EFFECTS OF VIBRATION ON THE VISCOELASTIC BEHAVIOR OF MONODISPERSE POLYBUTADIENES

G. V. Vinogradov, Yu. G. Yanovskii,
A. I. Isaev, V. P. Shatalov,
and V. G. Shalganova

UDC 532.135

The influence of cyclic deformation on the viscoelastic properties of monodisperse polybutadienes of various molecular weights is investigated.

The viscoelastic properties of polymers are largely determined by their molecular weight and molecular-weight distribution [1, 2]. The viscoelastic behavior of practically monidisperse polymers and narrow polymer fractions in small-amplitude cyclic deformation (such that the viscoelastic characteristics are a function only of the frequency) has been studied in [3-6]. Furthermore, the viscoelastic properties of monodisperse poly-α-methylstyrene, determined from tensile stress relaxation experiments, are described in [7].

Of considerable interest is the systematic study of the viscoelastic properties of monodisperse polymers of different molecular weights for both small deformation amplitudes and amplitudes large enough to affect the viscoelastic properties of the polymers [8]. This approach makes it possible to determine a fundamental mechanical characteristic, namely the relaxation spectra, of monodisperse polymers of various molecular weights, and how they vary under the influence of an increase in the deformation amplitudes. Also, it would be interesting to apply the method proposed in [9] for calculating the viscoelastic characteristics normally determined in continuous deformation under steady-state flow conditions, using the results of a determination of how the relaxation spectrum varies under the influence of an amplitude increase in cyclic deformation. This method is based on the fact that the limits of the relaxation spectrum exhibit a single-valued dependence on the deformation rate.

The Experiment. In order to measure the viscoelastic characteristics in cyclic deformation we used a vibration rheometer [10] and a frequency rheometer [11] operating on the electromagnetic transduction principle [1]. The measurements on the vibration rheometer, which operated in the forced-vibration regime, were carried out at frequencies from 6 to 110 Hz. Sinusoidal vibrations were maintained over the entire range of deformation amplitudes. The results were processed by a method proposed by Markovitz and others [12, 13]. The frequency rheometer measurements were carried out in the range from 300 to 2000 Hz. The experimental results were processed on a digital computer.

In cyclic deformation 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. The measurements were performed at various deformation amplitudes γ_0 and cyclic frequencies $\omega = 2\pi f$, where f is the vibration frequency. The value of γ_0 was used to estimate the deformation rate amplitude $\dot{\gamma}_{\max} = \gamma_0 f$. From η^* the complex shear modulus $G^* = \eta^* \times i\omega = G' + iG''$ was calculated, along with its components the elastic modulus G' and the loss modulus G''.

Concurrently with the dynamic characteristics, the effective viscosity $\eta = \tau/\dot{\gamma}$ was determined, where τ and $\dot{\gamma}$ are the tangential stress and shearing rate, respectively. The measurements were carried out on a capillary viscosimeter, which is described in [14]. All the tests were conducted at 22°C.

We assumed in the study that the shearing rates and cyclic frequencies were equivalent and we made use of the correlation of the effective viscosity and absolute value of the complex dynamic viscosity.

A. V. Topchiev Institute of Petrochemical Synthesis, Academy of Sciences of the USSR, Moscow. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 20, No. 3, pp. 389-397, March, 1971. Original article submitted April 14, 1970.

TABLE 1. Characteristics of the Polybutadienes

Sample No.	M_w	$\frac{M_w}{M_n}$	ρ_{25}	Microcyclicity		
				cis-	trans-	1,2
1	$3,8\cdot10^4$	1,22	0,895	45	45	10
2	$6,75\cdot10^4$	1,2	0,895	44,5	41,5	14
3	$1,02\cdot10^5$	1,1	0,895	44	42	14
4	$1,43\cdot10^5$	1,1	0,895	47,2	22	8,8
5	$2,4\cdot10^5$	1,1	0,895	45,2	45,6	9,2

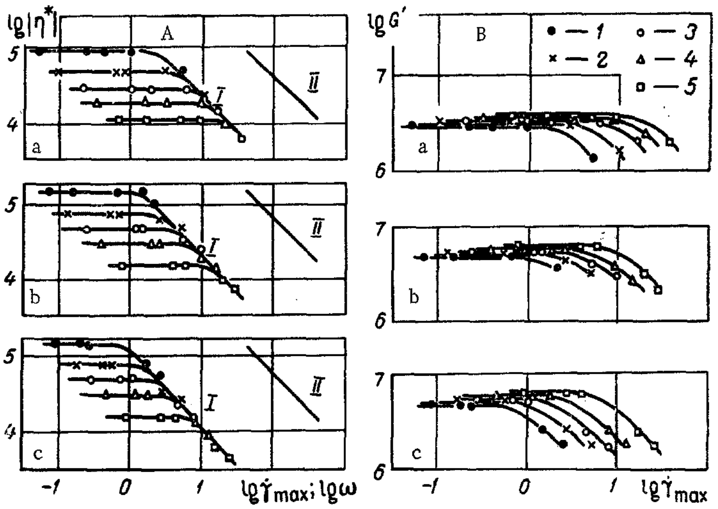

Fig. 1. Absolute value of the complex viscosity $|\eta^*|$, in P, versus γ_{max} at various frequencies (family of curves I) and the frequency ω for small deformation amplitudes (curves II) (A), and elastic modulus G' (B) versus deformation rate amplitude $\dot{\gamma}_{max}$. a, b, c) Sample Nos. 2, 3, and 4, respectively. Frequency ω, in sec^{-1}: 1) 40; 2) 80; 3) 125; 4) 200; 5) 400.

The Polymers. The objects of our investigation were polybutadiene samples, whose characteristics are summarized in Table 1.

EXPERIMENTAL RESULTS AND DISCUSSION

Curves showing the dependence of the absolute values of the complex dynamic viscosity on the deformation rate amplitude at various frequencies (family of curves I) and on the frequency in the amplitude interval where the complex viscosity is amplitude-independent (curve II) are presented in Fig. 1A. It is evident from the figure that for definite values of the deformation rate amplitude and a fixed frequency the curves of $|\eta^*| = \Phi_1(\dot{\gamma}_{max})$ for each polybutadiene merge into an envelope, which is shifted relative to curve II along the horizontal axis by the amount $\log a$, i.e., $\log\dot{\gamma} = \log\omega = \log\gamma_{max} + \log a$.

The curves in Fig. 1A are similar to the corresponding dependences described earlier in [8, 9] for polyisobutylene and polypropylene.

In order to explain the reasons for the shift of the dependence $|\eta^*| = \Phi_1(\dot{\gamma}_{max})$ relative to $|\eta^*| = \Phi_2(\omega)$ we consider the relationship between $\dot{\gamma}_{max}$ and ω. The envelope of the curves for $|\eta^*| = \Phi_1(\dot{\gamma}_{max})$ for different frequencies ω is reached when γ_{max} becomes equal to its critical value $\dot{\gamma}_{max}^{cr}$. These critical values were determined as described in [8]. The critical values of the deformation rate amplitudes are equal to $\gamma_0^{cr}f$, which, in turn, are equal to $\gamma_0^{cr}\omega/2\pi$, where γ_0^{cr} are the critical values of the deformation amplitude corresponding to arrival of the curves for $|\eta^*| = \Phi_1(\dot{\gamma}_{max})$ at the envelope. The values of γ_0^{cr} depend only slightly on the frequency (in the experimental frequency range γ_0^{cr} varies by 8%) and may be regarded as approximately constant. Therefore, $\gamma_0^{cr}/2\pi \approx \text{const} = a$. Consequently, $\dot{\gamma}_{max}^{cr}$ is proportional to the cyclic frequency ω, but is not equal to it. The curve for $|\eta^*| = \Phi_1(\dot{\gamma}_{max}^{cr})$ is shifted along the

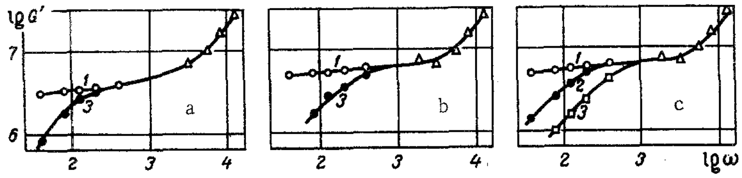

Fig. 2. Elastic modulus G' versus frequency ω. 1) Small deformation amplitudes; 2, 3) deformation rate amplitudes of 3.16 and 10 $\sec^{-1}$. a, b, c) Sample Nos. 2, 3, and 4, respectively.

horizontal axis relative to the dependence $|\eta^*| = \Phi_2(\omega)$ exactly by the amount a. The latter quantity is an important characteristic of the viscous properties of a polymer, insofar as it determines the deformation rate amplitude limit at which the complex viscosity begins to depend on the amplitude. With an increase in the molecular weight this limit shifts toward lower values of $\dot{\gamma}_{max}$, because for higher-molecular samples the viscosity anomaly sets in at small shearing rates.

The deformation work corresponding to the transition from the flat parts of curves I to the envelope can be calculated from the relation

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

It is essential to note that for each polymer the value of E_{cr} is (with 13% error) invariant with respect to the cyclic deformation conditions. The quantities E_{cr} and a obtained for polybutadiene samples having various molecular weights are listed below:

M_w	$6.75 \cdot 10^4$	$1.02 \cdot 10^5$	$1.43 \cdot 10^5$
E_{cr}	$1.42 \cdot 10^6$	$8.31 \cdot 10^5$	$3.23 \cdot 10^5$
$\log a$	1.2	1.5	1.66

An important fact here is the reduction of E_{cr} as the molecular weight increases. This happens because for a specified value of the deformation rate amplitude a higher degree of viscosity anomaly is observed for higher-molecular samples, i.e., the ratio of the maximum Newtonian viscosity to the viscosity determined for a given $\dot{\gamma}_{max}$ turns out to be larger.

The dependences of the elastic modulus G' on the deformation rate amplitude at various frequencies and on the frequency at various deformation rate amplitudes are shown in Figs. 1B and 2, respectively. Also shown in Fig. 2 are data obtained with the frequency rheometer using electromagnetic transducers (light triangles). Curves 1 in Fig. 2 refer to the values of G' obtained for small amplitudes that do not affect the value of G". Curves 2 and 3 were obtained for large deformation rate amplitudes. It is evident from the figure that at these amplitudes the low-frequency part of the dependence $G'(\omega)$ is cut off. Inasmuch as $\log \dot{\gamma} = \log \omega = \log \dot{\gamma}_{max} + \log a$, it may be assumed that curves 2 and 3 yield the dependence of G' on the corresponding values of the shearing rates in continuous deformation.

The frequency dependence of the loss modulus G" is shown in Fig. 3, where it was calculated from continuous deformation experiments on the basis of capillary viscosimeter data on the shear stress as a function of the shearing rate, because it is known that in nearly Newtonian flow regimes $\tau = G''$. The validity of this approach was confirmed by direct cyclic-deformation experiments using sample No. 1. The corresponding data are represented by the light circles in Fig. 3.

Using the method of Ninomiya and Ferry [15], we calculated the relaxation time distribution function $H_{in}(\theta)$ from the dependences $G'(\omega)$ and $G''(\omega)$ for the small-amplitude interval where G' and G" are amplitude-independent. By analogy with the incipient viscosity concept, which is independent of the shearing rate for small values of the latter, we also refer to the indicated relaxation time spectra as "incipient." The effective relaxation spectra $H_e(\theta)$, which afford characteristics determined for the polybutadienes at various values of $\dot{\gamma}_{max}$ in correspondence with the continuous deformation rates, were calculated in the same way as the incipient spectra.

The incipient relaxation spectra for monodisperse polybutadienes are shown in Fig. 4, where they form a family of curves having an envelope. The latter corresponds to the incipient relaxation spectrum

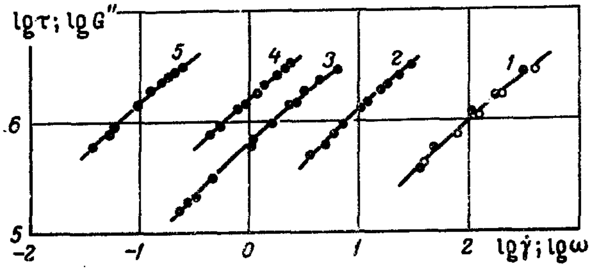

Fig. 3

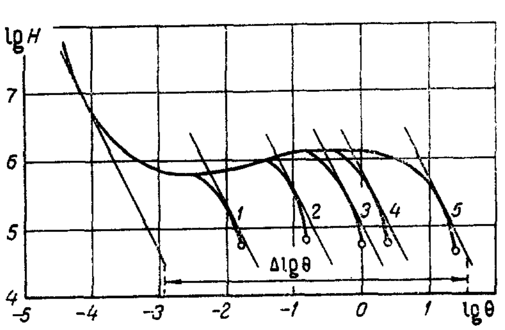

Fig. 4

Fig. 3. Shear stress τ versus shearing rate $\dot{\gamma}$, and loss modulus G'' versus frequency ω. 1-5) Sample Nos. 1-5, respectively; ●) in continuous deformation; ○) in cyclic deformation.

Fig. 4. Incipient relaxation spectra for monodisperse polybutadienes. 1-5) Sample Nos. 1-5, respectively. H in dyn/cm^2; θ in sec.

of the polybutadiene having the largest molecular weight of those investigated. Three intervals are distinguished in the curves for $H_{in}(\theta)$: a large-time interval, corresponding to the flow regime; a small-time interval, corresponding to the glass transition; and a rubber elasticity plateau, which is situated between the other two intervals. In the rubber-elastic plateau interval the relaxation time distribution function, beginning with definite molecular weights, has a minimum and a maximum. The width of the rubber-elastic plateau on the relaxation time scale decreases with the molecular weight. This reduction is primarily attributable to the displacement of the large-time interval of the spectrum toward smaller relaxation times, so that the variation of the relaxation spectra with decreasing molecular weight is outwardly analogous to the cutoff of the relaxation spectrum under the influence of deformation at various shearing rates [8, 16].

The data given in Fig. 4 can be used to construct the dependence of the width of the rubber-elastic plateau on the molecular weight of the polybutadienes. In order to estimate the width of the rubber-elastic plateau from the curves for $\log H_{in} = \psi(\log \theta)$ we draw equal-slope tangents to those curves in the transition intervals from the rubber-elastic plateau to the flow regime and glass-transition regime. We then determine the plateau width from the value of $\Delta \log \theta$, as indicated schematically in Fig. 4. The tangents are usually plotted with a slope of 1/2. However, for polymers having a very narrow molecular-weight distribution the transition from the rubber-elastic plateau to the flow and glass-transition intervals is distinguished by a much steeper slope than for polydisperse polymers. It is impractical, therefore, to use a slope of 1/2 for the tangents. The transition limits to the flow and glass-transition regions for polybutadienes were determined for tangents having slopes varying from $-1/2$ to -3. The corresponding data on the width $\Delta \log \theta$ of the rubber-elastic plateau as a function of $\log M_w$ are given in Fig. 5A. It is evident from the latter that the width of the rubber-elastic plateau depends only slightly on the choice of the tangent slope. This choice has a particularly inconsequential effect on the slope of the rubber-elastic plateau width as a function of $\log M_w$; this slope has a value of 3.6. According to [1] this slope should be 2.4. However, as remarked earlier [7], similar dependences were obtained experimentally with a slope of 3.4. Below we use data obtained for tangents drawn to the curves in Fig. 4 with a slope of -2. Extrapolation of the dependence $\Delta \log \theta = \psi_1(\log M_w)$ to a zero value of $\Delta \log \theta$ gives the molecular weight at which the rubber-elastic plateau is formed: $M_3 = 1.4 \cdot 10^4$. The average molecular weight of the chains between linkage sites, when determined from the simple relation $M_e = \rho RT(G')^{-1}$, is equal to $3.5 \cdot 10^3$. Hence it follows that the rubber-elastic plateau for the given polybutadiene samples sets in when $M_w \simeq 4M_e$.

Using the incipient relaxation spectra, we can calculate the values of the maximum Newtonian viscosity $\eta_{\max} = \lim_{\dot{\gamma} \to 0} \eta$. According to [1], for the stationary flow case, i.e., for $\omega \to 0$,

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

The value of $\eta_{\max}$ calculated from Eq. (2) for monodisperse polymers of various molecular weights differs from the experimentally measured value according to capillary viscosimeter data by no more than 20%.*

---

*All numerical calculations of the spectra in the present study were carried out on a digital computer.

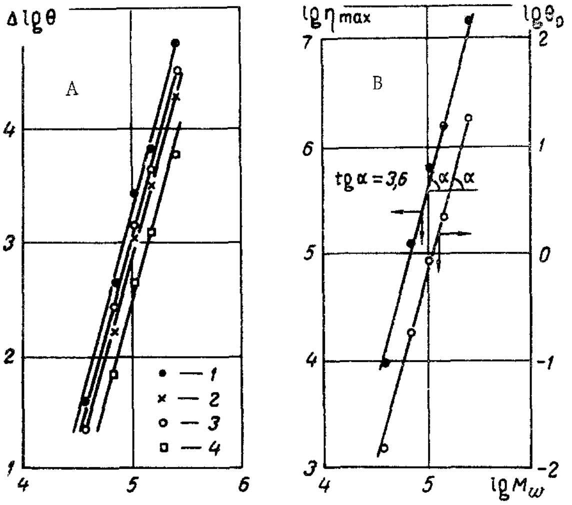

Fig. 5

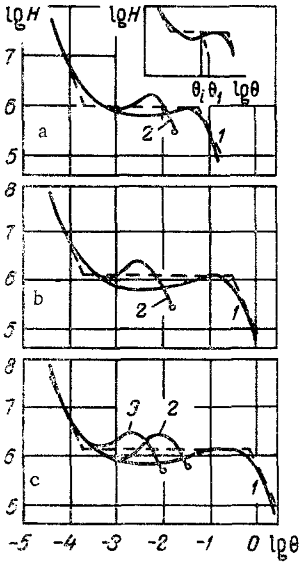

Fig. 6

Fig. 5. Width of the rubber-elastic plateau (A), and maximum Newtonian viscosity and maximum relaxation time (B) versus molecular weight, according to the relaxation spectra shown in Fig. 4. Slopes of tangents: 1) $-1/2$; 2) -1; 3) -2; 4) -3.

Fig. 6. Incipient (curve 1) and effective (curves 2 and 3) relaxation spectra for monodisperse polybutadienes. a, b, c) Sample Nos. 2, 3, and 4, respectively. Curves 2a, 2b, 2c, and 3c correspond to the following shearing rates γ, in $\sec^{-1}$: 160, 316, 145, and 460.

The dependence of the maximum Newtonian viscosity on the molecular weight of the polymer is shown in Fig. 5B, where $\eta_{\max} = CM_w^n$ with $n = 3.6$. Also shown in the same figure is the molecular-weight dependence of the maximum relaxation times θ_0 determined from the incipient relaxation spectra for the polymers (light circles in Fig. 4). The dependence $\theta_0(M_w)$ also has a slope of 3.6. As we know [18, 19], the dependence of $\log \eta_{\max}$ on $\log M_w$ has a jog corresponding to the critical molecular weight M_w^{cr}. If we assume that the dependence $\eta_{\max}(M_w)$ has roughly the same slope as the dependence $\theta_0(M_w)$ in the interval of smaller values of M_w as well, as shown in Fig. 5B, the implication is that the critical molecular weight must correspond to the critical value of θ_0. In this case the experimentally observed sharp rise of the viscosity for molecular weights above the critical value could be accounted for by a sharp rise of the maximum relaxation times of the polymers for $M_w > M_w^{cr}$.

We now consider the variations experienced by the incipient relaxation spectra of the polymers under deformation with various values of $\dot{\gamma}_{\max}$ or with the corresponding shearing rates in continuous deformation. The result is shown in Fig. 6, from which it is clear that under the action of large shearing rates the incipient relaxation spectrum of a monodisperse polymer experiences a very special kind of variation. The latter consists in a cutoff of the large-time part of the spectrum and a shift of the maximum toward smaller relaxation times. The significant thing here is that the maxima of the effective relaxation spectra are higher than for the incipient spectra. The possibility of this kind of variation of the incipient relaxation spectrum in the rubber-elastic plateau interval was postulated earlier in [17]. Clearly, a maximum in the effective relaxation spectrum for polymeric systems ought to be observed for polymers whose incipient relaxation spectra also have a maximum.

Figure 7 gives the dependence of the effective viscosity on the shearing rate (dark circles) and of the absolute value of the complex viscosity on the cyclic frequency for small deformation amplitudes (light circles). The ranges of the experimentally measured values of η and $|\eta^*|$ are given by the solid curves. The heavy dashed curves indicate the postulated values of the effective viscosity in the interval where variations of η are impossible for reasons to be stated below. The thin dashed curves indicate the dependence of the effective viscosity on the shearing rate according to calculations by the method proposed in [9]. The following relation is used:

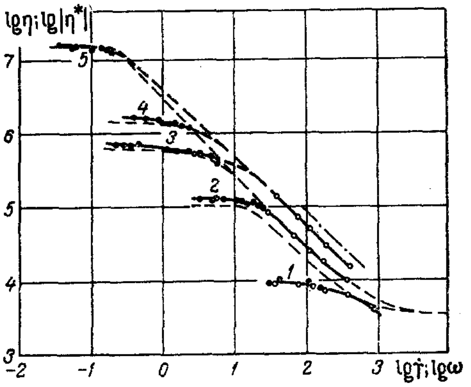

Fig. 7. Effective viscosity (in P) versus shearing rate, and absolute value of the complex dynamic viscosity versus frequency for small deformation amplitudes. 1-5) Sample Nos. 1-5, respectively; ●) in continuous deformation; ○) in cyclic deformation.

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

The upper limit in Eq. (3) is chosen as shown schematically in the upper part of Fig. 6. For a given i-th value of the shearing rate in continuous deformation a secant, approximated by a trapezoid, is drawn parallel to the large-time part of the spectrum. Then on the secant corresponding to the i-th shearing rate the value of $\theta_1 = 2.8\ \theta_i$ is found. The transition coefficient, equal to 2.8, was found in [9].

The values found for the effective viscosity η according to Eq. (3) do not differ by more than 60% from the experimentally measured values of $|\eta^*| = \Phi_2(\omega)$. This disparity is explained by the rather coarse approximation of the spectrum.

The dependence of the effective viscosity on the shearing rate can also be calculated from the effective relaxation spectra $H_e(\theta)$ given in Fig. 6. The following relation is used:

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

in which θ_2 is the maximum relaxation time on the effective relaxation spectra for a given deformation rate (light circles in Fig. 6). The data of the calculations are represented in Fig. 7 by a dot–dash curve. A comparison of these values of $\eta(\dot{\gamma})$ with the absolute value of the complex viscosity $|\eta^*| = \Phi_2(\omega)$ shows that for polybutadiene sample Nos. 3 and 4 the calculated values of $\eta(\dot{\gamma})$ are 60% higher than the measured values of $|\eta^*| = \Phi_2(\omega)$. For sample No. 2 the values of η and η^* concur. The observed discrepancy between $\eta(\dot{\gamma})$ and $|\eta^*| = \Phi_2(\omega)$ for the high-molecular polybutadiene samples is probably related to the fact that for large deformation rate amplitudes, as in the case of high shearing rates, the monotonicity of the function $\eta(\dot{\gamma})$ is disrupted in continuous-deformation regimes. Thus, according to the capillary viscosimeter data a sharp jog is observed in the flow curve, so that when the shear stresses attain certain values the flow rate jumps very suddenly. In cyclic deformation at large amplitudes the high-molecular samples are observed to break away from the measurement surfaces. These effects, of course, deserve special consideration. For the time being, however, we point out that the method proposed in [9] for polydisperse polymers can be used for an approximate calculation of the shearing-rate dependence of the effective viscosity of monodisperse polybutadienes.

The authors wish to thank E. K. Borisenkova for conducting the measurements on the capillary viscosimeter, as well as G. V. Gulyaev for assisting with the computer calculations.

LITERATURE CITED

1. J. D. Ferry, Viscoelastic Properties of Polymers, Wiley, New York (1961).
2. A. Tobol'skii, Properties and Structures of Polymers [in Russian], Khimiya (1964).
3. R. L. Ballman and R. H. Simon, J. Polymer Sci., A2, 3557 (1964).
4. S. Onogi, T. Masuda, and T. Ibaragi, Kolloid-Z., 222, 110 (1968).
5. R. H. Valentine, J. D. Ferry, T. Homma, and K. Ninomiya, J. Polymer Sci., A2, 479 (1968).
6. J. L. Den Otter, Dynamic Properties of Some Polymeric Systems, Dissertation, Leyden (1967).
7. T. Fujimoto, N. Osaki, and M. Nagasawa, J. Polymer Sci., A2, 129 (1968).

8. G. V. Vinogradov, Yu. G. Yanovskii, A. I. Isaev, and V. A. Kargin, Dokl. Akad. Nauk SSSR, 187, 1075 (1969).
9. G. V. Vinogradov, Yu. G. Yanovskii, and A. I. Isaev, Inzh.-Fiz. Zh., 3, 377 (1970).
10. A. I. Isaev and Yu. G. Yanovskii, Zavod. Lab., 36, 1525 (1970).
11. G. V. Vinogradov and Yu. G. Yanovskii, Zavod. Lab., 31, 115 (1965).
12. H. Markovitz, J. Appl. Phys., 23, 1070 (1952).
13. H. Markovitz, P. M. Yavorsky, R. C. Harper, L. J. Sapas, and T. W. De Witt, Rev. Sci. Instrum., 23, 430 (1952).
14. G. V. Vinogradov and N. V. Prozorovskaya, Plastmassy, No. 5, 50 (1964).
15. K. Ninomiya and J. D. Ferry, Colloid Sci., 14, 36 (1954).
16. R. I. Tanner, Trans. ASME, Ser. F, 90, 555 (1968).
17. K. Osaki, M. Tamura, M. Kurata, and T. Kotaka, J. Phys. Chem., 69, 4183 (1965).
18. G. V. Vinogradov, A. Ya. Malkin, and V. G. Kulichikhin, Vysokomolekul. Soedin., A10, 2522 (1968).
19. R. Porter and J. Johnson, Chem. Rev., 66, 1 (1966).