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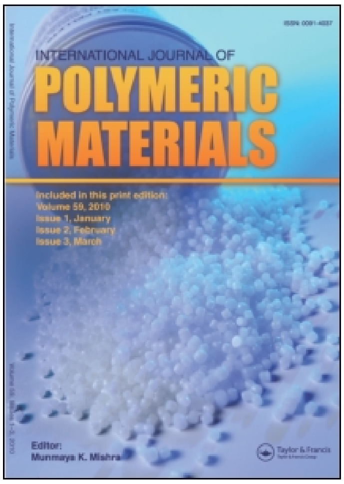

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Viscoelastic Characteristics of Polymers of Narrow Molecular-Mass Distribution in Various Physical States According to Data on Small-Amplitude Oscillating Shear

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Viscoelastic Characteristics of Polymers of Narrow Molecular-Mass Distribution in Various Physical States According to Data on Small-Amplitude Oscillating Shear

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This work is concerned with the results of dynamic investigations of 1,2-polybutadienes of narrow molecular-mass distribution over a wide temperature-frequency range covering various physical states of the material, from the fluid to the glassy state. The limits of applicability of the use of the temperature-frequency reduction are given. The experimental results have been obtained under the following test conditions: at variable frequency and constant temperature; at variable temperature and constant frequency.

INTRODUCTION

The small-amplitude deformation of polymers makes it possible to characterize their linear viscoelastic properties. An important feature of this method is that the structure of the polymer remains unchanged over a wide range of variation of deformation parameters (frequency and temperature). Important is the possibility of estimation of the conditions of transition of polymers from one physical state to another, the entire range of states including the fluid, high-elastic or rubbery, leathery and glassy states.[1] From an experimental standpoint, the most important task is to measure directly the quantitative characteristics of these states. For high-molecular-mass samples, under isothermal conditions, this requires a sufficiently wide frequency range (over tens of decimal orders), from the infralow to the ultrasonic region, which presents considerable experimental difficulties. In this connection, there naturally arises the question of the possibility of using the principle of temperature-time reduction or, which is the same thing, of temperature-frequency reduction in the region of the various physical states. The temperature-frequency reduction, which is an indirect method of estimating the relaxational properties of materials, is very extensively used in modern literature, though the possibility of its simultaneous application for high-molecular polymers of narrow MMD in extreme states, such as the fluid state, on the one hand, and the transient state (the leathery state) approaching the glassy state, is not quite clear.

The present work is concerned with new important results of dynamic investigations; these results have been obtained over a wide temperature–frequency range, which has enabled us to cover the various physical states of the material, in particular, to estimate the limits of the applicability of the method of temperature–frequency reduction. The results have been obtained under the following test conditions: at variable frequency and constant temperature, at variable temperature and constant frequency, at constant temperature and constant frequency. In the last case, we studied structurizing systems, whose properties sharply changed with time.

METHODS AND OBJECTS OF INVESTIGATION

The tests were carried out on an instrument for measuring the dynamic characteristics of polymers—a mechanical spectrometer,[2] operating under the regime of forced non-resonance oscillations in the range of circular frequencies ω from 10^{-4} to 1.6×10^{3} sec^{-1} at temperatures from -150 to 300°C. The instrument enables one to study the various materials, from viscofluid to solids. Its operation is based on a number of specially devised methods which considerably shorten the time of measurements in the region of frequencies below 0.628 sec^{-1} and increases the accuracy of phase measurements.[3–5] Let us consider briefly the essence of these methods.

The study of the dynamic viscoelastic properties of polymers must be carried out after the transient processes are complete; the duration of these processes may reach hundreds of oscillation periods. That is why the measurements carried out in the infralow frequency region take a rather prolonged period of time. The duration of the transient process depends on the properties of the object under study and the form of the perturbation function of the input signal. By varying the perturbation function of the input signal it is possible to alter the mode and duration of the transient process as a whole.

For this purpose, the required law of oscillation of the object is specified in the instrument with the aid of a controlling system which regulates the value of the applied mechanical stress. Picking out and analyzing the real and imaginary components of the controlling stress and taking into account the shape of the sample, we can calculate the dynamic characteristic of the polymer. The length of the transition process is given by

$$\tau = \frac{A\eta'(\omega)}{K+AG'(\omega)}$$

and the control error is

$$\Delta\theta = 1-\frac{K}{K+AG'(\omega)}$$

Here K is a dimensionless amplification factor of the controlling system; A is the form factor; η' and G' are, respectively, the dynamic viscosity and storage modulus of the polymer. At large K values the forced vibrations of the sample are set up sufficiently rapidly and the controlling mechanical stress assumes a stationary form.

In order to increase the accuracy of phase measurements, there has been devised the compensation method of measurements. The compensation of the mechanical resistance to movement, which is created by a mobile system, rules out the necessity of determination of the "constants" of the instrument. The magnitude of compensation signals has the same effect as the decrease of viscoelastic resistance to the movement of the sample: they are both proportional to the components of the compensating mechanical torque, M'_t and M''_t, and are chosen so that the registered components of mechanical resistance, M'_1 and M''_1, are commensurate with each other. In this case they are measured with satisfactory accuracy. Knowing M'_t and M''_t, M'_1 and M''_1, it is easy to calculate the values of $G' = M'_1+M'_t/\alpha'A$ and $G'' = \eta'$. $\omega = M''_1+M''_t/\alpha'A$, where α' is the specified vibration amplitude. The error of the measurement of the components of the complex modulus of the polymer will be governed by the sensitivity of the measuring instrument or by the error of specification of M'_t and M''_t.

The block-diagram of the mechanical spectrometer is given in Figure 1. The polymer sample 1 is placed between coaxial cylinders 2 which are secured in clamps 3. In the case of solid samples, they are set in the form of plates directly in clamps 3. The mobile system of the instrument, which includes the inner cylinder, the upper clamp, and an angle-of-rotation transducer, is directly connected to a mechanical torque generator 7. The immobile outer cylinder is secured, through the lower clamp 3, to the normal-stress compensator 8.

The signal from the angle-of-rotation transducer is transmitted, through a

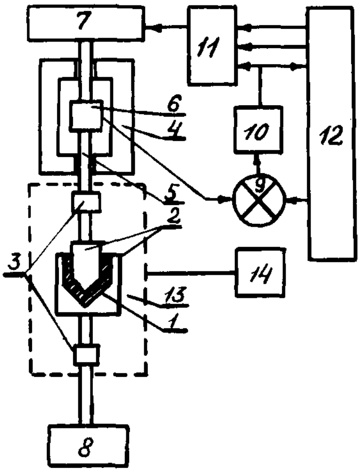

FIGURE 1 The block-diagram of a mechanical spectrometer (for the designations, see the text).

comparison device 9 and an amplifier 10 to the summator 11. Connected to the output of the comparison device 10 is the analyzer 12, from which the oscillation program signal is transmitted to comparison device 9 and the compensation signals to the summator 11, these signals displacing the control signal in a closed circuit. The closed follow-up circuit incorporates mechanical torque generator 7, angle-of-rotation transducer 6, comparison device 9, amplifier 10, and summator 11. The working unit with the polymer sample is placed in a thermocryochamber 13 connected to a programmed temperature controller 14.

The frequency and amplitude of oscillations specified with the aid of a magnetoelectric torque generator. The amplitude of angular rotations may vary from 6′ to 150′ at high linearity of the transformation coefficient, and the torques may vary from 0.3 to 3000 N. The mechanical torque generator used is a wire coil wound in the form of a frame and placed on an elastic suspension in a homogeneous field of a permanent magnet.

The error in the measurement of the loss angle is 0.05–0.1°. The range of shear modulus measured is 5–10 ^{10}Pa.

The instrument is fully automated, the results of measurements and calculations are read from the display and are recorded on a digital printer in terms of dynamic storage and loss moduli as a function of circular frequencies on a logarithmic scale.

The principal object under study was 1,2-polybutadiene having the molecular masses $M(1{,}3;\ 1{,}9;\ 3{,}3)\times 10^5$ and a narrow molecular-mass distribution, the polydispersity ratio being $M_w/M_n \leqslant 1{,}3$. The content of

1,2-units for the formation of various molecular masses varied within the range of 78,3 ÷ 81,0%. Since these polymers have a relatively high glass-transition temperature, one should have expected that the transition to the glassy state would be realized in a sufficiently low frequency range.

The kinetics of the structure–formation process were studied for the case of the copolymerization of spiran and cyclic siloxanes. The materials used for this purpose were octamethylcyclotetrasiloxane and 2,2,4,4,6,6-hexamethyl-8,8,10,10-tetraphenylspiro(7,5)hexasiloxane. It is well known[6] that the introduction of spirocyclic compounds into organic cyclo-siloxanes and the subsequent copolymerization result in the formation of polymers of network structure.

EXPERIMENTAL AND RESULTS OF DISCUSSION

Measurements carried out at variable frequencies and constant temperature enable us to obtain fundamental information on the basic regularities of the viscoelastic behaviour of a polymeric system in the various physical states, and also to establish the interrelationship between the molecular mass of the polymer and the conditions under which these states are attained.[7–11] However, depending on the test temperature, the various states of the material are attained at various loading rates (frequencies). Let us consider the results of a typical experiment of a similar type, carried out with 1,2-polybutadienes.

Figure 2 presents data for a sample with a molecular mass of $M = 1.35 \times 10^5$, obtained in the range of circular frequencies $\log \omega$ from -3.4 to $+3.2$ at temperatures from -33 to $+120°\text{C}$; these data describe the fluid, high-elastic (rubbery), leathery, and glassy states of the material.

In the region of the fluid state (the terminal zone)—the left branches of the $G'(\omega)$ and $G''(\omega)$ curves—there is observed a sharp change of the quantities G' and G'' with frequency; the slope of these curves tends to two and unity, respectively. The flow behaviour in the terminal zone is determined by the parameters η_0 (the initial viscosity), A_G (the high-elasticity coefficient), G_0 (the initial high-elasticity modulus), which are sufficiently simply calculated from data of synamic measurements.[8] It has been shown[7–11] for linear polymers, such as 1,4-polybutadienes, polystyrenes, polyisoprenes, polymethylphenylsiloxanes, that, as a function of molecular mass, $\eta_0 = A_1 M^\alpha$, and the values of α vary insignificantly and, on an average, are equal to 3.5. Analogous relation have been obtained for 1,2-polybutadienes.

The plateau and maxima on the $G'(\omega)$ and $G''(\omega)$ curves for linear high-molecular-mass polymers of narrow MMD constitute a typical manifestation of the viscoelastic behaviour of polymers of narrow MMD in the

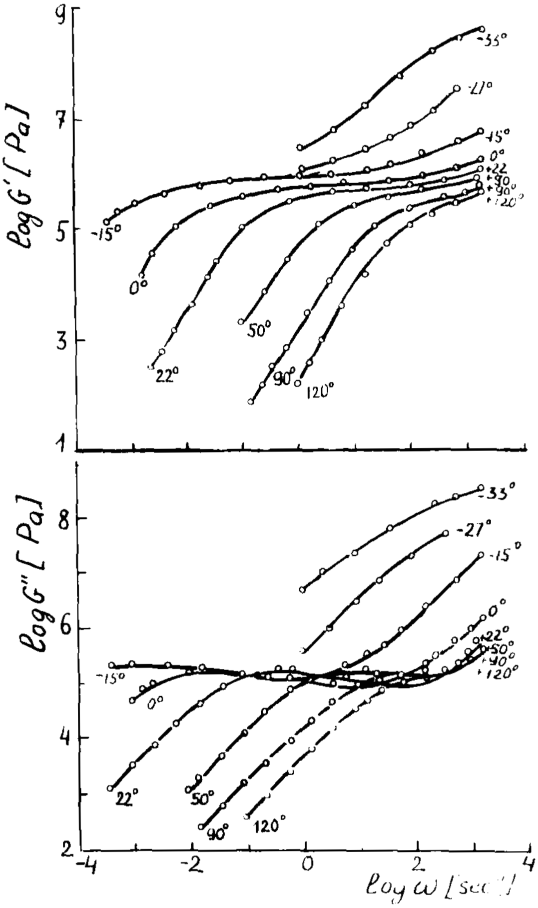

FIGURE 2 The dependence of the storage modulus G' and the loss modulus G'' on frequency ω at various temperatures for 1,2-polybutadiene with molecular mass $M = 1.35 \times 10^5$.

region of the high-elastic (rubbery) state. According to literature data[7–11] and the data of the present work, the values of the storage modulus on the plateau, G'_{pl}, and the loss modulus at the maximum, $G''_{\max}$, for polymers of various homologous series vary by not more than one decimal order. For high-molecular samples ($M/M_{\mathrm{cr}} \geqslant 10$, where M_{cr} is the critical molecular mass) and height of the plateau, G'_{pl}, and the quantity $G''_{\max}$ are practically independent of molecular mass, and the ratio $G''_{\max}/G'_{\mathrm{pl}} \simeq 0.4$. As a function of molecular mass, the frequency corresponding to the maximum of the loss modulus, $\omega_{\max}$, varies in inverse proportion to the initial viscosity. Depending on temperature, the quantities G'_{pl} and $G''_{\max}$ vary insignificantly, and $\omega_{\max}$ varies in the same manner as the initial viscosity. Of importance is the frequency dependence of the absolute value of the complex dynamic modulus G^*. There is an empirical rule for correlating this function with the dependence of shear stress under steady flow conditions if we assume that the rate of shear is numerically equal to the circular frequency.[12] The limit of this correlation is determined by the frequency $\omega_{\max}$ corresponding to the maximum of the $G''(\omega)$ curve; to the right of the maximum is the region of the transition to the high-elastic state, in which steady flow conditions cannot be attained.

From the frequency dependences of the dynamic characteristics presented in Figure 2 and obtained over a wide range of temperatures it is clearly seen that the form and character of the $G'(\omega)$ and $G''(\omega)$ curves are substantially dependent on the test temperature. At elevated temperatures the high-elasticity plateau degenerates (see the surves at 90 and 120°C) and with increasing frequency the system passes almost immediately from the fluid to the glassy state. The temperature coefficients (shift factors) in the region of the fluid and leathery states (a_T^f and a_T^g, respectively) differ sharply from each other (Figure 3), which points to the existence of the various temperature dependences of the relaxation times corresponding to the long-term and short-term parts of the relaxation spectrum of the system. The last circumstances is a spectacular evidence of the boundary possibilities of the use of the principle of temperature–time reduction. Indeed, within a single physical state, the fluid or the leathery state, the

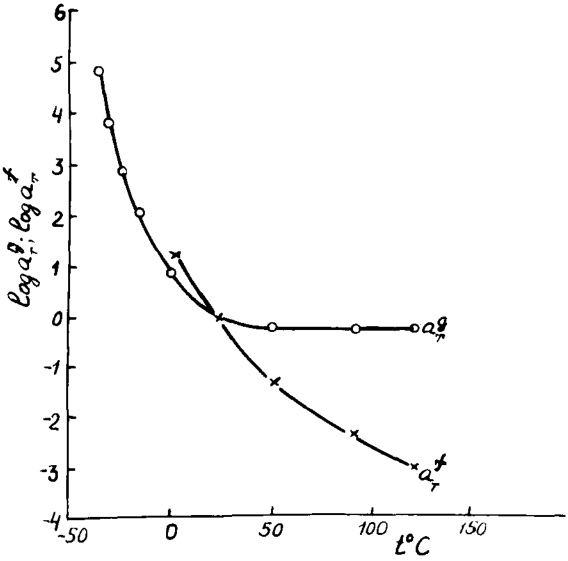

FIGURE 3 The temperature dependence of the shift factors a_T^f and a_T^g.

temperature dependence of the viscoelastic dynamic characteristics are unambiguously described by their own shift factors, a_T^f and a_T^g; therefore use may be made of the method of temperature–time reduction. At the same time, in the region of the high-elastic state, the temperature–time reduction method cannot be utilized since it is still not clear how the change of the form of the $G'(\omega)$ and $G''(\omega)$ curves can be taken into account unambiguously: the contraction of the region of the high-elasticity plateau with increasing temperature, the extension of the region of transition from the high-elastic to the fluid state with decreasing temperature, and other effects. A consequence of what has been said is the conclusion that the $G'(\omega)$ and $G''(\omega)$ curves, which are obtained by direct measurements at a given test temperature over a wide frequency range and describe the various physical states of the material—the fluid, high-elastic (rubbery) and glassy states, cannot be presented at other temperatures by shifting them along the frequency axis by the value of any averaged shift factor a_T, as presupposed by the method of temperature–time reduction.

The data presented in Figure 2 makes it possible to trace out the shift of the characteristic points on the $G''(\omega)$ curves as a function of temperature. This includes the values of the loss modulus at the maximum, $G''_{\max}$, and at the minimum, $G''_{\min}$, and the values of the corresponding frequencies, $\omega_{\max}$ and $\omega_{\min}$. The $G''_{\max}(t^\circ)$, $G''_{\min}(t^\circ)$, $\omega_{\max}(t^\circ)$, and $\omega_{\min}(t^\circ)$ curves are shown in Figure 4.

Using the $G'(\omega)$ and $G''(\omega)$ curves obtained at 22°C (Figure 2) and the

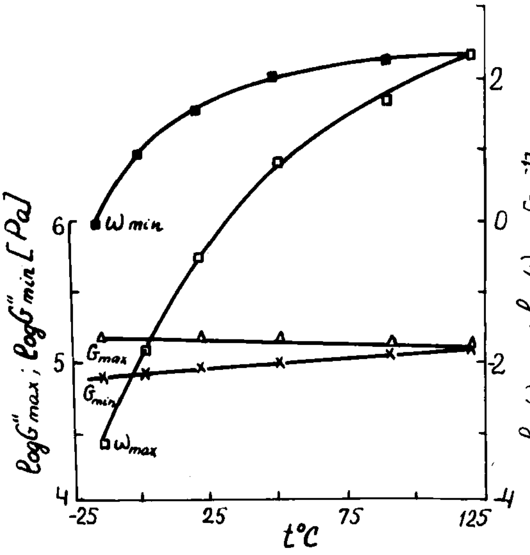

FIGURE 4 The temperature dependence of the quantities $G''_{\max}$, $G''_{\min}$, $\omega_{\max}$ and $\omega_{\min}$.

principle of temperature–time reduction for the leathery state, we constructed the $G'_r(\omega)$ and $G''_r(\omega)$ graphs reduced to 22°C, which describe all the physical states, from the fluid to the glassy state, and cover the frequency range of about twelve decimal orders (Figure 5); the frequency range from $\log \omega = -3.4$ to $\log \omega = +3.2$ was obtained by direct measurements. On the $G'(\omega)$,

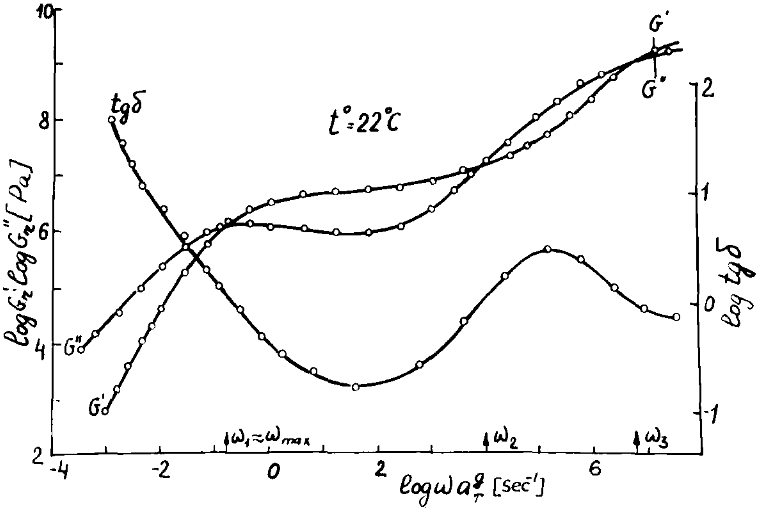

FIGURE 5 The dependence of the reduced storage modulus G'_r and the reduced loss modulus G''_r and the loss angle tan δ on the reduced frequency ωa_T^q for 1,2-polybutadiene with $M = 1.35 \times 10^5$ at a temperature of 22°C.

$G''(\omega)$ and $\tan \delta(\omega)$ curves there can be distinctly seen the characteristic regions of the states of the system. We may provisionally assume the following division. To the fluid state there correspond the values of tan δ from the maximum values to 1; this corresponds to the frequency $\omega_1 \approx \omega_{\max}$, which may serve as the boundary of this state. The region of the high-elastic state ends at the second point of intersection of the $G'(\omega)$ and $G''(\omega)$ curves in the range of mean values of frequency, in which case tan δ passing through a minimum again becomes equal to 1 at the frequency ω_2. The curve $G''(\omega)$ passes through a minimum. It should be noted that the minimum of the $G''(\omega)$ and $\tan \delta\ (\omega)$ curves practically divides in half the region of the high-elastic state. Beyond the region of the high-elastic state (the right part of Figure 5) the values of G' and G'' increase sharply, the quantity G' rising more sharply than G''. This is the region of transition to the glassy state. The values of tan δ also increase here, passing through a maximum, and then, for the third time, tan δ becomes equal to unity. The frequency corresponding to the maximum on the curve of $\tan \delta(\omega)$ vs. $\omega'_{\max}$ divides in half the region of the leathery state. The values higher than ω_3 correspond to the glassy state.

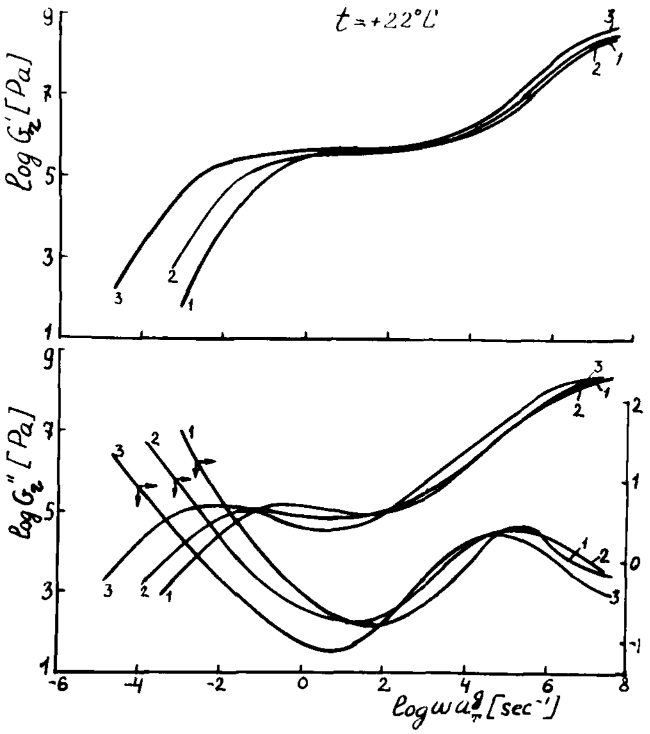

FIGURE 6 The dependence of the reduced storage modulus G' and loss modulus G'' and tan δ on the reduced frequency ωa_T for 1,2-polybutadienes of various molecular masses at a temperature of 22°C. The curves 1-3 correspond to the following molecular masses, respectively: $(1.35, 1.9, 3.3) \times 10^5$.

Analogous results have been obtained for polybutadienes having the molecular masses $(1.9 \text{ and } 3.3) \times 10^5$ (Figure 6). Of importance here is the dependence of the quantities $G''_{\min}$ and $\omega_{\min}$, ω_2, ω_3 and $\omega_{\max}$ on molecular mass. From the data of Figure 6 it can be seen that as the molecular mass increases the minimum values of the loss modulus $G''_{\min}$ become proportional to $M^{-0.4}$ and the corresponding frequencies $\omega_{\min}$ decrease proportionately to $M^{-0.6}$. The values of ω_2, ω_3, $\omega_{\max}$ practically remain unchanged with change of the molecular mass of the polymer.

Let us now consider the results of dynamic experiments obtained under the conditions of variable temperature and constant frequency. Figure 7 shows the curves of $G'(t^\circ)$, $G''(t^\circ)$ and $\tan \delta(t^\circ)$ for polybutadiene with $M = 1.35 \times 10^5$, which were measured at the frequency $\omega = 1 \text{ sec}^{-1}$. It is seen that as the temperature falls the system passes from the fluid to the high-elastic state, this being represented by the steeply rising branches of the $G'(t^\circ)$ and $G''(t^\circ)$ curves; here the $G'(t^\circ)$ curve changes more strongly and the

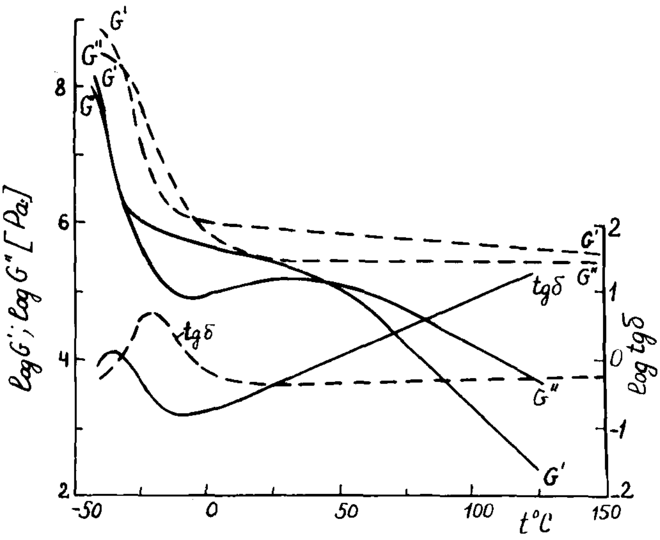

FIGURE 7 The dependence of the storage modulus G', the loss modulus G'' and tan δ on temperature t° for 1,2-polybutadiene with $M = 1.35 \times 10^5$. The solid lines correspond to the frequency $\omega = 1\ \mathrm{sec}^{-1}$; the dotted line corresponds to $\omega = 10^3\ \mathrm{sec}^{-1}$.

values of tan δ are sufficiently high (>1). In the region of the high-elastic state, on the $G''(t^\circ)$ curve there is observed a maximum and a minimum and the values of G' in the same temperature range very by about one decimal order. Mechanical losses decrease and pass through a minimum. As the temperature decreases further, the moduli G' and G'' again increase sharply, which is a consequence of the transition to the glassy state and on the tan $\delta(t^\circ)$ curve there appears a maximum. It may be assumed that this maximum corresponds to the glass-transition temperature of the polymer. In the same figure, the dotted lines show the analogous dependences obtained at the frequency $\omega = 10^3\ \mathrm{sec}^{-1}$. An important feature of these dependences is an extremely extended high-elasticity plateau—up to the temperature at which the polymer undergoes thermal destruction. In the interval from zero to maximal positive temperatures the material behaves as a cured polymer. What has been said corresponds to the absence of a maximum and a minimum on the $G''(t^\circ)$ curve; the values of tan δ are nearly constant and are equal to 0.4. As the temperature decreases the material passes into the glassy state. The maximum on the tan $\delta = f(t^\circ)$ curve at the frequency $\omega = 10^3\ \mathrm{sec}^{-1}$ is shifted to the side of higher temperatures. The tan δ vs $f(t^\circ)$ curves obtained at various frequencies allow us to determine the shift of the glass-transition temperature of the system as a function of frequency.

Analogous data have been obtained for polybutadienes with $M = (1.9$ and $3.3) \times 10^5$. Figure 8 shows the temperature dependencies of the elastic

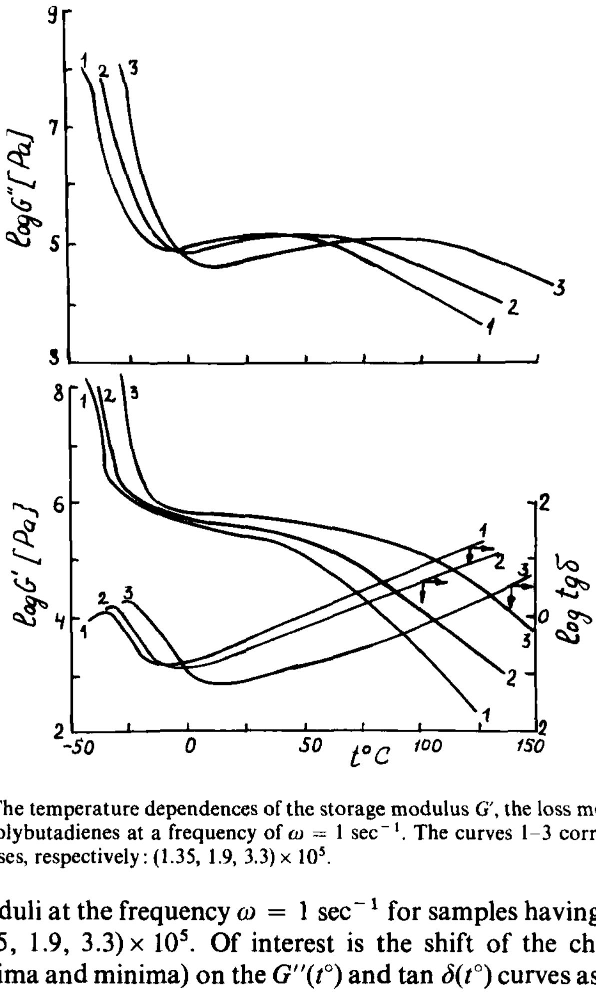

FIGURE 8 The temperature dependences of the storage modulus G', the loss modulus G'' and $\tan\delta$ for 1,2-polybutadienes at a frequency of $\omega = 1\ \sec^{-1}$. The curves 1–3 correspond to the molecular masses, respectively: $(1.35, 1.9, 3.3) \times 10^5$.

and loss moduli at the frequency $\omega = 1\ \sec^{-1}$ for samples having molecular masses $(1.35, 1.9, 3.3) \times 10^5$. Of interest is the shift of the characteristic points (maxima and minima) on the $G''(t^\circ)$ and $\tan\delta(t^\circ)$ curves as a function of molecular mass. The minimum and maximum on the $G''(t^\circ)$ curve determine, to a certain extent, the remoteness of the system from the glass–transition temperature (of course, at the given frequency). An important problem is to elucidate the quantitative regularities governing the change of the form of the $G''(t^\circ)$ curves as a function of frequency. As regards the maximum of $\tan\delta(t^\circ)$ corresponding to the glass–transition temperature, here the dependence on molecular mass is weak. It should however be noted that the polymers investigated differed somewhat in their microstructure, as has been pointed out above.

We shall now consider the dynamic experiments carried out under the conditions of constant frequency and constant temperature with systems, whose viscoelastic characteristics vary in time (t) as a result of the formation of a spatial structure. The kinetics of the process of formation of a network polymer can be deduced from the change of the storage and loss moduli with time. A typical curve for such a process is presented in Figure 9 in the form of the $G'(t)$ and tan $\delta(t)$ curves for the case of the copolymerization of spiran and cyclic siloxanes. Observing the variations of the above-indicated

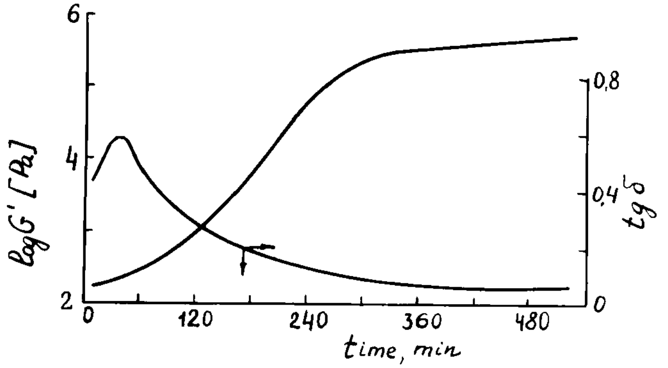

FIGURE 9 The time dependence of the storage modulus G' and tan δ for the copolymerization of spiran and cyclic siloxanes. The temperature is 90°C, the frequency $\omega = 10\ \text{sec}^{-1}$. The contents of the spiro ring is 7.0 mol.%.

dependences, we can follow the process from its initial phase, at the stage of formation of a spatial network, up to its completion. The $G'(t)$ and tan $\delta(t)$ curves can be used to estimate the duration of the induction period of the process, which is associated with the rebuilding of the molecules of the spiro ring into polycyclic blocks and to determine the dependence of this period on the contents of the spiro ring. The appearance of a network structure is fixed from the increase of the storage modulus on the tan $\delta(t)$ curve; to this moment there corresponds a maximum. The lengths of the induction period, as estimated from the yield of the gel fraction (6) and from the tan $\delta(t)$ curve nearly coincide. Moreover, the dependences of the elastic modulus on time and the rate of growth of the yield of the gel fraction during the reaction at various contents of the spiro ring are also quantitatively similar. The constant values of the storage modulus correspond to the completion of the structure–formation process. At any stage of the process, the data of dynamic investigations enable one to evaluate the elasticity and dissipation losses; the latter at least qualitatively characterize the regularity of the formation of a network structure, which is clearly seen from a comparison of the $G'(t)$ and tan $\delta(t)$ curves obtained at different contents of the spiro ring. An increase in the contents of the spiro ring leads to a sharp increase of the storage modulus and of the amount of the end product, which is rather simply accounted for by the formation of a denser network of chemical bonds. A decrease of dissipation losses in this case is due to the formation of a more regular network structure. It should be noted that the yield of the gel fraction upon completion of the process is about the same for the various contents of the spiro ring, but the viscoelastic properties of the final system are different. This is evidence of the high sensitivity and of the important role of the rheological estimation of processes of this kind, which allows one to gain additional information (apart from that obtained by chemical methods) on the structure of the polymer being formed and to arrive at quantitative estimates of its mechanical properties.

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