THE VISCOSITY OF AN ORIENTED SOLUTION

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The effects of oriented linear macromolecules are examined in relation to the viscosity of a polymer solution in simple shear and in axially symmetric extension. The effective viscosity is calculated for a solvent containing uniformly distributed rigid rods oriented along the tension axis.

The flow laws for polymer solutions indicate that the rheological behavior is dependent on the mode of deformation because flow causes structural rearrangement, e.g., orientation and deformation of the macromolecules, reversible or irreversible damage, or formation of supermolecular structures. Orientation is the simplest and most natural consequence here.

Here I compare two modes of deformation frequently used: axially symmetric extension and simple shear. In the first case, the preferred orientation always coincides with the shear direction, while in the second the molecules in the limit lie in shear planes, which lie at $\pi/4$ to the tension direction, i.e., the orientations in these two cases are substantially different as regards the relation to the principal axes of the strain tensor, which is especially important in relation to viscosity effects in such symptoms. A medium containing oriented chains should show induced viscosity anisotropy dependent on the flow.

The effective viscosity of a macromolecular solution increases with the deformation rate in tension but decreases in simple shear. These opposing effects can be considered as due to marked viscosity anisotropy. The polymer has least effect on the viscosity for shear in planes parallel to the preferred orientation [1], while it is probably largest for axially symmetric tension.

We consider these effects via the corresponding simple hydrodynamic problem on the basis of the following model. The solvent (viscosity η_0) contains uniformly distributed rigid cylindrical rods (length l, radius r_0, $l \gg r_0$) oriented along the z axis (see [2] for the viscosity of a dilute suspension of viscoelastic spheres). The solvent adhered to the rods, i.e., the speed of the solvent at the surface of a rod equals the speed of the rod itself. The medium on average is subject to axially symmetric strain along the z axis with a strain rate k_0.

Consider the motion of the solvent near a rod via the equations of hydrodynamics:

$$\frac{\partial p}{\partial r} = \eta_0 \left(\frac{\partial^2 v_r}{\partial r^2} + \frac{\partial^2 v_r}{\partial z^2} + \frac{1}{r} \frac{\partial v_r}{\partial r} - \frac{v_r}{r^2} \right), \tag{1}$$

$$\frac{\partial p}{\partial z} = \eta_0 \left(\frac{\partial^2 v_z}{\partial r^2} + \frac{\partial^2 v_z}{\partial z^2} + \frac{1}{r} \frac{\partial v_z}{\partial r} \right), \tag{2}$$

$$\frac{\partial v_r}{\partial r} + \frac{\partial v_z}{\partial z} + \frac{v_r}{r} = 0, \tag{3}$$

where p is pressure; we neglect gravitational and inertial forces. Let the axis of the rod coincide with the z axis. We seek a solution for the radial component of the velocity of the solvent in the form

$$v_r = v_r(r). \tag{4}$$

Then (3) gives the velocity component along the z axis as

$$v_z = u(r) z, \tag{5}$$

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where

$$u(r) = -\left(\frac{\partial v_r}{\partial r} + \frac{v_r}{r}\right).$$

We eliminate the pressure from (1) and (2), and then use (4) and (5) to show that for $v_r(r_0) = v_z(r = r_0) = 0$ we have

$$v_z = \left[\varkappa_0 (r^2 - r_0^2) + \varkappa \ln\frac{r}{r_0}\right] z.$$

Here $\varkappa_0$ should be zero because $\partial v_z/\partial r \to 0$ as $V \to \infty$. The velocity distribution is

$$v_r = -\frac{\varkappa}{2}\left[r \ln\frac{r}{r_0} - \frac{r}{2} + \frac{r_0^2}{2r}\right], \tag{6}$$

$$v_z = \varkappa z \ln\frac{r}{r_0}, \tag{7}$$

where $\varkappa$ is a constant to be determined. The action radius R is the distance out to which the flow of the solvent is governed by the rod, which is defined by $(r_0/R)^2 = c$, where c is the volume concentration of the rods. We note that $R < l/2$ and that the model does not describe the behavior of solutions whose concentration is $c = (2r_0/l)^2$ or less. The mean strain rate k_0 can be put as

$$k_0 = -\frac{2}{R} v_r(R),$$

and substitution from (6) gives

$$k_0 = \varkappa\left[\ln\frac{R}{r_0} - \frac{1}{2} + \frac{1}{2}\left(\frac{r_0}{R}\right)^2\right] = \frac{\varkappa}{2}[c - \ln c - 1]. \tag{8}$$

We put $\gamma = 1/(c - \ln c - 1)$ to get from (8) that

$$\varkappa = 2k_0\gamma, \tag{9}$$

where γ is dependent only on the bulk concentration.

From (7) and (9) we get the shear stress at the surface of a rod as

$$\sigma_{rz}(r = r_0) = \eta_0 \left.\frac{\partial v_z}{\partial r}\right|_{r=r_0} = 2\frac{k_0}{r_0}\eta_0\gamma z. \tag{10}$$

Then the force extending a rod in the z section is

$$F(z) = 2\pi r_0 \int_z^{l/2} \sigma_{rz} dz = \frac{1}{2}\pi\eta_0 k_0 \gamma (l^2 - 4z^2). \tag{11}$$

Note that F(z) is not dependent on the radius of the rod and is dependent only on l and the proportion of the volume filled by the rods. The F(z) averaged over the rod length is

$$F_{av} = \frac{1}{3}\pi\eta_0 k_0 \gamma l^2.$$

From (6) and (7) we get the viscous tensile force F_t for the solvent in a cylinder of radius R:

$$F_t = 6\pi\eta_0 k_0 \gamma\left[R^2 \ln\frac{R}{r_0} - \frac{1}{2}R^2 + \frac{1}{2}r_0^2\right] = 3\pi\eta_0 k_0 R^2.$$

The following is the stress in the medium averaged over the volume with allowance for the forces in the rods:

$$\sigma_{av} = \frac{F_{av} + F_t}{\pi R^2} = 3\eta_0 k_0\left[1 + \frac{1}{9}\gamma c\left(\frac{l}{r_0}\right)^2\right]. \tag{12}$$

From (12) we see that the rods, when completely oriented in the tension direction, give an effective viscosity

$$\eta_{eff} = 3\,\eta_0 \left[1 + \frac{1}{9}\,\gamma c \left(\frac{l}{r_0} \right)^2 \right],$$

i.e., the viscosity is increased by a factor $1 + (1/9)\gamma c(l/r_0)^2$. As would be expected, the precise effect from the oriented rods is dependent on c and on l/r_0.

The calculations show, for example, that c = 0.01 and $l/r_0 = 100$ (a reasonable figure for a polymer) imply a viscosity increased by a factor 4 in tension, or by a factor 80 in c = 0.1.

The viscosity is increased on account of a marked increase in the true strain rate in the solvent relative to the mean strain rate for the medium as a whole. This may produce nonlinearity in the relation of strain rate to stress for the solvent, which results in nonnewtonian flow of the medium as a whole at comparatively low average strain rates.

NOTATION

z	is the direction of stretching;
η_0	is the viscosity of solvent;
l, r_0	are the length and radius of rod;
k_0	is the averaged deformation rate of medium;
p	is the pressure;
v_r, v_z	are the velocity components of solvent;
$\varkappa$	is the constant;
c	is the volume concentration of rods;
R	is the distance at which the rod affects solvent flow;
σ_{rz}	is the shear stress at rod surface;
F(z)	is the tensile force;
$F_{av} - F(z)$	is the force averaged along rod length;
F_t	is the tensile force for solvent;
σ_{av}	is the averaged stress in medium;
η_{eff}	is the effective viscosity of medium.

LITERATURE CITED

1. V. N. Tsvetkov, V. E. Eskin, and S. Ya. Frenkel', Structure of Macromolecules in Solution [in Russian], Nauka, Moscow (1964).
2. R. Roscoe, J. Fluid. Mech., 28, 273 (1967).