POLYMER FLOW THEORY*

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Isothermal steady flow of an incompressible medium consisting of long elastic molecules is examined.

As a dense flowing medium, a polymer system (dilute and concentrated polymer solutions and melts) is described by a velocity v_i and velocity gradients $\nu_{ik} = \partial v_i/\partial x_k$.

When regarded as an assembly of linear polymeric molecules of identical length, the system is also determined by certain internal parameters characterizing the states of the system, which, bearing in mind the relation of the theory being developed to the theory of dilute polymer solutions [1], it is natural to assume to be mean square values of the components of the distance between the ends of a molecule $\langle h_i h_k \rangle = \int w(\mathbf{h})\, h_i h_k d\mathbf{h}$, where $w(\mathbf{h})$ is a distribution function depending on the velocity gradients. The values of the parameters in the moving and in the motionless fluid are connected by the relation

$$\langle h_i h_k \rangle = \alpha_{ij}\alpha_{kj} \langle h_j^2 \rangle_0. \tag{1}$$

The internal strain tensor α_{ik} may be expanded, for small gradients, in the series

$$\alpha_{ij} = \delta_{ij} + \tau_{ijqp}\nu_{qp} + \ldots; \tag{2}$$

where the relation

$$\sum_{j=1}^{3} \tau_{jjqp}\nu_{qp} = 0 \tag{3}$$

holds, because

$$\sum_{i=1}^{3} \langle h_i^2 \rangle = \langle h^2 \rangle = \langle h^2 \rangle_0 \left(1 + \frac{4}{3}\tau^2 \nu_{(nr)}\nu_{(nr)} + \ldots \right). \tag{4}$$

To describe the mechanical and optical-mechanical behavior of polymer systems, we proceed from expressions for the free energy, the dielectric constant tensor, and the dissipation function, represented in additive form, which is possible, since the polymeric molecule is a macrosystem. In spite of entanglement, the total intermolecular interaction energy is small in comparison with the internal energy of a chain, and the macromolecule in the systems examined manifests itself as an entity. For unit volume

$$F = \bar{n} \int w(\mathbf{h}) A(\mathbf{h})\, d\mathbf{h},$$

$$\varepsilon_{ik} = \delta_{ik} + 4\pi \bar{n} \int w(\mathbf{h}) \beta_{ik}(\mathbf{h})\, d\mathbf{h},$$

$$\Psi = \bar{n} \int w(\mathbf{h}) \psi(\mathbf{h}, \nu_{ik})\, d\mathbf{h}. \tag{5}$$

We shall expand the integrand expressions in even powers of h_i (because the ends of the molecule are indistinguishable), and the dissipation function, moreover, in symmetric and asymmetric combinations of the velocity gradient tensor $\nu_{(ik)}$ and $\nu_{[ik]}$. With an accuracy to terms of third order,

$$F = F_0 + g \langle h^2 \rangle; \tag{6}$$

$$\varepsilon_{ik} = \varepsilon_0\delta_{ik} + \varepsilon_1 \left(\langle h_i h_k \rangle - \frac{1}{3} \langle h^2 \rangle \delta_{ik} \right) + \varepsilon_{ikjl} \langle h_j h_l \rangle; \tag{7}$$

$$\Psi = (\alpha_1 + \alpha_2 \langle h^2 \rangle)\, \nu_{(jn)}^2 + \alpha_3 \langle h_n h_l \rangle \nu_{(jn)}\nu_{(jl)} + \alpha_4 \langle h_n h_l \rangle \nu_{(jn)}\nu_{[jl]} + \alpha_5 \langle h_n h_l \rangle \nu_{[jn]}\nu_{[jl]}. \tag{8}$$

The tensor $\varepsilon_{ikjl} \neq 0$ only in the case of solutions, if the dielectric constant of the solvent differs from that of the polymer (macroshape effect).

Using the formula [2]

$$\sigma_{ik} = \alpha_{kj} \frac{\partial F}{\partial \alpha_{ij}} + \frac{\partial \Psi}{\partial \nu_{ik}} \tag{9}$$

and omitting terms with velocity gradient powers above the first, we obtain the stress tensor

$$\sigma_{ik} = -p\,\delta_{ik} + 2g \langle h_i h_k \rangle + 2(\alpha_1 + \alpha_2 \langle h^2 \rangle)\nu_{(ik)} + (\alpha_3 + \alpha_4) \langle h_l h_k \rangle \nu_{(il)} + (\alpha_3 - \alpha_4) \langle h_l h_i \rangle \nu_{(kl)} + (\alpha_4 + \alpha_5) \langle h_l h_k \rangle \nu_{[il]} + (\alpha_4 - \alpha_5) \langle h_l h_i \rangle \nu_{[kl]}, \tag{10}$$

which proves to be asymmetrical, this being associated with the presence of internal rotation.

From (7) and (10) we obtain the relations observed experimentally [3] between the elastic stresses and the optical properties of the system. We shall obtain expressions for the effective viscosity in two simple cases. From this point on we shall use the experimental fact: $\sigma_{22} \approx \sigma_{33}$ [3], and shall assume that for zero velocity gradients the Trouton relation $\eta_{\parallel} = 3\eta_{\perp}$ [4] holds. It may be verified that it is necessary, to satisfy these conditions, that

$$\alpha_3 = \alpha_4, \quad \alpha_5 = 0.$$

In simple shear ($\nu_{12} \neq 0$) we shall assume, as in the theory of flow of dilute solutions [1], that the

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component normal to the plane of flow does not change: $\langle h_3^2 \rangle = \langle h_3^2 \rangle_0 = s$. We shall omit terms with odd powers of velocity gradient in the diagonal components, since the latter should not depend on the sign of the gradient.

From (1), (2), and (4), we have

$$\langle h_1^2 \rangle = s[1 + \tau_1^2 \nu_{12}^2 + \ldots];$$
$$\langle h_2^2 \rangle = s[1 + (2\tau^2 - \tau_1^2)\nu_{12}^2 + \ldots];$$
$$\langle h_1 h_2 \rangle = s[(\tau_{1212} + \tau_{2112})\nu_{12} + \ldots]. \qquad (11)$$

For the shear viscosity we obtain the expression

$$\eta_\perp = \alpha_1 + \alpha_2 \langle h^2 \rangle + \frac{\alpha_3}{2}(3\langle h_2^2 \rangle - \langle h_1^2 \rangle) =$$
$$= \mu + s[(2\alpha_2 + 3\alpha_3)\tau^2 - 2\alpha_3\tau_1^2]\nu_{12}^2 + \ldots, \qquad (12)$$

which decreases when $\tau \ll \tau_1$ ("rigid" molecules) and increases when $\tau \gg \tau_1$ ("elastic" molecules), in conformity with the ideas and experiments of Peterlin [5]. For "rigid" molecules there are numerous data showing a decrease in viscosity both for melts [6] and for concentrated [7] and dilute [8] solutions.

When there is simple tension ($\nu_{22} = \nu_{33} = -\nu_{11}/2$), we establish from condition (4) that $\tau_{iiqq} = \tau\delta_{iq}$, and then

$$\langle h_i^2 \rangle = s[1 + 2\tau\nu_{ii} + 4\tau^2\nu_{ii}^2 + \ldots],$$
$$\langle \underset{i \neq k}{h_i h_k} \rangle = s[\tau_{ikii}\nu_{ii} + \tau_{kikk}\nu_{kk} + \ldots]. \qquad (13)$$

The tensile viscosity,

$$\eta_\parallel = 3(\alpha_1 + \alpha_2\langle h^2 \rangle) + \alpha_3(2\langle h_1^2 \rangle + \langle h_2^2 \rangle) =$$
$$= 3\mu + 3s\alpha_3\tau\nu_{11} + 9s(2\alpha_2 + \alpha_3)\tau^2\nu_{11}^2 + \ldots \qquad (14)$$

increases with increase of velocity gradient, which corresponds with experimental data [9].

Thus, the theory put forward gives a qualitatively true picture of the phenomena observed in the flow of polymer systems.

NOTATION

v_i—velocity; ν_{ik}—velocity gradient tensor; h_i—distance between ends of molecule; α_{ik}—internal strain tensor; δ_{ik}—Kronecker symbol; τ, τ_1, τ_{ijqp}—relaxation time; $\overline{n}$—number of macromolecules in unit volume; for a macromolecule in the system: $A(\mathbf{h})$—free energy, $\beta_{ik}(\mathbf{h})$—dielectric susceptibility tensor, $\overline{\psi}(\mathbf{h}, \nu_{ik})$—dissipation function; g—viscoelastic shear modulus; α_i—phenomenological constants; $\mu = \alpha_1 + 3s\alpha_2 + s\alpha_3$—initial shear viscosity; p—hydrostatic pressure. Subscripts i, k = 1, 2, 3 number the vector and tensor components. The summation convention is employed.

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