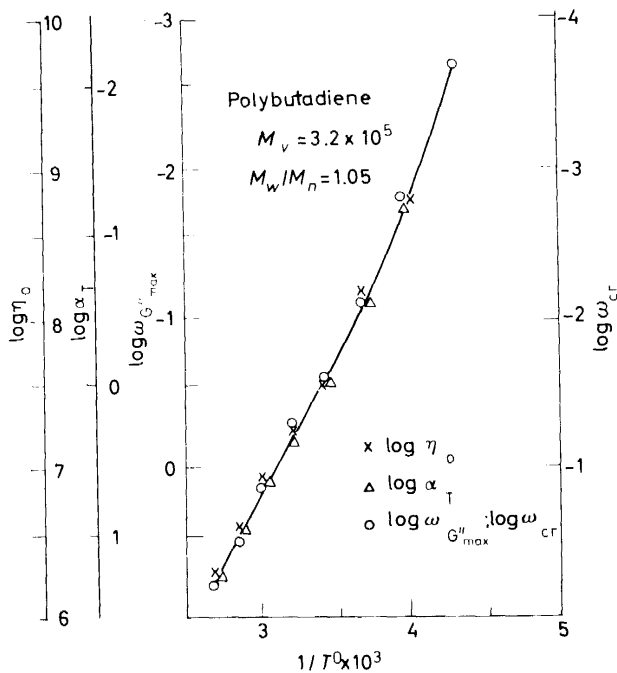


Figure 3. The temperature dependence of initial viscosity, reduction coefficient and frequencies corresponding to the maximum of loss modulus and to the appearance of a disproportionality of its variation with frequency for high-molecular-weight polybutadiene.

the temperature variation of initial viscosity and frequencies corresponding to the maxima and to the transition to the slow increase of the loss modulus is described by a single relationship.

The frequency dependence of the storage modulus is presented in *Figure 4*. When the region of low frequencies, in which the storage modulus varies proportionally with the square of frequency, is attained, the following set of

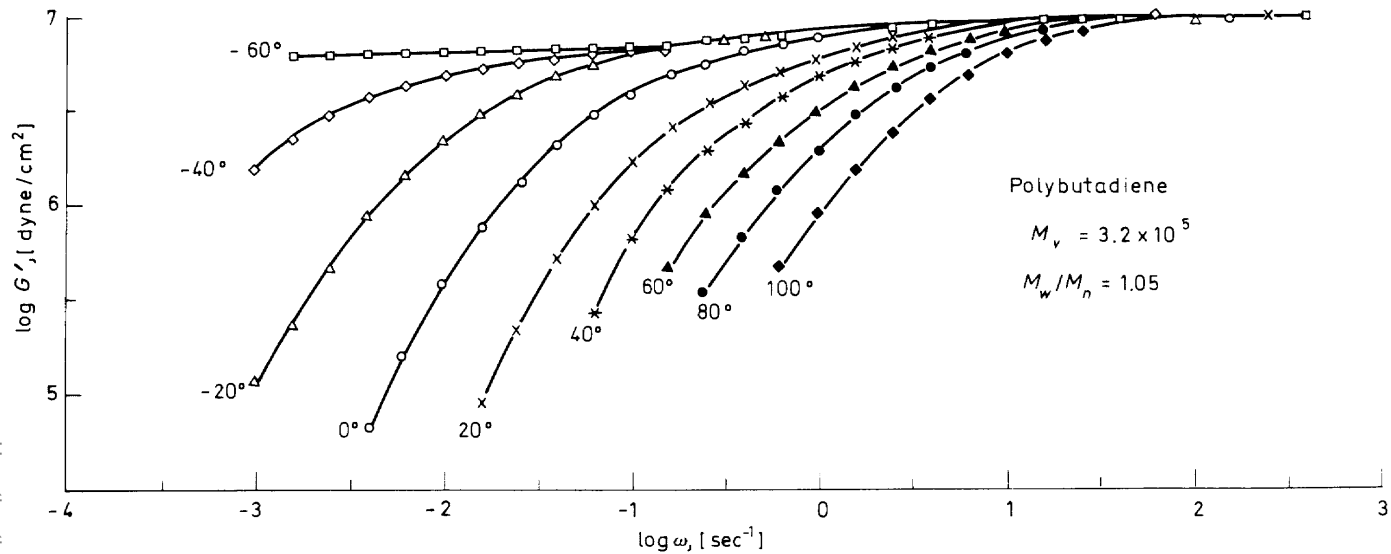


Figure 4. The frequency dependence of storage modulus for high-molecular-weight polybutadiene.

simple relations must then be strictly satisfied:

$$\eta'_0 = \lim_{\omega \rightarrow 0} \frac{G''}{\omega} = \lim_{\dot{\gamma} \rightarrow 0} \frac{P_{12}}{\dot{\gamma}} = \lim_{\dot{\gamma} \rightarrow 0} \frac{\tau}{\dot{\gamma}} = \eta_0$$

$$A_{G,0} = \lim_{\omega \rightarrow 0} \frac{G'}{\omega^2} = \lim_{\dot{\gamma} \rightarrow 0} \frac{P_{11} - P_{22}}{2\dot{\gamma}^2} = \frac{1}{2} \zeta_0$$

$$G_0 = 2 \frac{\eta_0^2}{\zeta_0} = \frac{(G'')^2}{G'}$$

Here η'_0 and η_0 are the initial values of dynamic viscosity and viscosity at steady flow, respectively; $A_{G,0}$ and ζ_0 are the initial values of elasticity and normal-stress coefficients; G_0 is the initial value of shear modulus for steady flow.

The temperature dependence of the elasticity coefficient is shown in Figure 5. Since the activation energy of the development of normal stresses

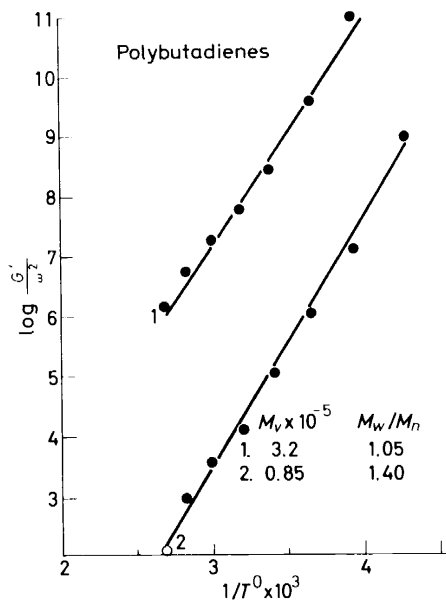


Figure 5. The temperature dependence of elasticity coefficient for high-molecular-weight polybutadienes.

exceeds, by a factor of two, the activation energy of viscous flow, the high-elasticity modulus at zero shear is independent of temperature. At temperatures from -20 to 40°C , when the quadratic dependence of the storage modulus on frequency is reliably established, the high-elasticity modulus at zero shear for a PB sample of molecular weight equal to 3.2×10^5 is found to be equal to $(3.6 \pm 0.4) \times 10^6 \text{ dyn cm}^{-2}$.

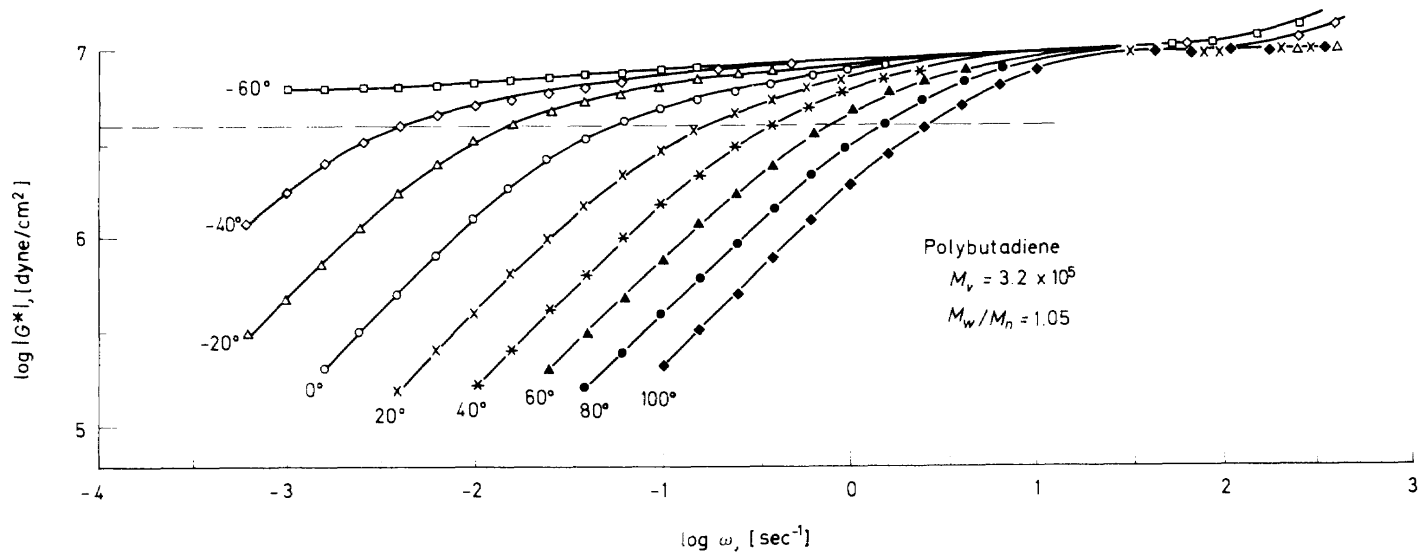


Figure 6. The frequency dependence of the absolute value of complex modulus for high-molecular-weight polybutadiene.

INTERRELATION OF THE STRUCTURE OF POLYMERS

The viscoelastic properties of polymers are most fully described by the frequency dependence of the complex modulus (G^*). The dependence $G^*(\omega)$ presented in *Figure 6* is important because in a number of works there has been established an empirical correlation between this function and the dependence of shear stress on the rate of shear for steady flow régimes, in which case it is assumed that the shear rate is numerically equal to the circular frequency. At this point, on the basis of what has been said, one can establish the limit of this kind of correlation. It is given by the dashed line, which corresponds to the maxima of the dependences $G''(\omega)$. Above the dashed line is the zone that is forbidden for the correlation. It is impossible to realize a steady flow with parameters corresponding to this zone since it describes the transition of the polymer to the high-elastic state and offers its characterization in this state. Of importance is the fact that in the region of high values the complex modulus varies more slowly with decreasing temperature, depending on frequency. This enables one to predict the considerable increase of anomalous viscosity as the temperature falls in the region of high shear stresses.

We complete the consideration of the viscoelastic properties of high-molecular-weight narrow fractions by resorting to the frequency dependence of complex viscosity. It is presented in *Figure 7*. This Figure very clearly

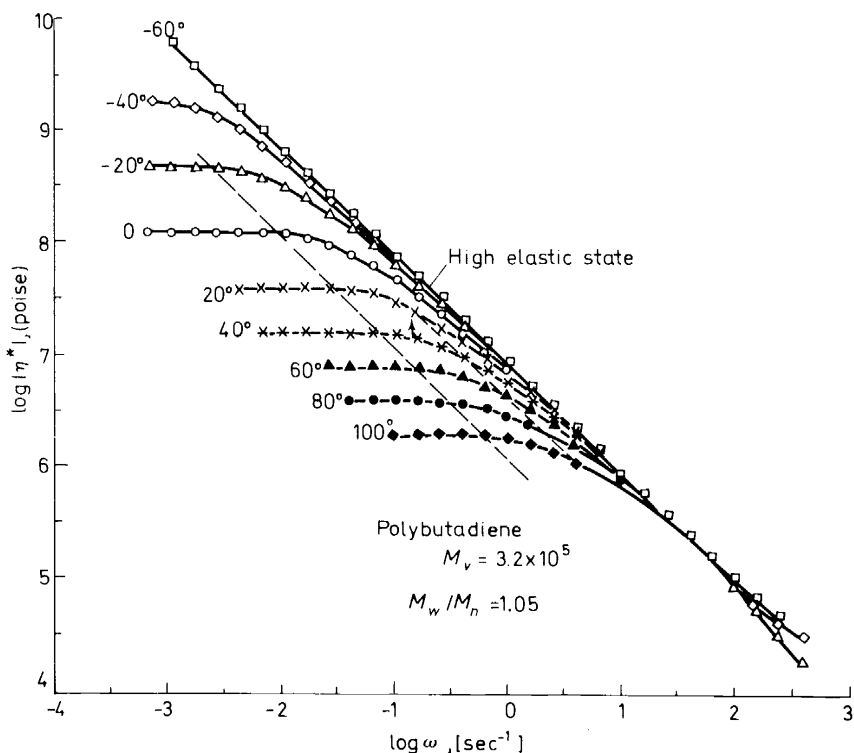


Figure 7. The frequency dependence of the absolute value of complex viscosity for high-molecular-weight polybutadiene.

shows how the change of temperature shifts the region of independence of complex viscosity on frequency and, hence, of viscosity on shear rate for steady flow régimes. The point marked on the curve for 20°C with an arrow corresponds to the spurling effect (the equality $\omega = \dot{\gamma}$ is assumed here). From the data of *Figure 7* one can easily see the scale of the manifestation of anomalous viscosity which can be observed for high polymers of narrow MWD.

Let us now dwell on the results of the experiments carried out by Borisenkova on a capillary constant-pressure viscometer over a wide temperature range. They are presented in *Figure 8*. An excellent correlation is observed

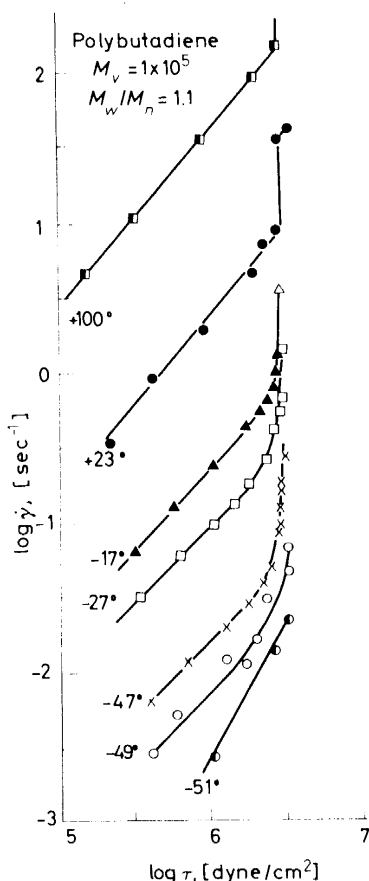


Figure 8. The dependence of apparent shear rate on shear stress on capillary wall and the effect of spurt for high-molecular-weight polybutadiene.

between the data of capillary viscometry and the dynamic characteristics of polybutadienes. Over the entire temperature range studied the critical shear stress corresponding to the spurt remains constant. As the temperature falls, however, a new fact is established on the basis of measurements of complex

shear modulus : approximately below $1.5 T_g$ in the region of high shear stresses, anomalous viscosity manifests itself stronger and stronger.

MODEL BINARY MIXTURES OF LINEAR POLYMERS OF NARROW MWD

Let us now consider the simplest binary mixtures, in which both components are high-molecular-weight compounds ($M/M_c \gg 5$). A number of works have been published in recent years, which give the results of thorough measurements of the viscoelastic properties of well characterized blends of polystyrenes⁹⁻¹⁴ and poly(methyl methacrylates)¹⁵. In the case of polybutadienes with $M/M_c \approx 15$ and $M/M_c > 50$, more clear-cut results could have been expected. The measurements should be made over a wide temperature range, taking into account the fact that all the works published up to the present time refer to a constant temperature. Accordingly, Barancheeva and Yanovsky studied mixtures containing 0.2, 0.5, and 0.8 volume fractions of the lower-molecular-weight component. The basic results obtained are presented in *Figures 9-12*.

The graphs showing the dependence $G''(\omega)$ are the most spectacular, and the frequency dependences of $|G^*|$ and $|\eta^*|$ are the least interesting. The character of the temperature dependence of $\omega_{G''_{\max}}$ and of the initial values of parameters describing the viscoelastic properties of binary mixtures is just the same as for the initial starting components. This is illustrated by the data given in *Figure 11*.

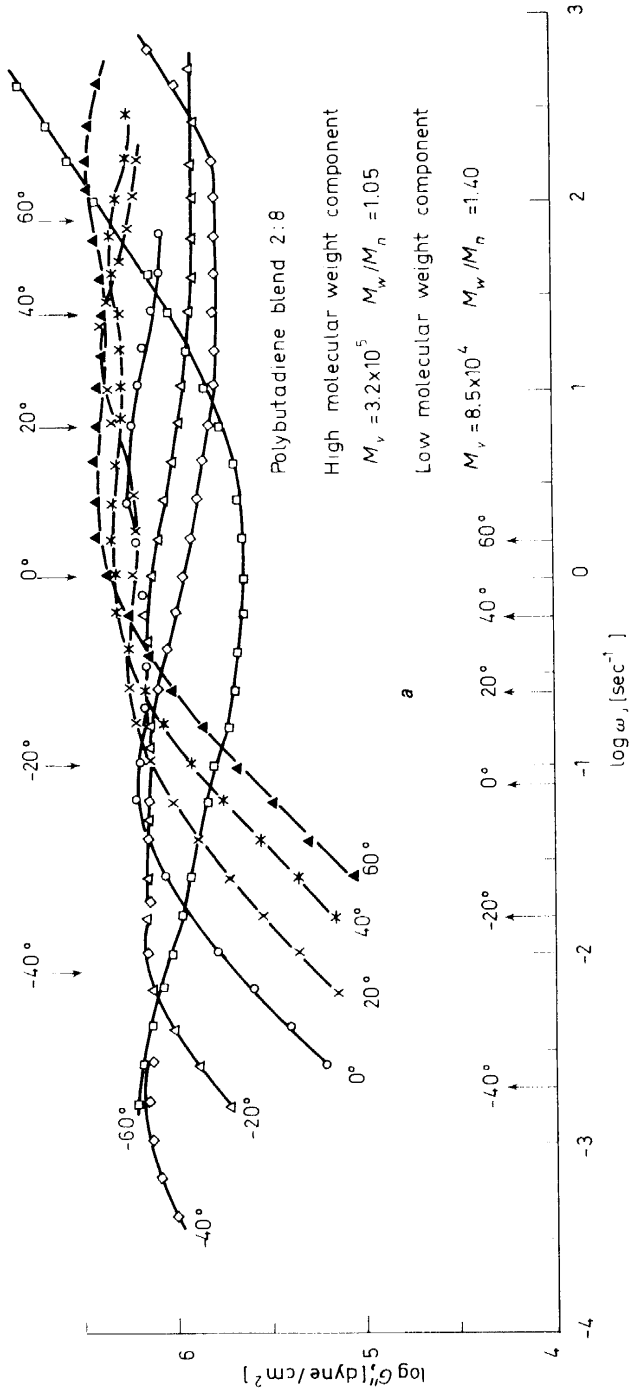
For the sake of simplicity and more vividness let us compare the frequency dependence of the loss moduli of the starting components with those of their mixtures at two temperatures, as shown in *Figure 13*. Let us first consider the case of a relatively small content of a lower-molecular-weight component. At higher temperatures, two maxima are observed for the loss modulus, though slightly pronounced. As the temperature falls, there appears on the frequency dependence of the loss modulus a plateau covering the entire range of frequencies situated between the maxima of both components. This means that with decreasing temperatures the components exhibit their individuality in the mixture in a lesser degree.

With equal fractions of the components the curves of $G''(\omega)$ show a characteristic inflexion point. This point corresponds to a frequency close to the frequency of the maximum of loss modulus of the higher-molecular-weight component and is evidence that it has assumed the high-elastic state. For the mixtures concerned we observed, at all the temperatures under study, a maximum for the loss modulus that coincide with the loss modulus of the lower-molecular-weight component.

In mixtures with a lower content of the higher-molecular-weight component, its presence is recognized by the characteristic change of the course of the curves of $G''(\omega)$ in a frequency region in which this component has passed to the high-elastic state.

The consideration of the viscoelastic properties of binary mixtures leads to the following conclusions:

(1) Over a wide range of compositions of binary mixtures there is observed a transition of the high-molecular-weight component to the high-elastic state.



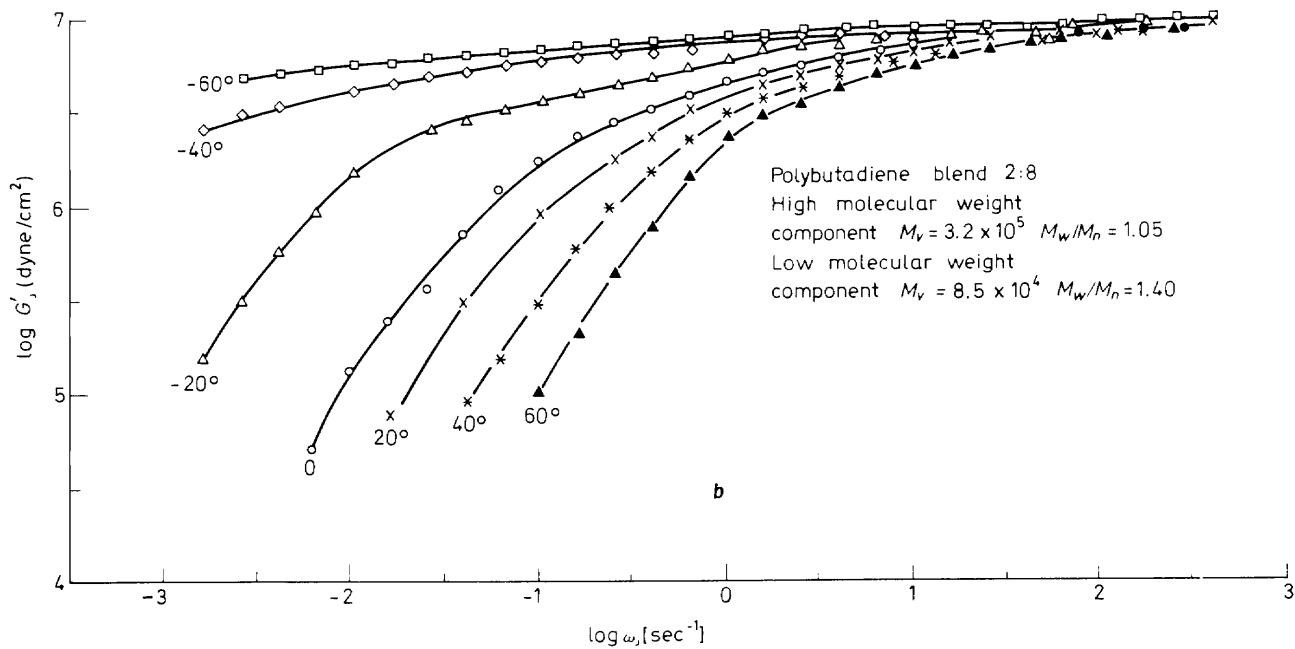


Figure 9. The frequency dependence of the components of complex modulus for a binary mixture of polybutadienes, containing 0.2 volume fractions of the lower-molecular-weight component: a—loss modulus; b—storage modulus.

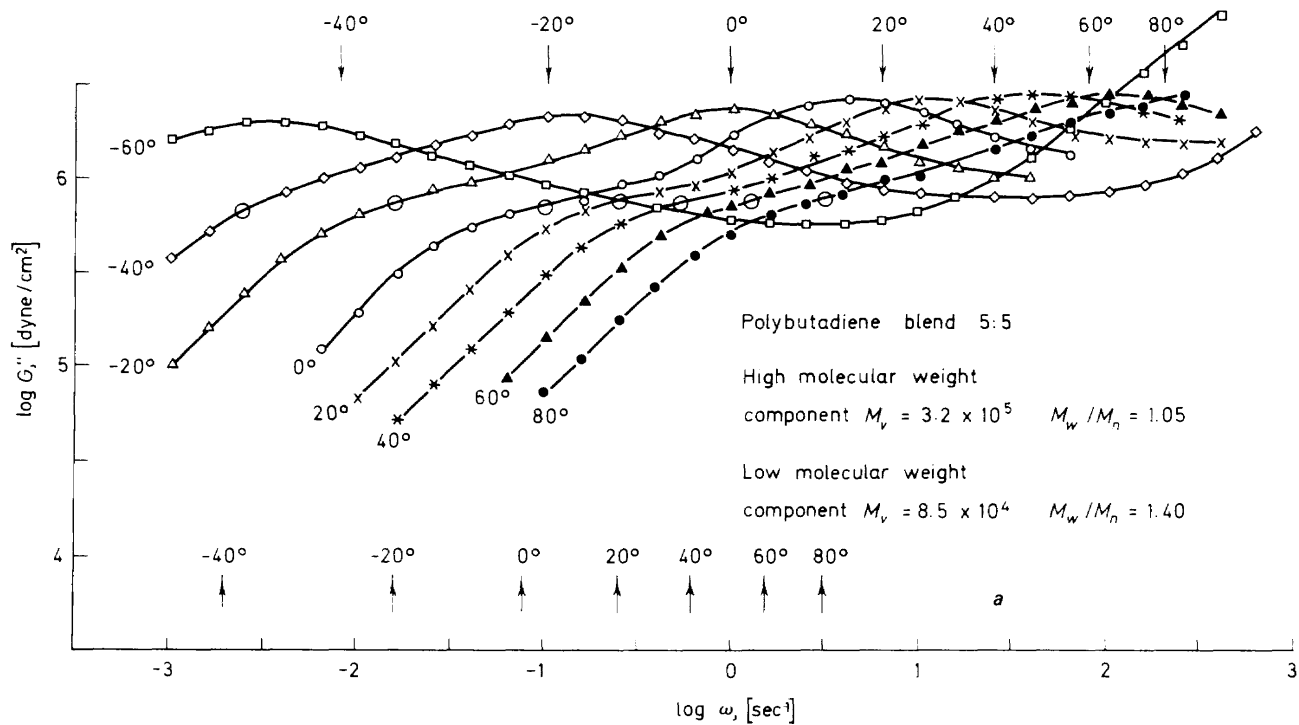


Figure 10. The frequency dependence of the components of complex modulus and absolute values of complex modulus and viscosity for a binary mixture of polybutadienes, containing equal fractions of the components: a—loss modulus; b—storage modulus; c—complex modulus; d—complex viscosity.

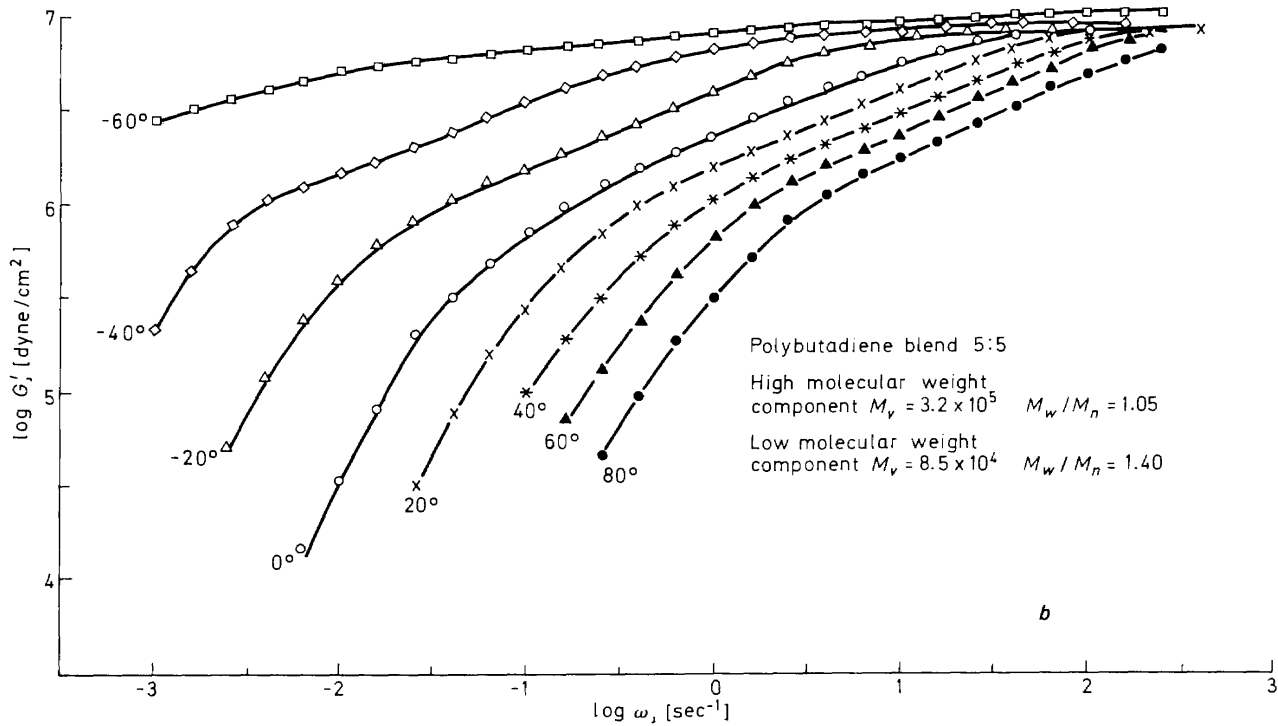


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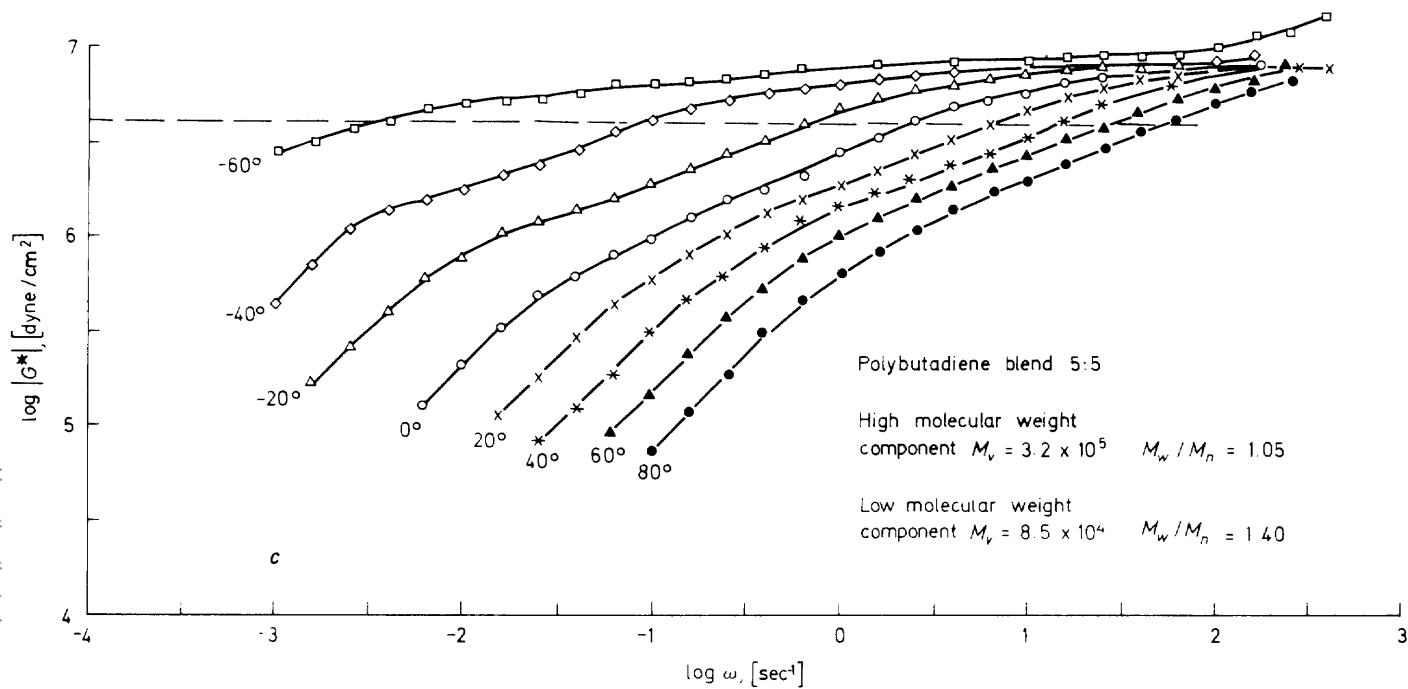


Figure 10—cont.

INTERRELATION OF THE STRUCTURE OF POLYMERS

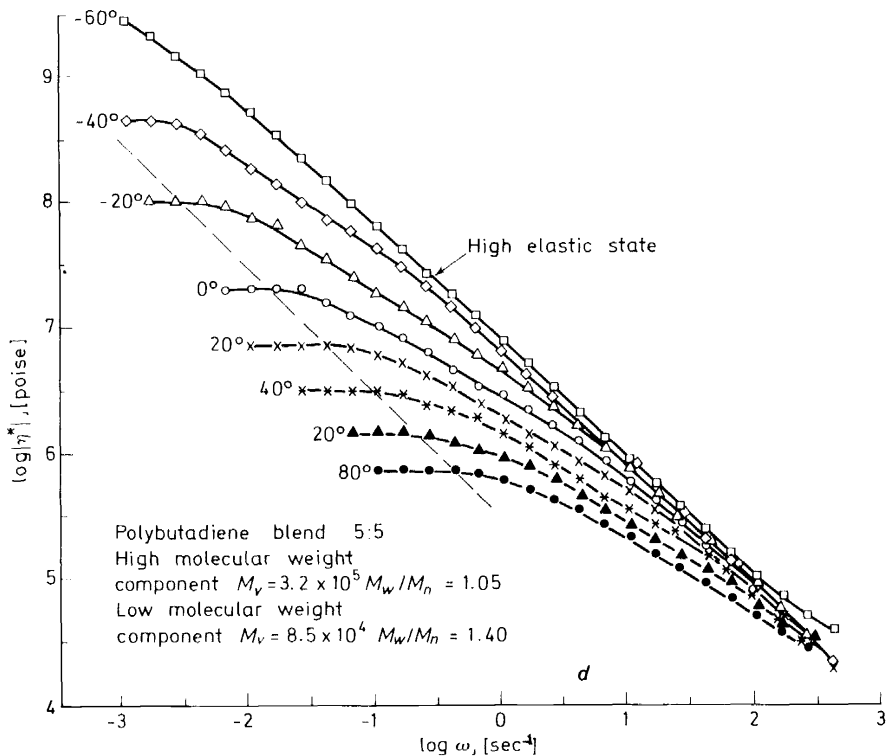


Figure 10—cont.

(2) Over a wide frequency range the viscoelastic properties of polymers (polydisperse systems) cannot be described by theories that introduce averaged parameters similar to the characteristic mean relaxation time.

(3) The individual effect of the components on the properties of mixtures becomes stronger with rise of temperature.

(4) The specific features of the properties of high polymers are inconsistent with the conception of a single network of randomly intermingled macromolecules of different length, since the concept of randomly intermingled chains by no means implies a separate manifestation of these properties. This point of view has been put forward in works from our laboratory^{6, 19} and also by the school of Sh. Onogi¹⁰.

From a comparison of the relaxation spectra of mixtures with those of original components it follows that the methods known from the literature¹⁶⁻¹⁸ for calculating the relaxation spectra of mixtures are inapplicable in this case.

Based on the consideration of the viscoelastic properties of high-molecular-weight linear polymers, one can draw important conclusions concerning the flow régimes in the ducts and, in particular, concerning the flow curves.

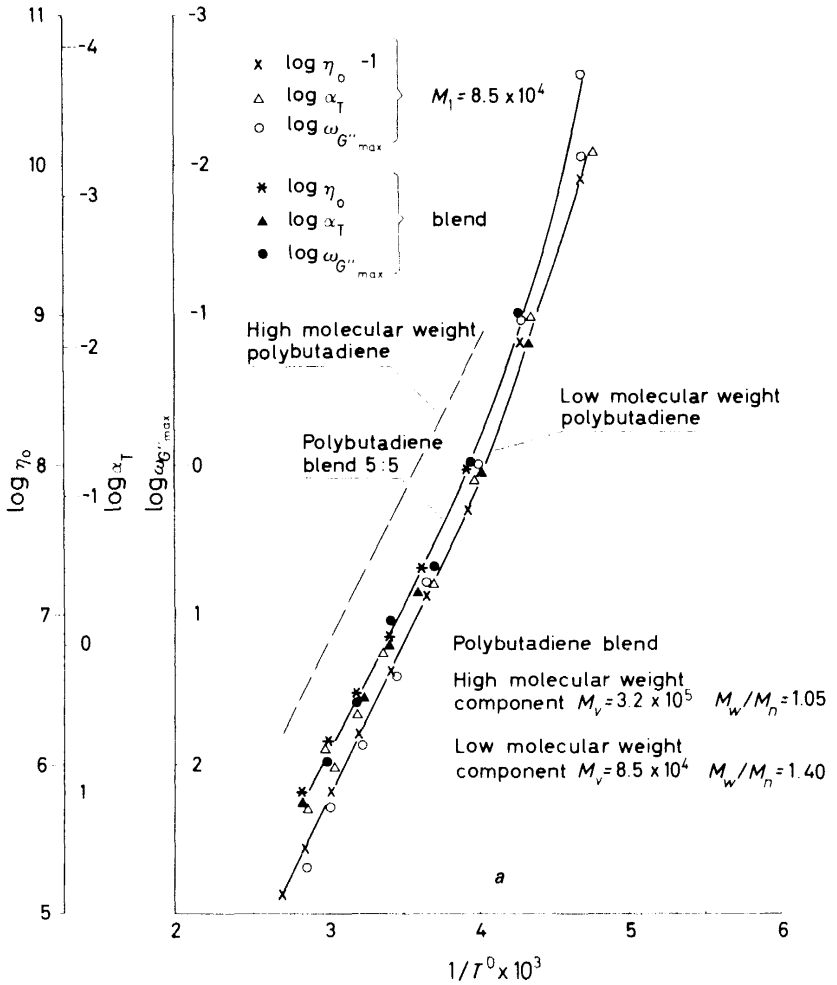


Figure 11. The temperature dependence of parameters characterizing the viscoelastic properties of polybutadienes and their binary mixtures containing equal fractions of the components: a - frequency corresponding to the maxima of the dependences of the loss modulus, initial viscosity and reduction coefficient; b - elasticity coefficient.

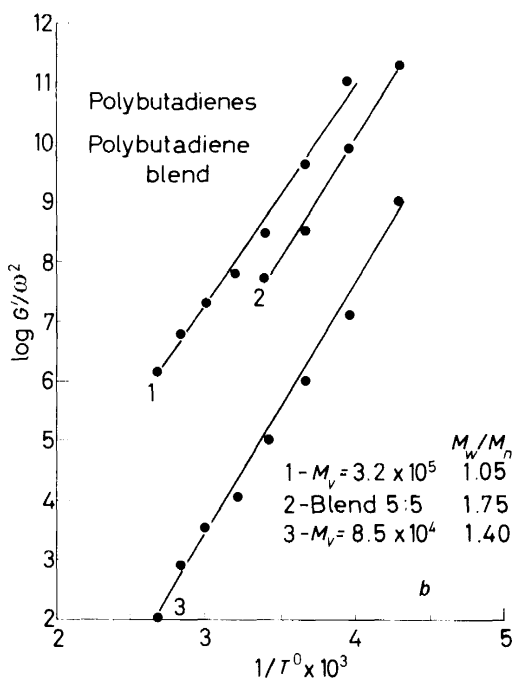
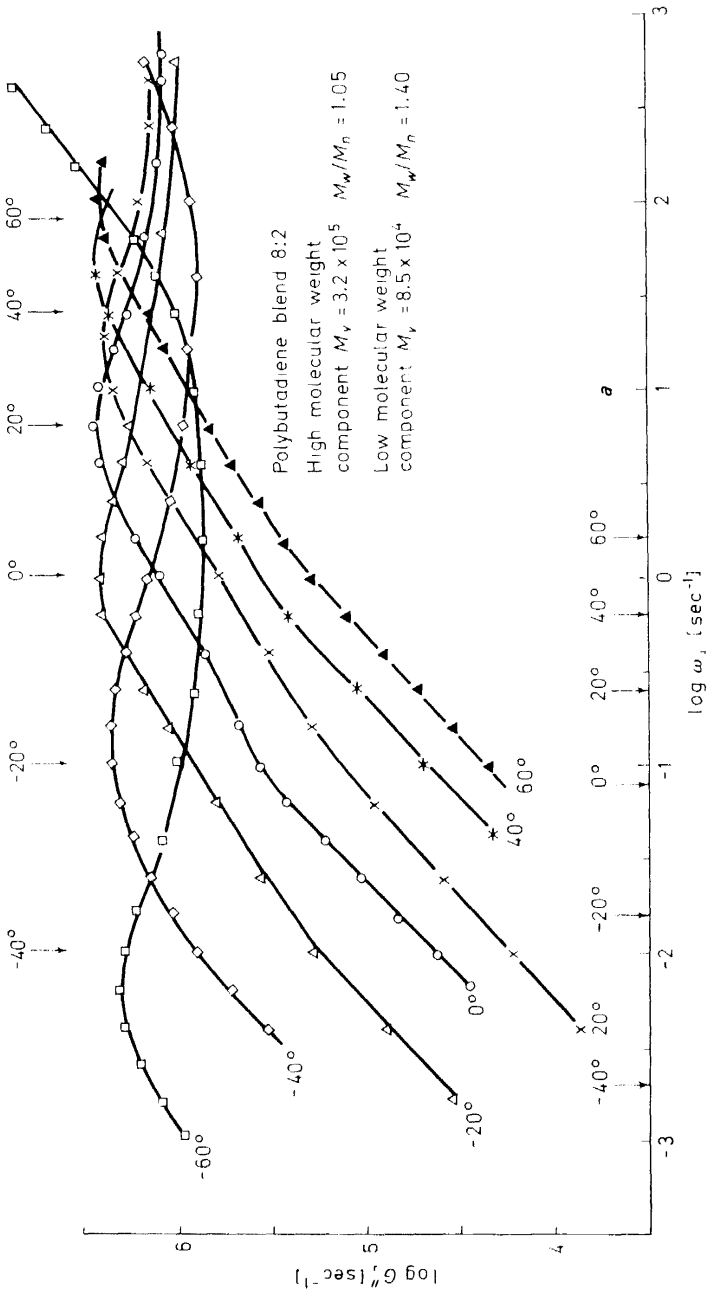


Figure 11—cont.

At a high content of the high-molecular-weight component when its transition to the high-elastic state in the mixture is sufficiently sharp (especially at elevated temperatures) one should expect the occurrence of a spurt at low shear rates corresponding to frequencies close to the value of $\omega_{G'_{\max}}$. The spurt due to the high-molecular-weight component, however, cannot be sharply pronounced since the system contains a low-molecular-weight component which is still in the fluid state, a circumstance that hampers the intensive development of wall slippage. To the transition to the high-elastic state of the low-molecular-weight component there must correspond a second spurt at a shear stress typical of a given polymer-homologous series. In the interval of shear stresses and rates between two spurts, a sharply pronounced anomalous viscosity should be expected to occur. Under these conditions of deformation there occurs the flow of the low-molecular-weight component filled with the high-molecular-weight component, whose mechanical loss is reduced since it is already in the high-elastic state.

The sharpness of the manifestation of a spurt in mixtures for the high-molecular-weight component depends on its content. It must increase with increasing difference of the molecular weights of the components.

When the concentration of the high-molecular-weight component decreases over a range of shear rates corresponding to the frequencies of the transition of both components to the high-elastic state, non-Newtonian flow of the



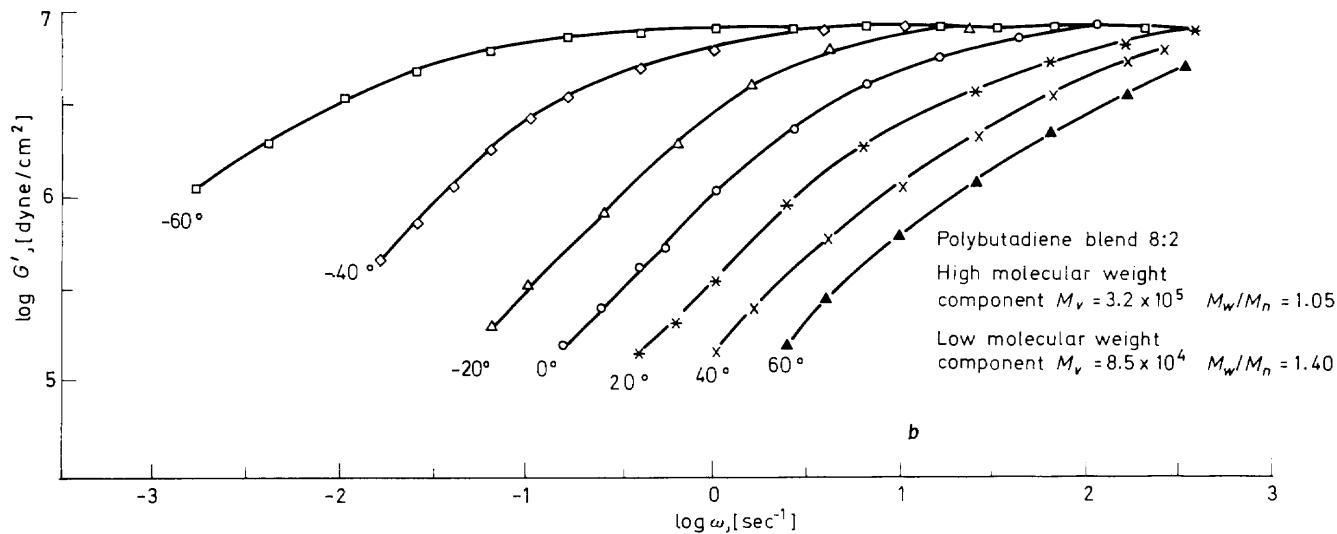


Figure 12. The frequency dependence of the components of complex modulus for a binary mixture of polybutadienes, containing 0.8 volume fractions of the lower-molecular-weight component: a—loss modulus; b—storage modulus.

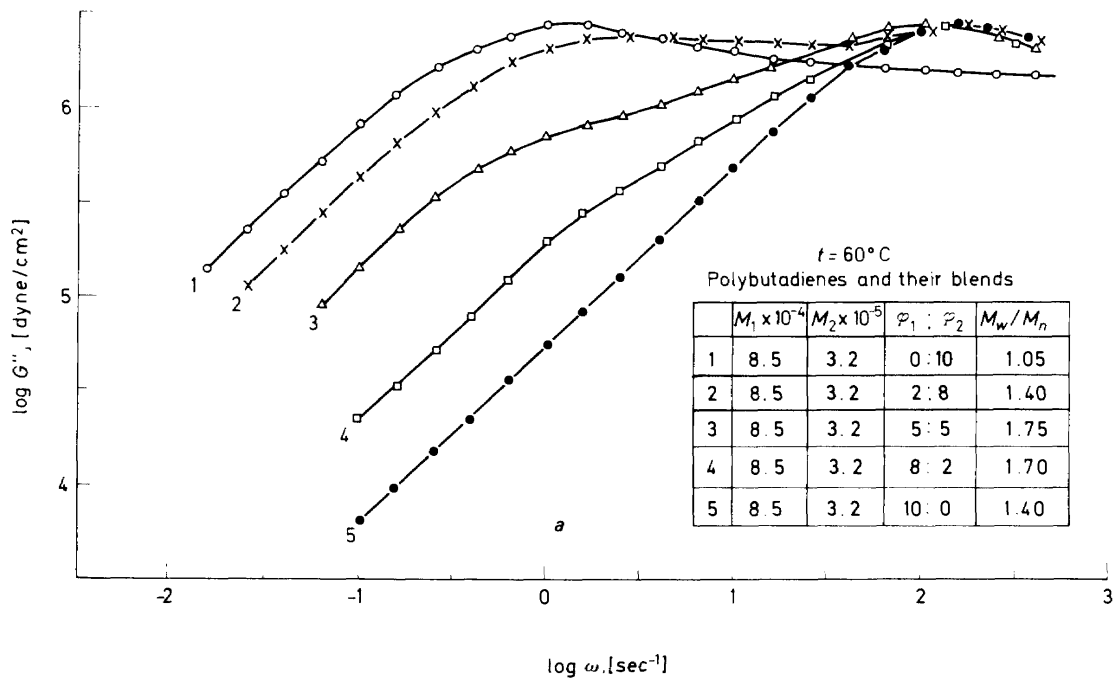


Figure 13. The frequency dependence of the loss modulus for high-molecular weight polybutadienes and their mixtures: a, b—loss modulus and relaxation spectrum at 60°C ; c, d—at -20°C .

INTERRELATION OF THE STRUCTURE OF POLYMERS

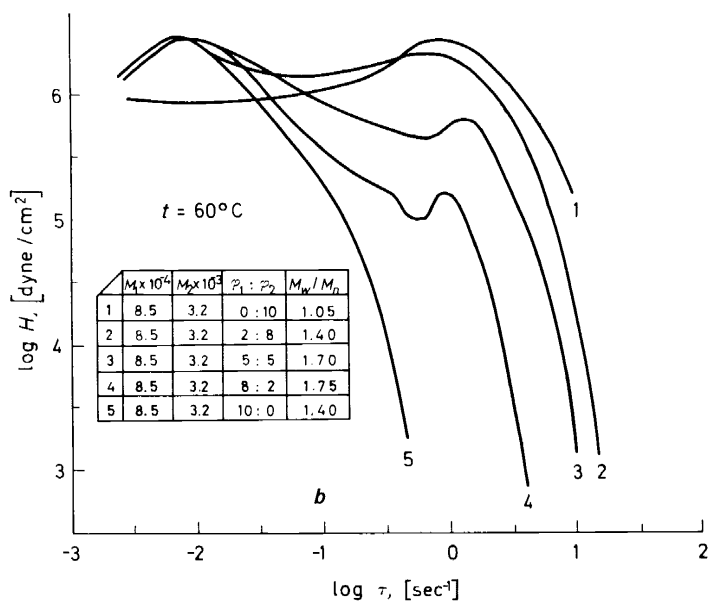


Figure 13—cont.

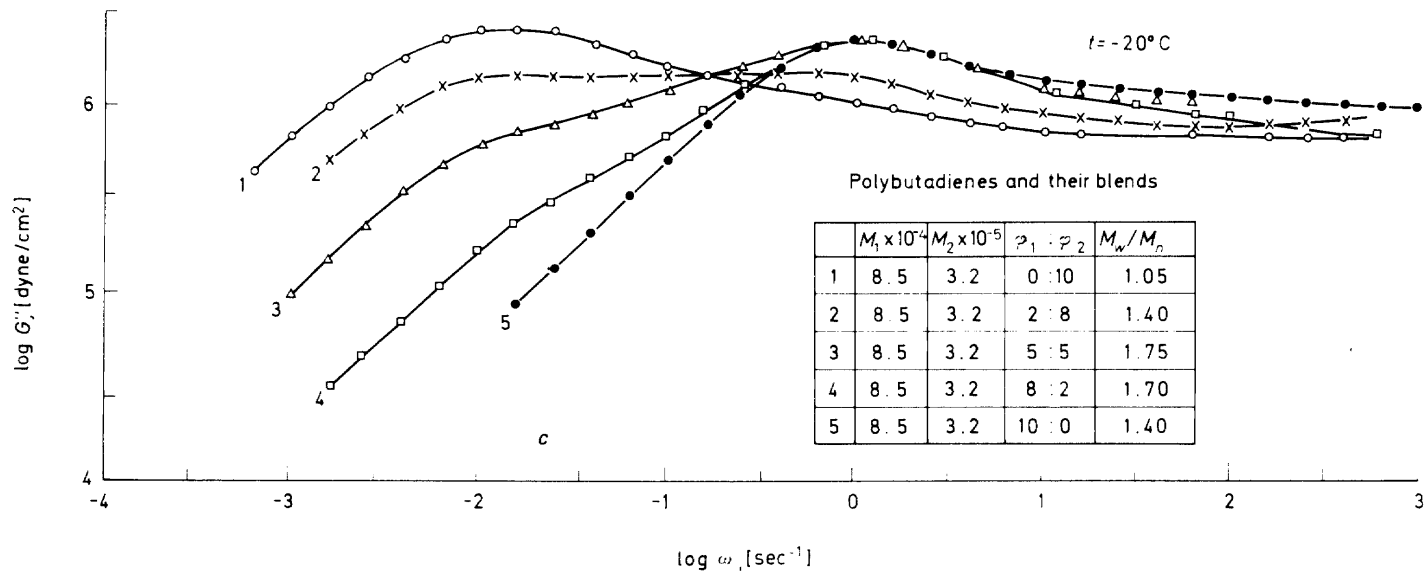


Figure 13—cont.

INTERRELATION OF THE STRUCTURE OF POLYMERS

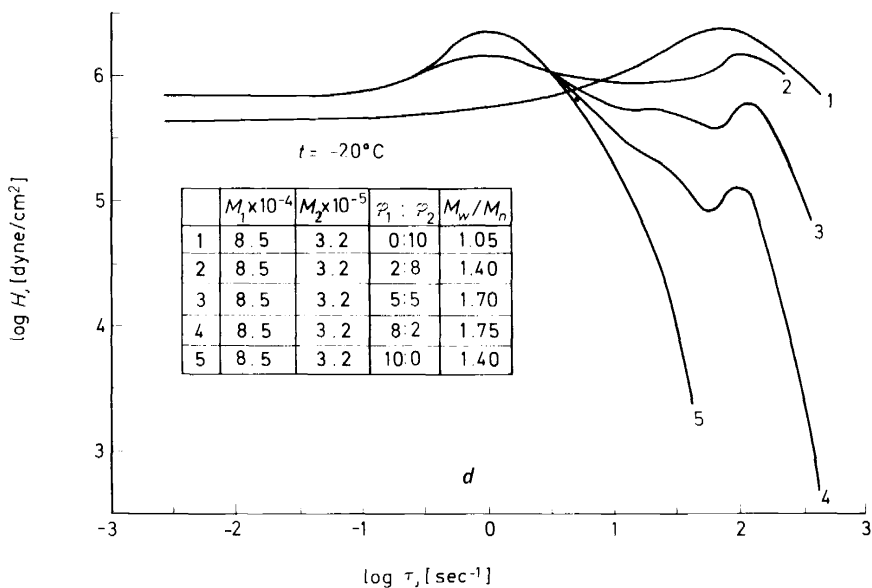


Figure 13—cont.

mixture must be observed. The most prominent anomalous viscosity may be expected at a ratio of the components close to 5:5 (Figure 13).

In the region of high content of the low-molecular-weight component, it exerts a predominating effect: anomalous viscosity is reduced and there arises a spurt at the rates of shear of the low-molecular-weight component.

What has been said above is in excellent agreement with the experimental results obtained by Borisenkova on a capillary viscometer (see Figure 14).

Moreover, the concept of the transition of the high-molecular-weight component to the high-elastic state when the low-molecular-weight component is still in the fluid state permits a quantitative estimation of the dependence of viscosity on shear rate up to the critical rate corresponding to the occurrence of a spurt. This approach is based on the simple idea of the additivity of losses as suggested by Malkin. And the meaning of this is as follows. With increasing frequency, after the maximum of the loss modulus is attained, the loss modulus is lowered, and this decrease may cover the range of several decimal orders of frequency. Hence, after the critical shear rate corresponding to the transition of the high-molecular-weight component to the high-elastic state is reached, with further increase of the rate of shear the dissipation losses caused by them will be reduced, which implies a decrease of viscosity under the conditions of steady flow. Thus, there arises a new concept concerning the nature of anomalous viscosity in polydisperse systems.

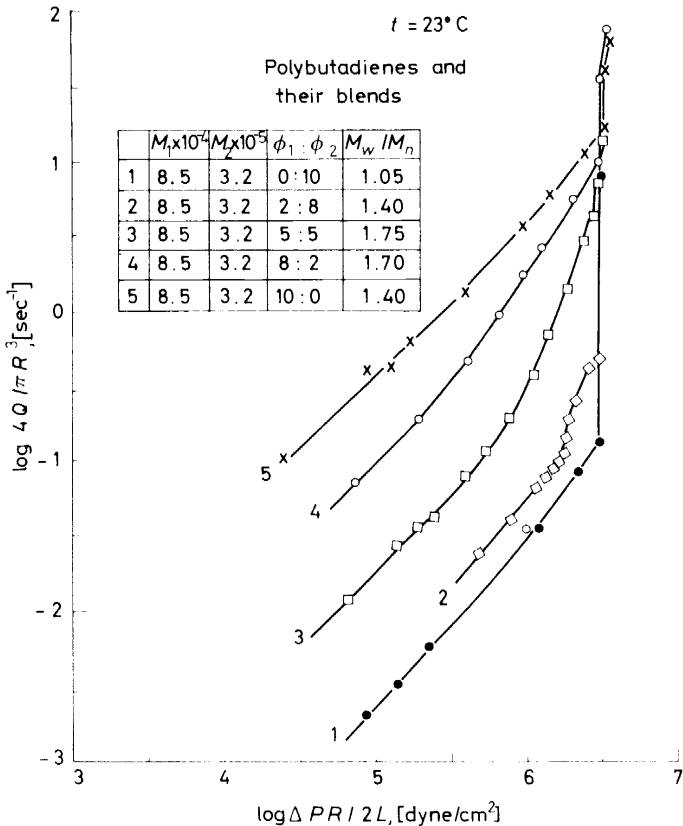


Figure 14. The dependence of apparent shear rate on shear stress on the capillary wall and the spurt effect for high-molecular-weight polybutadienes and their mixtures.

THE SPURT EFFECT AND THE DEFORMABILITY OF POLYMERS IN THE HIGH-ELASTIC STATE

The limits of steady flow régimes for high-molecular-weight linear polymers are determined by the spurt, which in its turn is caused by loss of adhesion to the solid surface and by wall slippage. There then arises a question of the possibility of suppression of wall slippage under the action of hydrostatic pressure. The experiments performed by Podolsky and Smirnova on a rotational viscometer show that the critical stress of the spurt does not vary and the spurt occurs with equal intensity at pressures of up to 600 atm. Since the application of pressure increases the initial viscosity, there will accordingly be observed a decrease of the critical shear rate—a phenomenon undesirable from the viewpoint of the processability of polymers.

Let us now dwell on the proof that only limited deformation values can be attained under the conditions of transition of polymer into the high-elastic state. The relevant experiments have been conducted by Isaev and

INTERRELATION OF THE STRUCTURE OF POLYMERS

Katsyutsevich on a rotational vibrorheometer, which can be used to subject polymers to cyclic deformations of various amplitudes.

The frequency dependence of the loss modulus at low amplitude for the polymers under investigation is shown in *Figure 15*. The arrow along the abscissa indicates the lowest frequency at which the experiments were conducted. This frequency corresponds to the high-elastic state of polymers or

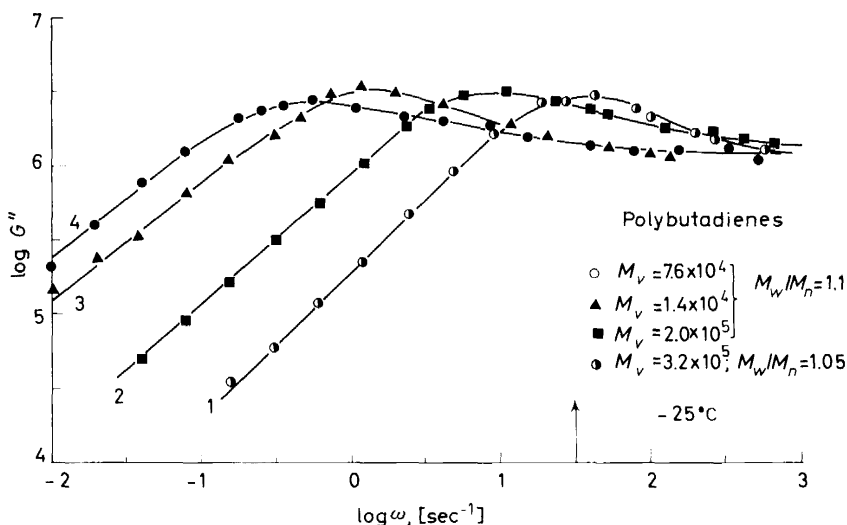


Figure 15. The frequency dependence of loss modulus for polybutadienes.

to their transition to this state (this refers to polybutadiene with a molecular weight of 7.6×10^4).

The results of experiments with higher amplitudes being specified are presented in *Figure 16*. From this figure it follows that at frequencies above 5 Hz there exists a critical deformation amplitude, above which the amplitude of shear stress decreases. The latter quantity is controlled by the detachment of the polymer from measuring surfaces. Under these conditions the bob and the external cylinder can be moved apart without any resistance offered by the polymer. It is essential that the value of critical amplitude of deformation is only 25 per cent, whereas under the deformation conditions prior to the spurt the high-elastic deformation alone may go beyond 150 per cent.

The results of experiments on high-amplitude deformation of polybutadienes presented in *Figure 16* is of great interest from another point of view, too. If under the influence of cyclic large-amplitude deformation the polymer is torn away from the bounding surfaces, this means that it will offer a low resistance to shear in the axial direction. Thus, by specifying the vibration régime of rotation of one of the surfaces that confine the polymer within the concentric clearance it can be brought to a spurt. Then, under the pressure acting in the axial direction the polymer will be pushed from the

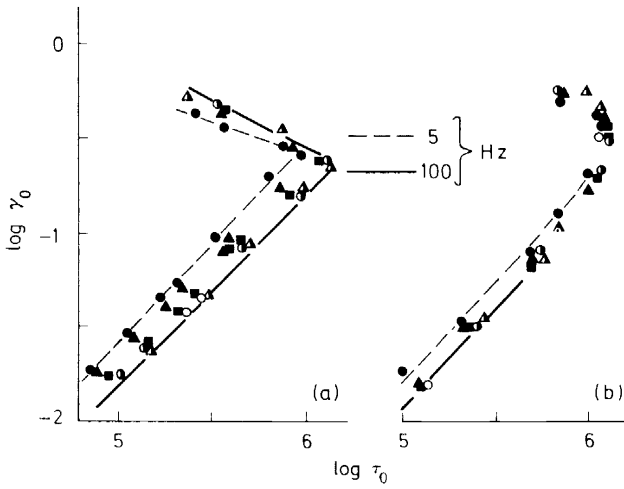


Figure 16. The dependence of the deformation amplitude on the amplitude of shear stress: a—molecular weight 7.6×10^4 , b—molecular weight 3.2×10^4 .

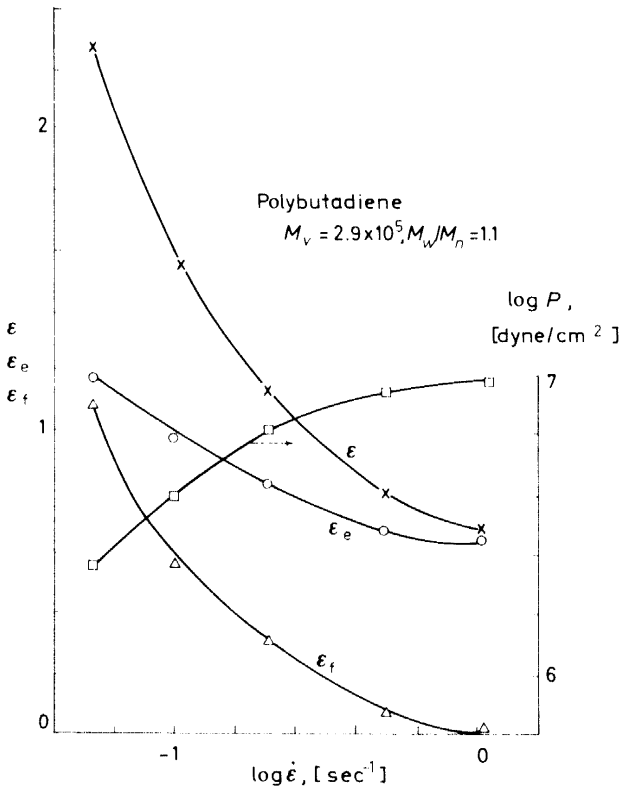


Figure 17. The dependence of true stress (ϵ), irreversible (ϵ_t) and reversible (ϵ_e) deformations on the rate of deformation in uniaxial extension.

concentric clearance with a low resistance and high velocity. There is another circumstance which is also essential. It is known that under the conditions of spurt the stream of polymer has a regular undistorted shape. The processability of polymers under spurt conditions may therefore be of interest not only from the point of view of acceleration of their flow but also in respect of the structure of extruded polymers.

The estimation of the deformability of high-molecular-weight polymers in uniaxial extension deserves attention. The relevant data obtained by Volosevich are given in *Figure 17*. From this figure it is seen that with increasing rate of deformation the possibility of accumulation of both irreversibility and reversible deformations falls rapidly and at stresses corresponding to the spurt under the shearing conditions in uniaxial extension at the initial stage of deformation the samples undergo rupture.

POLYMER SOLUTIONS

How does the introduction of solvents and oligomers into high-molecular-weight linear polymers affect their rheological properties and the effects considered above? The relation between the basic parameters characterizing the viscoelastic properties of concentrated solutions (depending on the molecular weight of the polymer with its volume fraction being higher than 0.1–0.3), based on the data obtained in our laboratory²⁰, is presented in *Table 1*. Note that here H_{\max} is the maximal value of the function which describes the relaxation spectrum of the polymeric system in the region of the terminal zone and the high-elasticity plateau.

For flexible-chain polymers of the polybutadiene type the effect of the solvent on the viscoelastic properties of concentrated solutions is insignificant²¹.

As the concentration of polymer is decreased the network density of macromolecules is also diminished. In this way the change of the density is facilitated under the influence of deformation. Consequently, anomalous viscosity becomes more prominent. Its occurrence is shifted to the side of lower shear stresses and rates (by a square law, depending on the concentration).

In the case of concentrated solutions, just as for bulk polymers, with increasing rate of deformation there is observed a transition to the high-elastic state. It is accompanied by the spurt effect and by the reduction of dissipation losses for the components of the polymeric system that have already passed into the high-elastic state. This transition and the development in the polymeric system of non-Newtonian flow are relaxation processes. For concentrated polymer solutions these processes are governed by a certain characteristic (for example, maximal) relaxation time. Such a characteristic relaxation time or a spectrum of characteristic times can therefore be used for a model description of the non-Newtonian behaviour of polymeric systems. By the molecular mechanism, the phenomena of anomalous viscosity caused, on the one hand, by the decrease of the network density and, on the other, by the reduction of dissipation losses upon transition of the polymer to the high-elastic state, are essentially different. It is necessary that the two mechanisms be taken into account. The complexity of the problem consists

Table 1. Effect of concentration and molecular weight of high-molecular-weight linear polymers of narrow distribution on the viscoelastic properties of their concentrated solutions

$$A_{G,0} = \lim_{\omega \rightarrow 0} \frac{G'}{\omega^2} \sim C^8; A_{G,0} \sim M^7$$

$$G_0 = \lim_{\omega \rightarrow 0} \frac{(G'')^2}{G} \sim C^2, G_0 - \text{independent of molecular weight}$$

$$\eta_0 \sim C^5; \eta_0 \sim M^{3.5}$$

$$\left. \begin{array}{l} G''_{\max} \sim C^2; G''_{\max} - \\ G'_{pl} \sim C^2; G'_{pl} - \end{array} \right\} \text{independent of molecular weight}$$

$$G'_{pl}/G''_{\max} = 2.5$$

$$\omega_{G''_{\max}} \sim C^{-2}; \omega_{G''_{\max}} \sim M^{-3.5}$$

$$\theta_{\max} = \frac{\eta_0}{G_0} \sim C^2; \theta_{\max} \sim M^{-3.5}$$

$$H_{\max} \sim C^2; H_{\max} - \text{independent of molecular weight.}$$

in the assessment of their relative role since with decreasing polymer concentration, even when the occurrence of the transition of the polymer to the high-elastic state is doubtless, this transition in the case of solutions cannot be as sharp as for the bulk polymer. Associated with this problem is another one, which is no less important.

For low-concentration solutions of high-molecular-weight polymers there can be obtained S-shaped flow curves having two branches of Newtonian flow. As the polymer concentration decreases, however, the transition from the non-Newtonian flow to the spurt becomes smoother and, just as in the case of bulk polymers, at high outputs, there is observed a flow of the polymeric system in the duct outwardly similar to the upper Newtonian branch of flow curves. But this resemblance is misleading, since no laminar flow of polymeric systems occurs under the conditions of spurt²². Hence, from the shape of the dependence of the output on the pressure drop in the duct one cannot draw a conclusion about the nature of the deformation of the polymeric system. A study into the structure of the flow of polymer solutions is probably needed in order to obtain criteria for differentiation between the two cases considered above.

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