

Polarization-Optical Investigation of Polymers in Fluid and High-Elastic States Under Oscillatory Deformation

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Synopsis

The relationship was investigated between birefringence and oscillatory shear deformation of linear high molecular mass polymers exemplified by narrow- and broad-distribution polybutadienes and polyisoprenes. Polymer deformation at different frequencies and amplitudes was carried out in an annular gap. The stress field uniformity was not below 95%. It was shown that in oscillatory deformation of polymers in the fluid and high-elastic states, birefringence contains a time-independent steady component and an oscillatory component with a frequency equal to that of the assigned oscillation. A linear interrelation was found to exist between the amplitude of the oscillatory component of birefringence and that of the shear stresses, with a proportionality factor equal to the stress-optical coefficient of the polymers. The phase of the oscillatory component of birefringence coincides with that of the shear stresses. Measurements of the steady component of the birefringence make it possible to find the steady component of the first normal stress difference resulting from the assignment of shear oscillations to the polymer. On the basis of the experimental data obtained for polybutadienes and polyisoprenes, and the literature data for polystyrene solutions, a master curve was constructed that generalizes the dependence of the steady component of the first normal stress difference in the linear and nonlinear deformation regimes on the product of the square of the deformation amplitude and the storage modulus measured at low amplitudes. This dependence is valid in the linear and nonlinear deformation regimes. It is invariant with frequency, amplitude deformation, molecular mass, and molecular mass distribution of the polymers. It is shown by visual observation of deformation that the abrupt drop in resistance of polymer to shear in large-amplitude deformation is due to polymer rupture near the surface of the inner cylinder and is accompanied by a slip-stick process. This is the phenomenon of spurt early observed in capillary viscometers at high shear stresses and recently investigated in coaxial cylinder devices at large amplitude deformation.

INTRODUCTION

Polarization-optical methods of stress measurement are widely applied in the static and cyclic regimes of deformation of solids.^{1,2} In recent years these methods have been further developed with reference to the evaluation of the stress state arising in polymer flow and are based on simple relationships between the polarization-optical and rheological characteristics of polymers.³⁻⁶

In characterizing the properties of polymeric systems, the regimes of their oscillatory (harmonic) shear deformation,⁷ which supply abundant information on their viscoelastic behavior, are of great importance. In distinction to the static regimes of polymer deformation, where the value of birefringence unambiguously

characterizes their stress state, this is insufficient in the case of cyclic deformation. As shown in references 8–11, for low-concentration polymer solutions in cyclic deformation the polarization-optical properties must be characterized by two values, namely, the birefringence and the phase angle between birefringence and deformation. The situation is similar to the case of the characterization of rheological properties under oscillatory deformation regimes: not only the value of stress but also the phase-shift angle between stress and deformation must be registered. Moreover, it is well known from references 12 and 13 that in oscillatory deformation of polymers in the glassy state and in the range of transition from the glassy to the high-elastic state, the stress-optical coefficient is a complex value depending on the oscillation frequency.

In connection with the above, the following questions are posed in the present investigation. First, what is the relationship between the values of stress and birefringence of polymers in their oscillatory deformation in the fluid and high-elastic states? Also, on the one hand, what is the relationship between the phases of birefringence and deformation and, on the other, between the phases of stress and birefringence? It should be emphasized that oscillatory deformation of polymers is a nonstationary process, and therefore there arises the question of the applicability of the stress-optical law to such deformation regimes. Besides, the present investigation will answer the question whether the stress-optical coefficient of polymers depends on the frequency and amplitude in their oscillatory deformation in the fluid and high-elastic states.

Thus, this investigation serves the purposes of experimental substantiation of the polarization-optical method for studying the processes of oscillatory deformation of polymers in the fluid and high-elastic states, which will make it possible to determine, on the basis of polarization-optical measurements, the storage (G') and loss (G'') moduli, shear stresses τ , maximal tangential stresses τ_{\max} , and the first normal stress difference σ_N . The rheo-optical method has the advantage of contactless measurement (without any mechanical pickup devices such as dynamometers, and so on) of the dependence of the indicated parameters on the frequencies and amplitudes of harmonic oscillations with simultaneous visualization of the deformation process. The possibility of visual observation of the deformation process makes it possible to evaluate the nature of its critical regimes, in particular, to find out how the spurt phenomenon, known from the data of capillary viscometry and recently detected in large-amplitude cyclical deformation of polymer, develops.¹⁴

Also an attempt is made here to generalize the results of experimental investigations into the steady component of the first normal stress difference arising in oscillatory deformation of polymers.

EXPERIMENTAL

Method

To solve the problems posed, the authors devised a dynamovibro-optimeter combining a vibrorheometer¹⁵ with the optical equipment widely used in the photoelasticity method.^{1,2} The device, presented schematically in Figure 1, includes an optical arrangement, a working cell provided with a drive for assigning oscillations and steady rotation, and a recording circuit.

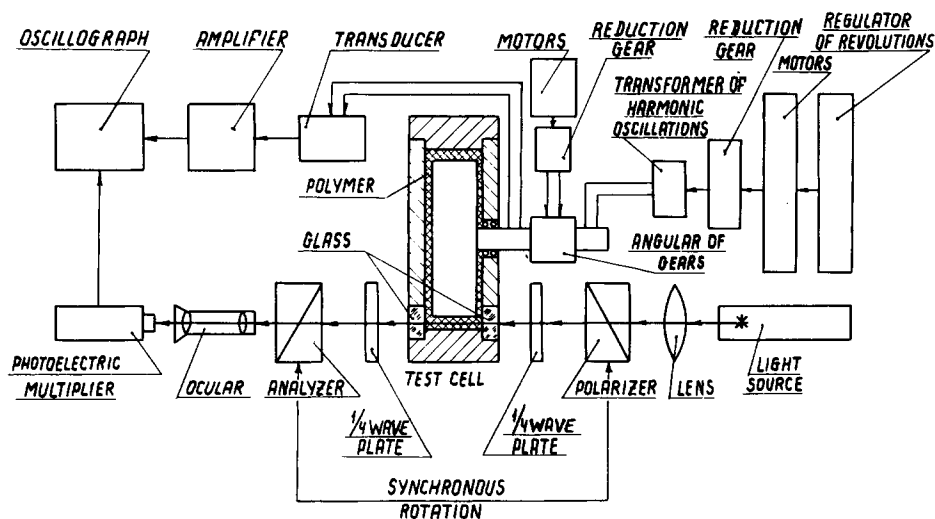


Fig. 1. Key diagram of dynamovibro-optimeter.

The optical arrangement consists of sources of laser monochromatic light with a wavelength of 6.33×10^{-5} m and white light (incandescent lamp) fed with direct current, a polarizer and analyzer provided with a device for their synchronous rotation, two plates $\lambda/4$, and a system of lenses.

The working cell consists of coaxial cylinders with a specimen of a transparent polymer placed in the gap between them. The inner cylinder is replaceable, its diameter being 4.0×10^{-2} or 4.14×10^{-2} m, while that of the outer cylinder is 4.2×10^{-2} m, which ensures 0.95 and 0.98 uniformity of the stress field with gaps of 1×10^{-3} and 3×10^{-4} m, respectively. The end faces of the working cell are covered with lids provided with windows in which grade K-8 optical glasses are inserted. Polarized light passes along the cylinder generatrix. Their lengths are 1×10^{-2} or 2×10^{-2} m. The coaxiality of the cylinders is ensured by using two precision ball bearings. The play of the inner cylinder during its rotation does not exceed 1×10^{-5} m. The polymer is inserted by means of a piston-type loading device, which is screwed into one of the lids of the working cell.

The oscillations are assigned with the aid of electric motors connected with regulator revolutions, a reducing gear, and an eccentric mechanism, which converts rotation to oscillatory motion. The ranges of the frequencies are from 10^{-3} to 2 cps, and those of the deformations, from 0.01 to 5 relative units. The recording system includes a strain gauge for measuring a deformation, an amplifier, a photoelectric multiplier, and a loop oscillograph.

Besides oscillatory shear at different frequency and amplitude (according to the harmonic law), also realized was polymer deformation in steady shear in the range of 10^{-4} – 10^3 sec $^{-1}$. Polymer deformation under constant shear rate is achieved with the aid of two motors via a reducing gear and angle transmission. The recording system and the optical arrangement are the same as with oscillating shear. The device also permits visual observation of the polymer behavior in the gap through an inspection tube.

Materials

The objects of investigations were narrow- and broad-distribution polybutadienes and polyisoprenes, which had previously been widely investigated in oscillatory deformation¹⁴ and extrusion in capillaries.^{16,17} The characteristics of the investigated narrow-distribution specimens are given in Table I. Besides the specimens listed in the table, a specimen D was investigated, which simulates an industrial polybutadiene and is a 16-component mixture of equal amounts of specimens of narrow-distribution polybutadienes with molecular masses from 65,000 to 320,000 ($M_w/M_n = 3.0$), and also a specimen H simulating an industrial polyisoprene and representing a six-component mixture of equal amounts of narrow-distribution polyisoprenes with molecular weights from 65,000 to 830,000 ($M_w/M_n = 2.0$). All measurements were obtained at room temperature.

RESULTS AND DISCUSSION

In the dynamovibro-optimeter the birefringence of the polymer in oscillatory deformation is determined by recording the intensity of the circular-polarized light flux at the analyzer output. Figures 2(a), 2(b), and 2(c) depict typical patterns of oscillation in photocurrent and deformation in time at a constant frequency of 0.1 cps and three different deformation amplitudes. Each peak on the photocurrent curve corresponds to the intensity minimum of the light flux, which corresponds to a definite order of isochromatic fringes. It is easy to pinpoint the position of the zero-order isochrome, which, in the case of a small amplitude, is the darkest and is hence located above the other peaks [Fig. 2(a)]. During each deformation cycle, the peak corresponding to the zero isochrome appears three times. This is in line with the fact that during each deformation cycle the values of the birefringence as well as the deformation pass through zero three times. The figure shows that the zero isochrome precedes the deformation by an angle of $\varphi_{\Delta n}$. With an increase in deformation amplitude [Fig. 2(b)] one observes a gradual lowering of the peak corresponding to the position of the zero isochrome, which indicates that the birefringence is not equal to zero at any time of the cycle. This signifies that a steady component of the birefringence appears. With a further growth in amplitude [Fig. 2(c)] the zero isochrome disappears completely, and the peak corresponding to the first-order isochrome is reduced. A further increase in amplitude results in the gradual disappearance of the peaks corresponding to the first-order, second-order, etc., isochromes. It can also be seen from Figure 2 that any isochrome of a higher-than-zero order may appear two or four times during the oscillation cycle (provided it does not correspond to the minimum level of birefringence during the cycle).

TABLE I
Characteristic of Polymers Studied

Specimen code	Polymer	M_w/M_n	$M_v \times 10^{-5}$	Isomeric composition			
				cis-1,4	trans-1,4	1,2	3,4
A	Polybutadiene	1.2	0.76	45.0	45.0	10.0	—
B	Polybutadiene	1.1	1.41	47.2	44.0	8.8	—
C	Polybutadiene	1.1	3.01	45.0	41.0	14.0	—
E	Polyisoprene	1.61	1.48	72.0	20.8	—	6.2
F	Polyisoprene	1.14	2.40	77.4	14.6	—	8.0
G	Polyisoprene	1.10	3.80	79.0	15.2	—	5.8

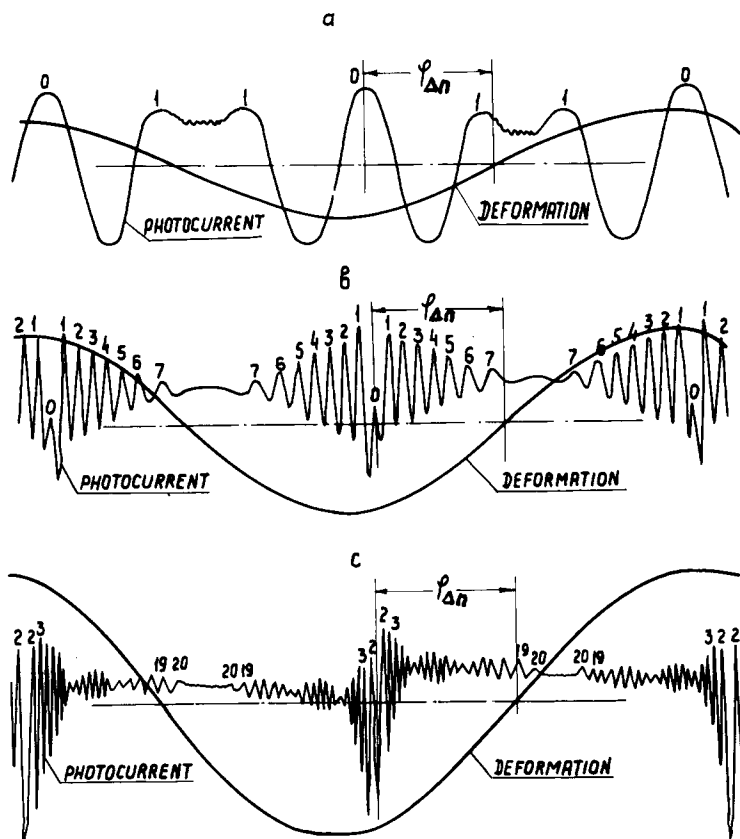


Fig. 2. Typical photorecording of deformation and intensity of light flux at analyzer output for specimen B at frequency of 0.1 cps and deformation amplitudes of 6.3×10^{-2} (a), 3.8×10^{-1} (b), and 1.1 (c). Specimen height 2×10^{-2} m, gap width 1×10^{-3} m.

With increasing deformation amplitude, the number of peaks in the oscillation cycle increases, corresponding to an increase in maximum values of birefringence and hence to the appearance of peaks corresponding to higher-order isochromes. Thus, with an increase in oscillation amplitude, on the one hand, the minimum level of birefringence increases because of the growth in the steady component of birefringence (the low-order isochromes disappear) in the oscillation half-cycle; and, on the other hand, the maximum level of birefringence increases (high-order isochromes appear).

Figure 3 exhibits the dependence of the birefringence on the time for one oscillation half-cycle, as plotted on the basis of the photorecording of the intensity of the light flux represented in Figure 2(c). The dots on this curve correspond to an integral order of the isochrome, and their position on the scale ωt corresponds to the position of the peaks on the time dependence of the photocurrent, i.e., to the isochrome number. The minimum number of an integral order of the isochrome was determined during a gradual increase of the amplitude and by observing the number of peaks that have disappeared. The order of the first remaining isochrome was taken to be one unit higher than that of the vanished isochrome. The fractional minimum order of the isochrome was found by linear extrapolation of the time dependence of the birefringence corresponding to the half-cycle in question up to the intersection, with a similar dependence for the adjoining half-cycle.

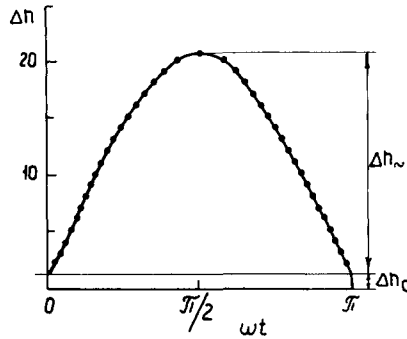


Fig. 3. Time dependence of birefringence during oscillation half-cycle plotted from photo of Figure 2(c).

From Figure 3 it follows that the value of the birefringence in cyclical deformation of polymers (Δn) is equal to

$$\Delta n = \Delta n_c + \Delta n_{\sim}$$

where Δn_c and Δn_{\sim} are the steady and oscillatory components of the birefringence, respectively. Note that the time dependence of the birefringence during oscillations is a π periodic function. An expansion of this dependence in a Fourier series showed that the amplitude of the first harmonic of birefringence plays the determining role. The contribution from the amplitudes of the higher harmonics does not exceed 5% of the amplitude of the first harmonic. Hence, one can assume that the value of birefringence during oscillations varies by the following law:

$$\Delta n = \Delta n_c + \Delta n_0 \sin(\omega t + \varphi_{\Delta n}) \quad (1)$$

where Δn_0 is the birefringence amplitude, $\varphi_{\Delta n}$ is the phase shift between birefringence and deformation. The variation of birefringence in oscillatory deformation of polymers can be explained on the basis of the shear and normal stresses arising in this case. When a polymer is assigned deformation by the law $\gamma_0 = \gamma_0 \sin \omega t$, the following shear stress appears in the polymer:

$$\tau = \Delta_0 \sin(\omega t + \varphi_0) \quad (2)$$

where γ_0 and τ_0 are the deformation and stress amplitudes, respectively, φ_0 is the phase-shift angle between the shear deformation and stress, ω is the circular frequency, and t is the time. Besides, the first normal stress difference (σ_N) develops in the polymer, which according to reference 18 has the following form in the range of linear behavior of the polymer:

$$\sigma_N = \sigma_c + \sigma_0 \sin(2\omega t + \varphi_N) \quad (3)$$

where σ_c is the steady component of the first normal stress difference, σ_0 is the amplitude of the oscillatory component of the first normal stress difference of the frequency 2ω and φ_N is the angle of the phase shift between the oscillatory component of the first normal stress difference and the deformation.

According to references 1 and 2, the maximum tangential stresses arising in solids (τ_{\max}) are equal to

$$\tau_{\max} = \sqrt{\left(\frac{\sigma_N}{2}\right)^2 + \tau^2} \quad (4)$$

The maximum shear stresses in oscillatory deformation contain a steady, $\tau_{\max,c}$, and an oscillatory $\tau_{\max \sim}$, component, i.e., $\tau_{\max} = \tau_{\max,c} + \tau_{\max \sim}$. Since the shear stresses in oscillatory deformation contain no steady component, from eq. (4) it follows that $\tau_{\max,c} = \sigma_c/2$. For the oscillatory component of the maximum shear stresses, we obtain from eqs. (2)–(4)

$$\tau_{\max \sim} = \left\{ \left[\frac{\sigma_0 \sin(2\omega t + \varphi_N)}{2} \right]^2 + \left[\tau_0 \sin(\omega t + \varphi_0) \right]^2 \right\}^{1/2} \quad (5)$$

For the case of oscillatory deformation of polymers in the linear regime, it is well known from a number of theoretical investigations^{16–22} that, with an assigned frequency ω , the functions $\sigma_c(\gamma_0)$ and $\sigma_0(\gamma_0)$ are determined by the formulas

$$\sigma_c = \gamma_0^2 \cdot G'_\omega = \gamma_0^2 \cdot G(\omega) \quad (6)$$

$$\sigma_0 = \gamma_0^2 \left| \frac{1}{2} G_{2\omega}^* - G_\omega^* \right| \quad (7)$$

where G'_ω is the storage modulus at frequency ω , and $G_{2\omega}^*$ and G_ω^* are the complex shear modulus at frequency 2ω and ω , respectively.

We shall now see how eqs. (6) and (7) agree with experiment. The authors of references 23–27 carried out mechanical measurements of the first normal stress difference in oscillatory deformation of polymer solutions and melts. The common qualitative feature of these experiments is the fact that the first normal stress difference in oscillatory deformation regimes of polymer solutions and melts contains a steady component and an oscillatory component of double frequency, as predicted by all theories. As regards the steady component of the first normal stress difference, σ_c , the authors of references 25–27 demonstrate the validity of relation (6). However, for the oscillatory component of the first normal stress difference, no quantitative agreement of the theoretical formula (7) and experiment was obtained in references 25 and 26. As indicated in references 27 and 28, this is because the relationship between the rigidity of the test specimen and the dynamometer measuring the normal stresses was not taken into consideration. Therefore, in order to ensure reliable measurement of the oscillatory component of the first normal stress difference, Faitelson and Alekseyenkov²⁷ increased the rigidity of the dynamometer to 6.81×10^7 N/m, using a piezotransducer for measuring the displacements. In this case, too, however, the dynamometer rigidity proved to be ten times less than that of the specimen. Therefore, a correction was introduced into the experimental value of the normal force in order to find its true value. After that, formula (7) agreed with experiment.

The effects of the rigidity of the measuring devices in the Weissenberg rheogoniometer and of the viscoelastic properties of the specimens on the results of the measurement of normal stresses have been considered.²⁸ It was shown that the appropriate corrections can be introduced,²⁶ and this brought eq. (7) in line with the results just mentioned. Thus, the foregoing consideration of the theoretical investigations and experiments work on the measurement of the first normal stress difference show that eqs. (6) and (7) are correct.

The highest values of σ_c and σ_0 at a given value of deformation amplitude can be achieved at frequencies corresponding to the transition to the high-elastic state when the storage modulus G' reaches the value G'_p corresponding to the high-elasticity plateau and $G_\omega^* \simeq G_{2\omega}^* = G_p^*$. Taking into account relation (7) and the fact that $\tau_0 = \gamma_0 |G_\omega^*|$, we obtain from Eq. (5):

$$\tau_{\max} \sim = \gamma_0 \left[\frac{1}{4} \gamma_0^2 \left| \frac{1}{2} G_{2\omega}^* - G_{\omega}^* \right|^2 \sin^2 (2\omega t + \varphi_N) + |G_{\omega}^*|^2 \sin^2 (\omega t + \varphi_0) \right]^{1/2}$$

Then, considering that $\sin \alpha \leq 1$ and $G_{2\omega}^* = G_{\omega}^* = G_p^*$, we obtain the following estimate for τ_{\max} ~:

$$\tau_{\max} \sim \leq \gamma_0 |G_p^*| \left[\frac{\gamma_0^2}{16} + 1 \right]^{1/2}$$

From the last inequality it follows that if we assume that the linear behavior of polymers in oscillatory deformation persists even up to deformation amplitudes of the order of unity, then even in the region of the high-elasticity plateau, $\tau_{\max} \sim \leq 1.03\tau_0$. It follows that the contribution from the oscillatory component of the first normal stress difference to the oscillatory component of the maximum shear stresses does not exceed 3%, in other words, it can be assumed with a sufficient degree of accuracy that the amplitude of the maximum shear stresses $\tau_{\max,0} = \tau_0$. The foregoing indicates that for polymers in the fluid and high-elastic states the maximum tangential stresses vary according to the law

$$\tau_{\max} = \tau_{\max,c} + \tau_0 \sin (\omega t + \varphi_0) \quad (8)$$

A comparison of eqs. (1) and (8) shows that they have the same structure. Therefore, for measuring stresses in oscillatory deformation of polymers in the fluid and high-elastic states by the optical method, it is very important to find a correlation between $\varphi_{\Delta n}$ and φ_0 on the one hand and between Δn_0 and τ_0 on the other. Figures 4 and 5 depict, respectively, the dependence of Δn_0 on τ_0 and of $\varphi_{\Delta n}$ on φ_0 for the investigated specimens of polybutadienes and polyisoprenes over a wide range of frequencies and amplitudes of deformation. The values of τ_0 and φ_0 used in plotting these graphs are borrowed from reference 14 at those deformation amplitudes for which the present authors measured the phases and amplitudes of birefringence. From the dependence of $\varphi_{\Delta n}$ on φ_0 it follows that $\varphi_{\Delta n} = \varphi_0$, i.e., the phases of birefringence and stresses with respect to the assigned deformation coincide and hence coincide with respect to one another as well. According to references 1 and 2, static loading under the relationship between the maximum tangential stresses and the birefringence is determined by the formula

$$\tau_{\max} = \frac{\Delta n \lambda}{2CH} \quad (9)$$

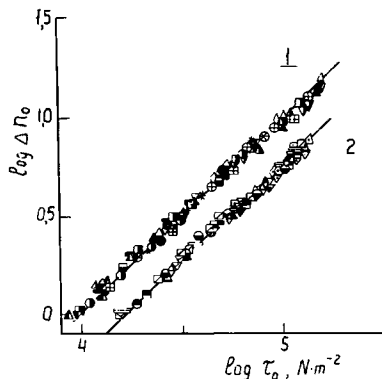


Fig. 4. Dependence of birefringence amplitude on stress amplitude for polybutadienes (1) and polyisoprenes (2) at different frequencies. Key for symbols in Figures 4–6 is shown on Figure 7.

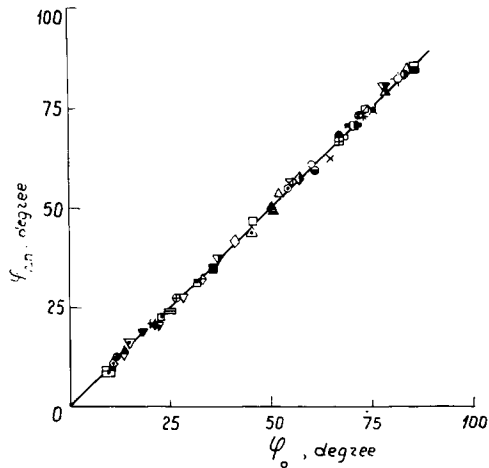


Fig. 5. Comparison phase shift of birefringence relative to deformation and stress with respect to deformation for polybutadienes and polyisoprenes at different frequencies.

where Δn is the order of the isochrome, λ is the wavelength, C is the stress-optical coefficient, and H is the thickness of the polymer layer. In Figure 4 the dots show the experimental results, and the solid line, the results of calculations by the formula $\Delta n_0 = 2\tau_0 CH/\lambda$. The values of the stress-optical coefficients, equal to $C = 3.3 \times 10^{-9} \text{ m}^2/\text{N}$ and $c = 1.9 \times 10^{-9} \text{ m}^2/\text{N}$, are borrowed from reference 16, where they were found experimentally in stationary flow regimes for the investigated polybutadienes and polyisoprenes, respectively. It should be noted that the frequency range realized corresponds to the fluid and high-elastic states of the polybutadienes and polyisoprenes at hand, and the dependence of Δn_0 on τ_0 is invariant with frequency, deformation amplitude, molecular mass, and molecular mass distribution of the polybutadienes and polyisoprenes.

This suggests two important possibilities. First, the stress-optical coefficient in oscillatory deformation of polymers in the fluid and high-elastic states is independent of frequency and of stress and deformation amplitudes. Second, the values of the coefficient C found in stationary regimes of polymer flow can be used for nonstationary deformation regimes. The results obtained open up the possibility of determining the dynamic characteristics of polymers at different frequencies and amplitudes on the basis of polarization-optical measurements alone. Thus, the applicability of the stress-optical law to nonstationary deformation regimes of polymers in the fluid and high-elastic states has been substantiated experimentally.

It has been shown above that the value of birefringence of polymers in oscillatory deformation contains a constant component Δn_c . By using the measured value of Δn_c , it is possible to calculate the constant component of the first normal stress difference by the formula

$$\sigma_c = 2\tau_{\max,c} = \frac{\Delta n_c \lambda}{CH}$$

The results of these measurements for the investigated polybutadienes and polyisoprenes are presented in Figure 6 as dependences of σ_c on γ_0^2 at different frequencies. It is well known that in linear regimes of polymer deformation the relationship between σ_c and γ_0 is quadratic and corresponds to eq. (6). The data

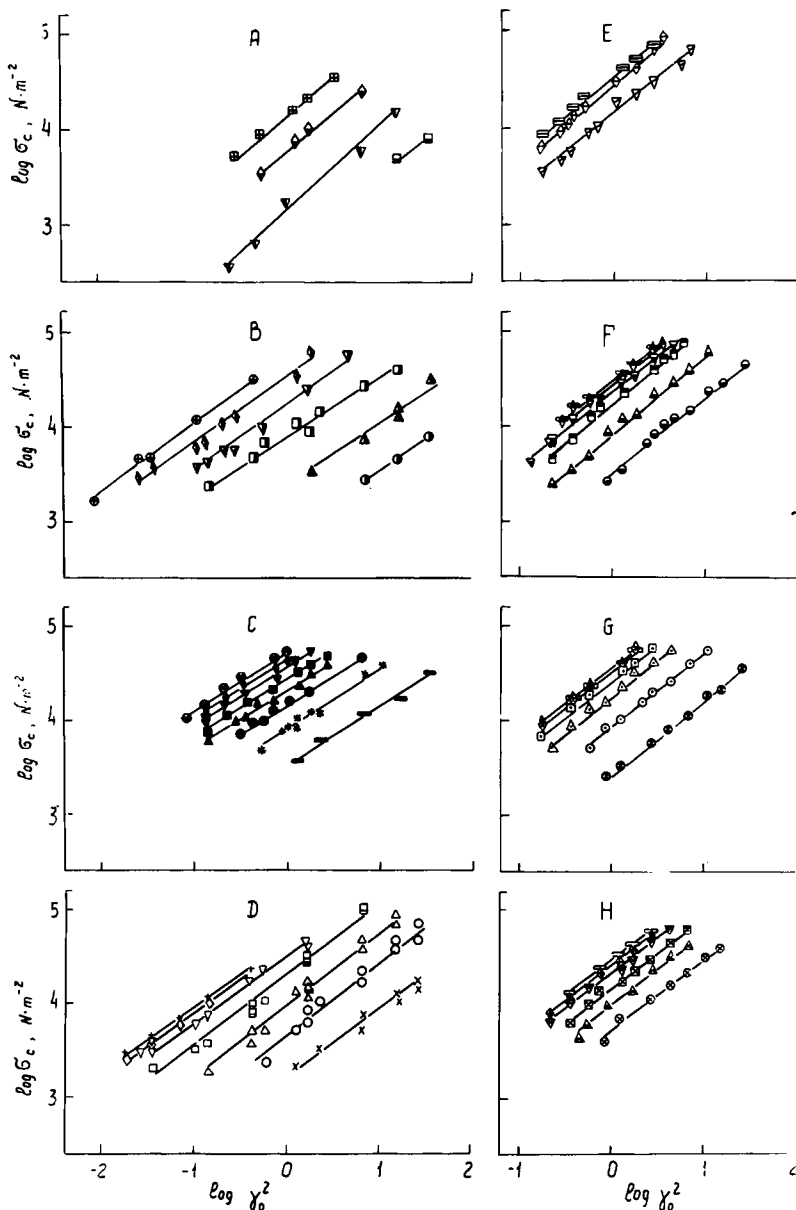


Fig. 6. Dependence of constant component of first normal stress difference on square of deformation amplitude at different frequencies. Specimens A, B, C, D, E, F, G, and H; (\blacktriangledown) data of mechanical measurements for specimen A.

obtained show that there is a deviation from the quadratic law due to the non-linear behavior of the polymer in the deformation amplitude range under review. In Figure 6, for the specimen of polybutadiene A, we also give the values of σ_c obtained using the mechanical method on a cone-plate-type device at a frequency of 0.3 cps. It can be seen that the data of polarization-optical and mechanical measurements of σ_c are in good agreement.

It is important to note here that on a cone-plane device the values of the normal force at a given frequency and amplitude pass over to the stationary value

within rather long periods of time from the beginning of deformation. On the other hand, the values of Δn_c reach the stationary value more rapidly, practically within a few cycles from the moment of assignment of oscillations. This drastic difference in the time during which σ_c reaches the stationary value is evidently due to the insufficient rigidity of the dynamometer of the normal force in the cone-plane device, which was equal to 10^5 N/m.

The set of obtained data demonstrates the prospects of measuring by the polarization-optical method the stresses arising in polymers on their oscillatory deformation. The method under consideration has an important advantage over the mechanical method. It was noted above that the polarization-optical method is "contactless" and the working cell may be extremely rigid. This is particularly important when measuring normal stresses.^{27,28}

Figure 6 shows the dependence of the steady component of the first normal stress difference on the square of the amplitude at different frequencies. As the frequencies increase, their effect on this dependence weakens, and when the frequencies corresponding to the high-elasticity plateau are achieved, the frequency dependence practically disappears.

Let us consider the dependence of σ_c on $\gamma_0^2 G'$. This dependence for the investigated polybutadienes and polyisoprenes is presented in Figure 7 (the values of G' in the linear region are borrowed from reference 14). The figure also shows the experimental data on σ_c obtained from the dependences $\sigma_c(\gamma_0)$ given in reference 26 for polystyrene solutions at different frequencies. Reference 26 also gives the frequency dependences of the storage moduli in the linear region. It can be seen that with such plotting one obtains a mastercurve for the investigated polybutadienes and polyisoprenes and the literature data²⁶ on polymer solutions. Besides, the dependence obtained is invariant with deformation frequency.

At low $\gamma_0^2 G'$, the values of σ_c are proportional to them. This is reflected by the dashed line in Figure 7. At high amplitudes this equality fails, and the value of σ_c becomes less than $\gamma_0^2 G'$. At high values of γ_0 this divergence may be as large

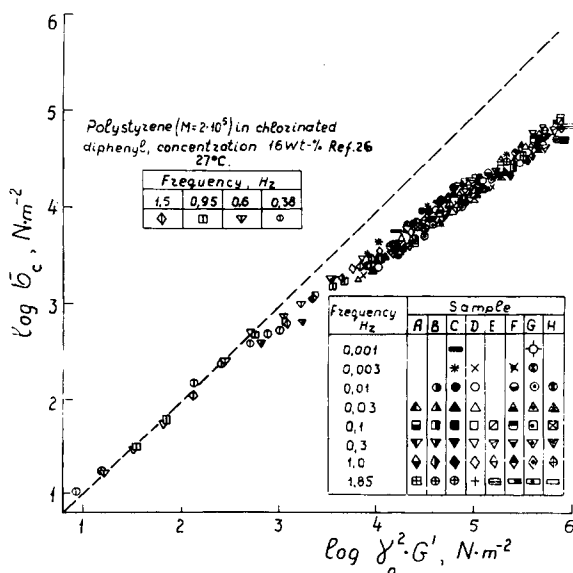


Fig. 7. Generalized characteristic of steady component of first normal stress difference.

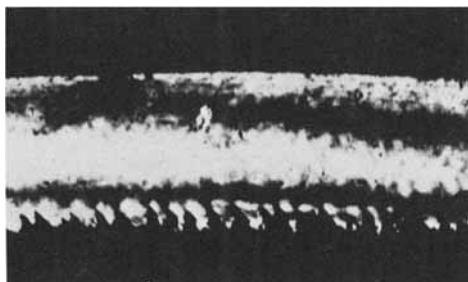
as tenfold. It is important, however, that for different polymers all the experimental data are described by one and the same dependence over a wide frequency range.

It has been shown that when certain critical values of deformation amplitudes, $\gamma_{0(cr)}$, are exceeded, linear polymers show a drastic drop in resistance to shear in their large-amplitude oscillatory deformation.¹⁴ This phenomenon is most pronounced in narrow-distribution polymers. Therefore, it is interesting to visually observe the development of this process. The experiments were conducted on a specimen of polybutadiene C during deformation with a frequency of 0.1 cps. At $\gamma_0 < \gamma_{0(cr)}$, stable deformation of the polymer in the gap and its complete sticking to the working surfaces was observed [Fig. 8(a)]. Further, when the amplitude $\gamma_{0(cr)}$ is achieved, the polymer begins to slip-stick near the surface of the inner cylinder.

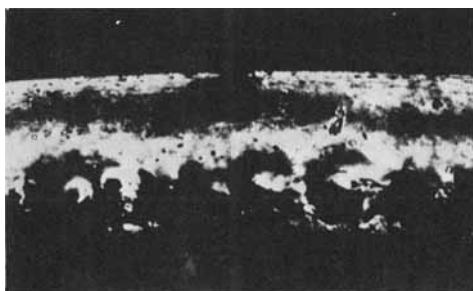
This process is well observed visually. At amplitudes γ_0 slightly exceeding



(a)



(b)



(a)

Fig. 8. Typical photos illustrating behavior of polymer in gap between coaxial cylinders. Specimen C. Frequency 0.1 cps. Deformation amplitudes: (a) 6.06×10^{-1} ; (b) 1.03; (c) 1.496.

$\gamma_{0(cr)}$, the polymer shows ruptures in the most stressed layer near the surface of the inner cylinder. These ruptures form a "saw" [Fig. 8(b)]. When the deformation ceases, the rupture zones are rapidly healed (within a few seconds). With further increase in amplitude, the rupture of the polymer extends uniformly to the entire region adjoining the internal cylinder. The "saw" disappears, and a dark region forms in the polymer near the internal cylinder, which is a continuous zone of polymer ruptures [Fig. 8(c)]. In this case after the deformation ceases, the healing of the ruptures takes more and more time. In continuity rupture regimes, no quantitative treatment of the measurement results is possible.

The authors are indebted to Dr. E. P. Plotnikova in carrying out the measurements of first normal stress difference on the rheogoniometer.

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Received March 24, 1977