

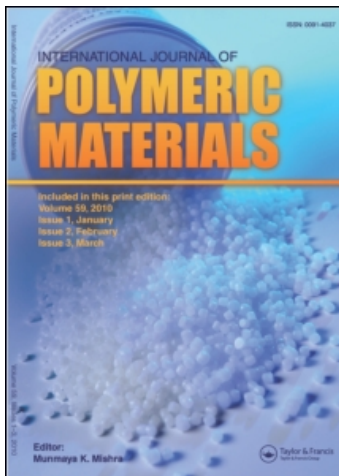
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The Rheology and Molecular-Mass Characteristics of 1,4-cis-Polyisoprenes and Butyl Rubbers†

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The interrelationship of the molecular-mass characteristics and the rheological properties of 1,4-cis-polyisoprenes and butyl rubbers has been examined. Commercially produced polymers were subjected to mechanical breakdown (polyisoprenes) and to ozonolytic or catalytic (by AlCl_3) degradation (butyl rubbers) until the most probable distribution was attained. The molecular-mass characteristics of the polymers was determined by the GPC method. We have plotted curves showing the dependences of the apparent and complex viscosities on the rate of shear and the frequency, of the storage and loss moduli on the frequency, and of the initial values of viscosity and of the first-normal stress coefficient on the molecular-mass characteristics of the polymers studied.

We have obtained the logarithmic relaxation-time H-spectrum from the molecular-mass characteristic on the one hand and from the storage modulus on the other. These two kinds of relaxation-time spectra are in satisfactory agreement with each other. The initial viscosity has been evaluated from the relaxation-time spectra. The data obtained agree well with the experimentally determined values of viscosity.

1. INTRODUCTION

One of the most important problems in the field of polymer rheology is concerned with the interrelation between molecular characteristics, namely molecular masses (MM) and their distribution (MMD), and the main

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rheological characteristics (such as the relaxation spectra). The extensive application of the GPC method substantially facilitates solution of the problem.

In spite of the wide commercial use of 1,4-cis-polyisoprene (PI in this country) and butyl rubber (BR), there are only scarce data in the literature concerning the relationship between the rheological and molecular characteristics of these polymers over a wide range of their variation. The present work aims at bridging this gap.

Especial attention must be drawn to the problem of the change of MM and MMD of the polymers under the effect of their mechanical and chemical degradation. Polyisoprenes are very susceptible to the processes of mechanical degradation. As regards butyl rubbers, they are subjected to chemical degradation by ozonolysis for the purpose of preparation of oligomers with active groups (like carboxyl) at the ends of the molecules. Degradation of BR with the action of AlCl_3 is realized for cleaning of reactors.

2. EXPERIMENTAL

The molecular masses and MMD of the samples were determined on a gel chromatograph "Waters-200" with styrogel columns at a temperature of 25°C and with the rate of elution 1 ml/min. Two sets of columns were used, the pore sizes being as follows: 3×10^3 , 10^4 , 3×10^5 Å and 10^4 , 3×10^4 , 10^5 , 3×10^5 Å. Chloroform was used as the eluent. The concentration of the samples varied from 0.1 to 0.3%, depending on the molecular mass expected. The calibration was made by polystyrene standards with the use of the principle of the universal Benoit relation and the Mark-Houwink constants for PS^1 , BR^2 , PI^3 in chloroform at 25°C . The average molecular masses and molecular-mass distributions were calculated from gel-chromatograms by means of computer. For a number of samples we measured the intrinsic viscosity on a Ubbelohde viscometer in chloroform at $25 \pm 0.1^\circ\text{C}$. The characteristics of the samples used are presented in Table I.

The investigation of the rheological properties under stationary and dynamic conditions was conducted on a Weissenberg rheogoniometer R-18 with a cone-and-plate unit. The angle of the cone is 2° ; the amplitude of the vibrations of the plate in dynamic tests did not exceed 0.003 rad. The measurements were carried out in a temperature range of 25 – 140°C and a range of deformation rates and frequencies of 10^{-2} to 10^2 s^{-1} .

The data obtained on the rheogoniometer were compared with the results of the tests carried out on the mechanical spectrometer DChP-2⁴ over a frequency range of 2.5×10^{-3} to 1.5×10^4 s^{-1} ; the error did not exceed 10%.

The BR† samples were prepared by the ozonolytic (samples 1–3, 6, 7, 10) and

† The Mooney viscosity is 74 at 100°C , and the content of isoprene units is 1.64 mole %.

TABLE I
The molecular characteristics of the polymer investigated

Type of elastomer	Sample no.	$\bar{M}_n \times 10^3$	$\bar{M}_w \times 10^3$	$\bar{M}_z \times 10^3$	\bar{M}_w/\bar{M}_n	$[\eta]_{gr}$, litre/g	$[\eta]_{exp}$, litre/g	$\log \eta_0, N \cdot m^{-2} \cdot s$	
								experimental	calculated
PI	1	64.2	123	206	1.92	1.16	1.15	2.9	3.3
	2	148	225	318	1.52	—	—	4.1	3.9
	3	132	270	445	2.05	2.09	2.15	4.4	4.52
	4	170	363	627	2.14	—	—	5.08	5.0
	5	245	611	1140	2.49	—	—	6.0	6.07
	6	340	660	991	1.94	4.1	3.93	6.3	5.86
	7	353	898	1640	2.54	5.06	4.8	6.6	6.6
BR	1	2.48	4.63	8.13	1.87	—	—	—	—
	2	2.41	6.66	13.2	2.76	—	—	0.3	0.4
	3	2.71	8.4	52	3.1	—	—	0.78	0.9
	4	4.1	9.2	17.1	2.24	—	—	—	—
	5	7.42	31.3	67	4.22	0.3	0.31	—	—
	6	4.7	37.6	126	8	—	—	1.85	1.8
	7	5.3	114	448	21.5	0.53	0.51	3.16	2.7
	8	10.5	236	685	22.5	—	—	—	—
	9	18.3	244	562	13.3	—	—	5.15	4.85
	10	21.7	295	571	13.6	1.11	1.08	5.3	5.22
	11	202	484	961	2.4	1.55	1.56	6.4	6.3

catalytic (by the action of an excess of AlCl_3 , samples 4, 5, 8) degradation of solutions of commercial BR (sample 11) for different periods of time. The samples obtained after the degradation were reprecipitated by ethanol and dried in vacuum to constant weight. As the degree of degradation increases the polydispersity first increases, passes through a maximum and then monotonically decreases; after 50 ruptures per molecule the MMD approaches the most probable value. When a large amount of elastomer undergoes degradation in the absence of effective mixing, there is observed a bimodal MMD, which is evidently associated with the non-uniform distribution of the degrading agent in the bulk of the reaction mass and with the formation of local portions which have undergone increased degradation.

The PI† samples (1, 3, 4, 5) were prepared by plasticization of a gel-free commercial sample (sample 7) on rolls. The PI samples 2 and 6 were synthesized under laboratory conditions over a lithium catalyst.

To determine the presence of long-chain branching in the samples investigated, use was made of the procedure based on the comparison of the intrinsic viscosities, which were determined experimentally on the Ubbelohde viscometer, $[\eta]_{exp}$ and calculated from gel-chromatograms $[\eta]_{gc}$. The algorithm of the calculation of the long-chain branching has been described in the literature.⁵ As can be seen from Table I, the discrepancy between $[\eta]_{exp}$ and $[\eta]_{gc}$ measured for several samples does not exceed the experimental error ($\pm 5\%$), which points to the absence of long-chain branching in the samples.

3. RESULTS AND DISCUSSION

3.1 Correlation of steady-state and complex viscosities

At present it has been experimentally established that there exists a correlation between η (steady-state viscosity) and η^* (the complex viscosity) at $j = \omega$, a fact which has been pointed out by Cox and Merz.⁶

Figure 1 shows typical results of these dependences, which allows one to change over from the characteristics of steady-state flow to dynamic characteristics and vice versa. Analogous results have been obtained for the other BR and PI samples. However, as was pointed out in the literature,⁷ such a correlation is not valid over the entire range of j and ω , since at certain j or ω values there takes place a transition of the polymer to the rubbery (quasi-cured) state. As the temperature is raised and the molecular mass decreases the zone allowed for the correlation shifts to higher values of j and ω and for samples with $\bar{M}_w > 5M_c$ at temperatures above 80°C it covers the entire j and ω range studied.

† The Mooney viscosity is 80 at 100°C and the content of cis-groups is 97%.

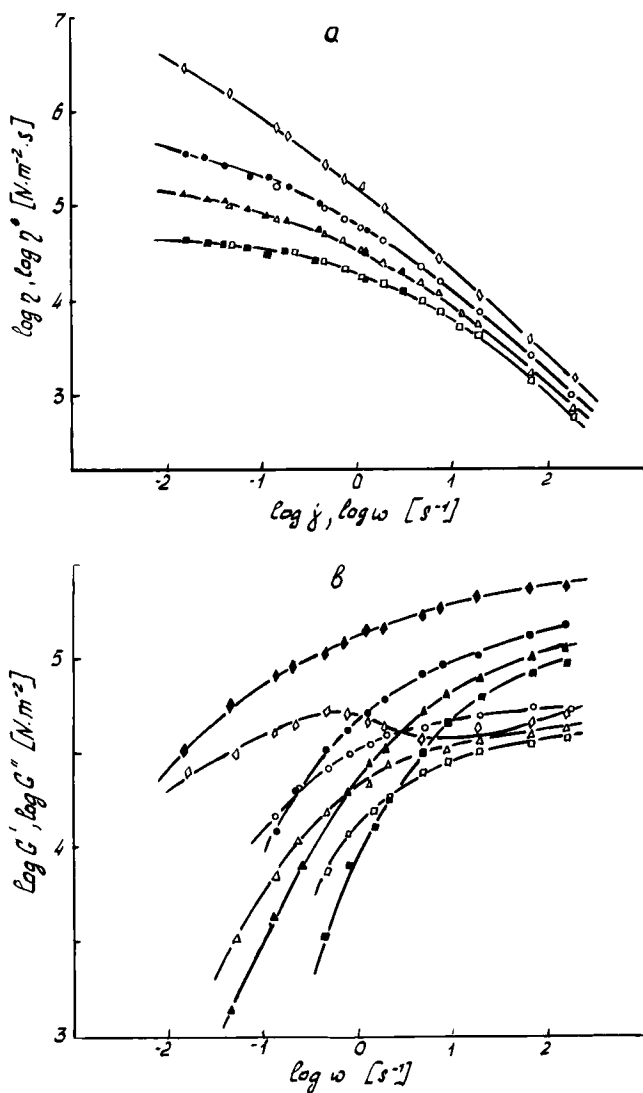


FIGURE 1 Dependences (a) of the apparent (\bullet , \blacktriangle , \blacksquare) and complex (\diamond , \circ , \triangle , \square) viscosities on the rate (frequency) of shear deformation and (b) of the storage (\blacklozenge , \bullet , \blacktriangle , \blacksquare) and loss moduli on frequency for BR sample 10 at the following temperatures: 25°C (\blacklozenge , \diamond), 80°C (\bullet , \circ), 110°C (\blacktriangle , \triangle), and 140°C (\blacksquare , \square).

In order to elucidate the effect of MMD on the rheological characteristics, the experimental data were reduced to 100°C through the use of the Williams-Landel-Perry equation.⁸ Figure 2 presents the temperature dependence of the shift factor a_T for BR and PI since these polymers have the same glass-transition temperature.⁹

3.2 Steady-state viscosity and dynamic characteristic of polymers

The results of the reduction in the $\log \eta a_T - \log(j a_T) (a_T)$ and $\log G'(\log G'' - \log(\omega a_T))$ coordinates are given in Figures 3-6 where the numbers at the curves correspond to the numbers of the samples in Table I. The spread of the points does not exceed $\pm(10-15)\%$.

As can be seen from Figures 5 and 6 for $\bar{M}_w > 5 M_c$ the height of the G' plateau and the magnitude of the G'' maximum are practically independent of molecular mass and MMD. For samples of wide MMD, in contrast to the case of monodisperse samples, the transition to G'_{pl} and G''_{max} is smoother. The higher the poly-dispersity the more distinctly this regularity manifests itself,

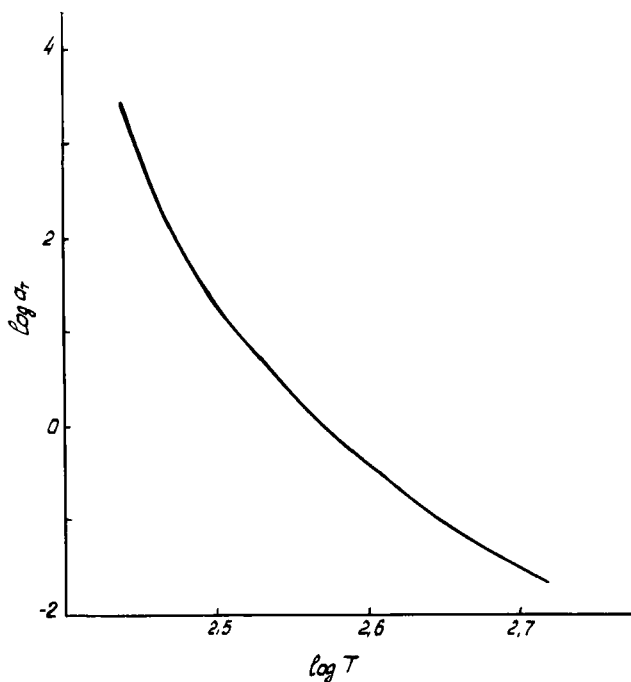


FIGURE 2 Temperature dependence of the shift factor a_T .

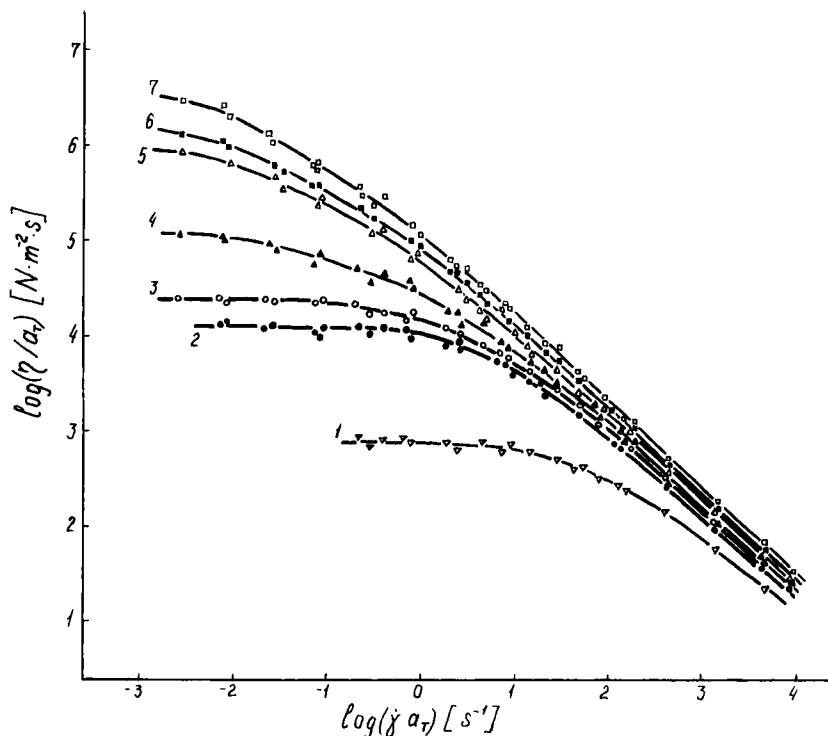


FIGURE 3 Dependences of viscosity on rate of shear for PI samples, reduced to 100°C.

increasing the region of the non-proportional variation of G' with ω . As the value of ω and the molecular mass decrease the slope of the $G'(\omega)$ and $G''(\omega)$ curves increases, and in the region of frequencies corresponding to Newton flow there is fulfilled the relation $G' \propto \omega^2$ and $G'' \propto \omega$, which is characteristic of monodisperse polymers.⁷

For the samples studied, master temperature-invariant curves in the $\log(\eta/\eta_0) - \log(\dot{\gamma}\alpha_T)$ coordinates¹⁰ have also been constructed (Figures 7 and 8). It should be noted that the master curve describes the flow properties of samples with a polydispersity (M_w/M_n) of up to 10 well. For elastomers with $\bar{M}_w/\bar{M}_n > 5$ the points are found to lie somewhat lower, and the deviation is larger the higher the polydispersity is, this being associated with the stronger manifestation of non-Newtonian behaviour.

3.3 The dependence of the initial (largest Newtonian) viscosity on the molecular parameters

The relationship between the initial viscosity and the molecular mass is

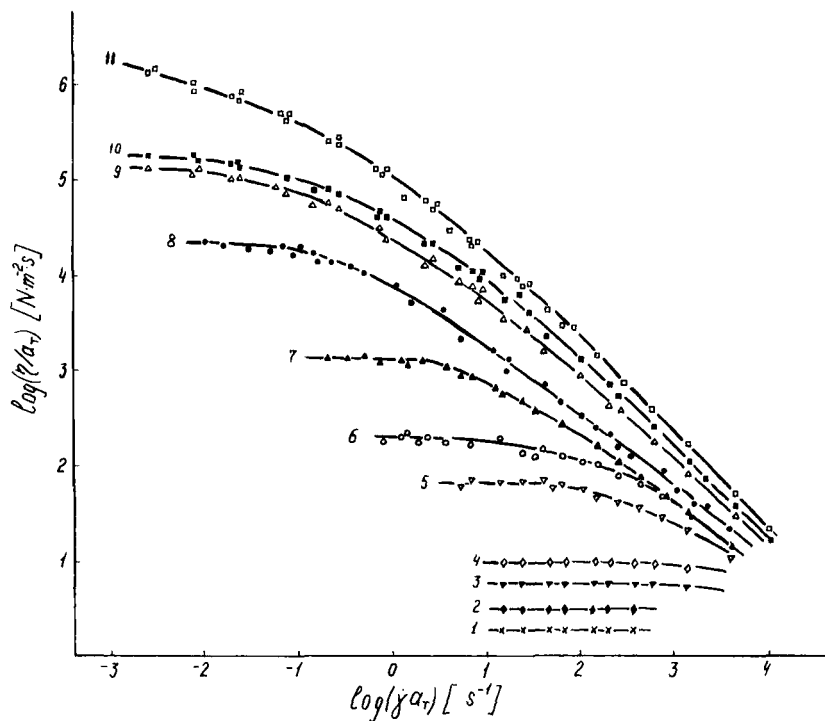


FIGURE 4 Dependences of viscosity on rate of shear for BR samples, reduced to 100°C.

expressed by the well-known formula :

$$\eta_0 = KM^a \quad (1)$$

where $a \approx 3.5$ for $M > M_c$.

The dependence of the initial viscosity at 100°C on the mass-average molecular mass for PI, as follows from Figure 9(a), is nicely described by an equation of the form

$$\eta_0^{100} = 1.75 \cdot 10^{-18} M_w^{4.1} \text{ Pa} \cdot \text{s} \quad (2)$$

An attempt has been made to take into account the width of MMD by means of the relation proposed in the literature:¹²

$$\eta_0^{100} = K \bar{M}_w^a \exp[-K_p a (M_w/M_n - 1)], \text{ Pa} \cdot \text{s} \quad (3)$$

In the coordinates $\log \eta_0$ vs. $\log \bar{M}_w / \exp[K_p (\bar{M}_w / \bar{M}_n - 1)]$, the experimental data lie on a straight line (Figure 9(b)). The coefficient K_p was determined by the method of least squares. Taking the values of the coefficients K , K_p and a into account, the dependence of η_0 on the molecular characteristics for BR

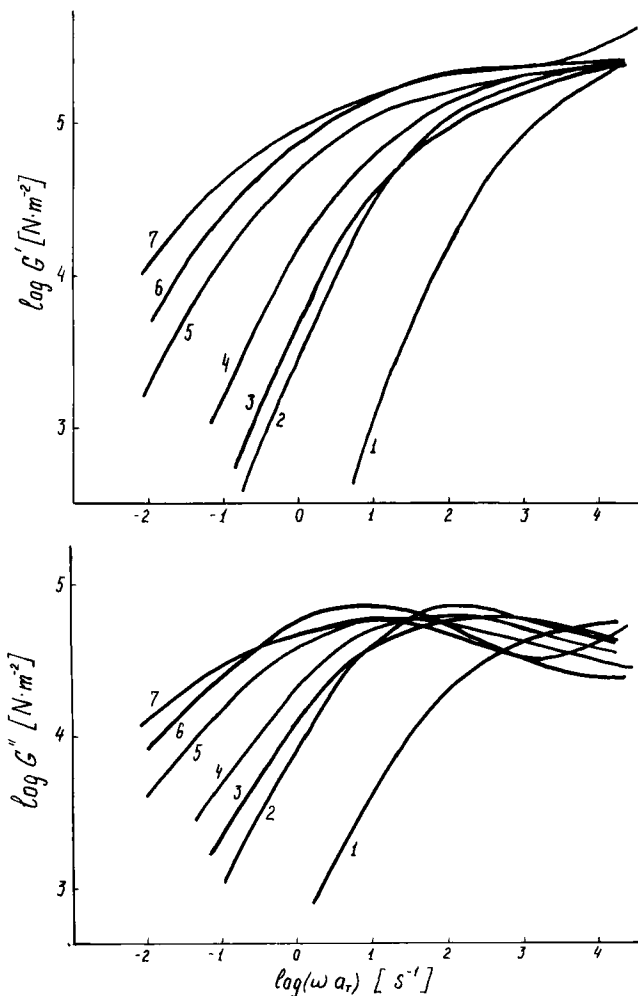


FIGURE 5 Dependences of storage and loss moduli on frequency for BR samples, reduced to 100°C.

samples with $\bar{M}_w \exp [-K_n(M_w/M_n - 1)] \geq M_c$ has the form :

$$\eta_0^{100} = 2.3 \cdot 10^{-13} \bar{M}_w^{3.4} \exp [-0.043 \cdot 3.4 (M_w/M_n - 1)] \text{ Pa} \cdot \text{s} \quad (4)$$

Thus, for PI and BR we have obtained the relationships between the initial viscosity at 100°C and their molecular parameters. If the polymer samples differ significantly in molecular-mass distribution, it is necessary to introduce a collection factor for polydispersity into Eq. (1), and also for branching in the case of the presence of long-chain branches.

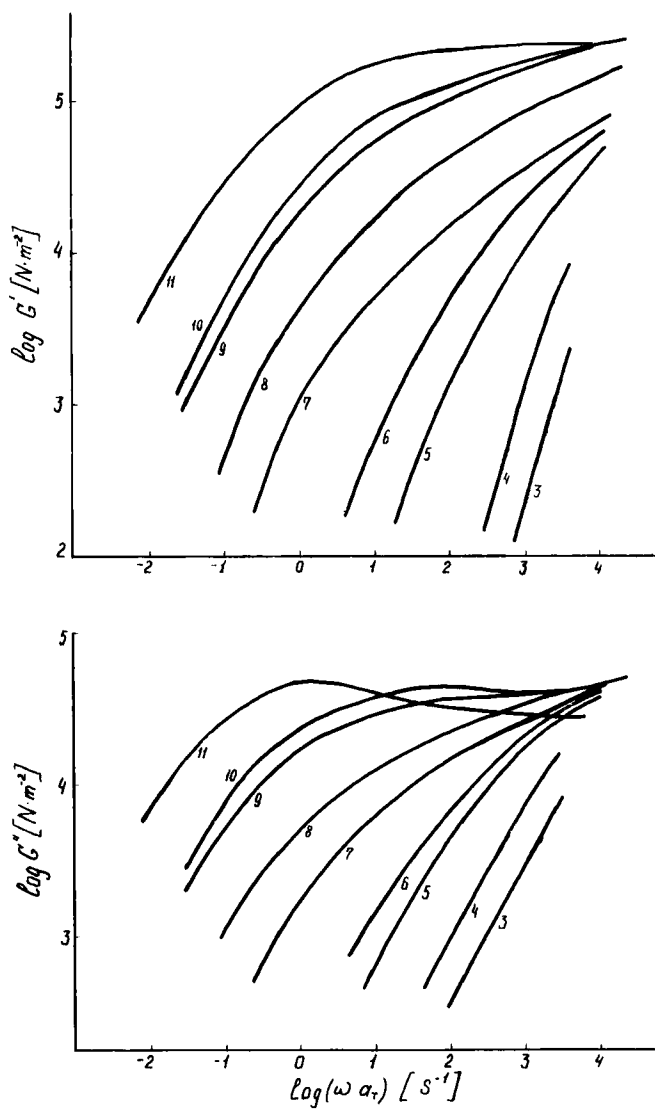


FIGURE 6 Dependences of the storage and loss moduli on frequency for BR samples, reduced to 100°C.

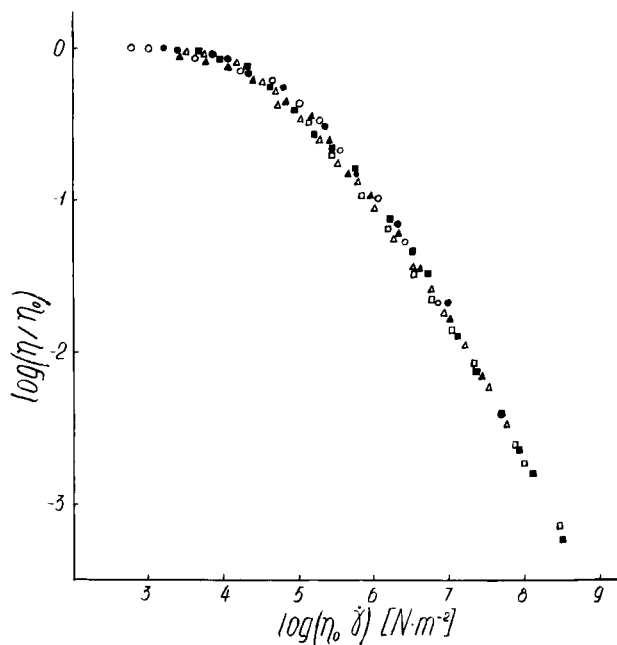


FIGURE 7 Temperature-invariant characteristic curve for the viscosity of polyisoprene: ●—sample No. 2, ○—sample No. 3, ▲—sample No. 4, △—sample No. 5, ■—sample No. 6, □—sample No. 7.

3.4 Molecular parameters and the initial normal stress coefficient (ξ_0)

The available experimental data show that the use, for the initial normal stress coefficient, of M_w as the argument with the aid of which it is possible to describe experimental data on the flow properties well, does not lead to satisfactory results. The quantity ξ_0 is more strongly affected by the higher moments of MMD.

To establish the relationship between ξ_0 and the molecular parameters, use was made of the relation proposed in the literature:¹³

$$\xi_0 = K \bar{M}_w^{(2a-1)} M_z \quad (5)$$

Figures 10(a) and 11(a) illustrate the applicability of a relation of this kind to PI and BR at 100°C with the following numerical coefficients:

$$\text{for PI} \quad \xi_0 = 5 \times 10^{-43} \bar{M}_w^{7.5} \cdot \bar{M}_z, \text{ N} \cdot \text{m}^{-2} \cdot \text{s}^2 \quad (6)$$

$$\text{for BR} \quad \xi_0 = 6.3 \times 10^{-35} \bar{M}_w^{5.8} \bar{M}_z, \text{ N} \cdot \text{m}^{-2} \cdot \text{s}^2 \quad (7)$$

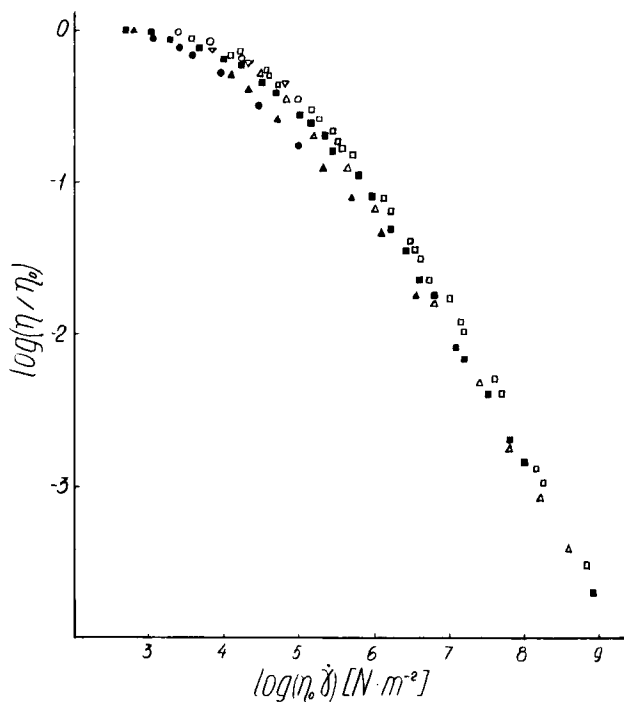


FIGURE 8 Temperature-invariant curve for the viscosity of BR samples: ∇ —sample No. 5, \circ —sample No. 6, \triangle —sample No. 7, \bullet —sample No. 8, \blacktriangle —sample No. 9, \blacksquare —sample No. 10, \square —sample No. 11.

It should be remarked that the coefficient a in Eqs. (2) and (4) coincide with the value of a in Eqs. (6) and (7). For PI samples the coefficient a is somewhat greater than for BR, i.e. for PI samples the quantities ξ_0 and η_0 depend on M_w more strongly.

As has been shown in the literature,¹⁴ for polymethylsiloxanes it is possible to linearize experimental data in the coordinates $\log \xi_0$ and $\log (\bar{M}_w \cdot \bar{M}_z)$. As can be seen from Figures 10(b) and 11(b) for PI samples this condition is fulfilled, whereas for BR samples no linearization can be realized.

Figures 10 and 11 do not give the corresponding values for BR samples 1–4 since at 100°C these samples display practically Newtonian flow behaviour.

3.5 The dependence of the relaxation-time spectrum on molecular-mass distribution

One of the most important characteristics of polymers is their relaxation-time spectrum, which allows one to calculate all the characteristics of polymers under linear deformation conditions.

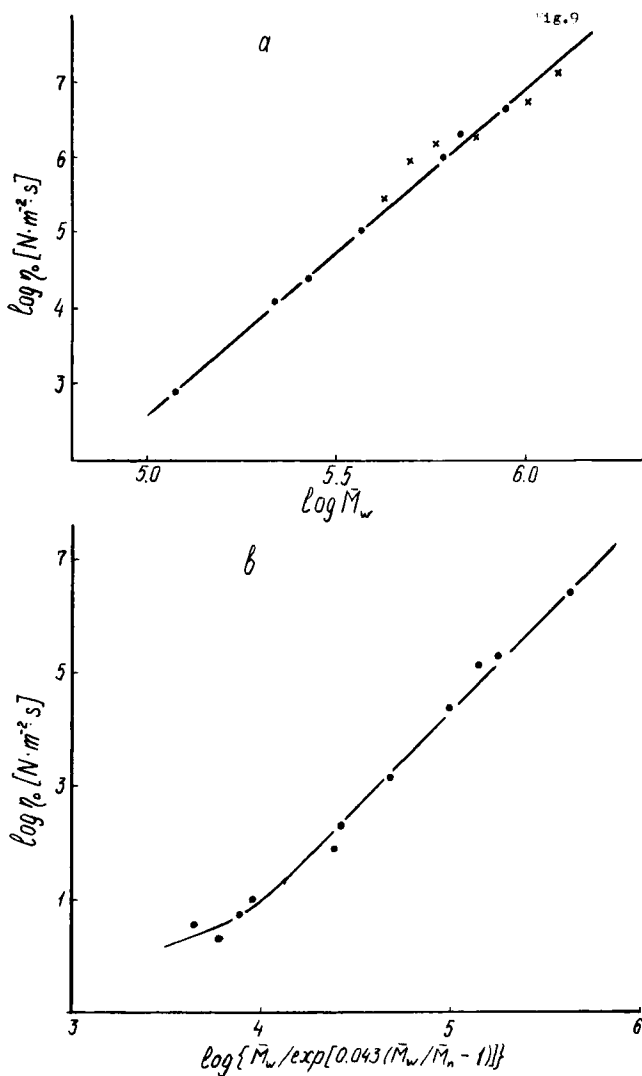


FIGURE 9 Dependence of the initial (largest Newtonian) viscosity at 100°C on the mass-average molecular mass for (a) PI and (b) BR; ● - data of the present work; × - data given in ref. 11.

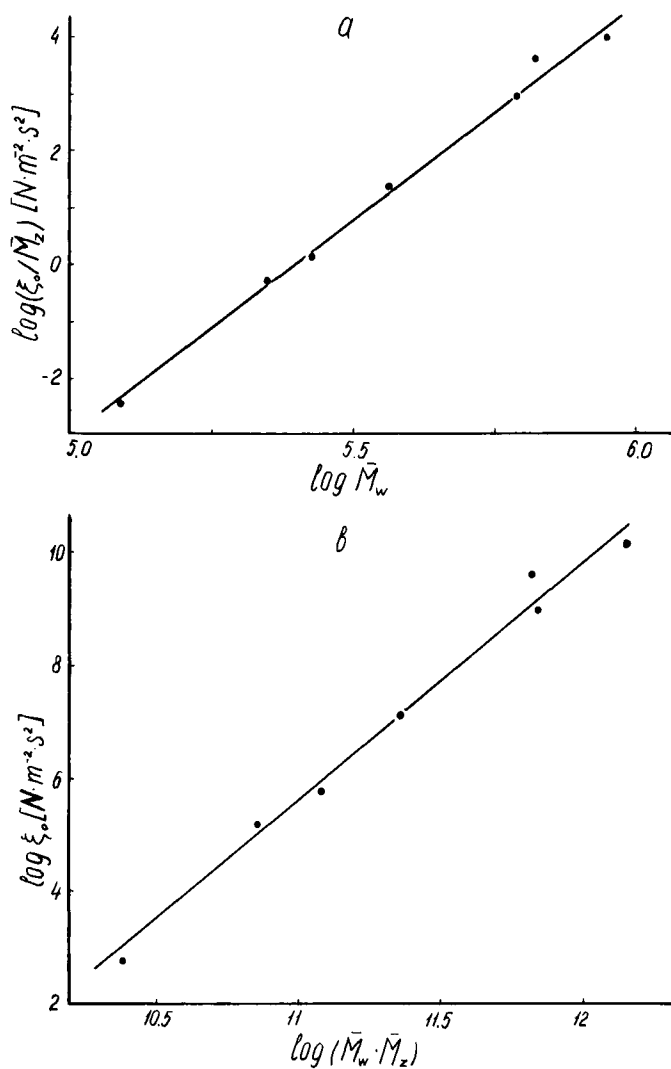


FIGURE 10 Dependence of the initial normal stress coefficient at 100°C on the molecular characteristics of PI.

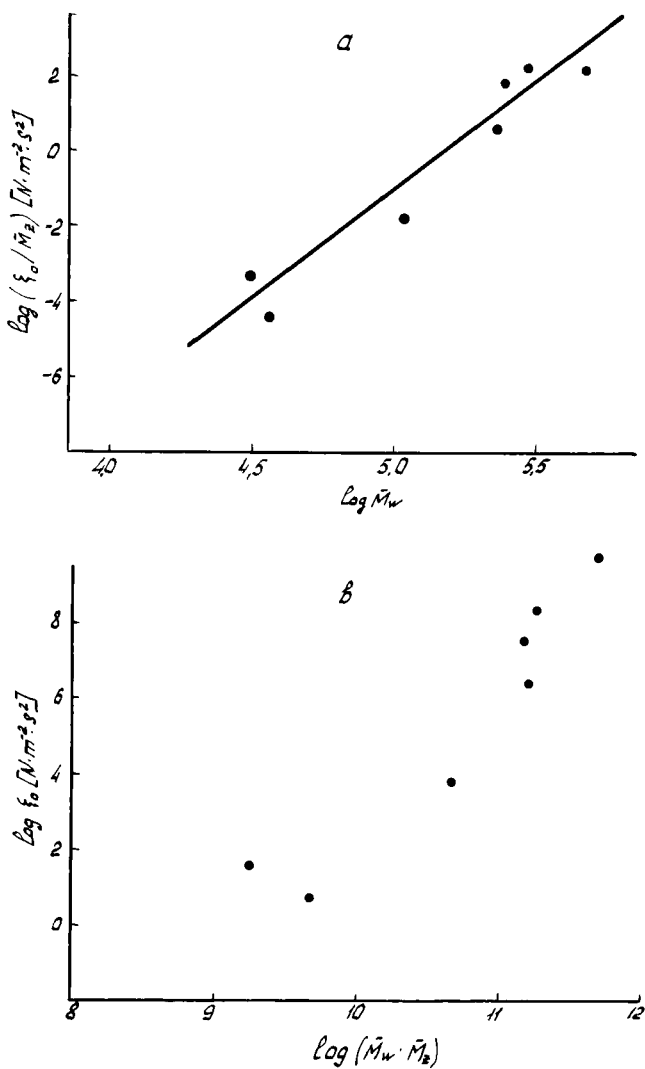


FIGURE 11 Dependence of the initial normal stress coefficient at 100°C on the molecular characteristics of butyl rubber.

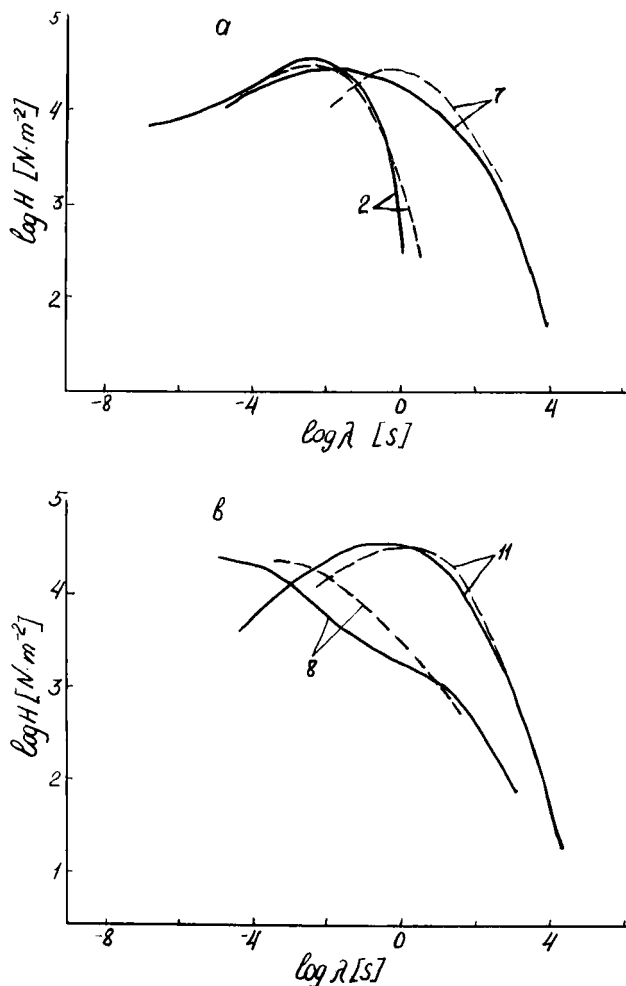


FIGURE 12 The relaxation-time spectra of (a) PI and (b) BR, calculated from MMD (—) and obtained from experimentally measured dependences of $G'(\omega)$ (---).

The expressions most frequently used for the calculation of the relaxation-time spectrum $H(\theta)$ do not take into account the molecular characteristics of a polymer. In this connection, it is interesting to compare the relaxation-time spectra calculated from data on molecular-mass distribution and from the dependences of the dynamic characteristics on the frequency.

From data obtained by gel permeation chromatography and the dependence of G' on ω reduced to 100°C there have been constructed logarithmic

relaxation time H-spectra according to Ninomiya and Yasuda¹⁵ and Ferry:¹⁶

$$H(\ln \theta) G'_{pl} = M_n f(M)/a$$

$$\theta G'_{pl} = KM^a \quad (8)$$

$$H(\theta) = AG'_{pl} \left(2 - \frac{d \log G'}{d \log \omega} \right) \Big|_{\omega^{-1}} \quad (9)$$

where G'_{pl} is the modulus on the rubbery (high-elasticity) plateau; $f(M)$ is the molecular-mass distribution (MMD) function. The values of K and a for PI and BR were taken from expressions (2) and (4). As follows from Figure 12, the relaxation-time spectra calculated from formulas (8) and (9) are in satisfactory agreement with a sufficiently narrow MMD for elastomers. The use of the Williams–Ferry method for the calculation of $H(\theta)$ for elastomers of wide MMD is not legitimate. Besides, the relaxation spectra calculated from molecular-mass data cover a wider range of relaxation times.

From the spectra calculated on the basis of molecular-mass characteristics there have been found the values of η_0 at 100°C for BR and PI samples; they are listed in Table I. This table also presents the values of η_0 obtained experimentally. As can be seen from Table I, the Newtonian viscosities calculated from the spectrum agree well with the experimentally determined values, which points to the reliability of the spectra calculated from the molecular-mass characteristics.

Thus, we have established the quantitative relationships between the main molecular and rheological characteristics of PI and BR over a wide spectrum of their molecular parameters, which permits one to determine, on the basis of the known molecular parameters, all the principal rheological characteristics over a wide range of temperatures, frequencies and deformation rates.

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