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Influence of Vibrations on the Viscoelastic Behavior of Monodisperse Polybutadienes

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The viscoelastic behavior of monodisperse polybutadienes is studied at different amplitudes of cyclic deformation. The concept of initial relaxation spectrum is introduced, this spectrum corresponding to small amplitudes. Under the action of high amplitudes the relaxation spectrum changed. This changed-effective spectrum can be calculated by means of the linear theory of viscoelasticity.

The initial spectra of monodisperse polybutadienes have maxima. Under the action of high amplitudes the long-time parts of the spectra are truncated and the maxima shift into the short-time regions. There is an unambiguous correspondence between the amplitude of the deformation rate on cyclic deformation and the rate of shear on continuous deformation.

It is shown that the length of the high-elasticity plateau, estimated on a logarithmic scale of relaxation times, and the maximum relaxation times of polybutadienes, as well as their initial Newtonian viscosities are dependent on molecular weight to a power of 3.6. The apparent viscosity is calculated, making use of the approximate initial relaxation spectrum concept, the law of change of its long-time boundary with the shear rate and the commonly known relation of the linear theory of viscoelasticity. The results of these calculations were found to agree approximately with the data obtained under conditions of continuous deformation.

INTRODUCTION

The viscoelastic properties of polymers depend largely on their molecular weight and molecular-weight distribution.^{1,2} References 3-6 reported studies of viscoelastic behavior of practically monodisperse polymers and narrow

polymer fractions during cyclic deformation at small amplitudes (when the viscoelastic characteristics are functions only of the frequency of vibration). Besides, the viscoelastic properties of monodisperse poly- α -methylstyrene, determined from experiments in stress relaxation on extension were described in Ref. 7.

Of considerable interest is a systematic investigation of the viscoelastic properties of monodisperse polymers of different molecular weights both at low deformation amplitudes and at such amplitudes of deformation which affect the viscoelastic properties of the polymers.⁸ This makes it possible to determine a fundamental mechanical characteristic, namely the relaxation spectra of monodisperse polymers of different molecular weights and how they vary with increasing deformation amplitude. Besides, it was interesting to try out the method suggested in Ref. 9 for calculating viscoelastic characteristics, which are usually determined during continuous deformation at steady-state flow regimes. This method requires knowledge of how the relaxation spectrum varies with increasing amplitude upon cyclic deformation and is based on the fact that the boundaries of the relaxation spectrum depend unambiguously on the rate of deformation.

EXPERIMENTAL

Viscoelastic characteristics during cyclic deformation were measured with a vibrorheometer¹⁰ and a frequency rheometer¹¹ operating on the principle of electromagnetic transducer.¹ Measurements with the vibrorheometer operating under conditions of forced vibrations were carried out at frequencies ranging from 6 to 110 Hz. A sinusoidal vibration regime was maintained throughout the whole range of deformation amplitudes. Results were treated by the method suggested by Markovitz and coworkers.^{12,13} Frequency rheometer measurements were made in the frequency range 3×10^2 to 2×10^3 Hz. The results of these experiments were processed on an electronic computer (EC).

The complex dynamic viscosity $\eta^* = \eta' - i\eta''$ was determined where, as usual, η' is the real component or the so-called dynamic viscosity and η'' is the imaginary component. Measurements were made at different cyclic deformation amplitudes γ_0 and circular frequencies $\omega = 2\pi f$, where f is the frequency of vibration. The amplitude of rate of deformation $\dot{\gamma}_{\max} = \gamma_0 \cdot f$ was estimated from γ_0 . The value of η^* was used to calculate the complex shear modulus $G^* = \eta^* \times i\omega = G' + iG''$ and its components: the storage modulus G' and the loss modulus G'' .

Simultaneously with the dynamic characteristics we determined the apparent viscosity $\eta = \tau/\dot{\gamma}$ where τ and $\dot{\gamma}$ are the tangential stress and shear rate,

respectively. The measurements were made with the capillary viscometer described in Ref. 14, all experiments being carried out at 22°C.

In this work shear rates and circular frequencies were assumed to be equivalent. The very good correlation of apparent viscosity and absolute value of complex dynamic viscosity is taken into consideration.

POLYMERS

The objects of study were polybutadiene samples characterised by the data of Table I.

TABLE I
Characteristics of polybutadienes

Sample No.	M_w	M_w	ρ_{26}	Microstructure		
		M_n		<i>cis</i>	<i>trans</i>	1,2
1	3.8×10^4	1.22	0.895	45	45	10
2	6.75×10^4	1.2	0.895	44.5	41.5	14
3	1.02×10^5	1.1	0.895	44	42	14
4	1.43×10^5	1.1	0.895	47.2	44	8.8
5	2.4×10^5	1.1	0.895	45.2	45.6	9.2

RESULTS AND DISCUSSION

Figure 1 shows the dependence curves of the absolute values of the complex dynamic viscosity on the amplitude of rate of deformation at various frequencies of vibration (set of curves 1) and on the frequency of vibration in the region of amplitude values where the complex viscosity is independent of them (curves 2). It is evident from the figure that at definite amplitude deformation rate and fixed frequency the $|\eta^*|$ vs. $\dot{\gamma}_{\max}$ curves for each polybutadiene emerge onto an envelope shifted along the abscissa axis relative to curve 2 by the value $\log a$, i.e. $\log \dot{\gamma} = \log \omega = \log \dot{\gamma}_{\max} + \log a$.

The curves presented in Figure 1 are analogous to similar dependencies described earlier in Refs. 8,9 for polyisobutylene and polypropylene.

To explain the shift of the dependence $|\eta^*|$ vs. $\dot{\gamma}_{\max}$ relative to $|\eta^*|$ vs. ω consider the relation between $\dot{\gamma}_{\max}$ and ω . The envelope of the $|\eta^*|$ vs. $\dot{\gamma}_{\max}$ curves at different ω is attained when $\dot{\gamma}_{\max}$ reaches its critical value $\dot{\gamma}_{\max}^{\text{cr}}$. These critical values were also determined as described in Ref. 8. The critical values of the deformation rate amplitudes equal $\gamma_0^{\text{cr}} \cdot f$, which in their turn are equal to $\gamma_0^{\text{cr}} \omega / 2\pi$, where γ_0^{cr} are the critical deformation amplitudes, corresponding to emergence of the $|\eta^*|$ vs. $\dot{\gamma}_{\max}$ curves onto the envelope.

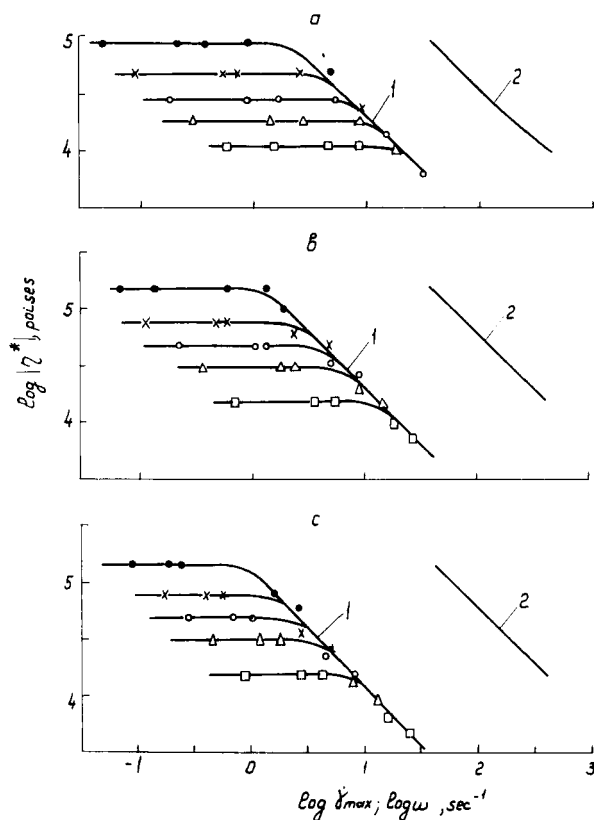


FIGURE 1 Absolute value of complex dynamic viscosity $|\eta^*|$ vs. deformation rate amplitude $\dot{\gamma}_{\max}$ at different frequencies (curve sets 1) and on frequency ω at small deformation amplitudes (curves 2): a, b, and c—samples Nos. 2, 3, and 4, respectively. Frequency, ω (sec^{-1}): ●—40, ×—80; ○—125; △—200; □—400.

The values of γ_0^{cr} depend little on the frequency (they vary by 8 percent over the range of frequencies used) and may approximately be assumed constant. Hence, the value $\gamma_0^{\text{cr}}/2\pi \approx \text{const} = a$. Therefore, $\dot{\gamma}_{\max}^{\text{cr}}$ is proportional to the circular frequency ω , but not equal to it. The curve of $|\eta^*|$ vs. $\dot{\gamma}_{\max}$ is shifted along the abscissa axis relative to the $\log |\eta^*|$ vs. $\log \omega$ by exactly the values $\log a$, which are given in Table II for the polybutadiene samples under discussion. The quantity a is an important characteristic of the viscous properties of a polymer, because it determines the boundary of the deformation rate amplitudes at which the complex viscosity becomes dependent upon it. With increasing molecular weight this boundary shifts towards lower values of $\dot{\gamma}_{\max}$ because with higher molecular weight samples the viscosity anomaly is displaced at lower shear rates.

TABLE II
Values of E_{cr} and a for different polybutadienes

M_w	6.75×10^4	1.02×10^5	1.43×10^5
E_{cr} , erg/cm ³	1.42×10^6	8.31×10^6	3.23×10^6
$\log a$	1.2	1.5	1.66

It is possible to calculate the work of deformation, corresponding to the transition from the horizontal sections of curves I to the envelopes:

$$E_{cr} = 4\pi^3 |\eta^*| (\dot{\gamma}_{max}^{cr})^2 \omega^{-1} \quad (1)$$

It should be noted here that for each polymer E_{cr} is invariant (to an accuracy of 13 percent) relative to the regimes of cyclic deformation. The E_{cr} values obtained for polybutadiene samples of different molecular weights are listed in Table II. It is important that E_{cr} decreases with increasing molecular weight. This is due to the fact that at a given deformation rate amplitude the anomaly viscosity is higher for higher molecular weight samples, i.e. the ratio of the initial Newtonian viscosity to the viscosity determined at a given $\dot{\gamma}_{max}$ is higher.

Figures 2 and 3 present the dependencies of storage modulus G' on deformation rate amplitude at various vibration frequencies and on frequency at various deformation rate amplitudes, respectively. Figure 3 also contains data obtained on a frequency rheometer with electromagnetic transducer

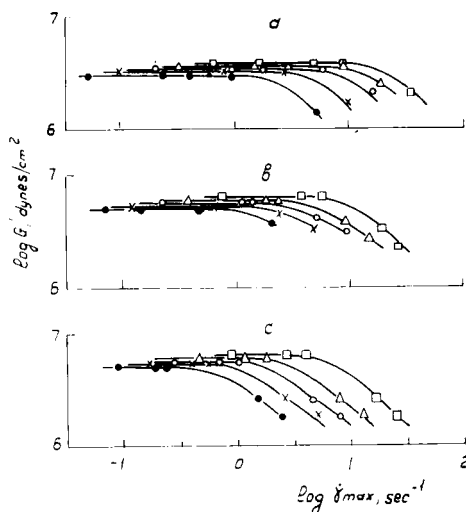


FIGURE 2 Storage modulus G' vs. deformation rate amplitude $\dot{\gamma}_{max}$ at different frequencies. Symbols have the same meaning as in Figure 1.

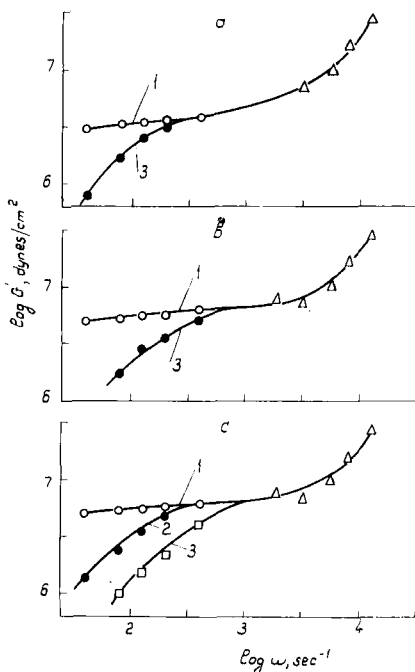


FIGURE 3 Storage modulus G' vs. frequency ω . Curve 1—small deformation amplitudes; curves 2 and 3—deformation rate amplitudes 3.16 and 10 sec^{-1} , respectively.

(open triangles). Curve 1 in Figure 3 refers to the G' values obtained at low amplitude, which do not affect G' . Curves 2 and 3 were obtained at high deformation rate amplitudes. It is evident from the figure that at these amplitudes of deformation rates the low-frequency part of the G' vs. ω dependencies are truncated. Since $\log \dot{\gamma} = \log \omega = \log \dot{\gamma}_{\max} + \log a$, it may be accepted that curves 2 and 3 give the dependence of G' on the corresponding values of shear rates on continuous deformation.

Figure 4 shows the frequency dependence of the loss modulus G'' calculated from experiments at continuous deformation from the data of capillary viscometry, it being known that at flow conditions close to Newtonian $\tau = G''$. The validity of this procedure was confirmed by direct experiments with polybutadiene sample No. 1. The corresponding data are represented in Figure 4 by open circles.

Using the method of Ninomiya and Ferry¹⁵ the relaxation time distribution functions $H_{\text{in}}(\theta)$ were calculated from the G' vs. ω and G'' vs. ω dependencies for the region of low amplitudes, where G' and G'' are independent of them. By analogy with the concept of initial viscosity, which is independent of the

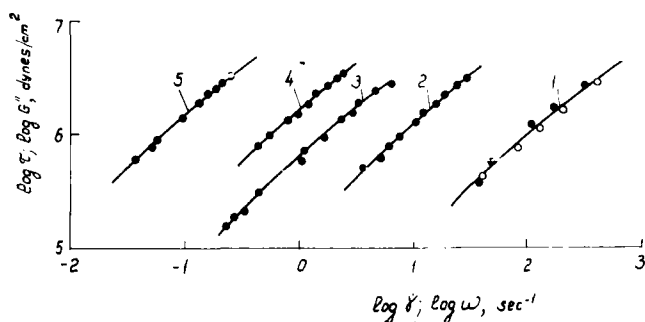


FIGURE 4 Shear stress τ vs. shear rate $\dot{\gamma}$ and loss modulus G'' vs. circular frequency ω . Curves 1–5—samples Nos. 1–5, respectively. ● and ○—continuous and cyclic deformation respectively.

rate of shear in the region of its low values, the relaxation time spectra in question may also be termed initial. The effective relaxation spectra $H_e(\theta)$, given by the characteristics of polybutadienes, determined at different values of $\dot{\gamma}_{\max}$ and corresponding rates of continuous deformation, were calculated in the same way as the initial spectra.

Figure 5 presents the initial relaxation spectra of monodisperse polybutadienes, these being a set of curves with an envelope. The envelope corresponds to the initial relaxation spectrum of the polybutadiene with highest molecular weight of those studied. Three regions can be distinguished on the H_{in} vs. θ curves: a long-time region corresponding to the region of flow, a short-time region corresponding to that of the glass transition, and the region of the high-elasticity plateau situated between them. In the high-elasticity plateau region the relaxation time distribution function has a minimum and a maximum, beginning from definite molecular weights. The length of the high-elasticity plateau on the relaxation time scale decreases with decreasing molecular weight. This occurs predominantly due to the shift of the long-time part of the spectrum towards smaller relaxation times, so that the change in relaxation spectra with decreasing molecular weight is outwardly similar to the effect of relaxation spectrum truncation under the influence of deformation at different shear rates.^{8,16}

From the data shown in Figure 5 the dependence of the length of high-elasticity plateau on the molecular weight of polybutadiene can be plotted. To estimate the high-elasticity plateau length from the $\log H_{in}$ vs. $\log \theta$ dependence curves tangents with equal angular coefficients are drawn to these curves at the transition from the high-elasticity plateau to the regions of fluidity and of glass transition. Then the length of the plateau is estimated by the value of $\Delta \log \theta$ as is shown schematically in Figure 5. Usually tangents with an angular coefficient of $-\frac{1}{2}$ are drawn. However, for polymers with

very narrow molecular weight distributions the transitions from the high-elasticity plateau to the fluidity and glass transition regions are much steeper than for polydisperse polymers. This makes it inconvenient to use an angular coefficient of $-\frac{1}{2}$. The boundaries of the transitions to the fluidity and glass-transition regions for polybutadienes were determined with tangents at angular coefficients varying from $-\frac{1}{2}$ to -3 . The corresponding data on the length of high-elasticity plateau $\Delta \log \theta$ as a function of $\log M_w$ are represented in

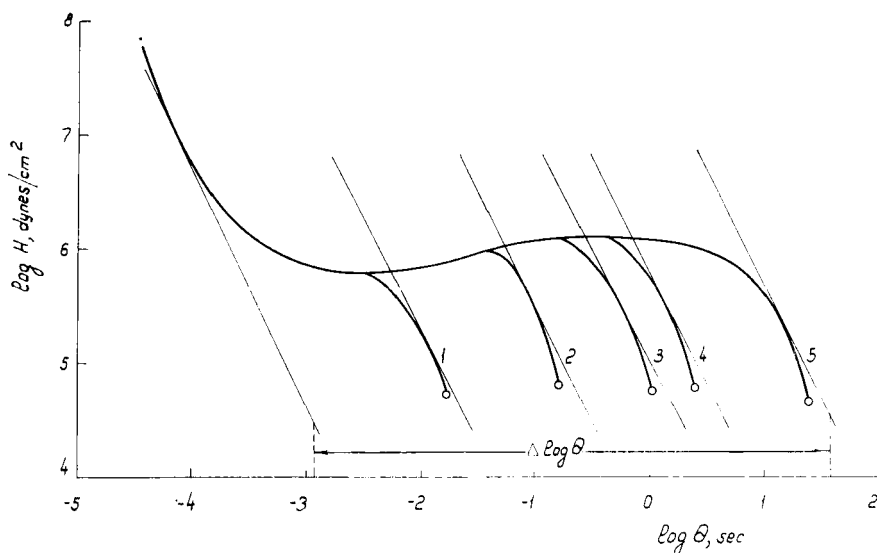


FIGURE 5 Initial relaxation spectrum of monodisperse polybutadienes. Curves 1-5—samples Nos. 1-5, respectively.

Figure 6. It is evident from this figure that the length of the high-elasticity plateau depends little on the choice of angular coefficient of the tangents. This choice has no effect on the angular coefficient of the dependence of the high-elasticity plateau length on $\log M_w$, which equals 3.6. According to Ref. 1 this angular coefficient should be 2.4. However, as has been indicated in the paper,⁷ such dependencies have been obtained experimentally with the angular coefficient 3.4. Below, use is made of data obtained by drawing tangents to the curves in Figure 5 with an angular coefficient of -2 . Extrapolation of the $\Delta \log \theta$ vs. $\log M_w$ dependence to a zero value of $\Delta \log \theta$ gave the molecular weight at which the high-elasticity plateau forms as being $M_w = 1.4 \times 10^4$. The average molecular weight of the network chain between entanglement nodes determined from the simple dependence

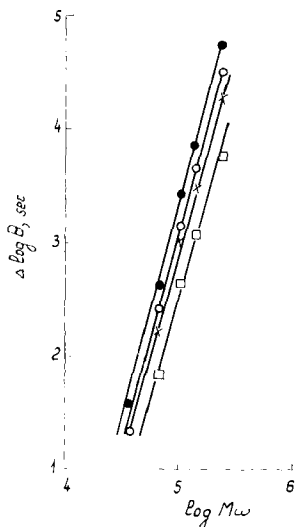


FIGURE 6 Dependence of length of high-elasticity plateau on molecular weight according to relaxation spectra presented in Figure 5. Angular coefficients of tangents: $\bullet = -\frac{1}{2}$; $\times = -1$; $\circ = -2$; $\square = -3$.

$M_e = \rho RT(G')^{-1}$, equals 3.5×10^3 . It follows from this that the high-elasticity plateau for the polybutadiene samples in question appears when $M_w \simeq 4M_e$.

The initial Newtonian viscosities $\eta_{\max} = \lim \eta|\dot{\gamma} \rightarrow 0$ can be calculated by making use of the initial relaxation spectra. According to Ref. 1 for the case of stationary flow, i.e. when $\omega \rightarrow 0$

$$\eta_{\max} = \int_0^{\infty} H_{in}(\theta) d\theta \quad (2)$$

The value of η_{\max} calculated from Eq. (2) for monodisperse polymers of different molecular weight differed from those measured experimentally by capillary viscometry by not more than 20 percent.†

Figure 7 shows the dependencies of the initial Newtonian viscosity on the molecular weight of polymer, namely $\eta_{\max} = cM_w^n$, where $n = 3.6$. The same figure presents molecular weight dependence of the maximum relaxation times θ_0 determined from the initial relaxation spectra of the polymers (open circles in Figure 5). The θ_0 vs. M_w dependence also has an angular coefficient of 3.6. As is known,^{18,19} the dependence of $\log \eta_{\max}$ on $\log M_w$ has a break corresponding to the critical molecular weight M_w^{cr} . If we assume that the

† All numerical calculations from spectra, given in this paper, were carried out by EC.

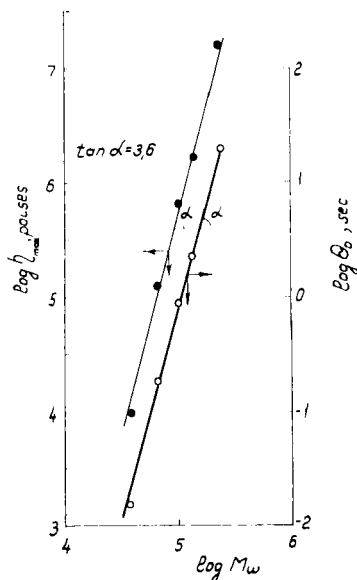


FIGURE 7 Dependence of initial Newtonian viscosity and greatest relaxation time on molecular weight.

η_{\max} vs. M_w dependence is symbatic with θ_0 vs. M_w in the region of lower M_w values than shown in Figure 7 as well, this means that the critical molecular weight should correspond to the critical value of θ_0 . In this case the sharp increase in viscosity observed experimentally at molecular weight values above critical could be attributed to the sharp increase in maximum relaxation times of polymers at $M_w > M_w^{cr}$.

Now let us consider the changes in the initial relaxation spectra of polymers when they are deformed at different $\dot{\gamma}_{\max}$ or corresponding shear rates under continuous deformation. This is shown in Figure 8, from which it is evident that under the action of considerable shear rates a peculiar change occurs in the initial relaxation spectrum of the monodisperse polymer. This change consists in truncation of the long-time part of the spectrum and a shift of the maximum into the region of smaller relaxation times. It is essential that the maxima of the effective relaxation spectra are higher than those of the initial ones. The possibility of such a change in the initial relaxation spectrum in the region of the high-elasticity plateau had been apprehended previously in Ref. 17. Evidently a maximum should be observed on the effective relaxation spectra of polymer systems for polymers whose initial relaxation spectra also have a maximum.

Figure 9 presents the dependencies of apparent viscosity vs. shear rate (black circles) and of absolute complex viscosity vs. circular frequency at

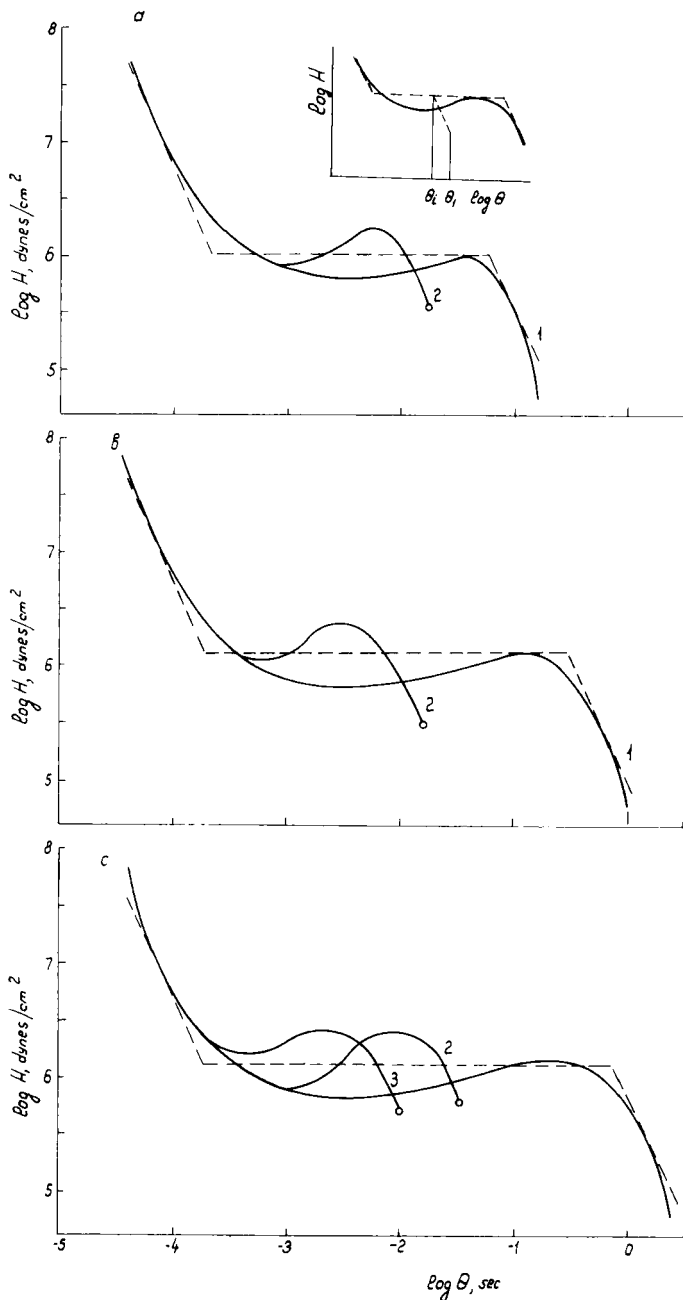


FIGURE 8 Initial (curve 1) and effective (curves 2 and 3) relaxation spectra of monodisperse polybutadienes. a, b, and c—samples Nos. 2, 3, and 4, respectively. Curves 2a, 2b, 2c, and 3c correspond to the shear rates. $\dot{\gamma}$ (sec⁻¹): 160, 316, 145 and 460.

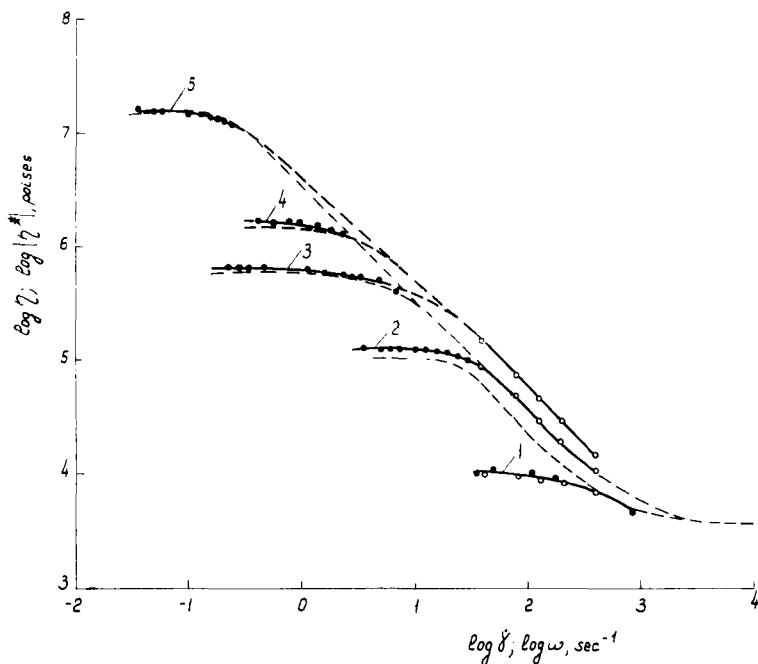


FIGURE 9 Dependence of apparent viscosity on shear rate and absolute value of complex dynamic viscosity on frequency at small deformation amplitudes. Curves 1–5—samples Nos. 1–5, respectively. ● and ○—continuous and cyclic deformation, respectively (see also text).

small deformation amplitudes (open circles). The regions of experimentally measured η and $|\eta^*|$ values are shown by solid lines. The thick dashed line represents supposed apparent viscosities in the region where measurement of η is impossible for reasons which will be indicated below. The thin dashed lines show the dependencies of apparent viscosity vs. shear rate, calculated by the method suggested in the Ref. 9. Use was made of the relation

$$\eta = \int_0^{\theta_1} H_{in}(\theta) d\theta \quad (3)$$

The upper limit in Eq. (3) is selected as shown schematically in the upper part of Figure 8. For a given i th value of shear rate on continuous deformation a secant is drawn parallel to the long-time part of the spectrum, approximated by a trapezoid. Then on the secant corresponding to the i th shear rate the value $\theta_1 = 2.8 \theta_i$ is found. The transition coefficient of 2.8 was found in Ref. 9.

The apparent viscosities η found from Eq. (3) differ by not more than

60 percent from the experimental values of $|\eta^*|$ measured as a function of ω . This difference is due to the rather rough approximation of the spectrum.

The dependence of the apparent viscosity on shear rate can also be calculated directly from the effective relaxation spectra $H_e(\theta)$ presented in Figure 8. For this purpose we used the relation

$$\eta = \int_0^{\theta_2} H_e(\theta) d\theta, \quad (4)$$

where θ_2 is the greatest relaxation time on the effective relaxation spectra at the assigned deformation rate (open circles in Figure 8). These calculations are illustrated in Figure 9 by a dash-dot curve. Comparison of these values of η vs. $\dot{\gamma}$ with the absolute value of complex viscosity $|\eta^*|$ vs. ω showed that for polybutadiene samples 3 and 4 the calculated values of η vs. $\dot{\gamma}$ was 60 percent higher than those of $|\eta^*|$ vs. ω measured experimentally. For polybutadiene sample 2 the values of η and $|\eta^*|$ coincided. The disagreement between η vs. $\dot{\gamma}$ and $|\eta^*|$ vs. ω observed for high-molecular polybutadiene samples is probably related to the fact that at high deformation rate amplitudes, as well as at high shear rates under conditions of continuous deformation the monotonic nature of η vs. $\dot{\gamma}$ is disturbed. Indeed, according to the data of capillary viscometry there is a sharp break in the flow curve, so that when certain shear stresses are reached the discharge increases jumpwise. On cyclic deformation at high amplitudes the high molecular weight samples come away from the measuring surfaces. However, these phenomena deserve special study. Here it should be noted that the method suggested in Ref. 9 for polydisperse polymers can be used for approximate calculation of the dependence of the apparent viscosity of monodisperse polybutadienes on shear rate.

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