DYNAMICS OF THREADS OF DILUTED POLYMER SOLUTIONS

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The article presents a quantitative description of the process of slow thinning of a thread of polymer solution taking the molecular structure into account.

The present article explains in extended version the results of the theoretical analysis of the formation of thin stable threads of polymer solutions, annotated by Bazilevskii et al. [1]. Such threads form when a drop of polymer solution is drawn out between two plates [1], when a jet of polymer solution undergoes capillary breakup [1, 2], etc. One of these cases is shown in Fig. 1.

It was shown in [1, 3] that the fact of thin stable threads existing indicates that polymer solutions are able to develop considerable resistance to the process of intense extension; this corresponds to an increase of Trouton (longitudinal) viscosity by several orders of magnitude compared with the shear viscosity of these solutions. This is in agreement with the results of the experimental works [4-6], which contain an evaluation of the stresses arising in intense tensioning of polymer solutions. These effects are explained by the orientation of the macromolecules in the direction of tension, which impedes the flow of the surrounding medium around them [1, 7].

Below we present the quantitative investigation of the phenomenon of formation of thin threads within the framework of the molecular hydrodynamic model of dilute polymer solutions suggested by Hinch [7], which is able to describe the appearance of considerable stresses under conditions of intense tension. This model is described by the equations

$$\frac{D}{Dt}\langle \mathbf{zz}\rangle = (\langle \mathbf{zz}\rangle\cdot\boldsymbol{\Omega}-\boldsymbol{\Omega}\cdot\langle \mathbf{zz}\rangle)+\frac{z^2}{3z_0^2+z^2}(\langle \mathbf{zz}\rangle\cdot\mathbf{E}+\mathbf{E}\cdot\langle \mathbf{zz}\rangle)-2\lambda\frac{z_0Nb}{z(Nb-z)}\left(\langle \mathbf{zz}\rangle-\frac{z_0^2}{3}\delta\right), \qquad (1)$$

$$\sigma=-p\delta+2\mu_0\left(1+5nz_0^3\frac{z^2}{3z_0^2+z^2}\right)\mathbf{E}+n\varkappa\frac{Nb}{Nb-z}\langle \mathbf{zz}\rangle . \qquad (2)$$

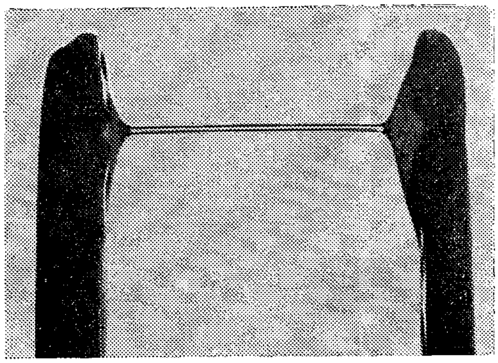

Fig. 1. Thread of polyoxyethylene in water formed by extending a drop of solution by tweezers. (Distance between the jaws of the tweezers approximately 5 mm.)

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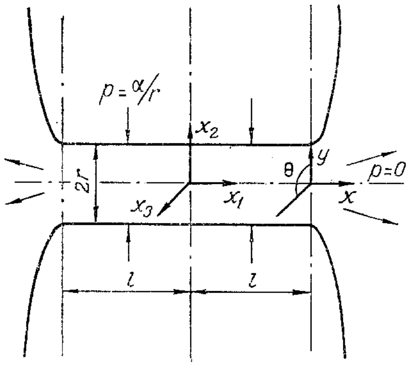

Fig. 2. Model of the thread.

For the case of uniform thinning of the thread, the tensors **Ω** and **E** have the form (the system of coordinates x_1, x_2, x_3 is shown in Fig. 2):

$$\mathbf{\Omega}=0,\ \mathbf{E}=\begin{vmatrix} -\frac{2}{r}\frac{dr}{dt} & & 0 \\ & \frac{1}{r}\frac{dr}{dt} & \\ 0 & & \frac{1}{r}\frac{dr}{dt} \end{vmatrix}$$

Let us examine the flow of polymer solution in the thread when the orientation of the macromolecules has become considerable:

$$z^2/z_0^2 \gg 1. \tag{3}$$

Since the liquid is being extended along the Ox_1 axis, the macromolecules also become oriented along this axis

$$\langle \mathbf{zz} \rangle = \begin{vmatrix} z^2 & \\ & 0 \end{vmatrix}.$$

It is obvious that under the given conditions the stress tensor σ has a diagonal structure, and its components σ_{22} and σ_{33} are equal to the capillary pressure α/r with the opposite sign.

When the behavior of the liquid in the thread has become largely non-Newtonian (i.e., in Eq. (2) the term $2\mu_0(1 + 5nz_0^3)E_{ii}$, describing the influence of Newtonian viscosity is small compared with the other terms of the sum), all that has been said above enables us to represent the system of equations (1), (2) in the form

$$\sigma_{11}=-p+\beta\frac{Z^2}{1-Z}, \tag{4}$$

$$\sigma_{22}=\sigma_{33}=-p=-\alpha/r, \tag{5}$$

$$\frac{dZ}{dt}=ZE_{11}-\frac{\lambda Z_0}{1-Z}, \tag{6}$$

$$E_{11}=-\frac{2}{r}\frac{dr}{dt}=\frac{v(l)}{l}, \tag{7}$$

where $Z = z/(Nb)$ (i.e., $N^{-1/2}\leqslant Z\leqslant 1$), $\beta=n\varkappa(Nb)^2$; $v(l)$ is the speed of the liquid at the point $x_1 = l$ in the coordinate system x_1, x_2, x_3.

Since the disintegration of a thread of polymer solution proceeds much more slowly than the purely inertial disintegration of a thread of water, it is natural to assume that the forces of inertia in the problem under examination are not substantial. In that case the thread is homogeneous, and σ_{11} is constant along the entire thread. The value of σ_{11} is determined by processes occurring at the borders of the thread. The liquid extruded from the thread emerges in a region (henceforth called macrovolumes) that has characteristic dimensions considerably exceeding the radius of the thread; in these regions the tensile strain to which the elements of the liquid are subjected in the thread is replaced by compressive strain along the flow line (the flow is of a nature that is close to radial).

If the liquid is able to manifest considerable excess stresses only under conditions of intense tension, then these stresses are instantaneously relaxed at the point where the type of strain changes (i.e., at the border of the thread), and $\sigma_{11} = 0$. This condition, in particular, was adopted in [1, 3] in the evaluation of the longitudinal viscosity of polymer solutions upon deformation in the thread. In this case viscosity was determined as $\mu_l = \frac{\alpha}{r} \Big/ \left(-\frac{2}{r}\frac{dr}{dt}\right)$; it was found to be several orders of magnitude larger than the initial shear viscosity.

If, upon flow in a macrovolume, i.e., under conditions of compressive strain, considerable excess stresses manifest themselves in a liquid, σ_{11} may be nonzero. To find σ_{11} in this case, we examine flow in a macrovolume. The equations of motion and continuity, written in the cylindrical coordinates x, y, θ (Fig. 2, $x = x_1 - l$) with a view to the axisymmetry of the problem, have the form [8] (without loss of generality we examine the macrovolume situated in the region $x_1 > 0$)

$$\rho\left(\frac{\partial v_{*x}}{\partial t} + v_{*y}\frac{\partial v_{*x}}{\partial y} + v_{*x}\frac{\partial v_{*x}}{\partial x}\right) = -\frac{\partial p}{\partial x} + \frac{1}{y}\frac{\partial}{\partial y}(y\tau_{yx}) + \frac{\partial \tau_{xx}}{\partial x}, \tag{8}$$

$$\frac{1}{y}\frac{\partial}{\partial y}(yv_{*y}) + \frac{\partial v_{*x}}{\partial x} = 0, \tag{9}$$

where τ_{xx} and τ_{yx} are the excess stress components, and v_{*x} and v_{*y} are the components of the flow velocity of the liquid in a macrovolume in the coordinate system x, y, Θ.

Let us examine the motion occurring near the axis of symmetry of the macrovolume, where the liquid undergoes uniaxial compression and the macromolecules relax. Taking it that the macromolecules are oriented along the flow line, and that the excess stress is due solely to the tension of the macromolecules, we can easily confirm with the aid of Eq. (2) that the only nonzero principal value of the tensor τ is $\tau = \beta Z_*^2/(1-Z_*)$ (Z_* is the degree of orientation of the macromolecule in the macrovolume), and

$$\tau_{yx} = \tau\frac{v_{*x}v_{*y}}{v_*^2}.$$

If we substitute this expression into the system of equations (8), (9), we find that motion along the axis of symmetry ($y = 0$, $v_{*y} = 0$, $\tau_{xx} = \tau$, $v_{*x} = v_*$) is described by the equation

$$\rho\left(\frac{\partial v_*}{\partial t} + v_*\frac{\partial v_*}{\partial x}\right) = \frac{\partial}{\partial x}(\tau - p) - \frac{\tau}{v_*}\frac{\partial v_*}{\partial x}.$$

In the inertialess approximation, integration of this equation from x = 0 to x = ∞ (where τ = 0, p = 0) determines the magnitude of σ_{11} in the thread:

$$\sigma_{11} = (\tau - p)_{x=0} = -\int_0^\infty \frac{\tau}{v_*}\frac{\partial v_*}{\partial x}\,dx. \tag{10}$$

Taking the viscosity forces into account (on the assumption that the flow in the macrovolume is radial) leads to the appearance of a term in Eq. (10) that has the order $\mu_0 v_*(0)/r$ ($v_*(0)$ is the velocity of the liquid at the point x = 0). In this case, when this value is small compared with the terms of Eq. (10), and as can be easily seen, this takes place when $\mu_0 v_*(0) \ll \alpha$, the viscosity forces may be neglected in the examination of the flow in the macrovolume. It must be pointed out that in the case of a thread with constant length, the last inequality is stronger than the above condition of neglecting the viscosity forces in flow in a thread.

The magnitude of the integral in Eq. (10) is determined by the kinematics and the associated degree of extension of the macromolecules at each point of the axis of symmetry of the macrovolume. This correlation is determined by Eq. (1), which for the indicated case has the form

$$\frac{\partial Z_*}{\partial t}+v_*\frac{\partial Z_*}{\partial x}=\frac{Z_*}{(1+3Z_0^2/Z_*^2)}\frac{\partial v_*}{\partial x}-\frac{\lambda Z_0\left(1-Z_0^2/(3Z_*^2)\right)}{1-Z_*}. \tag{11}$$

The first term of this equation has the order calculated for a thread of magnitude $\partial Z/\partial t$, which in its turn is smaller than $\partial Z/\partial t$ in a thread with macromolecules "frozen" into the liquid and with the same kinematics of the motion. Then in accordance with (6) and (7):

$$\frac{\partial Z_*}{\partial t}\lesssim ZE_{11}=Zv(l)/l.$$

In the case of a thread with constant length, the absolute value of the second term of Eq. (11) is of the order $Zv_*(0)/x_*$, where x_* is the x coordinate of the point of the macrovolume at which the macromolecules attain their equilibrium conformation, i.e., the degree of extension Z_0. If the flow in the macrovolume is taken to be radial, then the value x_* is determined from the condition $x_*^2/r^2 \lesssim Z/Z_0 \lesssim N^{1/2}$, i.e., the value of x_* cannot exceed the length on which relaxation would occur with the macromolecules "frozen" into the liquid.

Summing up all that has been said above, we may conclude that in the case of a thread with constant length, when $v(l) = v_*(0)$, the absolute magnitude of the ratio of the first to the second term of Eq. (11) in order of magnitude does not exceed $(r/l)N^{1/4}$. Thus, for sufficiently thin and long threads, i.e., when the condition $(r/l)N^{1/4} \ll 1$ is fulfilled (for most polymers $N^{1/4} \sim 10$), the first term of Eq. (11) is small compared with the second term of this equation, and it may be neglected. That means that the process of relaxation of macromolecules in the macrovolume proceeds much more rapidly than the process of extension of the macromolecules in the thread, i.e., the flow in the macrovolume may be considered steady at any instant.

If we substitute the value $\partial v_*/\partial x$, found from Eq. (11) modified in the described manner, into the integrand in (10), subsequent integration leads to the following result (taking (3) and the fact that $Z_0 \ll 1$ into account):

$$\sigma_{11}=-\beta\left(Z_*(0)+\ln(1-Z_*(0))\right)-\int\limits_0^\infty\frac{\beta Z_*}{(1-Z_*)^2}\frac{\lambda Z_0}{v_*}\left(1-\frac{1}{3}\frac{Z_0^2}{Z_*^2}\right)\left(1+3\frac{Z_0^2}{Z_*^2}\right)dx, \tag{12}$$

where $Z_*(0)$ is the degree of extension of the macromolecules at the point $x = 0$ and consequently in the thread, i.e., $Z = Z_*(0)$.

If we assume that the flow in the macrovolume is radial, then we can show that the integral in the last equation is of the order of magnitude

$$\frac{\beta Z^2}{1-Z}\frac{2\lambda Z_0}{v_*(0)Z}r\left(\frac{1}{1-Z}+\sqrt{\frac{Z}{Z_0}}(1-Z)\right).$$

For a thread of constant length, $v_*(0)$ is proportional to l, and all other magnitudes contained in this expression are independent of l according to the conditions of the problem; then, when l increases, the last expression may be made as small as ever required compared with the terms of Eq. (4). It will be shown below that in this case, in the thread $dZ/dt > 0$, and in accordance with Eq. (6), $E_{11}=v_*(0)/l \gtrsim \lambda Z_0/(Z(1-Z))$. If we substitute this last inequality into the presented expression, we find that the ratio of the value of the integral under examination and of the term $\beta Z^2/(1-Z)$ in Eq. (4) is not of a larger order of magnitude than $(r/l)N^{1/4}$. Thus, with $(r/l)N^{1/4} \ll 1$, and with a view to (5) and (12), Eq. (4) is transformed to the form

$$-\beta(Z+\ln(1-Z))=-\frac{\alpha}{r}+\beta\frac{Z^2}{1-Z}. \tag{13}$$

This equation unambiguously determines the correlation between the radius r of the thread and the degree of orientation Z of the macromolecules in the thread. It shows, in particular, that at the instant of disappearance of the thread ($r \to 0$) the macromolecules are subjected to maximum extension ($Z \to 1$). Equation (13) enables us to note that with high orientation of the macromolecules $(1-Z \ll 1)$, and this, according to (13), always takes place when $\alpha/(r\beta) \gg 1$, the first term of this equation is small compared with the third term of the same equation; this is equivalent to σ_{11} being small compared with the capillary pressure in the thread. That means that under these conditions the process of thinning of the thread amounts to uniaxial extension of the polymer solution by a tensile stress equal to the capillary pressure α/r. Neglecting the first term of Eq. (13) enables us to integrate the system of equations (6), (7), (13). As a result we have

$$Z = 3 - \sqrt{C - 2\lambda Z_0 t},$$

$$r = \frac{\alpha}{\beta} \frac{\sqrt{C - 2\lambda Z_0 t} - 2}{(3 - \sqrt{C - 2\lambda Z_0 t})^2}, \tag{14}$$

where C is the integration constant found from the initial condition $t = 0$, $r = r(0)$, i.e.,

$$C = \left(3 - \frac{\sqrt{1 + 4\frac{\beta r(0)}{\alpha}} - 1}{2\frac{\beta}{\alpha} r(0)}\right)^2.$$

Specifically, if we choose to begin counting the time at the instant of disappearance of the thread, we obtain $C = 4$; then $t < 0$ corresponds to the period of existence of the thread. In that case $|2\lambda Z_0 t| \ll C$ (taking into account that $1-Z \ll 1$), and equality (14) may be represented in the form

$$Z = 1 + \frac{1}{2}\lambda Z_0 t.$$

With low orientation of the macromolecules $(Z \ll 1)$, which is always the case when $\alpha/(r\beta) \ll 1$, expansion into series and neglecting the terms of higher order of smallness in Eqs. (6) and (13) lead to the following result of integrating the system of equations under examination:

$$Z = \frac{1}{3}\lambda Z_0 t + C,$$

$$r = \frac{\alpha}{2\beta}\left(\frac{1}{3}\lambda Z_0 t + C\right)^2, \tag{15}$$

where $C = \sqrt{\alpha/(2\beta r(0))}$.

In the general case, the solution of the system of equations (6), (7), (13) reduces to the integration of the equation

$$\left(\frac{2Z^2}{Z + (1 - Z)\ln(1 - Z)} - 1 + Z\right)\frac{dZ}{dt} = \lambda Z_0. \tag{16}$$

Hence it can be seen that the dynamics of the process of orientation of the macromolecules in thinning of the thread does not depend on the surface tension of the polymer solution. Moreover, by direct check we can convince ourselves that $1/3 < (\lambda Z_0)^{-1} dZ/dt < 1/2$, i.e., the value dZ/dt lies within the limits determined by the asymptotic solutions presented above. In the case of a thread with constant length this enables us to estimate the speed of the liquid at the point $x_1 = l$ with the aid of (6):

$$\frac{v(l)}{l} = E_{11} \simeq \frac{\lambda Z_0}{Z(1 - Z)}. \tag{17}$$

Then the above condition of neglecting the viscosity forces in flow in a macrovolume may be represented in the form

$$\frac{\mu_0 \lambda Z_0}{\alpha Z(1 - Z)} \ll 1. \tag{18}$$

On the basis of the solution found we can show that in the case $l = \text{const}$, the forces of inertia in flow, both in the thread and in the macrovolume, may be neglected when $\rho v^2(l)/2 \ll \alpha/r$, which, in accordance with (13) and (17), is equivalent to

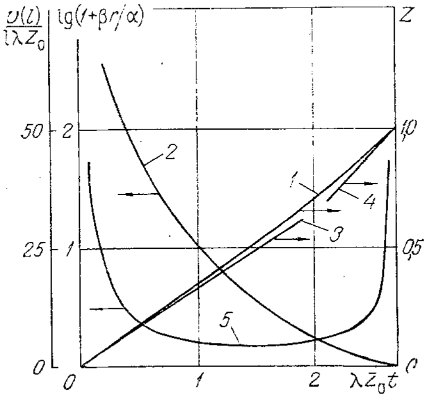

Fig. 3. Dependences of the change of the degree of extension of the macromolecules and of the radius of the thread on time (curves 1, 2); curves 3, 4 correspond to the dependences $Z = Z(t)$ describing the behavior of macromolecules in two limiting cases ($Z \ll 1$ and $1-Z \ll 1$); curve 5 represents the dependence of the change of speed of the liquid at the border of the thread.

$$\frac{\rho(\lambda Z_0 l)^2}{\beta Z^4(1-Z)} \ll 1. \tag{19}$$

If we adopt for a thread of solution of polyoxyethylene WSR-301 in water with a concentration 0.01% that $\rho = 1\ \mathrm{g\cdot cm^{-3}}$, $\mu_0 = 10^{-2}$ P, $\lambda = 5\cdot 10^2\ \mathrm{sec^{-1}}$, $Z_0 = 5\cdot 10^{-3}$, $\alpha = 70\ \mathrm{dyn\cdot cm^{-1}}$, $l = 0.2$ cm, $\beta = 10^5\ \mathrm{dyn\cdot cm^{-2}}$ (then, in accordance with (17), $v(l) \gtrsim 2\ \mathrm{cm\cdot sec^{-1}}$), the inequalities (18) and (19) may be represented as follows: $Z(1-Z) \gg 10^{-4}$, $Z^4(1-Z) \gg 10^{-6}$. These inequalities determine the range of application of the suggested theory for l = const. The obtained results also remain correct for threads of variable length if the rate of dilution of the macrovolumes 2U obeys the condition

$$1 - \frac{U}{v(l)} \gg \frac{r}{l} N^{1/4},$$

which is indispensable for neglecting the term $\partial Z_* / \partial t$ in Eq. (11) and the integral in equality (12), and, if possible, for neglecting the viscosity forces and the forces of inertia in flow in a macrovolume (which occurs, e.g., when conditions (18), (19) are fulfilled and when $U = \mathrm{const} > 0$). Figure 3 shows the results of the numerical solution of the equations describing the behavior of the thread of polymer solution in the general case (curves 1, 2, 5), and also the results of the asymptotic investigation of the problem (curves 3, 4). The beginning of counting the time in the given case was chosen at the instant corresponding to the formal situation $Z = 0$, $r = \infty$. It can be seen from the figure that the asymptotic solutions describe fairly well the process of orientation of the macromolecules under conditions that go far beyond the limits of the assumptions that were made; in practical calculations this makes it possible to use Eqs. (14), (15) jointly with Eq. (13), which establishes a correlation between Z and r.

The obtained results agree qualitatively with the experimental data for solutions of polyoxyethylene and polyacrylamide in a wide range of concentrations [1]. Instead of the viscosity of the solvent μ_0, which figures in Hinch's theory, we used in the calculations the greatest Newtonian viscosity of the polymer solution; this enabled us to take into account the interaction of the macromolecules in the case of highly concentrated solutions.

In conclusion, it must be pointed out that the thread of polymer solution is stable in relation to "rapid" perturbations of the radius (the time of development of the perturbation

$\Delta t \ll Z/(\lambda Z_0)$), since, as can be shown, in this case the force tensioning the thread $F = \pi r \alpha + \pi r^2 \tau$ increases at the place where the thread is thinned, and decreases at the place where it is wider (see [9, 10]).

NOTATION

t, time; r, radius of the thread; l, half the length of the thread; x_1, x_2, x_3, Cartesian coordinates (Fig. 2); x, y, Θ, cylindrical coordinates (Fig. 2); v, flow velocity of the liquid in the coordinate system x_1, x_2, x_3; v_*, flow velocity of the liquid in the coordinate system x, y, Θ; U, half-rate of dilution of macrovolumes; α, surface tension; $\langle \mathbf{zz} \rangle$, second moment of extension of the macromolecule; $z = \mathrm{Tr}(\langle \mathbf{zz} \rangle)^{1/2}$, distance between the ends of the macromolecule; b, length of the Kuhn segment; N, number of Kuhn segments in the macromolecule; $z_0 = b\sqrt{N}$, size of the macromolecule in equilibrium conformation; $Z = z/(Nb)$, degree of orientation of the macromolecule in the thread; Z_*, degree of orientation of the macromolecule in the macrovolume; $Z_0 = z_0/(Nb)$; Ω, rotation tensor; E, strain rate tensor; σ, stress tensor; τ, excess stress tensor; p, pressure; n, number of molecules in unit volume; k, Boltzmann constant; T, absolute temperature; $\varkappa = 3kT/(Nb^2)$, elasticity constant of the macromolecule; μ_0, viscosity of the solvent; μ_l, effective longitudinal viscosity; $\lambda = \varkappa/(6\pi\mu_0 z_0)$; $\beta = n\varkappa(Nb)^2$; $\tau = \beta Z_*/(1 - Z_*)$; C, integration constant; F, tension of the thread.

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