VISCOELASTIC PROPERTIES OF AMORPHOUS POLYMERS IN THE RUBBERLIKE ELASTIC STATE AS A FUNCTION OF THE NATURE AND LENGTH OF THE POLYMER CHAIN

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The effect of the fundamental molecular parameters on the behavior of polymers in the region of the rubberlike-elasticity plateau is analyzed to find "corresponding states" of different polymers and methods for reducing the experimental data to a generalized form.

The core problem in the description of the viscoelastic properties of polymers is to determine the parameters that can be used to characterize their individual features as simply as possible, along with functions that predict the dependence of the properties of polymers on their molecular structure and the parameters of whatever external influences are felt. The variation of the viscoelastic properties as a function of the temperature and time is similar for many amorphous linear polymers, so that the problem reduces to the selection of "corresponding states," in which the polymers are mechanically equivalent. This problem has been expounded in the literature since 1939, at which time A. P. Aleksandrov and Yu. S. Lazurkin demonstrated the equivalent influence of temperature and cyclic deformation frequency on the properties of a polymer [1]. This result was later formulated as the principle of temperature–time or temperature–frequency superposition and acquired significant development in the schools of Ferry [2] and Tobolsky [3]. Also of considerable theoretical importance is the equivalence of the temperature dependences of the relaxation times of various polymers for a proper choice of normalization temperature [4, 5].

In research on the properties of polymers in the fluid state the principle of "logarithmic additivity" has been established [6], and it has been shown [7] that the viscoelastic properties of linear polymers in the fluid state are determined primarily by two individual parameters, the glass-transition temperature T_g and the number of segments $N = M/M_c$, where M is the molecular weight of the polymer and M_c is the critical molecular weight corresponding to the formation of a three-dimensional linkage configuration [8, 9]. Then, adopting the quantities T_g and N as the arguments of the viscoelastic characteristics, one can derive a set of universal functions characterizing the principal features of the behavior of linear polymers in the fluid state.

It has been established in the investigation of polymers in the glassy state that the viscoelastic properties depend only slightly on the molecular characteristics of the polymers [2, 3]. Also, the elastic modulus of glassy polymers is of the order 10^{10} dyn/cm^2, irrespective of the nature of the polymer chain [10].

The rubberlike elastic state is the most characteristic state of polymers. It occurs in definite ranges of temperatures or application times, when the deformations of the polymers turn out to be mainly irreversible; this irreversibility has an entropy character. The rubberlike elastic state has been meagerly studied in the case of uncrosslinked polymers.

The rubberlike high-elasticity state is manifested in the temperature and frequency dependences of the elastic modulus, as we know, by what we call the rubberlike-elasticity plateau. It is also well known that the width of this plateau increases with the molecular weight [11]. For different polymers, however,

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TABLE 1. Characteristics of the Investigated Polymers

Polymer	ρ_{25}	$\|\eta\|$*	$M\cdot 10^{-5}$†	M_w/M_n	Microstructure‡			T_g	Antioxidant, %	Catalyst**
					cis-	trans-	1,2			
Polybutadiene PB-1	0,89	6,51	8,42	1,05	40	31,5	28,5	193	0,5	sec-BuLi
Polybutadiene PB-2	"	3,42	3,72	1,12	40,5	33,5	26	193	"	" "
Polybutadiene PB-3	0,895	1,63	1,43	1,1	47,2	44	8,8	180	0,6	" "
Polybutadiene PB-4	"	1,26	1,02	1,1	44	42	14	180	"	n-BuLi
Polystyrene	1,05	—	8,6††	1,1	Atactic			388	—	—

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*The value of $|\eta|$ was determined for solutions in toluene at 25°C.

†The molecular weights of the polybutadienes were calculated according to the equation $|\eta| = 1.56\cdot 10^{-4} M^{0.78}$, starting with the values found for $|\eta|$ (see [12).

‡The microstructure was determined by infrared spectroscopy.

**All the samples were prepared by anionic polymerization from "live" chains.

††The sample was prepared at the Mellon Institute in the USA; the molecular weight data were furnished by the Institute.

TABLE 2. Initial Viscosity of Polybutadienes at Various Temperatures (°K)

$M\cdot 10^{-3}$	$\eta_0\cdot 10^{-4}$								
	217,5	225	233,5	254	293	315	334	353	371
38	1260	295	115	18,6	1,26	—	—	—	—
143	—	—	—	—	200	72,5	39,8	22,9	14,1

the relationship between the molecular characteristics and width of the rubberlike-elasticity plateau, on the one hand, and the height of the plateau, on the other, has been investigated by diverse methods and with objects having different molecular weight distributions (MWD's). For this reason it is impossible to compare the data obtained by different authors in order to develop general laws.

The present article is concerned with the investigation of the effect of the fundamental molecular parameters on the behavior of polymers in the region of the rubberlike-elasticity plateau in order to find "corresponding states" of unlike polymers and methods for the reduction of the experimental data to a generalized form.

We used polymers having various chain rigidities and narrow MWD's, so that they could be regarded as essentially monodisperse, thus precluding the influence of the MWD and confining the investigation to the influence of the length and rigidity of the polymer chain (i.e., the number of segments) on the viscoelasticity in various temperature–time deformation regions.

EXPERIMENTAL METHOD

The objects of our study were polybutadiene and polystyrene having a polydispersity ratio no greater than 1.1. The latter was determined by ultracentrifuge sedimentation rate measurements. The physicochemical characteristics of the samples are listed in Table 1. The densities of the polybutadienes at various temperatures were found with the use of the bulk expansion coefficient given in [13], $7.5\cdot 10^{-4}$. Our antioxidants were N-phenyl-N'-isopropyldiamine (for the PB-1 and PB-2 samples) and ionol (for the PB-3 and PB-4). The temperature dependence of the density was taken from [14] for polystyrene. The glass-transition temperatures of all the samples were determined from the position of the loss maximum at a frequency of 1 Hz by means of a torsional pendulum executing freely damped oscillations.

The torsional pendulum used in the investigation is described in [15]. The dynamical characteristics, i.e., the elastic modulus G' and mechanical loss tangent tan δ, were calculated from the measurement results by conventional methods (see, e.g., [16]).

We obtained the dynamical characteristics over a wide frequency range by the temperature–frequency superposition method, plotting the dependence of the reduced modulus $G'_{re} = G'(\rho_0 T_0/\rho T)$ on the reduced frequency ωa_T (where ρ and ρ_0 are the densities of the polymer at temperatures T and T_0; ω is the cyclic frequency; and a_T is the temperature coefficient of shear).

In log–log coordinates the majority of the graphs of G'_{re} versus ω were essentially parallel to the horizontal axis and could not be used to determine the shear coefficient a_T of the curves along the axis over the entire temperature range.

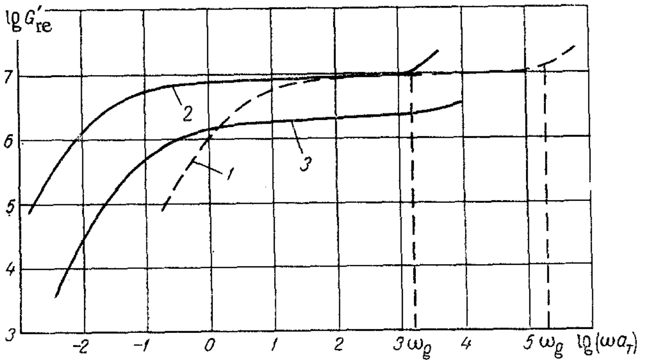

Fig. 1. Reduced elastic modulus G'_{re} versus reduced frequency for polybutadiene PB-4 at 265 (1) and 220°K (2), and for polystyrene at 473°K (3). Coordinates log (G'_{re}), dyn/cm^2; log (ωa_T), sec^{-1}.

TABLE 3. Coefficients of the WLF Equation for the Adopted Reduction Temperatures

Polymer	T_g	T_0	C_1^0	C_2^0
PB-1, PB-2	193	236	5,9	85,5
PB-3, PB-4	180	220	6,9	102

We used the following methods to determine the functions $a_T(T)$. It is well known (see, e.g., [8]) that a_T is independent of the molecular weight of polymers with $M > M_C$. Then the coefficient a_T can be determined at various temperatures from the expression $a_T = (\eta_T/\eta_{T_0})(\rho_0 T_0/\rho T)$ (where η_T and η_{T_0} are the initial viscosities of the polymer at temperatures T and T_0), by using the temperature dependence of the viscosity for samples in which such measurements are relatively easy to perform.

The foregoing method was used to determine the function $a_T(T)$ for the PB-3 and PB-4 samples. The values of the initial viscosity η_0 were determined on a constant-pressure capillary viscosimeter [17]; at low temperatures we used a polybutadiene sample with $M = 3.8 \cdot 10^4$ whose microstructure was close to that of PB-3 and PB-4. The resulting data are summarized in Table 2.

From these data we calculated the coefficients a_T and, assuming that the function $a_T(T)$ is described by the well-known Williams–Landel–Ferry (WLF) equation [2], we plotted the dependence of $(T - T_0)/\log a_T$ on $(T - T_0)$. From the graph of this dependence, which forms a straight line, we determined the coefficients C_1 and C_2 in the WLF equation.

For the PB-1 and PB-2 samples we determined the coefficients C_1 and C_2 in the WLF equation by the same method, except that, due to the absence of low-molecular samples having a similar microstructure, we determined the values of $\log a_T$ directly by shifting the dependences $G'_{re}(\omega)$ along the frequency axis in the temperature range from 260 to 373°K.

For the polystyrene (PS) we borrowed the function $a_T(T - T_0)$ from [18].

The reduction temperature T_0 for the various polymers was determined on the basis of the condition $T_0/T_g = \text{const}$, which, as will be shown presently, guarantees the analysis of the fundamental rubberlike elasticity characteristics of polymers in "corresponding states." The choice of values for the reduction temperature was dictated by the fact that the viscoelastic properties of PS, according to published data [18], are known for $T_0 = 473$°K, i.e., for $T_0/T_g = 1.22$. The values of T_g at a frequency of 1 Hz, T_0, and the coefficients C_1^0 and C_2^0 of the WLF equation for the investigated polybutadiene samples are given in Table 3.

RESULTS AND DISCUSSION

It is customarily assumed that the coefficients in the WLF equation are "universal" for calculations of the shear temperature coefficient a_T. Then, at a temperature differing from the glass-transition point by a certain amount (at $T = T_g + \Delta T$), the relaxation times must decrease relative to the relaxation times at T_g in the same proportion for different polymers. It is not clear, however, whether the different polymers turn out to be equivalent at $T_g + \Delta T$ with respect to the regions of transition from the rubberlike to the fluid and glassy states when all three regions are estimated from the frequency scale. Inasmuch as the curves for $G'_{re}(\omega a_T)$ are similar for dissimilar linear polymers, in order to solve this problem it is necessary to determine on those curves characteristic points in the transition regions from the rubberlike to the fluid and glassy states. If these characteristic points on the curves for $G'_{re}(\omega a_T)$ occupy the same

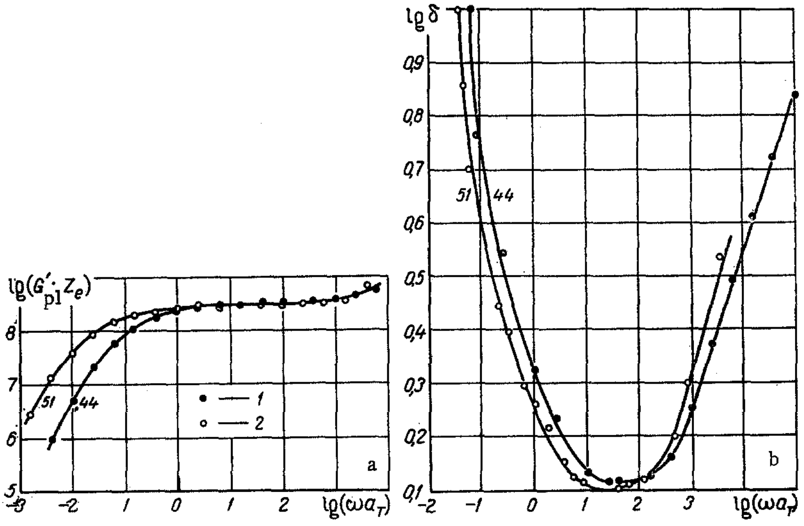

Fig. 2. Normalized elastic modulus $G'_{pl} \cdot Z_e$ (a) and mechanical loss tangent (b) versus reduced frequency at $T_0 = 1.22\ T_g$ for polystyrene (1) and polybutadiene PB-4 (2). The numbers attached to the curves indicate the number of dynamic segments in the polymer chains. Coordinates $\log(G'_{pl} \cdot Z_e)$, dyn/cm²; $\log(\omega a_T)$, sec⁻¹.

position on the frequency scale for different polymers, then these polymers may be regarded as equivalent from the standpoint of their rubberlike transition tendency.

Let us examine the experimental data for PS and PB-4 (Table 1), processed so that the reduction temperature in both cases differs by the same amount. This circumstance is illustrated in Fig. 1, for which the reduction temperature was assumed equal to 473°K for PS and to 265°K for PB, i.e., in both cases the reduction temperature was $T_g + 85°$.

We note first of all that the interval of rubberlike elasticity for monodisperse polymers corresponds to an almost constant value of the modulus G'_{re}. It is a well-known fact that the transition region from the rubberlike to the glassy state is virtually independent of the molecular weight and is therefore specific to a particular polymer homologous series. We denote the beginning of this transition by the point ω_g, which we determine from the graph of $G'_{re}(\omega a_T)$ as the value of ω at which the tangent to the graph of $G'_{re}(\omega a_T)$ at high frequencies reaches 10°. Taking into account the essentially inconsequential variation of the modulus in the vicinity of the rubberlike-elasticity plateau, we specify its low-frequency limit (transition into the fluid state) as the frequency ω_f at which G'_{re} decreases 0.2 of a decimal order (i.e., by 1/1.6) relative to its value at $\omega = \omega_g$. This definition of the plateau limits is conditional, but all that matters in the present study is that the assessment procedure be consistent for the various polymers. Thus, the characteristic point ω_g reflects the special features of the polymer homologous series, i.e., it is related to the segmental properties of the polymer chain, and the influence of the molecular weight on the width of the plateau is reflected in the distance of ω_f from the point ω_g on the frequency scale. The dependence of ω_g on the segmental properties is a consequence of the fact that the rubberlike-elasticity plateau degenerates as the molecular weight of the polymer decreases. The frequency ω_f moves closer to ω_g with decreasing molecular weight. In the limit as the molecular weight corresponds to the onset of the plateau, ω_f merges with ω_g. Then ω_g turns out to be an intrinsic characteristic of the viscoelastic properties of a polymer whose molecular weight is equal to the "segmental" molecular weight for the polymer homologous series.

It is apparent from Fig. 1 that with reduction to $T_0 = T_g + 85°$ the value of ω_g for polybutadiene is 2.1 decimal orders higher than for polystyrene. Consequently, the reduction to $T_0 = T_g + \text{const}$ does not guarantee the equivalence condition for different polymers in the sense that the characteristic transition to the glassy state for the different polymers will be observed at the same frequency.

We therefore choose for the polybutadienes a reduction temperature T_0 such that the complete attainment of the rubberlike elastic state corresponds to the same frequency as for polystyrene, i.e., in both cases we let $\log \omega_g = 3.2$. The value of $\log \omega_g$ 3.2 is attained for PB-4 at a reduction temperature of 220°K. A comparison of the reduction temperatures for polystyrene (473°K) and PB-4 (220°K) with the

TABLE 4. Characteristic Parameters for Various Polymers

Polymer	M_0	M_e	Z_e	$\bar{G}'_{pl} \cdot 10^{-6}$, dyn/cm^2	$G'_{pl} \cdot Z_e \cdot 10^{-8}$, dyn/cm^2
Polystyrene	104	$1{,}94 \cdot 10^4$	187	2,0	3,74
Polybutadiene PB-4	54	$2{,}0 \cdot 10^3$	37	8,7	3,22
Poly-α-methylstyrene	118	$1{,}2 \cdot 10^4$	101,6	3,4	3,46

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* The values of $\bar{G}'_{pl}$ are based on the data of [20].

TABLE 5. Relationship between the Glass-Transition Temperature and Monomer-Element Molecular Weight of Various Polymers

No.	Polymer	T_g	M_0	T_g/M_0
1	Polybutadiene (14% 1,2-; 42% trans-; 44% cis-)	180	54	3.34
2	Polybutadiene (8.8% 1,2-; 44% trans-; 47.2% cis-)	180	54	3.34
3	Polybutadiene (28% 1,2-; 31.5% trans-; 40% cis-)	193	54	3.57
4	Polystyrene	388	104	3.73
5	cis-Polyisoprene	223	68	3.28
6	Polyvinylacetate	306	86	3.56
7	Polyisobutylene	225	56	4.01
8	Polybutadiene (70% 1,2-; 30% 1,4-)	236	54	4.37
9	Polyvinylmethyl ether	263	58	4.53
10	Polyvinylethyl ether	256	72	3.56
11	Polyvinylpropyl ether	246	86	2.86
12	Polyvinyl-n-butyl ether	241	100	2.41
13	Polymethylacrylate	298	86	3.47
14	Polyethylacrylate	268	100	2.68
15	Polybutylacrylate	239	128	1.87
16	Polyvinylchloride	363	62.5	5.8

Note: The values for Nos. 1-4 are taken from the results of the present study, for Nos. 5-16 from [21]. In every case the values of T_g were measured by the dynamic method at a frequency of 1 Hz.

corresponding glass-transition temperatures yields the ratio $T_0/T_g = 1.22$. Analogous ratios were obtained for the other polybutadiene samples, whose reduction temperatures are indicated above. The constancy of the ratio T_0/T_g in correspondence with the above-indicated conditions is hardly fortuitous. On the contrary, it is reasonable to assume that this fact is attributable to the behavior of the temperature dependence of the relaxation characteristics of the polymers. In fact, an equal distance from the glass-transition temperature does not correspond to an equal molecular energy state; the latter is determined by the temperature ratio.

It is clear from Fig. 1 that at $T_0 = 1.22\ T_g$ the conditions for transition from the rubberlike to the glassy state equalize for polystyrene and polybutadiene, but the corresponding values of the elastic modulus do not become equal. The average values of the elastic moduli in the vicinity of the rubberlike elasticity plateau, $\bar{G}'_{pl}$, differ for polystyrene and polybutadiene; for the former it is $2 \cdot 10^6$ dyn/cm^2, and for the latter (PB-4) it is $8.7 \cdot 10^6$ dyn/cm^2. This disparity in the values of $\bar{G}'_{pl}$ is not related to a difference in the lengths of the molecular chains of dissimilarly structured polymers, but to the properties of the dynamic segment, mainly its rigidity.

The molecular weight M_e of the dynamic segment can be calculated from the average modulus $\bar{G}'_{pl}$ by using the well-known relation between M_e and $\bar{G}'_{pl}$ from the theory of rubber elasticity [19]. The segmental rigidity is characterized by the number of monomer elements contained in it, $Z_e = M_e/M_0$ (M_0 is the

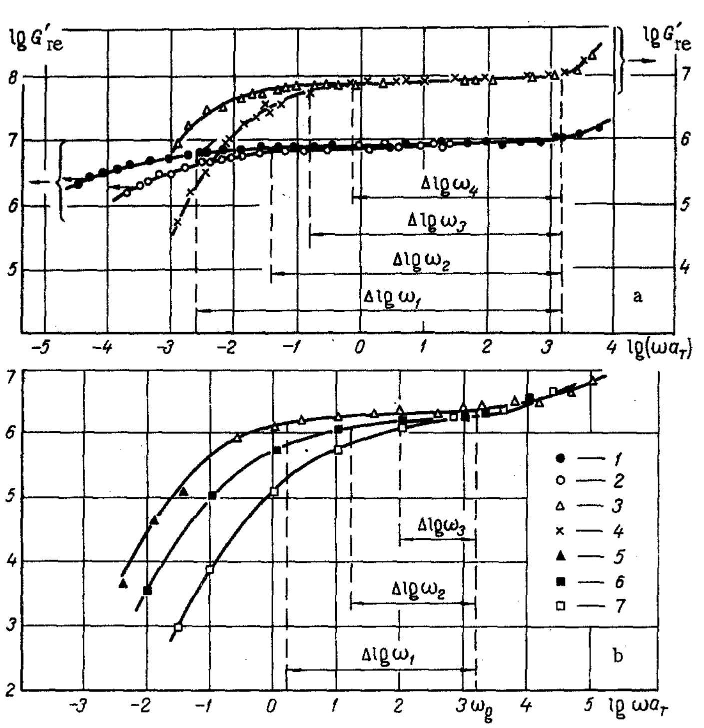

Fig. 3. Reduced elastic moduli G'_{re} versus reduced frequency. Coordinates $\log G'_{re}$, dyn/cm^2; $\log(\omega a_T)$, sec^{-1}. a) PB-1 (1); PB-2 (2); PB-3 (3); PB-4 (4); b) polystyrene with molecular weights $8.6 \cdot 10^5$ (5); $5.1 \cdot 10^5$ (6); $2.67 \cdot 10^5$ (7).

molecular weight of the monomer element). In polymers having different segmental rigidities and different monomer elemental structures the density of the three-dimensional fluctuation entanglement of physical bonds differs, as determined by the number N of segments per unit length, i.e., the frequency of entanglement nodes and the length l_0 of the monomer element. It is instructive, therefore, to compare the moduli, normalized on the number of linkage nodes per unit chain length and on unit monomer element length, i.e., the quantity $G'_{pl}/\mathcal{N}_0$. It is readily seen that $\mathcal{N}_0 Z_e = 1$, so that $Z_e = 1/\mathcal{N}_0$ and $\overline{G}'_{pl}/\mathcal{N}_0 = G'_{pl} \cdot Z_e$. This normalization of the moduli enables us to compare the properties of physical linkages that are equivalent in terms of the node frequency (spacing) and length of the monomer element. In other words, the characteristic parameter $\overline{G}'_{pl} \cdot Z_e = \rho RT/M_0$ may be regarded as the elastic modulus of a rubber for which the linkage node spacing is equal to the length of one monomer element.

A comparison of the dependences of $\overline{G}'_{pl} \cdot Z_e$ on ωa_T for polystyrene and PB-4 at $T_0 = 1.22\ T_g$ is made in Fig. 2a, from which it is evident that the indicated normalization procedure can be used effectively to align not only the values of ω_g, but also the elastic moduli in the vicinity of the rubberlike-elasticity plateau.

Processing of the experimental data given in [20] for monodisperse poly-α-methylstyrene yields for this polymer a value of the characteristic parameter $\overline{G}'_{pl} \cdot Z_e$ close to the corresponding values for polystyrene and polybutadiene. This conclusion is evident from the data presented in Table 4.

In order to ascertain the generality of the above-described method of reduction on the plateau height for dissimilar polymers, we use the relation $\overline{G}'_{pl} = \rho_0 RT_0/M_e$ and recognize that $T_0 = 1.22\ T_g$ to obtain $\overline{G}'_{pl} = (1.22\rho_0 R)T_g/M_0$.

As the latter equation attests, the comparison of different polymers on the basis of the characteristic parameter $\overline{G}'_{pl} \cdot Z_e$ is equivalent to their comparison on the basis of the ratio T_g/M_0 (we neglect the factor ρ_0, since it varies over the narrow interval from 0.85 to 1.00 g/cm^3 for the polymer group considered here). The values of $\overline{G}'_{pl}$ have not been determined for a large class of monodisperse polymers, but the values of T_g are reliably known for many polymers; consequently, in Table 5 a large number of amorphous polymers are compared on the basis of the ratio T_g/M_0.

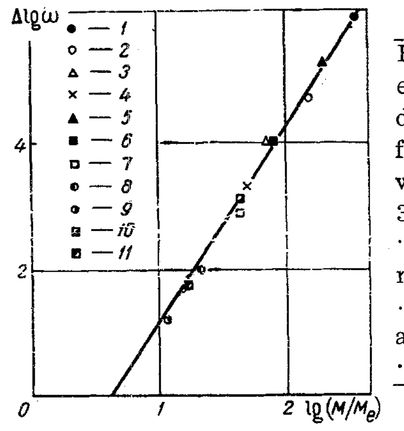

Fig. 4. Width $\Delta \log \omega$ of the rubberlike-elasticity plateau versus the number of dynamic segments in the polymer chain for various polymers. Polybutadienes with with molecular weights: 1) $8.42 \cdot 10^5$; 2) $3.72 \cdot 10^5$; 3) $1.43 \cdot 10^5$; 4) $1.02 \cdot 10^5$; 5) $5.1 \cdot 10^5$; 6) $1.8 \cdot 10^5$ [13]; polystyrene with molecular weights: 7) $8.6 \cdot 10^5$; 8) $5.10 \cdot 10^5$ [18]; 9) $2.67 \cdot 10^5$ [18]; polyvinyl-acetates with molecular weights: 10) $7.56 \cdot 10^5$; 11) $3.2 \cdot 10^5$ [24].

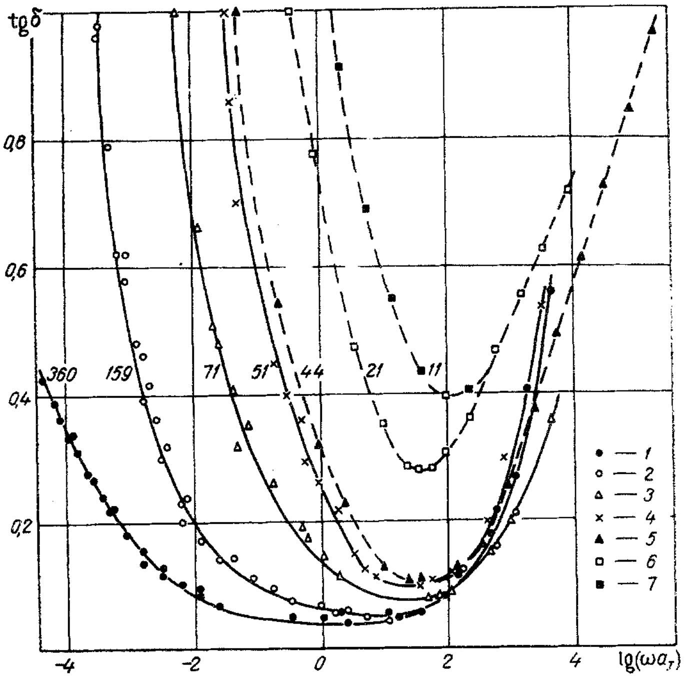

Fig. 5. Mechanical loss tangent versus reduced frequency. 1) PB-1; 2) PB-2; 3) PB-3; 4) PB-4; polystyrenes (dashed curves) with molecular weights: 5) $8.6 \cdot 10^5$; 6) $5.1 \cdot 10^5$; 7) $2.67 \cdot 10^5$. Abscissa $\log(\omega a_T)$, $\sec^{-1}$.

It is evident from Table 5 that for one group of polymers (Nos. 1-7) the ratio T_g/M_0 is close, on the average, to 3.62, with ±10% deviation from the average. As the length of the side substituents is increased the values of T_g/M_0 decrease (in the case of polybutylacrylate, for example, $T_g/M_0 = 1.87$), and with the addition of polar substituents they increase (for polyvinylchloride, for example, $T_g/M_0 = 5.8$). These data characterize the tendency of the polymer rigidity to vary as a function of the specific attributes of the intermolecular couplings and reveal that the method proposed above for normalization of the plateau modulus is only universal for nonpolar polymers without long side branchings in the monomer element.

As evinced by Fig. 2a, the widths of the rubberlike-elasticity plateaus for PS and PB-4 are close together when their molecular weights differ by a factor of approximately eight. This result is attributable to the fact that both of these polymers have similar numbers of dynamic segments (44 for polystyrene and 51 for polybutadiene) and, according to our earlier paper [22], the plateau widths for these polymers must be close (amounting to 2.9 and 3.3 decimal orders for these respective polymers). It is reasonable to assume that, with an equal number of segments in the polymer chains, these substances should be equivalent at $T_0 = 1.22\ T_g$.

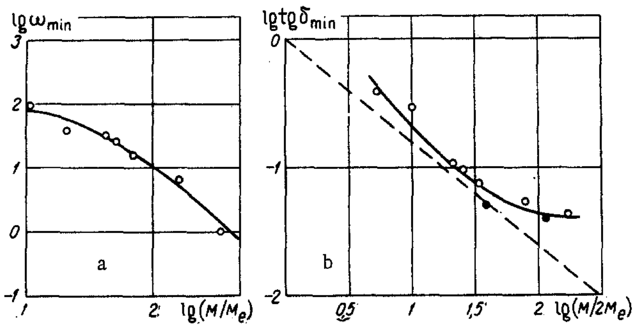

Fig. 6. Influence of the number of dynamic segments in the polymer chain on the reduced frequency corresponding to the minimum of the dependence $\tan\delta(\omega a_T)$ (a) ($\log\omega_{min}$, sec^{-1}) and the minimum value of the mechanical loss tangent (b) ($\log\tan\delta_{min}$).

As for the dependence of $\tan\delta$ on ωa_T, as seen in Fig. 2b, the values of $\tan\delta_{min}$ and the positions of these minima on the frequency axis for PS and PB-4 are close together, confirming the inference of Marvin's theory [23] concerning the proportionality of $\tan\delta_{min}$ to the number of segments, irrespective of the nature of the polymer chain. At this point a more general conclusion asserts itself regarding the equivalence of the dependences of $\tan\delta$ on ωa_T over the entire frequency range under the condition $T_0 = const \cdot T_g$ for polymers with strictly identical numbers of segments in the chain.

We now analyze the width of the rubberlike-elasticity plateau in the frequency dependence of the dynamic modulus.

The method of estimating the width of the plateau region on these curves was described above. It has been shown in [22] that the plateau width $\Delta\log\omega$ is directly proportional to X, where $X = \log(M/M_{pl})$ and M_{pl} is the molecular weight corresponding to the onset of the plateau. The experimental results of the present study permit us to confirm the conclusions and to refine the values found for the coefficients in our earlier work.

The dependence of the elastic moduli $G'_{re}(\omega a_T)$ for the polybutadienes and polystyrene and widths $\Delta\log\omega$ of the rubberlike plateau are given in Fig. 3a and 3b. Also shown in Fig. 3b are the experimental data of [18] for two polystyrene samples with molecular weights of $5.1 \cdot 10^5$ and $2.67 \cdot 10^5$. The molecular weights M_e of the dynamic segments for the investigated samples have the following values: $2.33 \cdot 10^3$ for PB-1 and PB-2; $2.0 \cdot 10^3$ for PB-3 and PB-4; $1.94 \cdot 10^4$ for polystyrene.

The dependence of the rubberlike plateau width $\Delta\log\omega$ on the logarithm of the number of segments M/M_e in the polymer chain is shown in Fig. 4. Also plotted in this figure are the analog-processed data of [13] for two polybutadiene samples (molecular weights of $5.1 \cdot 10^5$ and $1.8 \cdot 10^5$) and of [24] for two polyvinylacetate samples (molecular weights of $7.5 \cdot 10^5$ and $3.2 \cdot 10^5$). The molecular weights M_e of the dynamic segments for these polymers are $2.22 \cdot 10^3$ and $1.75 \cdot 10^4$, respectively. As apparent from Fig. 4, which is plotted in log–log coordinates, the plateau width exhibits a power-law dependence on the number of dynamic segments in the polymer chain. The power exponent, which is equal to 3, is universal for all the given polymers. It is important to note that the relationship between $\Delta\log\omega$ and $\log(M/M_e)$ is independent of the choice of reduction temperature. It is only important at each reduction temperature to estimate $\Delta\log\omega$ by the same method and to calculate M_e from the value of $\bar{G}'_{pl}$. For example, the data of [13] for polybutadiene at $T_0 = 298$°K and the experimental data given in this article for the polybutadienes provide comparable results on the dependence $\Delta\log\omega(\log M/M_e)$.

The line given in Fig. 4 intercepts the horizontal axis at $\log(M/M_e) \approx 0.6$. This fact indicates that linear polymers have a critical molecular weight M_{pl}, at which the frequency dependence of the elastic modulus begins to acquire a rubberlike-elasticity plateau. It is evident from the cited data that $M_{pl} = 4M_e$. Consequently, the dependence $\Delta\log\omega(\log M/M_e)$ can be described by the relation

$$\Delta\lg\omega = 3\lg(M/4M_e). \qquad (1)$$

This dependence is universal both for a typical thermoplast having a long rigid chain, such as polystyrene, as well as a typical elastomer having a very flexible chain, such as polybutadiene.

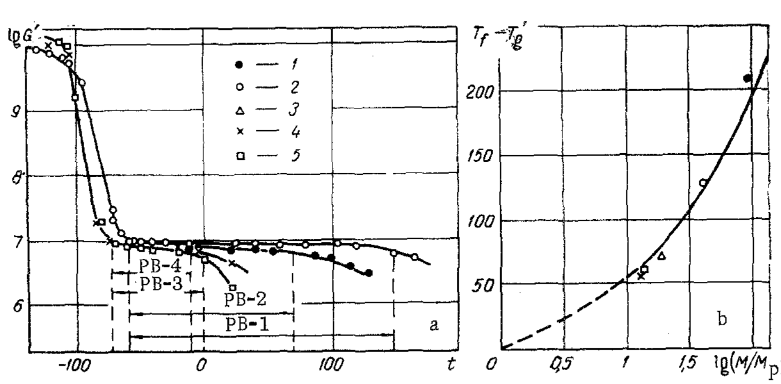

Fig. 7. Elastic modulus versus temperature at 1 Hz for polybutadiene (a) and relationship between the width of the rubber-like-elasticity plateau on the temperature curves of the elastic modulus and the number of dynamic segments in the polymer chains (b). Coordinates log G', dyn/cm^2; t, °C. 1) PB-1; 2) PB-2; 3) PB-3; 4) PB-4; 5) polystyrene: $M = 8.6 \cdot 10^5$.

It has already been demonstrated above that under the condition $T_0 = \text{const} \cdot T_g$ the dependence $\tan\delta \cdot (\omega a_T)$ is determined solely by the number of dynamic segments in the polymer chain, irrespective of the nature of the latter. The numbers attached to the curves in Fig. 5 indicate the number of dynamic segments for each sample. It is clear from the figure that for monodisperse polymers the dependence $\tan\delta(\omega a_T)$ has in the plateau region a distinct minimum, which shifts toward higher frequencies as the number of segments is diminished. Moreover, the minimum value of $\tan\delta(\omega a_T)$ is lower, the greater the number of dynamic segments composing the polymer chain.

This result admits the following interpretation. We know that the value of $\tan\delta$ for vulcanized rubbers decreases more rapidly, the higher the crosslink density. The fluctuation linkage configuration in unvulcanized rubber differs from the chemical crosslink configuration in that each linkage has a definite lifetime, i.e., disappears and reappears at a definite frequency. Only at frequencies commensurate with or greater than the natural frequencies of the generation and disintegration of the temporal linkages can this network produce an effect analogous to the spatial network of chemical bonds. From this point of view the position of the minimum for $\tan\delta(\omega a_T)$ on the frequency axis must be attributable to a certain characteristic ("mean") frequency of disintegration and generation of physical linkages in the polymer. The dependence of the position ω_{min} of the minimum of $\tan\delta(\omega a_T)$ along the frequency axis on the number of segments in the polymer chain is shown in Fig. 6a. As the molecular weight increases the mobility of the chain as a whole is reduced, causing an increase in the "mean" lifetime of the linkages; this effect is equivalent to the position ω_{min}.

With increasing molecular weight the value of $\tan\delta_{min}$ also decreases. This behavior is illustrated in Fig. 6b, in which the number of dynamic segments in the polymer chain for polystyrene and polybutadiene is adopted as the argument. This figure was plotted on the basis of our original experimental results as well as the data of [13, 18].

The dashed curve represents the dependence corresponding to the theoretical equation [23]

$$\operatorname{tg}\delta_{min} = 1.02\ (M/2M_e)^{-0.8}. \tag{2}$$

As seen in Fig. 6b, for $N = M/2M_e$ less than 70 the experimental and theoretical dependences are close. For $N > 70$, however, the value of $\tan\delta_{min}$ becomes constant, deviating from the theoretical. This result is probably a consequence of the fact that, beginning with a certain value of N, the ends of the polymer chains introduce a negligibly small contribution to the deformation losses, inasmuch as they are small relative to the total length of the polymer chain. The effect of the finite chain length is not incorporated in the theory of [23].

The concept of the rubberlike-elasticity plateau was treated above solely as an interval defined on the frequency curve of the dynamic modulus under isothermal conditions. However, there is a widely held view of the rubberlike plateau as a temperature interval ΔT corresponding to a constant modulus (or compliance) measured for a constant stress–time regime. A general quantitative correspondence between these two types of plateau was established in our earlier paper [22], using the following relation as the basis of the theoretical analysis:

$$\lg(M/M_{\mathrm{pl}}) = \frac{B\Delta T}{C + \Delta T}, \tag{3}$$

which was first proposed in [11, 25]. Here B and C are empirical constants. The width of the plateau on the frequency dependence of the modulus, according to [22], is expressed in terms of the ratio of these constants.

The temperature dependences of G' obtained in the present study at a frequency of 1 Hz for the polybutadienes are given in Fig. 7a. Their processing, which was analogous to that for Fig. 1, made it possible to find the plateau width for the various samples investigated. The relationship between ΔT and log (M/M_{pl}) is shown in Fig. 7b, from which it is apparent that the solid curve plotted according to Eq. (3) agrees well with the experimental data for values of the constants B = 3.22 and C = 1.22. The ratio $B/C = 2.6 \cdot 10^{-2}$, which is close to the value obtained in [25], although the values of the constants themselves differ for polyisobutylene and the polymers investigated in our work. It may be assumed that the cause of this discrepancy lies both in the disparity of the methods used to determine the thermomechanical curve and in the fact that the character of the rubberlike plateau depends on the MWD.

The results confirm the motion of equivalence between the rubberlike-elasticity plateaus in the temperature and frequency curves of the dynamical properties of a polymer (cf. Figs. 4 and 7b), as well as the universality of the plateau width as a function of the number of segments in the chain, irrespective of the chemical nature of the latter.

Therefore, the main inference to be drawn from the foregoing experimental facts is that the viscoelastic properties of different polymers are quantitatively determined by two parameters: the glass-transition temperature and the size of the dynamic segment. This conclusion was obtained earlier [7] in application to the properties of different polymers in the fluid state. In the present study it is confirmed and generalized for the rubberlike interval.

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LITERATURE CITED

1. A. P. Aleksandrov and Yu. S. Lazurkin, Zh. Tekh. Fiz., 9, 1261 (1939).
2. J. D. Ferry, Viscoelastic Properties of Polymers, Wiley, New York (1961).
3. A. V. Tobolsky, Properties and Structure of Polymers, Wiley, New York (1960).
4. M. L. Williams, R. F. Landel, and J. D. Ferry, J. Amer. Chem. Soc., 77, 3701 (1955).
5. J. Bishoff, E. Catsiff, and A. V. Tobolsky, J. Amer. Chem. Soc., 74, 3378 (1952).
6. G. M. Bartenev and L. A. Vishchnitskaya, Vysokomolek. Soed., 6, 751 (1964).
7. A. Ya. Malkin and G. V. Vinogradov, Vysokomolek. Soed., 7, 1134 (1965).
8. T. G. Fox and P. J. Flory, J. Amer. Chem. Soc., 70, 2384 (1948).
9. R. Porter and J. Johnson, Chem. Rev., 66, 1 (1966).
10. A. V. Tobolsky and E. J. Catsiff, J. Polymer Sci., 19, 111 (1956).
11. V. A. Kargin and T. I. Sogolova, Zh. Fiz. Khim., 23, 530 (1949).
12. J. T. Gruver and G. J. Kraus, J. Polymer Sci., Part A, 2, 797 (1964).
13. R. H. Valentine, J. D. Ferry, T. Homma, and K. Ninomiya, J. Polymer Sci., Part A-2, 6, 479 (1968).
14. I. V. Konyukh, M. P. Zabugina, and G. V. Vinogradov, Zavod. Lab., 13, 123 (1965).
15. E. A. Dzyura and Yu. G. Yanovskii, Zavod. Lab., 35, 1485 (1969).
16. K. H. Illers and E. Jenkel, Kolloid-Z., 160, 97 (1958).
17. G. V. Vinogradov and N. V. Prozorovskaya, Plast. Massy, No. 5 (1964).
18. S. Onogi, H. Kato, S. Ueki, and T. Ubaragi, J. Polymer Sci., Part C, 15, 481 (1966).
19. L. Treolar, Physics of Rubber Elasticity, Clarendon, Oxford (1958).
20. T. Fujimoto, N. Ozaki, and M. Nagasawa, J. Polymer Sci., Part A-2, 6, 129 (1968).
21. K. Schmieder and K. Wolf, Kolloid-Z., 134, 149 (1953).
22. A. Ya. Malkin, E. A. Dzyura, and G. V. Vinogradov, Dokl. Akad. Nauk SSSR, 188, 1328 (1960).
23. H. Högberg, S. E. Lovel, and J. D. Ferry, Acta Chem. Scand., 14, 1424 (1960).
24. S. Onogi, T. Masuda, and T. Ibaragi, Kolloid-Z., 222, No. 2, 110 (1968).
25. V. A. Kargin and G. L. Slomimskii, Zh. Fiz. Khim., 23, 563 (1949).