RHEOLOGICAL RELATIONSHIPS FOR CONCENTRATED POLYMER SOLUTIONS

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Using a network model for concentrated polymer solutions, an expression is calculated for the stress tensor, defined in terms of the moments of the distribution function and the kinetic equation for these moments. In the limiting case the results obtained coincide with known results for normal Newtonian liquids.

The basic problem in describing the motion of non-Newtonian liquids, including concentrated polymer solutions, consists in forming the rheological relationship relating the stressed state of the medium to its deformation characteristics.

For weakly concentrated polymer solutions (at concentrations $c \leq 0.01\%$ by weight) this problem has been solved completely in the literature (see, for example, [1, 2]). For solutions with medium and high concentrations ($c \geq 1\%$) the problem remains unclear to a significant degree. With growth in polymer solution concentration the macromolecules lose their individuality; their reaction to external perturbations takes on an ever more complex character.

In contrast to the phenomenological approach widely employed in the rheology of polymer systems, the present study will formulate a rheological relationship for concentrated polymer solutions from the molecular-kinetic position.

We will first describe the model used for a concentrated solution of a high-molecular-weight polymer in a low-molecular-weight solvent.

In weakly concentrated polymer solutions in a state of thermodynamic equilibrium, the macromolecule chains form low-density entanglements with an effective radius on the order of 10^{-4}-10^{-5} cm [1] and are so dissociated that their mutual interaction is negligibly small. With growth in concentration of the polymer, these separated entanglements accumulate and impinge upon each other, forming physical intermeshings and engagements. Due to the action of intermolecular forces at contact points labile bonds are formed, creating a homogeneous system filling the entire volume [3]. We assume that because of the low density of the macromolecule segments per unit volume the structural node points are formed primarily by four subchains, containing two macromolecules each. We will term the distance from node to node the subchain (Fig. 1). The subchains consist of segments, the basic kinematic units of the structural network. The number of such segments S per unit volume will serve as an effective parameter of the network model.

In the process of isothermal, homogeneous, and incompressible transverse flow the network deforms, the subchains are oriented along flow lines and stretched elastically, while the stresses developed in the subchains are concentrated in the weakest parts of the network – the node points. In order to avoid consideration of the complex kinetics of the process of node formation and destruction under the influence of these stresses, we assume that the characteristic lifetimes of these nodes are all the same and much greater than the characteristic flow time.

To derive the rheological relationship we will initially consider a model of a freely permeable structural network with freely articulated segments. The assumption of free network permeability eliminates the effect of one node upon another through the solvent, while the assumption of freely articulated segments allows us to regard the interaction of the latter with the solvent as occurring because of formation of network nodes with an effective coefficient of friction $\zeta \approx 12\pi a\bar{\eta}S$, where a is the effective node radius and $\bar{\eta}$ is the

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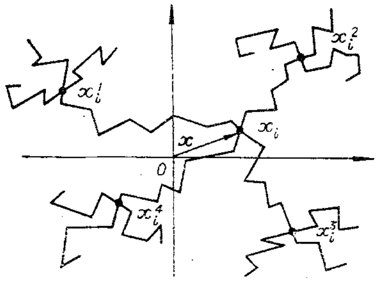

Fig. 1

viscosity of the medium. In the expression for ζ it is assumed that in an effective network friction node there are as many segments (with Stokes friction) as there are in two subchains.

We choose an arbitrary node and locate a corresponding coordinate system such that its origin coincides with the center of mass of the four nodes neighboring the given one (averaged over Brownian motion) (see Fig. 1). We will now consider the basic forces acting upon the chosen node in the flow process [2, 4]: 1) hydrodynamic resistance of the node to the solvent; 2) an elastic force, since the nodes are elastically bonded to the freely articulated segments; 3) an effective diffusion force, produced by Brownian motion of the nodes. We assume that the hydrodynamic resistance force is proportional to the node's velocity with respect to the medium in unit volume:

$$f_i^1 = -\zeta\left(\dot{x}_i - \nu_{ji}x_j\right), \tag{1}$$

where $\dot{x}_i = [\partial x_i(t)]/(\partial t)$ is the mean node velocity; x_i and x_j are the coordinates of the node and medium in the given accompanying coordinate system; $\nu_{ji}x_j$ is the value of the velocity of the medium would have at the point where the node is located, if the node were absent; and ν_{ji} is the macroscopic velocity gradient tensor.

In the extended freely articulated subchain there acts a contracting entropic force, equal in value [2] to

$$F = (3kTh)/(b^2S), \tag{2}$$

where h is the distance between ends of the subchain; k is the Boltzmann constant; T is the absolute temperature, °K; and b is the segment length.

Denoting by x_i^α ($\alpha = 1, 2, 3, 4$) the coordinates of nodes surrounding the given node, in accordance with Eq. (2) for the elastic force we have

$$f_i^2 = \frac{3kT}{Sb^2}\sum_\alpha \left(x_i^\alpha - x_i\right) = -\frac{12kT}{Sb^2}x_i. \tag{3}$$

The effective diffusion force occurring because of Brownian motion of the network nodes will be [5]

$$f_i^3 = -kT\,(\partial/\partial x_i)\ln W, \tag{4}$$

where W is the density distribution function of the probability of finding a node at distance **x** from the origin per unit volume.

Neglecting inertial forces (in view of the significant viscosity of the media considered) we may write the condition for equilibrium of forces acting on the node as

$$f_i^1 + f_i^2 + f_i^3 \approx 0. \tag{5}$$

We then find the expression for mean node velocity,

$$\dot{x}_i = \zeta^{-1}\left(\zeta x_j \nu_{ji} + f_j^2 + f_i^3\right). \tag{6}$$

The condition for continuity of density of probability of finding a node with mean velocity $\dot{x}_j$ has the form

$$\partial W/\partial t + \operatorname{div}(WU) = 0, \tag{7}$$

where

$$\mathbf{U} = \zeta^{-1}(\zeta x_j \nu_{ji}\mathbf{e}_i + \mathbf{f}^2 + \mathbf{f}^3).$$

On the basis of Eqs. (6), (7) (considering that $\nu_{ii} = 0$) we write the kinetic equation

$$\partial W/\partial t + x_i\nu_{ji}(\partial W/\partial x_i) = (kT/\zeta)\Delta W + [12kT/(Sb^2\zeta)]\nabla(\mathbf{x}W). \tag{8}$$

It may be seen that its stationary ($\partial/\partial t = 0$) equilibrium ($\nu_{ij} = 0$) solution, normalized to unity, will be

$$W_0 = [12/(2\pi S b^2)]^{3/2} \exp [(-12/Sb^2)(\mathbf{x}^2/2)].$$

From this it follows that in the unperturbed state the value of the mean square deviation of a node from the coordinate origin will be

$$\langle \mathbf{x}^2 \rangle_0 = 0.25 S b^2.$$

It will now be convenient to transform Eq. (8) to dimensionless variables, using $\sqrt{(1/3)\ \langle \mathbf{x}^2 \rangle_0}$, as a result of which we obtain

$$\partial W/\partial t + x_j \nu_{ji} (\partial W/\partial x_i) = (1/\varkappa)[\Delta W + \nabla(\mathbf{x} W)], \tag{9}$$

where

$$\varkappa = \zeta S b^2 / 12kT.$$

To calculate the stress tensor we define it as follows. Let $\mathbf{l}$ be the positive direction of the normal from an imaginary plane, dividing some space into two subspaces – positive and negative. The force $\mathbf{P}(\mathbf{l})$ on a unit surface with which the positive subspace acts upon the negative is related to the stress tensor at the given point P_{ji}:

$$\mathbf{P}(\mathbf{l}) = P_{ji} l_i \mathbf{e}_i,$$

where $\mathbf{e}_i$ are basis vectors. One node acts on the solvent with force $\zeta(\dot{\mathbf{x}} - \mathbf{x}_j \nu_{ji} \mathbf{e}_i)$, and if in a unit volume there are z nodes, we have

$$\mathbf{P}(\mathbf{l}) = \int\limits_{\mathbf{l}\mathbf{x} \leqslant 0} z W(t, \mathbf{x})(-\mathbf{x}\mathbf{l})\, \zeta\left(\dot{\mathbf{x}} - \mathbf{e}_i \nu_{ji} x_j\right) dV, \tag{10}$$

where $-\mathbf{xl}$, multiplied by the unit area, is equal to the volume in which nodes may be found in the negative semispace such that their mean position is located in the positive semispace.

In accordance with Eq. (5), considering the symmetry of the integrand for the replacement of $\mathbf{x}$ by $-\mathbf{x}$, Eq. (10) may be written as

$$P_{ji} = -p\delta_{ji} - (1/2)\, z \int x_j (f_i^2 + f_i^3)\, W dV. \tag{11}$$

Equation (11) takes into account hydrostatic pressure. Substituting Eqs. (3), (4) in Eq. (11), after transformations we have

$$P_{ji} = -p\delta_{ji} + (1/2) z [(12kT/Sb^2)\langle x_j x_i \rangle - kT\delta_{ji}],$$

where $\langle x_j x_i \rangle \equiv \int x_j x_i W dV$ are moments of the distribution function. Replacing $\mathbf{x}$ by a dimensionless variable, we finally obtain

$$P_{ji} = -p\delta_{ji} + (1/2) z k T (< x_j x_i > - \delta_{ji}). \tag{12}$$

The number of nodes z per unit volume can be related to the network model parameter as follows: $z \approx Nn/2S$, where n is the number of segments in a macromolecule and N is the number of macromolecules per unit volume.

Thus, the stressed state in the model chosen is characterized by an anisotropy tensor $(\langle x_j x_i \rangle - \delta_{ij})$, which goes to zero at equilibrium.

Multiplying Eq. (9) by $x_j x_i$ and integrating over all space, we find the equation for the moments of the distribution function:

$$(d/dt)\langle x_j x_i \rangle = \langle x_i x_k \rangle \nu_{kj} + \langle x_j x_k \rangle \nu_{ki} - (2/\varkappa)(\langle x_j x_i \rangle - \delta_{ji}). \tag{13}$$

It has been considered here that

$$\text{as } x \to \infty \ W \to 0, \ \nu_{ii} = 0.$$

From Eqs. (12), (13) it is evident that $\varkappa$ is the stress relaxation time after termination of deformation $(\nu_{kj} = \nu_{ki} = 0)$.

For the case where $(d/dt)\langle x_j x_i \rangle = 0$, in accordance with Eq. (13) we have

$$P_{ji} = -p\delta_{ji} + 0.5\varepsilon\varkappa(\langle x_i x_k \rangle \nu_{kj} + \langle x_j x_k \rangle \nu_{ki}),$$

where $\epsilon = 0.5zkT$.

As an example of the employment of the relationships obtained, we will consider stationary Couette flow. Using the matrix notation

$$\|\langle x_i x_j\rangle\| \equiv M;\ \|\nu_{ij}\| \equiv \nu = \begin{Vmatrix} 0 & 0 & 0 \\ G & 0 & 0 \\ 0 & 0 & 0 \end{Vmatrix};\ \|P_{ij}\| \equiv P,$$

in which for a stationary flow from Eqs. (12), (13) we have

$$\left.\begin{aligned} M\nu + \nu^T M &= (2/\varkappa)(M - E) \\ P &= -pE + \varepsilon(M - E) \end{aligned}\right\}, \tag{14}$$

where E is the unit matrix; ν^T is the transposed matrix ν. Solving Eq. (14), we obtain

$$M = \begin{Vmatrix} 1 + 0.5(\varkappa G)^2 & 0.5\varkappa G & 0 \\ 0.5\varkappa G & 0 & 0 \\ 0 & 0 & 0 \end{Vmatrix};\ P = pE + \varepsilon \begin{Vmatrix} 0.5(\varkappa G)^2 & 0.5\varkappa G & 0 \\ 0.5\varkappa G & 0 & 0 \\ 0 & 0 & 0 \end{Vmatrix}.$$

It hence follows that $\tau = 0.5\epsilon\varkappa G$; $p_{11} - p_{22} = 0.5\varkappa^2 G^2$. Calculation of the coefficients proceeding G directly in terms of molecular-kinetic parameters is not difficult. However, their dependence on the thermodynamic state of the polymer–solvent system and, consequently, in the general case, their dependence on the invariants of the velocity deformation or shear stress tensor permits their determination from experiment. Denoting the viscosity by $\eta = 0.5\epsilon\varkappa$, for one-dimensional flow we have $\tau = \eta(G)\,G$, $p_{11} - p_{22} = \tau\varkappa(G)\,G$. The functions $\eta(G)$ and $\varkappa(G)$ may be written with rheological relationships known beforehand for some class of media (for example, [6, 7]) or established from data of viscometric and rheogoniometric measurements, respectively.

To this point the chain of the network model has been considered freely articulated. We will now expand the model to the case where the chain rigidity is considered. Since in this case the most probable chain equilibrium state does not change (only the chain deformation velocity changes), Eqs. (1), (3), and (4) remain in force.

Following Serf [2], we assume that the internal chain viscosity force depends on the rate of change of its length in the following manner:

$$f_i^{4\alpha} = \gamma(\delta h_i^\alpha/\delta t), \tag{15}$$

where $h_i^\alpha = x_i^\alpha - x_i$ is the difference between the coordinates of the chain's beginning and end; γ is a constant; $\delta h_i^\alpha/\delta t$ denotes that component of the rate of change h_i^α which is independent of rotation of the chain as a whole; the internal viscosity force is produced by braking of rotation.

The operator $\delta/\delta t$ is quite complex, and thus we will limit ourselves to an approximate expression for $\delta h_i^\alpha/\delta t$. In accordance with Eq. (5) we write the node velocity in the form

$$dx_i/dt = x_j\nu_{ji} - (kT/\zeta)(d/dx_i)\ln W - (12kT/\zeta S b^2)\,x_i = x_i\nu_{ji} - (kT/\zeta)(\partial/\partial x_i)\ln(W/W_0). \tag{16}$$

The equilibrium distribution function W_0 depends only on x^2, and W for an arbitrary flow depends on quadratic forms of the type $x_i x_i$, $x_i\nu_{(ik)}\nu_{(kj)}x_j$, $x_i\nu_{[ik]}\nu_{[kj]}x_j, \ldots$, and their derivatives. Here $\nu_{(ij)} = 0.5(\nu_{ij} + \nu_{ji})$; $\nu_{[ij]} = 0.5(\nu_{ij} - \nu_{ji})$. Clearly, this function must be such that $W \to W_0$ for $\nu_{(ij)} = \nu_{[ij]} \to 0$. Expanding $\ln(W/W_0)$ in a series in these quadratic forms and retaining only terms not dependent on rotation, in correspondence with the Hamilton–Kelley theorem from Eq. (16) we obtain

$$\delta x_i/\delta t = Ax_i + Bx_j\nu_{(ji)} + Cx_j\nu_{(jk)}\nu_{(ki)} + 0(x^3).$$

The coefficients A, B, C are unknown functions of the basic invariants of tensor $\nu_{(ji)}$. For incompressible ($\nu_{ii} = 0$) plane ($\nu_{(ik)}\nu_{(kl)}\nu_{(li)} = 0$) flows, in the second approximation for the deformation-rate gradient we may write

$$\delta x_i/\delta t \approx B_0 x_j\nu_{(ji)}.$$

In accordance with Eq. (15) for the node we have

$$f_i^4 = \sum_\alpha f_i^{4\alpha} = -4\gamma(\delta x_i/\delta t).$$

Consequently, the chain internal viscosity (rigidity) force acting on a given node is expressed in the form

$$f_i^4 \approx -4\gamma x_j\nu_{(ji)}. \tag{17}$$

The stress tensor, considering Eq. (17), may be obtained from Eq. (11), adding to f_i^2 and f_i^3 the term f_i^4. Performing calculations completely analogous to those used in deriving Eq. (12), we obtain

$$P_{ji} = -p\delta_{ji} + \varepsilon\ (\langle x_j x_i \rangle - \delta_{ji}) + \alpha\varepsilon\varkappa\ \langle x_j x_k \rangle\ \nu_{(ki)}, \tag{18}$$

where $\alpha = 4\gamma\zeta^{-1}$, and the value x_j is made dimensionless with $\sqrt{Sb^2/12}$.

Since Eq. (17) has second-order accuracy in ν_{ji}, Eq. (18) should be reliable only to terms of second-order smallness in ν_{ji}. Expanding $\langle x_j x_k \rangle$ in a series in velocity gradients

$$\langle x_j x_k \rangle = c_0 \delta_{jk} + c_1 \nu_{(jk)} + 0(\nu_{(jk)}),$$

we find that

$$P_{ji} = p\delta_{ji} + \varepsilon(\langle x_j x_i \rangle - \delta_{ji}) + 0.5\alpha\varepsilon\varkappa\ [\langle x_j x_k \rangle \nu_{(ki)} + \nu_{jk} \langle x_k x_i \rangle]. \tag{19}$$

Considering the internal viscosity force equation (17) in the expression for node velocity, we have

$$dx_i/dt = \zeta^{-1}[\zeta x_j \nu_{ji} - (12kT/Sb^2)x_i - kT(\partial/\partial x_i)\ \ln W - 4\gamma x_j \nu_{(ji)}]. \tag{20}$$

Substituting Eq. (20) in Eq. (7), we find

$$\partial W/\partial t + x_j[\nu_{ji} - \alpha\nu_{(ji)}](\partial W/\partial x_i) = (1/\varkappa)[\Delta W + \nabla(\mathbf{x}W)]. \tag{21}$$

From Eq. (21) we have

$$d\langle x_j x_i \rangle/dt = \langle x_k x_j \rangle[\nu_{ki} - \alpha\nu_{(ki)}] + \langle x_k x_i \rangle[\nu_{kj} - \alpha\nu_{(kj)}] - (2/\varkappa)(\langle x_j x_i \rangle - \delta_{ji}). \tag{22}$$

For stationary Couette flow from Eq. (22) we find directly

$$\begin{gathered}
\langle x_1 x_2 \rangle = [2 + (1 + \psi)\rho^2]/[2(1 + \psi\rho^2)]; \\
\langle x_2 x_2 \rangle = [2 + \psi(1 + \psi)\rho^2]/[2(1 + \psi\rho^2)]; \\
\langle x_3 x_3 \rangle = 1;\ \langle x_3 x_1 \rangle = \langle x_2 x_3 \rangle = 0; \\
\langle x_2 x_1 \rangle = [(1 - \psi)\rho]/[2(1 + \psi\rho)],
\end{gathered}$$

where

$$\psi = \alpha/(2 - \alpha);\ \rho = \varkappa G\ [1 - (\alpha/2)].$$

Therefore, omitting terms higher than second order in ν_{ji}, we have

$$\begin{gathered}
p_{11} = -p + 0.5\varepsilon[1 - (\alpha/2)](\varkappa G)^2;\ p_{22} = -p + 0.25\varepsilon\alpha(1 - \alpha)(\varkappa G)^2; \\
p_{33} = -p;\ p_{21} = p_{12} = 0.5\varepsilon\varkappa G;\ p_{31} = p_{13} = p_{23} = p_{32} = 0.
\end{gathered}$$

In the absence of internal viscosity, i.e., $\alpha = 0$, $p_{22} = -p$.

Consequently, consideration of internal viscosity leads to appearance of a second difference in normal stresses:

$$p_{22} - p_{33} = 0.25\varepsilon\alpha(1 - \alpha)(\varkappa G)^2 = \beta(G)G^2,$$

which is absent in the network model with freely articulated chains.

Thus, the stressed state in the network model chosen here may be characterized by τ, $p_{11} - p_{22}$, $p_{22} - p_{33}$.

The normal hydrodynamic equations in stresses and continuity together with Eqs. (19), (22) and the functions $\eta(G)$, $\varkappa(G)$, $\beta(G)$ established here allow consideration of the peculiarities of motion of concentrated polymer solutions and performance of concrete calculations.

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