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RELATIONSHIP BETWEEN THE FLOW PARAMETERS OF CONCENTRATED
HIGH-POLYMER SOLUTIONS AND THEIR MEAN-STATISTICAL
ORIENTATIONAL STRUCTURE

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The questions of the quality of polymer processing, for example by the methods of extrusion technology, and the production of high modular polymeric materials largely depend on the existence of a monitorable relationship between the external parameters of the processing of polymer media and their internal microstructure.

In this work this problem is analyzed for concentrated solutions of high-polymers (CSH) with the help of the structural-phenomenological model of polymers [1, 2]. The model is based on structural representations of the uniform, isotropic fluctuation network (Fig. 1), describing the specific structural features of CSH, consisting of the fact that in the single-relaxation approximation the concentrated polymer solution in a low-molecular solvent is modeled as a collection of statistically distributed effective network sites (segments) of rubbing with the solvent, spatially linked with one another by elastic subchains with kinetic rigidity. Kinetic rigidity refers to the well-known fact that a subchain cannot assume some conformations by a relative displacement of its tips.

The determination of the mean-statistical orientational structures of CSH follows from their rheodynamic description and the construction of the model. An important question addressed by the microscopic description of CSH is taking into account the interaction of the structural units of flow with their environment in the field of shear, entropic, and diffusion forces. In this case, this is the interaction of the randomly distributed network sites of rubbing with the solvent, linked with one another by elastic subchains with rigidity. Unlike theories for weakly concentrated solutions of polymers with solitary macromolecules [3-5] the interaction is sought relative to the center of mass O of the sites x_i^α , neighboring the x_i chosen for the analysis. The result is the mean stress, i.e., the reaction to external effect G of the statistically distributed rubbing sites interacting with one another (by means of the bonds) and with the solvent.

The physics of the phenomenon is as follows. At rest, the effective site of CSH, driven by Brownian forces of thermal motion and entropy forces pulling toward the center, undergoes around the center of mass a random walk with a rapidly decreasing Gaussian probability density distribution function. The matrix of the components of the moments of the probability density distribution function of such a walk has an equivalent diagonal form, and the radius vector (Fig. 1) of the deviation equals $x = 0.25sb^2$ (b is the length of the segment of rubbing, s is the number of segments in the subchain of the macromolecule).

Under the action of the external ordering forces, aside from these forces a Stokes friction force, owing to the defect in the velocity of the random walk of the site and the solvent at this point, and an internal friction force, associated with the fact that the segments of the subchains cannot assume all possible conformations by means of the relative displacement of their tips (the property of kinetic rigidity), act on the site.

In this case of distinguished directions, the probability density distribution function of the position of the sites will become distorted. The radius vector, the probability of whose length characterizes the deviation of the sites from the position of equilibrium, in

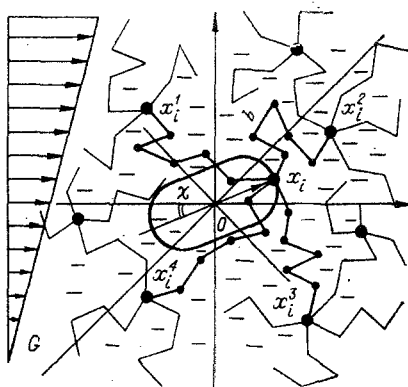


Fig. 1

the region of existence of the distribution function will now describe the configuration of an ellipse. The tensor of the moments of the distribution function will acquire not only diagonal, but also symmetric components. The angle χ of one of the principal axes of the ellipse to the direction of the flow is a quantitative measure of the most probable (for given G) orientational structure of the CSH.

Under the external action, however, the transition of the CSH from one equilibrium state to another is not realized instantaneously (as is achieved in practice for low-molecular liquids), but rather after some time, corresponding to the time of internal structural rearrangements, i.e., relaxation time.

It is necessary to have an equation for the transition, which at each moment in time will be determining for the stress tensor - this is the relation for the moments of the probability density distribution function, which describes the kinetics of the deviation of the position of the sites from their equilibrium states and characterizes the change in the mean-statistical orientational structure of the medium as a function of time.

Using this approach [1, 2], an expression for the stress tensor, determined in terms of the probability density distribution function of the positions of the rubbing sites, and the kinetic equation for these moments were obtained. In this case, the dimensionless system of equations of motion of the incompressible CSH for the case of a known constant flow rate has the form

$$H_0^{-1} \partial_t v'_i + v'_j \partial_j v'_i = -\partial_i p' + \partial_j \tau'_{ij}; \quad (1)$$

$$\tau'_{ij} = \text{Re}^{-1} \partial_j v'_i + \text{Re}_p^{-1} (\langle x_h x_i \rangle v'_{hj} + \langle x_h x_j \rangle v'_{hi} - H_0^{-1} \partial_t \langle x_i x_j \rangle - v'_j \partial_j \langle x_i x_j \rangle); \quad (2)$$

$$H_0^{-1} \partial_t \langle x_i x_j \rangle + v'_j \partial_j \langle x_i x_j \rangle = \langle x_h x_j \rangle (v'_{hi} - \alpha e'_{hi}) + \langle x_h x_i \rangle (v'_{hj} - \alpha e'_{hj}) - 2 \text{We}^{-1} (\langle x_i x_j \rangle - \delta_{ij}); \quad (3)$$

$$\partial_i v'_i = 0, \quad i, j = 1, 2, 3. \quad (4)$$

Here $p' = p/\rho \langle w \rangle^2$ is the hydrodynamic pressure; δ_{ij} is the Kronecker delta; $v_{ij}' = v_{ij}L/\langle w \rangle$ is the tensor of the velocity gradients; $e_{ij}' = e_{ij}L/\langle w \rangle$ is the symmetric tensor of the strain rates $v_i' = v_i/\langle w \rangle$; $\langle w \rangle$ is the mean velocity of the flow; L is the linear distance over which the liquid is in the varying velocity field; $\langle x_i x_j \rangle = \int x_i x_j W(x, t) dV$ are the moments of the probability density distribution function of the position of the rubbing sites (segments); V is the volume; $t' = t/T_*$ is the time; $H_0 = \langle w \rangle T_*/L$ is the homochronicity criterion; $\text{Re} = \rho \langle w \rangle L/\mu$, $\text{Re}_p = \rho \langle w \rangle L/\mu_p$ are, respectively, Reynolds number with a solvent viscosity μ and the viscosity of the polymer solution $\mu_p = 0.5\epsilon\kappa$ [for the viscosity in the limit $G \rightarrow 0$, see Eq. (6)]; $\text{We} = \kappa \langle w \rangle /L$ is Weissenberg's criterion for relaxational homochronicity; α is the kinetic rigidity of subchain segments in the network; $\kappa = \zeta s b^2/12kT$ is the time of internal structural rearrangements (characteristic relaxation time) after removal (application) of the strain; $\epsilon = 0.5zkT$ is the modulus of high elasticity. In the general case the coefficients ϵ , κ , α of the model are variable quantities [2].

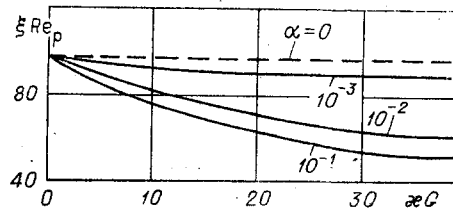


Fig. 2

In connection with the fact that for CSH $\mu \ll \mu_p$, in the case when the coefficients are constant their motion is characterized by the following set of primary complexes: H_0 , Re_p , We , α . Linear combinations of these complexes are used to construct other complexes which determine the flow process under study: $We/H_0 \equiv De = \kappa/T_x$ - Debor's criterion, $We/Re_p \equiv El = \kappa\mu_p/\rho L^2$ - the criterion of elasticity.

A new parameter describing the flow of CSH, compared with the well-known parameters for Newtonian liquids, is Weissenberg's criterion. It can be shown from the system (1)-(3) for the example of a stationary flow of CSH in channels that this criterion provides a quantitative measure of the mean-statistical orientational structure in the field of shear forces.

For the velocity field $v = v(y)$, $w = u = 0$ and for the usual boundary conditions $v_{ij} = G(y)$, $e_{ij} = 0.5G(y)$. From (3) we arrive at a system of algebraic equations for the moments

$$\begin{aligned} \langle x_2 x_3 \rangle &= \langle x_1 x_3 \rangle = 0, \quad \langle x_3 x_3 \rangle = 1, \\ (1 - 0,5\alpha)G(y)\langle x_1 x_2 \rangle - \kappa^{-1}(\langle x_1 x_1 \rangle - 1) &= 0, \\ (1 - 0,5\alpha)G(y)\langle x_2 x_2 \rangle - 0,5\alpha G(y)\langle x_1 x_1 \rangle - 2\kappa^{-1}\langle x_1 x_2 \rangle &= 0, \\ 0,5\alpha G(y)\langle x_1 x_2 \rangle + \kappa^{-1}(\langle x_2 x_2 \rangle - 1) &= 0. \end{aligned}$$

Therefore,

$$\begin{aligned} \langle x_1 x_2 \rangle &= \frac{(1 - \alpha)\kappa G(y)}{2(1 + 0,5\alpha(1 - 0,5\alpha)\kappa^2 G^2(y))}, \\ \langle x_1 x_1 \rangle &= \frac{1 + 0,5(1 - 0,5\alpha)\kappa^2 G^2(y)}{1 + 0,5\alpha(1 - 0,5\alpha)\kappa^2 G^2(y)}, \\ \langle x_2 x_2 \rangle &= \frac{1 + 0,25\alpha\kappa^2 G^2(y)}{1 + 0,5\alpha(1 - 0,5\alpha)\kappa^2 G^2(y)}. \end{aligned} \quad (5)$$

We note that a one-dimensional flow corresponds to the spatial variation of $\langle x_i x_j \rangle$.

According to (5), the expressions for the nonzero components of the stress tensor have the form

$$\tau_{12} = \frac{\epsilon\kappa}{2} \frac{1 + 0,25\alpha\kappa^2 G^2(y)}{1 + 0,5\alpha(1 - 0,5\alpha)\kappa^2 G^2(y)} G(y); \quad (6)$$

$$P_{11} - P_{22} = \frac{\epsilon}{2} \frac{(1 - \alpha)\kappa^2 G^2(y)}{1 + 0,5\alpha(1 - 0,5\alpha)\kappa^2 G^2(y)}; \quad (7)$$

$$P_{22} - P_{33} = 0. \quad (8)$$

By the method of orthogonal transformations [6], representing the components of the symmetric tensor $\langle x_i x_j \rangle$ in terms of their principal values, we find the orientation angle χ of the mean-statistical structure of the CSH to the direction of the flow (see Fig. 1):

$$\frac{\langle x_1 x_1 \rangle - \langle x_2 x_2 \rangle}{2\langle x_1 x_2 \rangle} = 0,5\kappa G(y) = \text{ctg } 2\chi. \quad (9)$$

On the channel axis $G = 0$, $\chi_1 = 45^\circ$, and on the wall $\cotan 2\chi_2 = 0,5\kappa dv/dy|_c$, and, in addition, $\chi_1 > \chi_2$.

Thus, when a CSH flows in a channel, a mean-statistical orientational structure, which is controlled by orienting $\zeta sb^2 G(y)$ and disorienting (kT) effects, forms over the cross section of the channel.

If it is assumed that the angles of orientation of the structural and optical polarizability of the CSH are equal, then they can be measured directly by the method of birefringence [4]. The angles of orientation of the structural and mechanical ($P_{11} - P_{22}/2\tau_{12}$) polarizability are equal only under the assumption of freely linked (ideal, $\alpha = 0$) subchains of macromolecules of the CSH.

The velocity gradient is determined from Eq. (6) [2] or some empirical relation $\tau = f(G)$.

For example, expressing the velocity gradient on the wall of the pipe by the well-known method [7], independent of the properties of the liquid under study, $dv/dr|_c = -(3n' + 1/4n') \cdot 8\langle w \rangle / D$ [$n' = d \ln(D\Delta p/4L) / d \ln(8\langle w \rangle / D)$] and taking into account the property of the trigonometric function (9), we note that the theoretical region of variation $We = \kappa \langle w \rangle / L$ in circular and flat channels can fill in the range from 0 to ~ 15 and ~ 20 , respectively. These quantities correspond to a virtually maximally oriented structure of CSH at the wall of the channel ($\chi < 1^\circ$).

In connection with the fact that under the action of external mechanical forces orientational phenomena are always accompanied by thermal ($\epsilon \sim kT$) disorienting phenomena, which themselves give rise to $P_{11} - P_{22}$ (7) the quantity We must evidently be of the order of unity.

The well-known decrease in the viscosity of CSH as G increases, as is evident from (6), is associated with the orientational phenomena under the action of external forces owing to the property of the kinetic rigidity of the polymer. It is evident from Fig. 2 that the decrease in the resistance [$\zeta Re_p = (2L/\rho \langle w \rangle^2) \partial p / \partial x$, $L = 4h$] under conditions of a stationary flow of CSH in a flat channel is also determined by orientational phenomena. In addition, structures with higher rigidity are oriented more rapidly.

The results of this study could be useful for establishing relationships between the mean-statistical orientational structure and the parameters of Couette and Poiseuille flows of CSH [8].

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