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EFFECT OF THE MOLECULAR MASS ON THE SHEAR AND LONGITUDINAL VISCOSITY OF LINEAR POLYMERS

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The effect of the molecular mass of a polymer sample on the dependence of the stationary viscosity on the velocity gradient upon simple shear and uniaxial tension is studied. The model of the dynamics of a suspension of noninteracting dumbbells in the anisotropic medium is used. The theoretical results show that the asymptotic behavior of the shear viscosity does not depend on the molecular mass and corresponds to experimental data.

The study of the technological processes of polymer processing is an important practical problem whose solution requires a mathematical formulation of the behavioral laws of polymer fluids. In mathematical modeling of the flows of linear-polymer solutions and melts, the greatest difficulties are connected with nonlinear effects. For their description it is necessary to obtain a rheological constitutive relation and check its correspondence to the real flows of polymer fluids. The rheological constitutive relation has already been formulated by Altukhov and Pyshnograi [1, 2], and Kulicke and Wallbam calculated the simple stationary shear flow and their results agree with experimental data [3]. The indicated relation was derived as a zero approximation of the more general rheological constitutive relation with respect to small parameters related to the reaction of the macromolecular chain and the internal viscosity [4, 5]; therefore, this relation needs to be additionally substantiated. We now construct a rheological zero-approximation model by a different method and study the effect of the molecular mass and concentration of the polymer on its parameters.

Rheological Constitutive Relation. We use the microstructural approach that permits us to establish a relationship between the macro and microcharacteristics of a polymer system [6, 7]. In the theory of polymer viscoelasticity, a monomolecular approximation, in which one macromolecule moving in an effective medium formed by a solvent and other macromolecules is considered instead of a set of macromolecules in the solvent volume, is the most efficient. To study relatively slow motions, one can use the Kargin–Slonimskii–Rouse model. In this model, the macromolecular dynamics is simulated by the motion of $N+1$ centers of friction (beads) connected sequentially by elastic forces (springs), and the equations of the dynamics of a macromolecule have the form

$$m\frac{d}{dt}u_i^\alpha = P_i^\alpha + Q_i^\alpha + \Phi_i^\alpha, \tag{1}$$

where m is the mass of a bead, u_i^α is the velocity of a particle with number α, P_i^α is the force of hydrodynamic entrainment, Q_i^α is the elastic force, and Φ_i^α is a random (Brownian) force.

It is noteworthy that the application of this approach leads to rheological constitutive relations of different complexity (see the review of publications in [6, 7]). The simplest rheological model [1, 2] allows one to simulate the stationary viscosimetric flows of linear-polymer solutions and melts qualitatively and quantitatively. We now consider it in more detail. We simulate the dynamics of a macromolecule by an elastic dumbbell that corresponds to the slowest relaxational process of a polymer chain.

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In the inertia-free case ($m = 0$), the equations of the dynamics of a macromolecule (1) in the laboratory coordinate system have the form

$$\dot r_i' = \nu_{ij} r_j' - 2T\mu\zeta_{ij}^{-1}(r_j' - r_j'') + \zeta_{ij}^{-1} f_j', \quad \dot r_i'' = \nu_{ij} r_j'' - 2T\mu\zeta_{ij}^{-1}(r_j'' - r_j') + \zeta_{ij}^{-1} f_j''. \tag{2}$$

Here r_i' and r_i'' are the ith Cartesian coordinate of the radius vector of the first and second beads, respectively, $2T\mu$ is the elasticity coefficient, T is the temperature in energy units, μ is the proportionality coefficient, ζ_{ij} is the tensor coefficient of friction, $\nu_{ij} = \partial v_i/\partial x_j$ is the velocity-gradient tensor, v_i is the ith component of the velocity vector, f_i' and f_i'' are the ith components of the vector of a random force (for the first and second beads, respectively), whose statistical properties are determined from an appropriate fluctuation-dissipative relation.

If the anisotropy of the polymer system is determined by the symmetric tensor a_{ij}, for the friction tensor ζ_{ij} we use the expression [2]

$$\zeta_{ij} = B\zeta(\delta_{ij} + 3\beta(a_{ij} - (a_{ll}/3)\delta_{ij}) + \text{æ} a_{ll}\delta_{ij})^{-1}. \tag{3}$$

Here ζ is the friction coefficient of the beads in a "monomeric" fluid (for spherical particles, we have $\zeta = 6\pi R\eta_{\rm s}$, where R is the particle radius and $\eta_{\rm s}$ is the viscosity of the solvent), B is the measure of amplification of the friction coefficient, β and æ are the scalar anisotropy coefficients that take into account, respectively, the isotropic and anisotropic contributions to the dependence of ζ_{ij} on a_{ij}, and δ_{ij} is the Kronecker symbol.

We pass to the new coordinates

$$\rho_i = (r_i' - r_i'')/\sqrt{2}, \qquad \rho_i^0 = (r_i' + r_i'')/\sqrt{2}. \tag{4}$$

The coordinate ρ_i^0 describes the motion of the center of gravity of a dumbbell and ρ_i is the relative motion of the beads. Then, in coordinates (4), Eqs. (2) take the form

$$\dot\rho_i = \nu_{ij}\rho_j - 4T\mu\zeta_{ij}^{-1}\rho_j + f_i, \qquad \dot\rho_i^0 = \nu_{ij}\rho_j^0 + f_i^0. \tag{5}$$

We derive equations for the correlation moment $y_{ik} = \langle\rho_i\rho_k\rangle$, where averaging is performed over all possible realizations of random force $\boldsymbol{f}$. Differentiating y_{ik} with respect to time and using (5), we have

$$\frac{d}{dt} y_{ik} = \nu_{ij} y_{jk} + \nu_{kj} y_{ji} - 4T\mu\zeta_{ij}^{-1} y_{jk} - 4T\mu\zeta_{kj}^{-1} y_{ji} + \langle f_i\rho_k\rangle + \langle f_k\rho_i\rangle. \tag{6}$$

The desired correlation moments $\langle f_i\rho_k\rangle$ can be found from an appropriate fluctuation-dissipative relation; however, there is a different method. The equilibrium ($\nu_{ik} = 0$) value of the correlation moment y_{ik} was found in [7]: $y_{ik}^0 = \delta_{ik}/(4\mu)$. In addition, Eqs. (6) are linear in y_{ik}; therefore, in terms containing no velocity-gradient tensor as a factor, we should replace y_{ik} by $(y_{ik} - y_{ik}^0)$. As a result, we obtain

$$\frac{d}{dt} y_{ik} = \nu_{ij} y_{jk} + \nu_{kj} y_{ji} - 4T\mu\Big[\zeta_{ij}^{-1}\Big(y_{jk} - \frac{1}{4\mu}\delta_{jk}\Big) + \zeta_{kj}^{-1}\Big(y_{ij} - \frac{1}{4\mu}\delta_{ij}\Big)\Big]. \tag{7}$$

We note that the tensor y_{ik} describes the form and dimensions of a macromolecular sphere. Since the anisotropic properties of a polymer medium are determined by the dimensions and form of macromolecular spheres, one can determine the anisotropy tensor a_{ik}, which describes the deviation of a statistically nonequilibrium system from the equilibrium condition as follows:

$$a_{ik} = \frac{\langle\rho_i\rho_k\rangle}{\langle\rho^2\rangle_e} - \frac{1}{3}\delta_{ik} = \frac{4\mu}{3} y_{ik} - \frac{1}{3}\delta_{ik}. \tag{8}$$

Here $\langle\rho^2\rangle_e$ is the equilibrium value of the expression $\langle\rho_1^2\rangle + \langle\rho_2^2\rangle + \langle\rho_3^2\rangle$.

Using (3), we write Eqs. (7) in the form

$$\frac{d}{dt} a_{ik} - \nu_{ij} a_{jk} - \nu_{kj} a_{ji} + \frac{1 + (\text{æ} - \beta)I}{\tau_0} a_{ik} = \frac{2}{3}\gamma_{ik} - \frac{3\beta}{\tau_0} a_{ij} a_{jk}. \tag{9}$$

Here $\tau_0 = B\zeta/(8T\mu)$ is the initial relaxation time, γ_{ik} is the symmetrized velocity-gradient tensor, and $I = a_{jj}$.

For comparison of (9) with experimental data, we need an expression for the stress tensor of a polymer system; this expression can be obtained by the standard way [7] and has the following form in the generalized coordinates (4):

$$\sigma_{ik} = -p\delta_{ik} + 4nT\mu\langle \rho_i \rho_k \rangle .$$

Here p is the hydrostatic pressure and n is the number of macromolecules in a unit volume.

With allowance for (8), this expression can be written in the form

$$\sigma_{ik} = -p\delta_{ik} + 3\eta_0 a_{ik}/\tau_0, \tag{10}$$

where $\eta_0 = nT\tau_0$ is the initial value of the shear-viscosity coefficient.

Thus, expressions (9) and (10) form a rheological constitutive relation of a nonlinear anisotropic viscoelastic fluid with the parameters τ_0, η_0, æ, and β, which in turn should depend on the molecular mass of a polymer M and its concentration c. The dimensional parameters τ_0 and η_0 are estimated by the formulas [1]

$$\eta_0 = \eta_0(c^*, M^*)\Big(\frac{c}{c^*}\Big)^{4,5}\Big(\frac{M}{M^*}\Big)^{3,4}, \qquad \tau_0 = \frac{\eta_0}{nT}, \tag{11}$$

where c^* and M^* are certain constants.

The induced-anisotropy parameters æ and β obviously depend neither on the molecular mass nor the concentration [1, 2]. To check this, we consider system (9), (10) for a stationary shear flow and a stationary flow of uniaxial tension.

Stationary Shear Flow. We study the nonlinear effects in a stationary shear flow when the velocity-gradient tensor has the form

$$[\nu_{ij}] = \begin{bmatrix} 0 & \nu_{12} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}.$$

From Eqs. (9) and (10), we derive the system of algebraic equations

$$\begin{gathered} a_{11} = 2\tau_N S a_{12} - 3\beta\tau_N(a_{11}^2 + a_{12}^2), \qquad a_{22} = -3\beta\tau_N(a_{22}^2 + a_{12}^2), \\ a_{12} = \frac{\tau_N}{3}\, S + \tau_N S a_{22} - 3\beta\tau_N a_{12}(a_{11} + a_{22}), \end{gathered} \tag{12}$$

where $\tau_N = 1/(1 + (\text{æ} - \beta)I)$, $I = a_{11} + a_{22}$, and $S = \tau_0\nu_{12}$. In this case, the behavior of the polymer system is characterized by the shear viscosity η and by the first N_1 and second N_2 differences between the normal stresses:

$$\eta = \frac{\sigma_{12}}{\nu_{12}} = \frac{3\eta_0 a_{12}}{S}, \quad N_1 = \sigma_{11} - \sigma_{22} = \frac{3\eta_0}{\tau_0}(a_{11} - a_{22}), \quad N_2 = \sigma_{22} - \sigma_{33} = \frac{3\eta_0}{\tau_0}(a_{22} - a_{33}).$$

The solutions of system (12) are determined by the values of the parameters æ and β, whose influence on the form of the viscosimetric functions η, N_1, and N_2 is studied in [3, 8]. It is known from experiments that, for large shear velocities, the values of $\eta(\nu_{12})$ do not depend on the molecular mass:

$$\eta(\nu_{12}) = k\nu_{12}^{\alpha}, \quad \tau_0\nu_{12} \gg 1, \quad k \sim M^0 \quad (0 < \alpha < 1.5). \tag{13}$$

Let us analyze conditions (13) by choosing appropriate values of æ and β. In the calculations, the concentration c/c^* was assumed to be equal to 1, and the values of the molecular mass M/M^* were assumed to be equal to $\sqrt{10}$, $\sqrt[4]{10}$, 1 and $\eta_0(c^*, M^*) = 1$. Figure 1 shows the effect of the parameters æ and β on the dependence of the stationary shear viscosity η/η_0 on the shear velocity ν_{12} and the molecular mass (curves 1 correspond to $M/M^* = \sqrt{10}$, curve 2 to $M/M^* = \sqrt[4]{10}$, and curves 3 to $M/M^* = 1$). As is seen from Fig. 1, for large ν_{12} the values of η for various molecular masses differ in the case where æ $= 0.3$ and $\beta = 0.1$ (dashed curves), and coincide in the case where æ $= 0.3$ and $\beta = 0.2$ (solid curves). The other values of æ correspond to other values of β. Therefore, there is a functional dependence between æ and β, which can be determined from the condition that the asymptotic behavior of the stationary shift viscosity does not

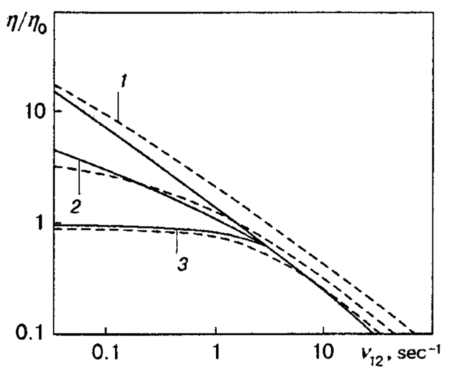

Fig. 1

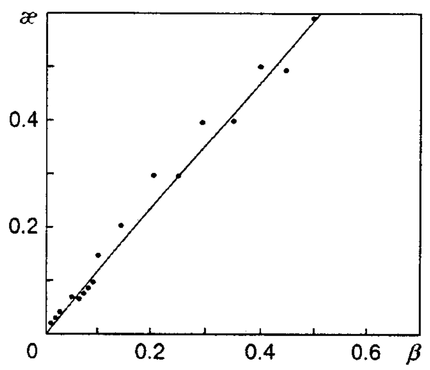

Fig. 2

TABLE 1

Sample number	$M \cdot 10^{-3}$		η_0, Pa · sec		τ_0, sec	
	Fig. 3	Fig. 5	Fig. 3	Fig. 5	Fig. 3	Fig. 5
1	200	327	$2.8 \cdot 10^2$	$9 \cdot 10^3$	0.33	0.84
2	350	467	$1.75 \cdot 10^3$	$5 \cdot 10^4$	3.66	6.64
3	517	687	$8.2 \cdot 10^3$	$1.4 \cdot 10^5$	25.32	27.4
4	813	805	$4.7 \cdot 10^4$	$6 \cdot 10^5$	288.25	137.4

depend on the molecular mass of a polymer. When $æ$ is varied from 0 to 1, the corresponding values of β are obtained (points in Fig. 2). One can see that the dependence $æ(\beta)$ can be described quite correctly by the linear function

$$æ = 1.2\beta. \tag{14}$$

The theoretical dependences were compared with the experimental data of [8], where the dependences of η and N on ν_{12} were obtained for solutions of linear polybutadiene of different molecular mass at $T = 298$ K. The molecular characteristics and rheological parameters of the solutions, which correspond to Fig. 3, are given in Table 1. The concentration of the samples is the same ($c = 6.76\%$). The value of τ_0 was determined from relation (11).

Figure 3a and b shows the shear viscosity η and the first difference between the normal stresses N_1 versus the shear velocity ν_{12} for $æ = 0.07$ and $\beta = 0.05$. As is seen, the theoretical curves agree with the experimental data. This makes it possible to conclude that the rheological zeroth-order approximation is applicable to the description of a stationary shear flow in quite a broad range of shear velocities. In this model, the parameters $æ$ and β depend weakly on the molecular mass.

Stationary Flow of Uniaxial Tension. The velocity-gradient and stress tensors have the diagonal form

$$[\nu_{ij}] = \begin{bmatrix} \nu_{11} & 0 & 0 \\ 0 & -\nu_{11}/2 & 0 \\ 0 & 0 & -\nu_{11}/2 \end{bmatrix}, \qquad [\tau_{ij}] = \begin{bmatrix} 2\sigma/3 & 0 & 0 \\ 0 & -\sigma/3 & 0 \\ 0 & 0 & -\sigma/3 \end{bmatrix}.$$

Here σ is the tensile stress and τ_{ij} is the deviatoric tensile tensor.

We now search for the longitudinal viscosity as a function of σ: $\lambda(\sigma) = \sigma/\nu_{11}$. From the rheological constitutive relations (9) and (10), we obtain

$$a_{22} = -\frac{3\beta a_{22}^2 + S/3}{1 + (æ - \beta)I + S}, \quad S = \frac{a_{11}(1 + (æ - \beta)I) + 3\beta a_{11}^2}{2a_{11} + 2/3}, \tag{15}$$
$$a_{11} = a_{22} + \sigma^*/3, \qquad I = a_{11} + 2a_{22},$$

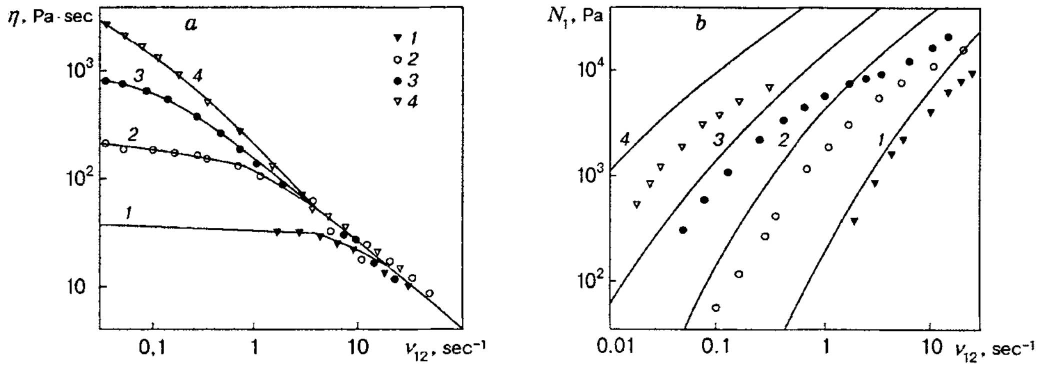

Fig. 3

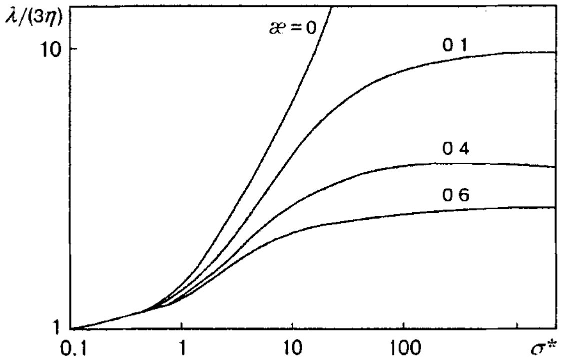

Fig. 4

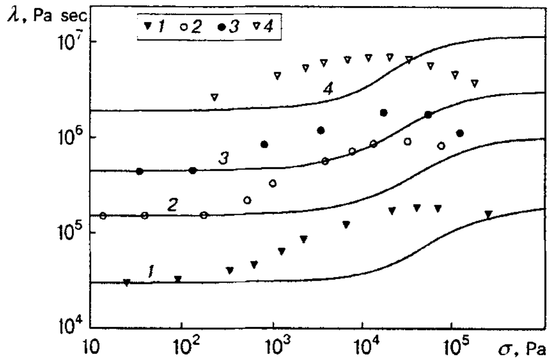

Fig. 5

where $S = \tau_0 \nu_{11}$ is the dimensionless tension velocity and $\sigma^* = (\tau_0/\eta_0)\sigma$ is the dimensionless tensile stress.

System (15) is a nonlinear system that was solved by the method of successive approximations and by the modified Newton method for verification.

We study the effect of the induced-anisotropy parameters æ and β on the dependence $\lambda(\sigma)$. With growth of σ, the longitudinal viscosity tends to limiting values, which increase as æ and β decrease. The calculation results for $\beta = 0.05$ are given in Fig. 4.

Figure 5 shows the longitudinal viscosity λ versus the tensile stress σ for polymers of different molecular mass and the experimental data of [9] (points), where polyethylene melts are examined at $T = 423$ K. The molecular characteristics and rheological parameters of the melts that correspond to Fig. 5 are listed in Table 1.

The parameters of the rheological model were estimated from formulas (11), and the values of æ and β [with allowance for (14)] were selected so that the theoretical dependences corresponded to the experimental data.

The theoretical curves in Fig. 5 agree with the experimental data, and one can explain the divergences in the region $10^2 < \sigma < 10^5$ by quite large values of polydispersibility of the samples used in [9].

It is known that as the polydispersibility increases, the nonlinear properties of a polymer are manifested in the field of smaller σ (or in the region of ν_{12} for shear). Owing to the use of the monomolecular approximation, this model represents the model of a monodisperse polymer and, consequently, does not describe the effects associated with polydispersibility. Probably, the application of the microstructural approach in deriving Eqs. (9) and (10) will allow us to describe these effects. Indeed, the dependences of the model parameters on the molecular mass of a polymer can be considered true, and the subsequent procedure will consist of averaging of the results with the use of a molecular-mass distribution.

Thus, the dependences (11) and the resulting relation (14), which were earlier used for stationary shear, remain valid for the flows of uniaxial tension; this shows the universality of this approach and the possibility of using the rheological model (9), (10) in describing the more complicated flows of linear-polymer solutions and melts, for example, the flows with a free surface, and a study of secondary flows, when the nonlinear effects play an important role.

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