JOURNAL OF APPLIED POLYMER SCIENCE VOL. 20, 25–40 (1976)

Polarization-Optical Investigation of Normal and Shear Stresses in Flow of Polymers

V. I. BRIZITSKY, G. V. VINOGRADOV, A. I. ISAEV, and YU. YA. PODOLSKY, *Institute of Petrochemical Synthesis of the USSR Academy of Sciences, Moscow, USSR 117912*

Synopsis

A method has been suggested for calculating the first difference of normal stresses characterizing the flow of polymers at high shear stresses. The calculations are based on the results of rheo-optical measurements in a slit of rectangular cross section. It has been found, for several samples of high molecular weight polybutadienes and polyisoprenes, that the flow behavior of the representatives of the given polymer homologous series having different molecular weights is characterized by a general relationship between the first normal stress difference and the shear stresses in those cases where the polymers are characterized by narrow molecular weight distributions. It has also been established that the first normal stress difference sharply increases in the region of shear stresses which immediately precedes the spurt—a jumpwise increase of the flow rate at a certain critical value of shear stress; while for polymers of wide molecular weight distribution the increase of the first normal stress difference in the region of high values of shear stresses is retarded. Equilibrium swell of the extrudate has been measured and the first normal stress difference determined by the rheo-optical method has been found to agree satisfactorily with the values calculated from the swelling ratios according to theoretical models.

INTRODUCTION

The deformation of linear polymers under the action of high stresses and at corresponding deformation rates may be accompanied by their transition from the fluid to the forced high-elastic state when the deformation takes place at temperatures much higher than the glass temperature.[1,2] This problem is of great importance for the processing of polymers since the transition indicated may lead to the disturbance of steady flow. When the polymer is flowing through a duct, the transition to the forced high-elastic state takes the form of a "spurt" of the stream, i.e., a manifold increase of the volume output at a certain critical value of pressure drop.[1,2]

There is ground to believe that the spurt of the flow of the polymer is associated with its high-elasticity and related phenomena. For this reason, visual observation of the flow under the regimes preceding the spurt is of interest. It provides a good opportunity to measure simultaneously the distribution of shear stresses and maximal tangential stresses and to compute on this basis the first normal stress difference. This is accounted for by the fact that the first normal stress difference at the shear stresses which are very close to the critical value cannot be measured by ordinary methods of rotational viscometry. It is because in the instruments usually employed, the detachment of

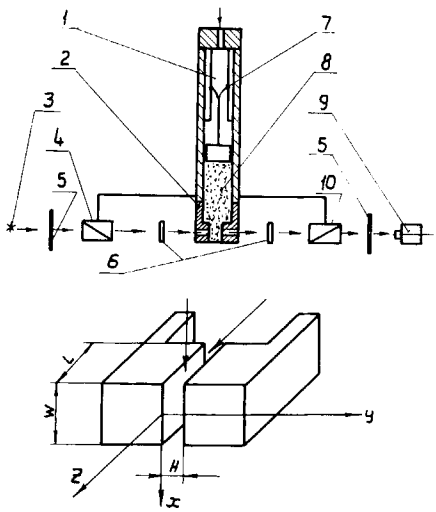


Fig. 1. Experimental setup (schematic): (1) nitrogen from pressure regulator; (2) working cell; (3) light source; (4) polarizer; (5) condenser; (6) quarter-wave plates; (7) flow meter; (8) sample; (9) camera (or screen); (10) analyzer. The flow of polymer in the z direction; light is directed toward the x axis.

polymers from the walls of the working part of the viscometer and the disturbed continuity of the flow are observed at shear rates and stresses which are much lower than the corresponding values recorded as critical in the capillary viscometer.[3] Nor are there fewer difficulties encountered when methods of capillary viscometry are used, in particular, when normal stresses are measured by means of pressure transducers located along the duct.[4–6] In this case, the first normal stress difference has to be found by linear extrapolation of the pressure along the capillary length up to the point where the extrudate leaves the capillary. This method requires the use of highly sensitive pressure transducers, which would not cause stream perturbations at that.

The task of measuring normal stresses and determining the character of their distribution in the stream during the flow of polymers at high rates can be solved by the rheooptical method which is based on the ability of high molecular weight compounds to exhibit, on deformation, the effect of birefringence and on the use of stress-optical laws for viscoelastic media.[7] The data reported in the literature,[8–16] indicating that the stress-optical laws are satisfied over a wide range of shear stresses, made the selection of this method sufficiently substantiated for a wide range of shear stresses.

Measuring the first normal stress difference by the rheo-optical method makes it possible to correlate the normal stresses with the extrudate swell, which is what has been done in this investigation.

EXPERIMENTAL

The experimental setup for carrying out rheo-optical investigations (Fig. 1) is a combination of a constant-pressure gas viscometer and an optical system designed for visual observation of the stream.[17,18]

The gas viscometer consists of a thermostated reservoir, a working cell, and

a system for regulating and measuring the pressure of nitrogen used to force the polymer through the working cell. The cell is shown at the bottom part of the figure. As seen, the cell includes a preexit container and a rectangular slit with two walls of optical glass, through which the stream is visually observed. The container is of a rectangular cross section 6 × 17 mm and 30 mm in length; it serves for observing the behavior of the polymer at the entrance into the rectangular slit. The entrance angle is 180°.

For calculation of the shear rate $\dot{\gamma}$ and the shear stress τ for a slit of rectangular form, the geometrical dimensions of the slit are of importance, particularly the ratio of the slit depth W (which is the linear size of the slit in the direction of illumination) to its width H, since it is this ratio that determines the extent of the perturbation effect of the front and rear walls of the slit.

Since the main objective of the present investigation is a study of polymers possessing a relatively low transparency and a high stress-optical activity, the geometrical dimensions of the slit for the rheo-optical unit in question have been chosen with account taken of these specific features; W and H are, respectively, equal to 6 and 2 mm. Such a ratio of W to H does not allow one to calculate the maximum values of shear rate $\dot{\gamma}_w$ and shear stress τ_w on the wall of the slit with the aid of formulas for a slit of infinite depth, since these formulas are applicable, with a sufficient degree of accuracy, to planar capillaries[15,19] with $W/H \geq 10$. Nevertheless, as will be shown below, strict calculation of $\dot{\gamma}_w$ and τ_w in certain special cases is possible for a rectangular slit with a lower ratio as well.

Entrance corrections have been estimated by using rectangular slits of different length L in our investigations, which made it possible to vary L/H within the limits of from 8 to 35. With this ratio of the geometrical dimensions of the slit and the preexit container, the loss of pressure in the preentrance region did not exceed 2% of the pressure drop in a slit of minimum length.

All the metallic surfaces of the working cell, which are in contact with the optical glasses, were polished and ground to fit the glasses. Before starting each experiment, with the working cell being assembled, the glasses were tested for mechanical strain. The working cell permits one to conduct experiments at pressures up to 200 atm and at temperatures from 20° to 90°C. For experiments that do not require visual observation of the stream, a provision is made for replacement of the rectantular slit with a capillary of circular cross section, with a diameter of D = 0.950 and a length of L = 23.65 mm. Three capillaries were used for investigation of extrudate swell. Their diameters and lengths are as follows: D = 0.950, 1.117, 1.010; L = 23.65, 46.6; 74.2 mm.

The constant-pressure gas viscometer of the setup in question is equipped with an automatic flowmeter. Its operating principle is based on the measurement of the linear velocity of the plunger, which transmits the nitrogen pressure to the polymer by the change of the ohmic resistance built into the viscometric reservoir of the slide wire whose movable contact is rigidly fixed to the plunger. The electrical signal of the slide wire is recorded by an electronic potentiometer.

The optical system shown in Figure 1 consists of a point light source, heat and light filters, condensers, a polarizer, and an analyzer, the last two units

TABLE I
Brief Description of Samples Investigated

Polybutadienes				Polyisoprenes			
	Isomeric composition				Isomeric composition		
$M_v \times 10^{-5}$	*cis*-1,4	*trans*-1,4	1,2-	$M_v \times 10^{-5}$	*cis*-1,4	*trans*-1,4	3,4-
0.80	46	45	9	3.75	79	15	6
1.35	47	44	9	5.75	69	25	6
3.20	45	46	9	8.30	85	10	5

being connected by a device designed for their synchronous rotation, and also quarter-wave plates, a screen and a cinema or photocamera. The optical system enables observation of isochromatic fringes in the case of circularly polarized light, and of isoclinic fringes when plane-polarized light is used.

All the optical measurements were carried out so that the focal plane passed through the middle of the planar stream. The adjustment of the focal plane to the middle of the duct was accomplished by focusing the objective first onto the front face of the glass next to the objective and then to the rear face of the second glass; simultaneously, the two positions of the objective on the optical bench were marked, after which the objective was set up in the middle position between the markings made.

Two types of light source were used: a white light and a monochromatic light source. Monochromatic light was produced with the aid of a mercury lamp and a green light filter which emits light with a wavelength of 5460 Å.

The objects under investigation are samples of polybutadienes and polyisoprenes of narrow molecular weight distribution (MWD; $M_w/M_n \leq 1.1$) which were synthesized by the method of anionic polymerization with butyllithium used as catalyst. The viscosity-average molecular weights (M_v) and the isomeric composition of the samples used are presented in Table I.

In addition to the samples listed in Table I, the authors have also investigated a system which simulates commercial polybutadiene and which is a 16-component mixture of equal quantities of samples of polybutadiene of narrow MWD with a molecular weight ranging from 65,000 to 320,000 (the M_w/M_n ratio for this mixture being 3.0). Besides, a sample of polydisperse polyisoprene ($M_v = 4.25 \times 10^5$; $M_w/M_n = 2.4$) was investigated.

The selection of such materials is accounted for by the fact that, on the one hand, the phenomenon of spurt reveals itself especially distinctly in linear polymers of narrow MWD,[1–3] and, on the other hand, the region of anomalous viscosity is clearly pronounced for polymers of wide MWD. All the results discussed below have been obtained by measurements at 25°C.

RESULTS AND DISCUSSION

Figure 2 presents flow curves showing the dependence of velocity gradient on shear stress for the polybutadienes (a) and polyisoprenes (b) studied. For samples of narrow MWD, we compare the results obtained for the flow of the polymers through a rectangular slit (squares) and a capillary (circles). In the first case, measurements were made by using slits of different lengths in order

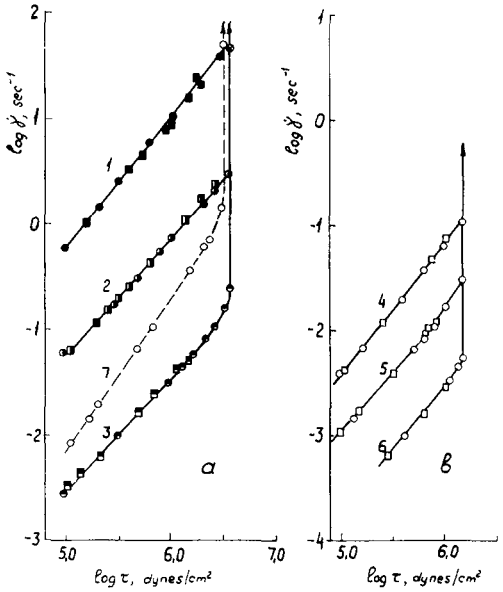


Fig. 2. Flow curves for polybutadienes (a) and polyisoprenes (b). Squares stand for rectangular slit, and circles for round capillary: (1, 2, 3) polybutadienes of narrow MWD with viscosity-average molecular weights ($\bar{M}_v$) 8×10^4, 1.35×10^5, and 3.2×10^5, respectively; (4, 5, 6) polyisoprenes of narrow MWD with the following values of $\bar{M}_v$: 3.75×10^5, 5.75×10^5, and 8.3×10^5, respectively; (7) model polydisperse polybutadiene with $\bar{M}_v = 2.4 \times 10^5$.

to take account of entry corrections according to the two-capillary method.[17] The calculation of the entry corrections has shown that they do not exceed 5 H for polybutadienes and 3 H for polyisoprenes over the entire range of shear stresses.

From Figure 2 it is seen that high molecular weight polymers of narrow MWD behave like Newtonian liquids when flowing in a capillary over a sufficiently wide range of shear stresses. Therefore, in the case of flow through a rectangular slit, the calculation of the velocity gradient and shear stresses may be carried out in a form brought up to numerical data, on the basis of the general solution of the problem for the isothermal steady flow of a noncompressible Newtonian liquid.[20]

For the position of the coordinate axes (see Fig. 1), the motion equation may be represented as follows:

$$\frac{\partial P}{\partial z} = \eta \left(\frac{\partial^2 V_z}{\partial x^2} + \frac{\partial^2 V_z}{\partial y^2} \right) \tag{1}$$

where V_z is the linear velocity of flow in the z direction; $\partial P/\partial z$ is the pressure gradient, and η is the viscosity.

With account taken of the complete adhering of the polymer to the walls of the duct, the boundary conditions are as follows:

$$\begin{gathered} V_z(x, 0) = 0 \\ V_z(x, H) = 0 \\ V_z(\pm W/2, y) = 0 \end{gathered} \tag{2}$$

The solution of eq. (1) obtained by Bussinesq using the method of separation of variables has the following form:

$$V_z = \frac{1}{\eta}\left(\frac{\partial P}{\partial z}\right)\left[(y/2)(y-H) + \frac{4H^2}{\pi^3}\sum_{n=1,3\ldots}^{\infty}\frac{1}{n^3}\cdot\sin\left(\frac{n\pi y}{H}\right)\frac{\cosh(n\pi x/H)}{\cosh(n\pi W/2H)}\right]. \quad (3)$$

From this equation we can easily find the velocity gradient in the y direction and its maximal value $\dot{\gamma}_w$ at the walls of the slit in the $x = 0$ plane:

$$\frac{\partial V_z}{\partial y} = \frac{1}{\eta}\left(\frac{\partial P}{\partial z}\right)\left[y - \frac{H}{2} + \frac{4H}{\pi^2}\sum_{n=1,3\ldots}^{\infty}\frac{1}{n^2}\cdot\cos\left(\frac{n\pi y}{H}\right)\cdot\frac{\cosh(n\pi x/H)}{\cosh(n\pi W/2H)}\right] \quad (4)$$

$$\dot{\gamma}_w = \pm\frac{1}{\eta}\left(\frac{\partial P}{\partial z}\right)\frac{H}{2}\left[1 - \frac{8}{\pi^2}\sum_{n=1,3\ldots}^{\infty}\frac{1}{n^2}\cdot\frac{1}{\cosh(n\pi W/2H)}\right] = \pm\frac{1}{\eta}\cdot\frac{\partial P}{\partial z}\cdot\frac{H}{2}\cdot K_1. \quad (5)$$

On the other hand, the flow rate of the polymer, Q, is

$$Q = \int_{-W/2}^{+W/2}\int_0^H V_z dx dy = -\frac{1}{\eta}\left(\frac{\partial P}{\partial z}\right)\frac{WH^3}{12}\left[1 - \frac{192}{\pi^5}\frac{H}{W}\cdot\sum_{n=1,3\ldots}^{\infty}\frac{1}{n^5}\tanh\left(\frac{n\pi W}{2H}\right)\right] = -\frac{1}{\eta}\frac{\partial P}{\partial z}\frac{WH^3}{12}\cdot K_2. \quad (6)$$

Eliminating $(1/\eta)(\partial P/\partial z)$ from eqs. (5) and (6) and assuming that $\tau_w = \eta\cdot\dot{\gamma}_w$, we can obtain formulas for calculation of the velocity gradient and the shear tangential stress at the walls of the slit in the $x = 0$ plane:

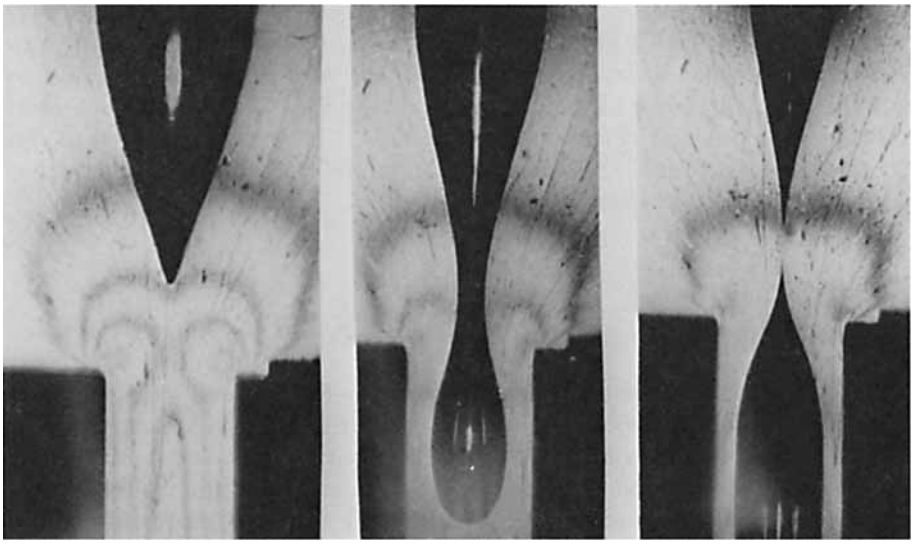
$$\dot{\gamma}_w = \pm\frac{6Q}{WH^2}\cdot\frac{K_1}{K_2} \quad (7)$$

$$\tau_w = \pm\frac{H}{2}\cdot\left(\frac{\partial P}{\partial z}\right)\cdot K_1.$$

As seen, eqs. (7) are analogous to the corresponding formulas used for calculation of $\dot{\gamma}_w$ and τ_w for the flow of Newtonian liquids through a rectangular slit of infinite depth,[20] with corrections introduced for the perturbation effect of the front and rear walls. Evaluation of the terms of the series, included in K_1 and K_2, has shown that they rapidly fall off. Thus, at $W/H = 3$, the ratio of the second term of the series to the first one is found to have values lower than 10^{-2} and 10^{-5}, respectively, for the coefficients K_2 and K_1. Therefore, with only the first term of the series being retained, we finally have

$$\dot{\gamma}_W = \pm 1.246\cdot\frac{6Q}{WH^2} \quad (8)$$

$$\tau_w = \pm 0.985\cdot\frac{H}{2}\left(\frac{\partial P}{\partial z}\right).$$



(a) (b) (c)

Fig. 3. Zone of entrance into the rectangular slit. Photographs taken at intervals of 1.5 sec show the action of tensile stresses in polybutadiene by the behavior of an air bubble.

Thus, the corrections for the shear rate and shear stress, which are introduced because of the effect of the front and rear walls, are 25% and 1.5%, respectively.

As seen from Figure 2, the $\dot{\gamma}(\tau)$ relations, which have been calculated with account taken of the corrections indicated, are in fact in good agreement with the data for a round capillary in these cases when the behavior of the polymer bears close resemblance to Newtonian behavior. The flow curve given in Figure 2 for polydisperse polybutadiene has been obtained only on a round capillary since the methods of treatment of the results of measurements on a rectangular slit used for samples of narrow MWD have been found to be inapplicable in this case because of the strong non-Newtonian behavior.

The qualitative observations of isochromatic fringes during the flow of polybutadienes of narrow MWD and comparison of the results obtained with the appearance of the emerging extrudate confirm practically completely the phenomena described in the literature.[21] Only a few facts need be added. The flow of the polymer as the viscoelastic medium is accompanied at any shear stress by the development of tensile stresses acting along the flow axis in the entrance region. This is evidenced by the observations of the behavior of foreign inclusions present in the entrance zone of the rectangular slit. For example, an air bubble entering the slit becomes gradually elongated (Fig. 3), and, eventually, undergoes rupture; the portion of the air bubble that has found its way into the duct again assumes a spherical form, which indicates the absence of tensile stresses in the zone of established flow. As regards the air left in the preentrance zone, it has the same fate.

As reported in the literature,[21] there are observed longitudinal oscillations in the optical pattern in the duct entrance zone, which arise simultaneously with the periodic slippage of the material in the duct. According to our ob-

servations made at stresses much lower than those at which longitudinal pulsations take place, feeble horizontal pulsations of interference bands arise in the entrance zone, while inside the duct the band pattern is still in parallel to the walls. This behavior of the polymer is due to the concentration of stresses at the entrance edges of the rectangular slit.

Let us now pass over to the calculation of normal stresses. It is known that the first normal stress difference σ, is equal to[11]

$$\sigma = \frac{2\tau_{xy}}{\tan 2æ} \tag{9}$$

where τ_{xy} is the shear stresses and æ is the extinction angle at a given point of the stream.

From this, it follows that the calculation of the first normal stresses difference, provided that the distribution of shear stresses is known, can be most simply made on the basis of the curve of distribution of the extinction angle determined by the method of isoclines. The application of this method, however, is fraught with a number of difficulties. First, even when the light is plane-polarized, the pattern of isoclinic fringes is overlapped by isochromatic fringes, which complicates the quantitative treatment of the photographs obtained. Secondly, for all the materials under investigation, the isocline of any parameter in the region of established flow was found to be a band smeared out over the major portion of the width of the rectangular slit. This made it impossible to assign the isocline of the given parameter to any definite point or any narrow region of the cross section of the rectangular slit. The fact that the extinction angle cannot be determined experimentally led to the necessity of its calculation.

It is known[10] that

$$\sin 2æ = \frac{\tau_{xy}}{\tau_{\max}} \tag{10}$$

where $\tau_{\max}$ is the maximum tangential stress at the given point.

Thus, in order to calculate the first normal stress difference, it is necessary and sufficient to know the values of shear and maximum shear stresses at each point of the stream. It has been pointed out above that the correction for the perturbation effect of the front and rear walls does not exceed 1.5% when τ_{xy} is calculated for the flow of a Newtonian liquid through the rectangular slit used in the present work. Therefore, τ_{xy} was calculated by the following formula[20]:

$$\tau_{xy} = \frac{\Delta P \cdot H}{2L} \tag{11}$$

Furthermore, a control estimation of the shear rate has been made. The following procedure was used. Into the polymer stream forced through the slit of rectangular cross section were introduced particles of aluminium (spheres 3–6 μ in diameter) and the velocity profile across the capillary cross section was determined from their velocity. Figure 4 presents the results of measurements at various pressures in the viscometer.

Here, the calculated velocity profiles, see eq. (3), are represented as solid lines, and those found experimentally are shown by dashed-and-dot lines.

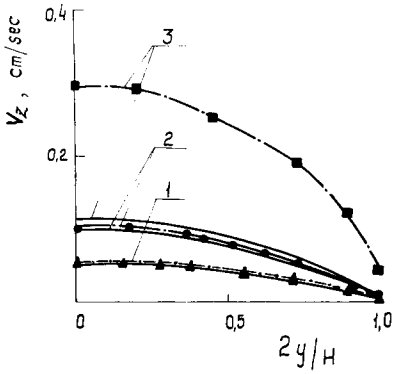


Fig. 4. Distribution of velocities along the width of the rectangular slit (L/H = 14.3) in the region of established flow for polybutadiene with $\bar{M}_v = 1.35 \times 10^5$ at various pressure drops ΔP, kg/cm^2: (1) 48; (2) 60; (3) 100.

As seen, the experimental profiles deviate markedly from the calculated data in the region of high shear stresses, which is associated with the manifestation of non-Newtonian behavior in this stress region even for polymers of narrow MWD. Graphic differentiation of the velocity profiles found experimentally enables one to calculate the velocity gradient at each point of the stream, from the value of which one can find shear stresses using the corresponding flow curves.

Another quantity which must be known in order to calculate the first normal stress difference is the maximum tangential stresses. Their distribution along the width of the stream have been obtained directly from the pattern of isochromatic fringes[18]:

$$\tau_{max} = \frac{n \cdot \lambda}{2CW} \tag{12}$$

where n is the serial number of the band, λ is the wavelength of the light source used, and C is the stress-optical coefficient for the given polymer. The distribution of bands along the slit width was recorded on photographic film with subsequent photometric treatment of the negative.

Figure 5 shows the distribution of isochromatic fringes for polybutadiene (a) and polyisoprene (b) having molecular weights 135,000 and 375,000, respectively, at different pressures, along the width of a slit with a length-to-width ratio of 14.3. As can be seen from Figure 5, at low pressures the distribution of bands along the cross section of the slit is linear. As the pressure increases, i.e., as the shear stress increases, the mode of distribution of bands becomes increasingly different from linearity, the distance between the bands decreasing near the duct walls. Moreover, at equal pressures the number of bands is always greater on polybutadienes than on polyisoprenes, which is associated with the different optical sensitivities of polybutadiene and polyisoprene. The high sensitivity of polybutadienes as compared with polyisoprenes results also in the bands being strongly concentrated at the duct walls. It should be noted in passing that the shear stress, at which the deviation of the distribution of bands across the cross section of the slit from linearity is first observed, approximately corresponds to the stress at which first distortions appear on the surface of the extrudate emerging from the capillary.

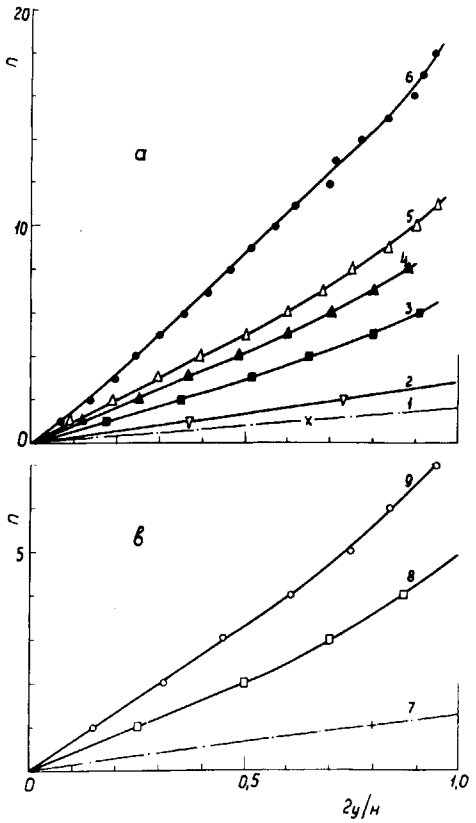


Fig. 5. Distribution of isochromatic fringes along the width of the rectangular slit (L/H = 14.3) in the region of established flow for polybutadiene with $\bar{M}_v = 1.35 \times 10^5$ (a) and polyisoprene with $\bar{M}_v = 3.75 \times 10^5$ (b) at various pressure drops ΔP, kg/cm^2: (1) 9; (2) 16; (3) 36; (4) 48; (5) 60; (6) 100; (7) 16; (8) 45; (9) 65.

As follows from eq. (12), the distribution of maximum shear stresses along the duct width must exactly correspond to the band distribution pattern. The stress-optical coefficient C entering into this formula was determined experimentally at rather low values of shear stresses for which it may be assumed, with a sufficient degree of accuracy, that $\tau_{xy} = \tau_{max}$. For the polymer homologous series studied, the values of the stress-optical coefficient has been found to be equal to 3.3×10^{-10} and 1.9×10^{-10} cm^2/dyne at 25°C for polybutadienes and polyisoprenes, respectively. The indicated value of C for polybutadiene is close to the literature data.[22,23]

Thus, the registration of the fringes pattern in circular polarized light of the polymer stream makes it possible to determine the values of shear stresses and maximum tangential stresses at each point of the stream. To illustrate, Figure 6 shows the distribution of maximum tangential stresses and shear stresses along the slit width for polybutadiene having a molecular weight of 135,000 at a pressure drop of P = 100 kgf/cm^2 in the rectangular slit.

As should be expected, in the central part of the stream, i.e., at low shear stresses, these values coincide, while upon approach to the walls, the value of

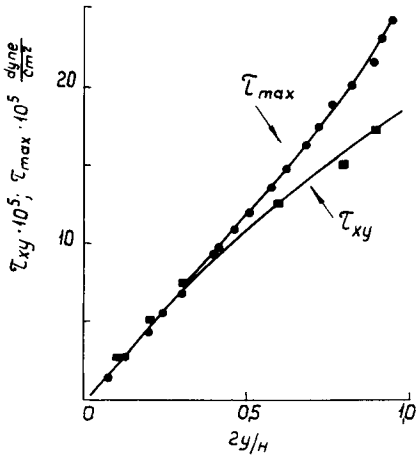


Fig. 6. Distribution of maximum tangential stresses (τ_{max}) and shear stresses τ_{xy} along the width of the rectangular slit (L/H = 14.3) in the region of established flow at a pressure drop of ΔP = 100 kg/cm^2 for polybutadiene with $\bar{M}_v = 1.35 \times 10^5$.

τ_{xy} becomes increasingly exceeded by the value of τ_{max}. It is the ratio of these quantities that makes it possible to calculate the relation between the first normal stress difference and the shear stress or the rate of shear. As seen from Figure 6, such a calculation can be made only in the region of high shear stresses, which is, on the one hand, a limitation on the method and, on the other hand, an advantage.

The results of such calculations for the samples of polybutadiene and polyisoprene studied are given in Figure 7. This figure also shows, for comparison, the dependences of the first normal stress difference on shear stresses, which have been determined by E. P. Plotnikova and A. Ya. Malkin using a cone-and-plate viscometer in the region of low shear stresses for polybutadiene having a molecular weight of 135,000.

From the data presented, it follows that the values of the first normal stress difference calculated by the method suggested are in good agreement with the corresponding values found at low shear stresses by direct measurements. Moreover, the relation between the normal stresses and shear stresses is independent of the molecular weight for polymers of narrow MWD within a single homologous series.

In the case of polybutadienes and polyisoprenes of narrow MWD the rate of growth of σ with increasing shear stress increases as the spurt region is approached. The critical value of the shear stress corresponding to the spurt is marked by the vertical arrows on the abscissa. The first normal stress difference value may exceed the shear stress corresponding to the spurt. This means that the phenomenon of the stream spurt is due in a large measure to the high-elastic properties of the polymer. Furthermore, it follows from this that one must be careful when extrapolating the parameters characterizing the high-elastic properties of polymers to the region of stresses at which the spurt is observed.

Quite different is the behavior of polydisperse polybutadiene. This follows from a comparison of Figures 2 and 7. Indeed, as seen from Figure 2, the

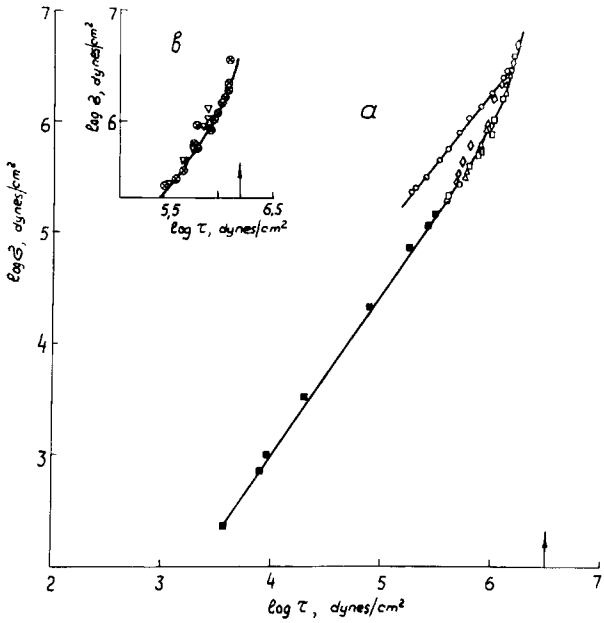


Fig. 7. Relation between the normal stresses and shear stresses for polybutadienes (a) and polyisoprenes (b). Filled symbols stand for a cone-and-plate device, open ones for a polarization-optical unit. Polybutadienes of narrow MWD have the following values of $\bar{M}_v$: (◇) 8×10^4; (□) 1.35×10^5; (△) 3.2×10^5. Polyisoprenes of narrow MWD have the following values of $\bar{M}_v$: (⊕) 3.75×10^5; (▽) 5.75×10^5; (⊗) 8.3×10^5; (○) model polydisperse polybutadiene with $\bar{M}_v = 2.4 \times 10^5$.

flow of a sample of polybutadiene of wide MWD reveals the non-Newtonian behavior, while the relation between σ and τ in double-logarithmic coordinates remains practically linear (Fig. 7).

The data given also show that for polybutadienes of narrow MWD, the shear stresses become equal to the first normal-stress difference at stresses approximately corresponding to the spurt of the stream in rotational-type devices.[3]

Hence, if the results obtained are combined with the literature data known for polymeric systems, important conclusions may be drawn concerning the relationship between the components of the stress tensor. It is known[24] that in the region of low shear stresses, $\sigma \sim \tau^2$. For polymers of narrow MWD, as the critical values of shear stress are approached, the exponent of the $\sigma(\tau)$ dependence begins to increase and may exceed 2; while for a polydisperse polymer, the angular coefficient of the dependence of normal stress on shear stress remains practically constant in the same range of shear stresses.

Let us now consider the problem of extrusion swelling. It is known that in the extrusion of polymer solutions and melts through ducts there is observed the effect of extrudate swelling.[20] The swelling ratio of the extrudate, B, which is equal to the ratio of the diameter of the extrudate to that of the duct, may reach several units. Some theoretical models have been proposed, which allow us to calculate the first normal stress difference on the basis of experimental data on extrudate swelling.[25-28] These models are based on the fact that the elastic energy stored by the polymer upon deformation in the

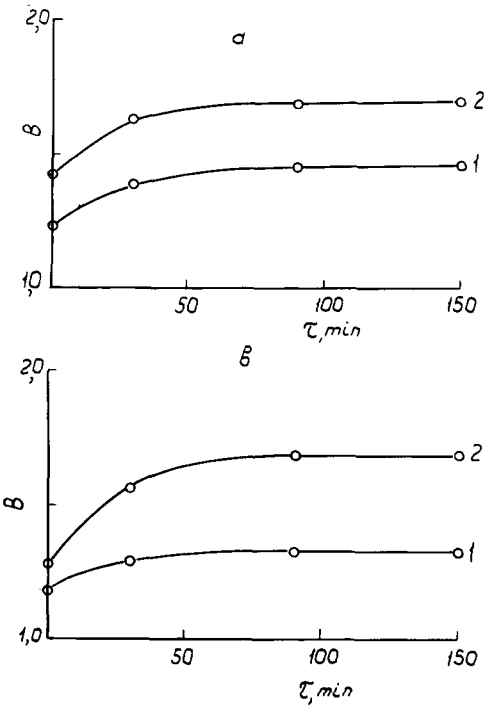


Fig. 8. Swelling ratio of the extrudate of polydisperse polybutadiene with $M_v = 2.4 \times 10^5$ (a) and polyisoprene $M_v = 4.25 \times 10^5$ (b) vs. time of aging in an aqueous–alcoholic solution at a temperature of 50°C. The ratio of the length of the duct to its diameter (L/D) is 70. The shear stresses τ (dynes/cm^2) are: (1) 7.95×10^4 and (2) 9.4×10^5 for polybutadiene and (1) 3.8×10^5 and (2) 8.9×10^5 for polyisoprene.

duct reveals itself in the form of longitudinal deformations when the polymer leaves the duct. The existing theories (literature sources are given on the left of the formulas) lead to the following results:

$$\text{Ref. 25:} \quad \sigma = \frac{2}{3}\tau_w B(6 \ln B)^{1/2} \tag{13}$$

$$\text{Ref. 26:} \quad \sigma = \frac{2}{3}\tau_w (B^4 + 2B^{-2} - 3)^{1/2} \tag{14}$$

$$\text{Ref. 27:} \quad \sigma = \tau_w \left\{ B^4 \left[1 + \frac{\partial \ln B}{\partial \ln (-\tau)} \right]^2 - 1 \right\}^{1/2} \tag{15}$$

$$\text{Ref. 28:} \quad \sigma = \frac{2}{3}\tau_w (B^4 - B^{-2})^{1/2}. \tag{16}$$

When the values of the swelling ratios are known, formulas (13)–(16) provide a relationship between the first normal stress difference and shear stresses. But up to the present time, no comparison has ever been made in the literature between the results of such calculations and the measurements of the first normal stress difference for the flow of polymers under the action of high shear stresses. A direct comparison has only been made[27,28] at low shear stresses, this being explained by the limited experimental possibilities in measuring the first normal stress difference (measurements have been made with the aid of the Weissenberg rheogoniometer).

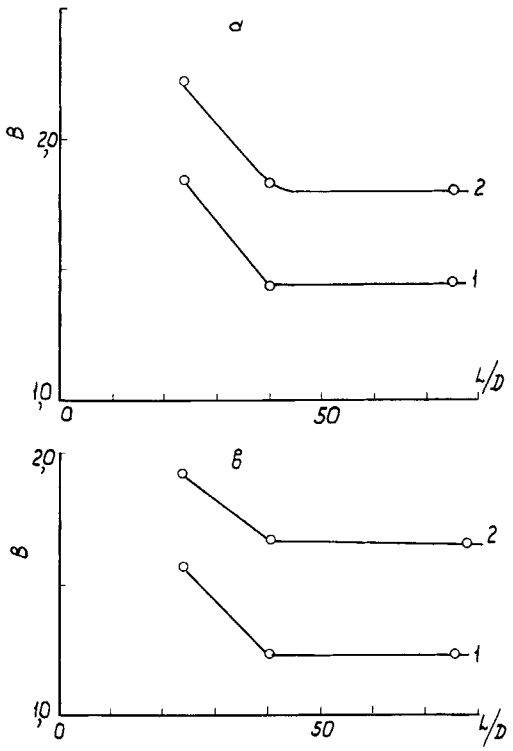


Fig. 9. Equilibrium value of the swelling ratio of the extrudate of polydisperse polybutadiene of $\bar{M}_v = 2.4 \times 10^5$ (a) and polyisoprene of $\bar{M}_v = 4.25 \times 10^5$ (b) as a function of the ratio of the length of the duct to its diameter (L/D). The temperature is 25°C. The shear stresses are (dynes/cm^2): (1) 7.95×10^4 and (2) 2×10^6 for polybutadiene; (1) 2.2×10^5 and (2) 1×10^6 for polyisoprene.

Though at high shear stresses the normal stress effect is least pronounced in the case of polymers having wide MWD, it is these polymers that are most convenient for a comparison to be made between the results of an experimental determination of normal stresses and their values calculated from the known models using the swelling ratio B. This is accounted for by the fact that in the case of polymers of narrow MWD the phenomenon of extrusion swelling at high shear stresses is accompanied by such strong distortions of the extrudate surface that the swelling ratio B cannot be determined in the region of high shear stresses. Therefore, the swelling ratios have been measured on samples of polybutadiene and polyisoprene of wide MWD.

To carry out such calculations, it is necessary to know the swelling ratio of the extrudate that satisfies two requirements. First, equilibrium values of the swelling ratio must be used in calculations. The point is that the diameter of the extrudate is changed with time after emerging from the duct due to the relaxation of stresses and deformations in it. To determine the duration of these processes, the kinetics of the increase of the extrudate diameter with time was studied.

In order to exclude the effect of gravitational forces on the dimensions of the extrudate and to speed up the relaxation processes, the extrudate was placed in an aqueous–alcoholic mixture at a temperature of 50°C. The den-

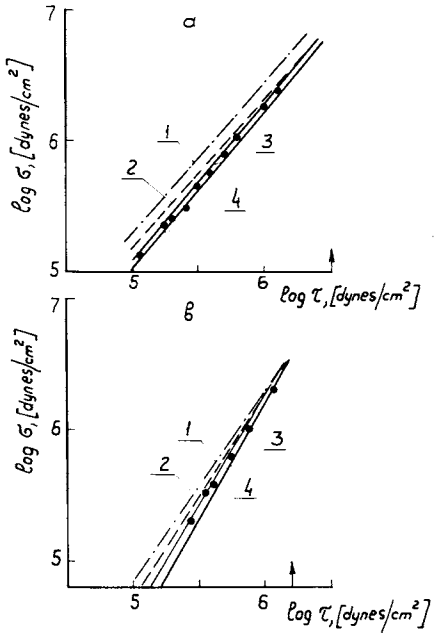


Fig. 10. Normal stresses vs. shear stresses for polydisperse polybutadiene of $\bar{M}_v = 2.4 \times 10^5$ (a) and polyisoprene of $\bar{M}_v = 4.25 \times 10^5$ (b). The dashes signify calculations based on the swelling ratio of the extrudate according to the following theories: (1) Mori[27]; (2) Metzner[26]; (4) Mendelson[25]; (3) Bagley[28]; the dots stand for experimental values.

sity of the mixture was equal to that of the polymer. The results of these measurements for polybutadiene (a) and polyisoprene (b) at two constant shear stresses are shown in Figure 8 in the form of time dependences of the swelling ratio. It is seen that the equilibrium values of the swelling ratio are attained after 1½ hr of aging of the extrudate in the aqueous–alcoholic mixture. It should be noted that if the polymers are aged for long periods of time, the shape of the extrudate is distorted—spiral or wave-like distortions are observed, this being caused by the action of surface tension forces. These data are not presented in Figure 8.

Secondly, use must be made in calculations of the value of swelling ratio due only to the shear flow of the polymer in the duct, which is not complicated by the effects arising at the duct entrance. For this purpose, the swelling ratio B must be measured in long ducts (at large values of the ratio of the length of the duct L to its diameter D). The results of measurements of equilibrium swelling ratios versus L/D given in Figure 9 for polybutadiene (a) and polyisoprene (b) at two values of shear stress have shown that at values of $L/D \geq 40$ further increase of this ratio does not affect the diameter of the extrudate. Therefore, all the calculations given below have been carried out on the basis of the equilibrium swelling ratios obtained in ducts with $L/D = 70$.

The results of calculations of $\sigma(\tau)$ with the aid of formulas (13)–(16) and their comparison with the experimental relations obtained by the rheooptical method are given in Figure 10. From this figure, it is seen that all the theories in question yield similar close results. Being highly important from

the theoretical point of view, this conclusion is also of great practical value for calculations of the swelling ratios of extrudates.

References

1. G. V. Vinogradov, A. Ya. Malkin, Yu. G. Yanovsky, E. K. Borisenkova, B. V. Yarlykov, and G. V. Berezhnaya, *J. Polym. Sci. A-2*, **10**, 1061 (1972).
2. G. V. Vinogradov, N. I. Insarova, B. B. Boiko, and E. K. Borisenkova, *Polym. Eng. Sci.*, **12**, 323 (1972).
3. G. V. Vinogradov, *Pure Appl. Chem.*, **26**, 423 (1971); *Rheol. Acta.*, **19**, 357 (1973).
4. C. D. Han, M. Charles, and W. Philippoff, *Trans. Soc. Rheol.*, **13**, 455 (1969).
5. C. D. Han, T. C. Yu, and K. U. Kim, *J. Appl. Polym. Sci.*, **15**, 1149 (1971).
6. C. D. Han, M. Charles, and W. Philippoff, *Trans. Soc. Rheol.*, **14**, 393 (1970).
7. A. G. Lodge, *Nature*, **176**, 838 (1955).
8. W. Philippoff, *Nature*, **178**, 811 (1956).
9. W. Philippoff, *J. Appl. Phys.*, **27**, 984 (1956).
10. W. Philippoff, *J. Polym. Sci.*, **18C**, I (1964).
11. W. Philippoff, *Trans. Soc. Rheol.*, **5**, 163 (1961).
12. W. Philippoff, and S. J. Gill, *Trans. Soc. Rheol.*, **7**, 33 (1963).
13. J. L. S. Wales, and H. Janeschitz-Kriegl, *J. Polym. Sci. A-2*, **5**, 781 (1967).
14. W. Philippoff, Proceedings of the 5th International Congress on Rheology, Vol. 4, Tokyo Press, Tokyo, 1970.
15. C. D. Han, and L. H. Drexler, *J. Appl. Polym. Sci.*, **17**, 2329 (1973).
16. H. Janeschitz-Kriegl, *Advan. Polym. Sci.*, **6**, 170 (1969).
17. G. V. Vinogradov, and N. V. Prozorovskaya, *Plastmassy*, **5**, 50 (1964).
18. M. M. Frocht, *Photoelasticity*, Vol. 1, Wiley, New York, 1941.
19. J. L. den Otter, *Rheol. Acta*, **10**, 200 (1971).
20. J. M. McKelvey, *Polymer Processing*, Wiley, New York, 1962.
21. G. V. Vinogradov, N. I. Insarova, B. B. Boiko, and E. K. Borisenkova, *Polym. Eng. Sci.*, **12**, 323 (1972).
22. N. K. Kalfoglou, and H. L. Williams, *J. Appl. Pol. Sci.*, **14**, 2481 (1970).
23. N. K. Kalfoglou, and H. L. Williams, *J. Macormol. Sci., Phy.*, **B4**, 381 (1970).
24. G. V. Vinogradov, A. Ya. Malkin, and V. F. Shumsky, *Rheol. Acta*, **9**, 155 (1970).
25. A. B. Metzner, W. T. Houghton, R. A. Sailor, and J. L. White, *Trans. Soc. Rheol.*, **5**, 133 (1961).
26. R. A. Mendelson, F. L. Finger, and E. B. Bagley, *J. Polym. Sci.*, **C35**, 177 (1971).
27. Y. Mori, and K. Funatsu, *Appl. Polym. Symp.*, **20**, 209 (1973).
28. E. B. Bagley, and H. J. Duffey, *Trans. Soc. Rheol.*, **14**, 545 (1970).

Received April 28, 1975