CHANGE IN THE STRUCTURE OF A POLYMER SOLUTION IN A LONGITUDINAL HYDRODYNAMIC FIELD

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There are two qualitatively different conditions for the stretching of liquid fibers formed by moderately concentrated polymer solutions [1]. If the longitudinal gradient of the drawing rate is rather small the structure of the solution remains unchanged. If this gradient exceeds a certain critical value, some of the solvent is expressed from the solution in and the liquid filament is converted into a slightly swollen fiber. The solvent released settles as droplets on the filament surface. This effect is of very great importance for a number of industrial processes pertaining to the production of filaments and films from polymer solutions. In addition, as was reported in [1], the drawing of a liquid filament, accomapnied by orientational formation of the solid phase, can serve as a most simple imitation of the formation of silk and gossamer filaments in nature.

This paper presents a qualitative theory for this phenomenon, based on investigation of the thermodynamic stability of a polymer solution in a longitudinal hydrodynamic field.

In accordance with current concepts we consider the described stratification of the polymer solution in drawing as consisting of two main stages:

1. cooperative ordering of the polymer molecules in individual regions of the solution, accompanied by formation of local quasi-crystalline, supramolecular structures containing a relatively small number of solvent molecules. This ordering is manifested in a considerable reduction of the number of configurations which the polymer molecules in the solution can assume.

2. closer packing of the ordered supramolecular structures and enhancement of the role of intermolecular interactions in their ensuring stability of the new state.

Similar stages were described by Flory [2], for instance, who pointed out, in particular, that the increase in free energy required for the precipitation of solid polymer from a solution or a melt is associated with the first stage, while the second stage of the process is usually accompanied by a reduction in the free energy of the system. Thus, the state attained after the first stage is a special kind of mesophase, and we arrive at the problem of investigating the conditions of thermodynamic equilibrium between the initial solution and this mesophase.

In accordance with the lattice theory of polymer solutions developed by Flory and Huggins, we regard the polymer molecule as a chain consisting of m monomer units (segments). For simplicity we assume that the segments in the molecule are freely articulated and that each segment is equal in volume to a solvent molecule. We regard the solution itself as a quasi-crystalline lattice with coordination number z, with each of its n cells occupied either by a polymer segment or by a solvent molecule.

In spite of the faults of the lattice model discussed in [3], the over-all qualitative results obtained from it are rather reliable. In the subsequent calculations two assumptions are most important.

1. The mean density of the segments is the same along the lattice. This assumption, which is valid for solutions in high and moderate concentrations, does not hold for dilute solutions in which the distance between the polymer molecules in the solution is considerable.

2. All the free cells of the lattice can be occupied with equal probability by segments of the polymer molecules or by solvent molecules. This hypothesis is only approximately valid if the considered solution is not athermal.

We can associate segments situated in z adjacent cells with each segment situated in a lattice cell. The lattice-cell segment can be chemically attached to one of these adjacent cells. We orient the lattice so that two possible bonds are parallel to the tensile axis (x-axis) of the solution: the type y and the type 1 bonds, oriented towards the positive and negative x-axes respectively. All the other bonds form angles $0 \leq \theta_k \leq \pi$ with the x-axis. When a tensile stress p is applied to the solution we assume that a tensile force $\tau = \sigma p$ (σ is the cross-section of the segment, i.e., the area of the central section of the cell) acts on each polymer molecule. If the position of one of the end segments of the polymer molecule is fixed ($x = x_0$), all other segments of the molecule can be regarded as being in a potential field $U = -\tau(x - x_0)$. A polymer molecule stretched in the x-direction will have minimum potential energy in this field. This we regard as the zero potential energy.

We consider the bond which connects the i-th and (i + 1)-th segments of the molecule and makes an angle θ_k with the x-axis. If this bond is of the y type the associated contribution to the potential energy of the molecule is zero, and $\theta_y = 0$. If $\theta_k \neq 0$, we assume th that this contribution $\varepsilon_k = \tau l_k = \tau h(1 - \cos\theta_k)$, where h is the length of the bond (the distance between the centers of adjacent cells). We distribute the z possible bonds on y groups in such a way that for bonds of each k-th group the values of θ_k or l_k are the same ($l_1 > l_2 > \ldots l_k > \ldots l_y$). Generally speaking, $y \leq z$, and we can introduce the quantities $g_k \geq 1$ which represent the number of bond types in different groups; these quantities act as statistical weights for the bonds.

We assume that jm cells of the lattice are already filled with segments of j polymer molecules, so that n − jm cells are free. The initial segment of the (j + 1)-th molecule can be placed in the lattice in n − jm different ways. The next segment of this molecule can be placed in any of the z adjacent cells which are free at this instant. As usual, we use in the calculation the mean fraction of free cells, and we find that the number of ways of placing the second segment is zn^{-1}

(n − jm − 1). In a similar way, it is easy to write expressions for the number of ways of placing all the subsequent segments. With such a method of calculation, however, the nature of the bond between any two successive segments is obscure and, hence, we use a slightly different method.

Let $q_{k,j+1}$ be the number of bonds of the k-th type in the (j + 1)-th polymer molecule under consideration. It is clear that the sum of these quantities with respect to k is m − 1—the total number of bonds in one molecule. Let the bond between the i-th and (i + 1)-th segments be of type 1 or y. A bond of type 1 (or type y) between these segments is possible only for the case in which the (i − 1)-th and i-th segments are connected by any bond, except a bond of type y (or type 1). Since $g_1 = g_y = 1$, the number of positions of the (i + 1)-th segment in these cases is $n^{-1}(n - jm - i)$. If the bond between the i-th and (i + 1)-th segments is of type k, in the general case for the number of positions of the (i + 1)-th segment we have:

(1) $g_k n^{-1}(n - jm - i)$—if the bond between the (i − − 1)-th and i-th segments is not of typek; and

(2) $(g_k - 1) n^{-1}(n - jm - i)$—if this bond is of type k.

We take into account that the relative frequency of occurrence of a type k bond in the (j + 1)-th polymer molecule is $(m - 1)^{-1} q_{k,j+1}$, and find for the number of positions of the (i + 1)-th segment connected with the preceding segment by a type k bond that

$$\frac{n - jm - i}{n}\left(g_k - \frac{q_{k,\, i+1}}{m-1}\right)^{q_{k,\, j+1}} \tag{1}$$

Recording the numbers $q_{k,\, j+1}$ and also the sequence of bonds in the (j + 1)-th polymer molecule we obtain an an expression for the number s_{j+1} of its configurations in the solution:

$$s_{j+1} = \frac{(n - jm)!}{(n - jm - m)!}\, n^{1-m} \prod_{k=1}^{y}\left(g_k - \frac{q_{k,\, j+1}}{m-1}\right)^{q_{k,\, j+1}}. \tag{2}$$

We note that this expression ignores the initial condition, according to which the probability of formation of a type k bond between the first and second segments is proportional to g_k. It was assumed, in fact, that the number of ways of placing the second segment is also determined by an expression of type (1), and not by the exact relationship given above. The use of asymptotic representation (2) is equivalent to the introduction of a large number of segments with negative numbers and is fully justified if m ≫ 1, which is assumed. In fact, it is clear from the foregoing that the successive construction of the bonds in the polymer molecule is a regular Markov process, whose asymptotic behavior is independent of the initial conditions. For the qualitative theory of the approximate relationship Eq. (2) is quite adequate, particularly since the increase in accuracy which can be obtained by taking the initial conditions into account is lost by the further approximation entailed in the use of Stirling formula for factorials, and so on.

For a system of n_1 polymer molecules distinguishable by the number and position of bonds of different types in each of them, the total number of configurations is equal to the product of the numbers s_j for each molecule. In calculating the number of configurations we assume that the total number of type k bonds in all molecules is equal to the mean value over the ensemble.

$$N_k = \sum_{j=1}^{n_1} q_{k,\, j} \approx \nu_k n_1 (m-1), \quad \sum_{k=1}^{y} \nu_k = 1.$$

The possibility of such an assumption follows directly from the concept of a polymer solution as a statistical system. If this hypothesis is incorrect, the applicability of statistical methods becomes questionable in principle. Assuming also that each polymer molecule is a cooperative system, i.e., assuming $q_{k,j} \gg 1$, as well as m ≫ 1, we can take

$$q_{k,\, j} \approx q_k = \nu_k (m-1).$$

The number of possible occurrences q_k of type k bonds in an ensemble of m − 1 bonds is obviously equal to the number of combinations of m − 1 taken q_k at a time. Hence, if the sequence of bonds in the molecules is not specified all the numbers s_j must be multiplied by

$$C_{m-1}^{q_1} C_{m-1-q_1}^{q_2} \ldots C_{m-1-q_1-\ldots-q_{y-2}}^{q_{y-1}}.$$

In considering indistinguishable polymer molecules, according to the "correct Boltzmann calculation" we have to introduce the factor $(n_1!)^{-1}$ into the expression for the total number of configurations. In addition, it is easy to see that in the above conclusion the x-axis can be oriented in either sense along the direction of stretching or, in other words, any of the terminal segments of the polymer molecule can be chosen as the initial segment. Hence, a factor 2^{-n_1} appears in the expression for the number of configurations. For this number we finally obtain the expression

$$\begin{gathered} s = [2^{n_1}(n_1)!]^{-1}\left(C_{m-1}^{q_1} C_{m-1-q_1}^{q_2} \ldots C_{m-1-q_1-\ldots-q_{y-2}}^{q_{y-1}}\right)^{n_1} \times \\ \times \prod_{j=1}^{n_1} s_j = \frac{1}{2^{n_1}(n_1)!}\,\frac{n!}{(n - n_1 m)!} \times \\ \times \left(\frac{n^{1-m}(m-1)!}{q_1!\, q_2!\, ,\ldots q_y!}\right)^{n_1} \prod_{j=1}^{n_1}\prod_{k=1}^{y}(g_k - \nu_k)^{q_k} \approx \\ \approx \frac{n!}{2^{n_1} n_1!\, n_2!}\,\frac{N!\, n^{n_1(1-m)}}{N_1!\, N_2! \ldots N_y!}\prod_{k=1}^{y}(g_k - \nu_k)^{N_k}, \\ n_2 = n - n_1 m\,. \end{gathered} \tag{3}$$

Here n_2 is the number of lattice cells filled by solvent molecules. The potential energy of the polymer molecule in the external force field is

$$E_j = \sum_{k=1}^{y} q_{k,\, j}\varepsilon_k = \tau h \sum_{k=1}^{y} q_{k,\, j}(1 - \cos\theta_k).$$

For the potential energy of a system of n_1 molecules we have

$$\begin{gathered} E = \sum_{j=1}^{n_1} E_j = \tau h n_1 (m-1)\sum_{k=1}^{y}\nu_k(1 - \cos\theta_k) = \\ = n_1(m-1)\sum_{k=1}^{y} a_k \nu_k. \end{gathered} \tag{4}$$

The total increase in energy due to replacement of some of the intermolecular bonds between solvent molecules and between segments of the polymer molecules by bonds between the segments and solvent molecules can be written in the form [4]

$$\Delta H = kT\chi m n_1 n_2 n^{-1},$$
$$kT\chi = Az\left({}^1/_2\varepsilon_{11} + {}^1/_2\varepsilon_{22} - \varepsilon_{12}\right). \qquad (5)$$

Here χ is the Huggins constant; A is the Avogadro number; ε_{11}, ε_{22}, and ε_{12} are the energies of intermolecular interaction between segments, between solvent molecules, and between segments and solvent molecules, respectively; k is the Boltzmann constant. The quantity χ can also be expressed in terms of specific evaporation energies or densities of cohesion energy of the solution components.

Equations (3)–(5) enable us to write the following expression for the statistical sum Q of a solution consisting of n_1 polymer molecules and n_2 solvent molecules:

$$Q = Q_1^{n_1} Q_2^{n_2} \frac{n!}{2^{n_1} n_1!\, n_2!} \frac{N!\, n^{n_1(1-m)}}{N_1!\, N_2! \ldots N_y!} \prod_{k=1}^{y} \times$$
$$\times (g_k - \nu_k)^{N_k} \times \exp\left[-\frac{n_1(m-1)}{kT} \sum_{k=1}^{y} a_k \nu_k - \frac{\chi m n_1 n_2}{n}\right]. \qquad (6)$$

Here Q_1 and Q_2 are the internal statistical sums of the molecules of polymer and solvent.

All the formulas are obtained on the assumption of ideal felxibility of the polymer chains. The theory can be extended to molecules of arbitrary rigidity by our introducing the additional energy $\varepsilon(k_1, k_2)$ associated with the replacement of a type k_1 bond by a type k_2 bond along the chain, as was done by Flory [2] in an investigation of the statistical thermodynamics of polymer molecules of arbitrary rigidity. Consideration of the deviations of actual flexibility from ideal flexibility complicates the calculations, but does not introduce fundamentally new concepts.

With the Stirling formula for the factorials and neglecting terms of order ln n and lower, we obtain from (6) the following expression for ln Q:

$$\ln Q = n_1 \ln Q_1 + n_2 \ln Q_2 - n_1 \ln \varphi_1 - n_2 \ln \varphi_2 +$$
$$+ n_1 \ln ({}^1/_2 m) - n_1 (m-1) -$$
$$- N \sum_{k=1}^{y} \nu_k \ln \frac{\nu_k}{g_k - \nu_k} - \frac{N}{kT} \sum_{k=1}^{y} a_k \nu_k - \chi m n_1 \varphi_2,$$
$$\varphi_1 = \frac{m n_1}{m n_1 + n_2}, \quad \varphi_2 = \frac{n_2}{m n_1 + n_2}.$$

Here φ_1 and φ_2 are the volume fractions of the polymer and solvent in the solution. Introducing r_1 and r_2, which are the number of moles of polymer and solvent, we obtain a relationship for the change in free energy of the system for a solution of pure polymer in pure solvent

$$\Delta F = RT\{r_1 \ln \varphi_1 + r_2 \ln \varphi_2 - r_1 \ln ({}^1/_2 m) +$$
$$+ r_1 m + \chi r_1 m \varphi_2 + r_1 m \times$$
$$\times \left[\sum_{k=1}^{y} \nu_k \ln \frac{\nu_k}{g_k - \nu_k} + \frac{1}{kT} \sum_{k=1}^{y} a_k \nu_k\right]\}, \quad m \gg 1. \qquad (7)$$

Here R is the gas constant.

The quantity ΔF from (7) can naturally be decomposed into two terms, namely ΔF_1, independent of the numbers ν_k in the system, independent of the volume concentration of the solution and ΔF_2, χ. The first term is the change in free energy due to mixing of the polymer and solvent molecules without disturbance of the ordering of the polymer molecules in the mixing process [2]. It is given by

$$\Delta F_1 = RT\,(r_1 \ln \varphi_1 + r_2 \ln \varphi_2 + \chi r_1 m \varphi_2). \qquad (8)$$

The second term is the change in free energy due to disorientation of the polymer molecules in the solution.

With the standard method it is easy to calculate all the partial quantities relating to different components of the solution [4]. For instance, for the molar chemical potentials μ_1 and μ_2 of the polymer and solvent in the solution we obtain the expression

$$\mu_1 = \mu_1^\circ + \Delta H_1 - T\Delta S_1 = \mu_1^\circ +$$
$$+ RT\left[\ln \frac{\varphi_1}{m} + (m-1)\varphi_1 + m \sum_{k=1}^{y} \nu_k \ln \frac{\nu_k}{g_k - \nu_k} +\right.$$
$$\left. + 1 + \ln 2 + \chi m (1 - \varphi_1)^2\right],$$
$$\mu_2 = \mu_2^\circ + \Delta H_2 - T\Delta S_2 = \mu_2^\circ +$$
$$+ RT\left[\ln (1 - \varphi_1) + \left(1 - \frac{1}{m}\right)\varphi_1 + \chi \varphi_1^2\right],$$
$$\Delta S_i = \frac{\partial(\Delta S)}{\partial r_i}, \quad \Delta H_i = \chi m \varphi_{i'}^2 \quad (i' \neq i). \qquad (9)$$

Here ΔS_i and ΔH_i are the partial entropy and enthalpy of the components, and μ_i^0 are the values of the chemical potentials for a pure polymer and a pure solvent.

The fractions ν_k of type k bonds in a solution in thermodynamic equilibrium are given by the solutions of the equations obtained by our equating to zero the derivatives of ΔF from (7) with respect to the different ν_k. Hence, we have a system of equations for ν_k:

$$\ln \frac{\nu_k}{g_k - \nu_k} + \frac{g_k}{g_k - \nu_k} -$$
$$- \ln \frac{\nu_i}{g_i - \nu_i} - \frac{g_i}{g_i - \nu_i} = \frac{a_i - a_k}{kT}$$
$$(k = 1, 2, \ldots, i-1, i+1, \ldots, y). \qquad (10)$$

The number i is selected arbitrarily from the sequence 1, 2, ..., y. Solving Eqs. (10), we obtain equilibrium values of ν_k as functions of $\varkappa = \tau h\,(kT)^{-1}$. These values should be used in Eqs. (7)–(9). We introduce $x_k = \nu_k(q_k - \nu_k)^{-1}$ and it is easy to show that a solution of system (10) satisfying the condition $\Sigma\nu_k = 1$ always exists and is unique. When $\varkappa = 0$, $\nu_k = z^{-1} g_k$ and as $\varkappa \to \infty$, we have $\nu_y \to 1$. We can also show that the sum contained in (7) and (9).

$$M(\varkappa) = \sum_{k=1}^{y} \nu_k \ln \frac{\nu_k}{g_k - \nu_k}, \qquad \varkappa = \frac{\tau h}{kT}$$

is a function of $\varkappa$ which increases monotonoically from $-\ln(z-1)$ to infinity when $\varkappa$ changes from 0 to ∞. The last conclusion can also be derived directly from (9), since the state of the polymer in the solution when $\varkappa$ increases must become less and less stable, and so the corresponding chemical potential will increase.

The change in free energy on transition from a pure polymer and a pure solvent to an ordered solution (i.e., to the mesophase state) is due entirely to mixing of the solvent and polymer molecules. For definiteness in calculation of the thermodynamic functions of the ordered solution the polymer molecules can be regarded as drawn in the stretching direction [2]. The number of possible configurations in this case is equal to the number n_1^* of segment positions on an axis containing n^*/m cells, multiplied by the Boltzmann factor $(n_1^*!)^{-1}$. After calculation we have for the free energy of formation of an ordered solution

$$\Delta F^* = RT \times$$
$$\times \left(r_1^* \ln \frac{r_1^*}{r_1^* + r_2^*} + r_2^* \ln \frac{r_2^*}{r_1^* + r_2^*} + \chi m r_1^* \varphi_2^*\right). \quad (11)$$

All quantities marked with an asterisk relate to the ordered solution. The arguments of the logarithms in (11) are the mole fractions of the polymer and solvent, as distinct from the volume fractions contained in (8), for instance. We use the previous method to obtain expressions from (11) for the chemical potentials of the components in the mesophase state

$$\mu_1^* = \mu_1^\circ +$$
$$+ RT\left[\ln \frac{\varphi_1^*/m}{1 - \varphi_1^*(1 - 1/m)} + \chi m (1 - \varphi_1^*)^2\right],$$
$$\mu_2^* = \mu_2^\circ + RT\left[\ln \frac{1 - \varphi_1^*}{1 - \varphi_1^*(1 - 1/m)} + \chi \varphi_1^{*2}\right]. \quad (12)$$

The initial polymer solution ceases to be stable on attainment of thermodynamic equilibrium between it and the mesophase, i.e.,

$$\mu_1 = \mu_1^*, \qquad \mu_2 = \mu_2^*. \quad (13)$$

These equations give, for instance, φ_1^* and the critical value of the parameter $\varkappa$ at which the appearance of a mesophase in the system becomes possible, i.e., at which the initial solution becomes stratified. When φ_1^* is known, it is easy to calculate the amount of solvent expressed.

We consider the situation in which $m \gg 1$. The first equation has the form

$$\ln(1 - \varphi_1) + \varphi_1 + \ln [1 +$$
$$+ \varphi_1^* m^{-1}(1 - \varphi_1^*)^{-1}] \approx \chi(\varphi_1^{2*} - \varphi_1^2).$$

We take

$$\varphi_1^* = 1 - m^{-1}\psi, \qquad \psi = \psi_0 + \chi\psi_1 + \ldots,$$
$$\psi_i = \psi_i(\varphi_1).$$

From the calculations we obtain, with accuracy to terms proportional to χ:

$$\varphi_1^* \approx 1 - m^{-1}\{(1 - \varphi_1)[e^{-\varphi_1} - (1 - \varphi_1)]^{-1} -$$
$$- \chi(1 + \varphi_1)e^{\varphi_1}[e^{-\varphi_1} - (1 - \varphi_1)]^2\}. \quad (14)$$

inclusively.

The solution has the form of (14) when the inequality

$$\chi \ll \frac{\psi_0}{|\psi_1|} = \frac{(1 - \varphi_1)e^{-\varphi_1}}{(1 + \varphi_1)[e^{-\varphi_1} - (1 - \varphi_1)]^3}$$

is satisfied.

Thus, expression (14) is valid for solutions which do not differ greatly from an athermal solution. As $m \to \infty$, $\varphi_1^* \to 1$. In the general case, when $m \gg 1$, solid phase formed from the solvent under the action of a longitudinal hydrodynamic field is in fact, a slightly swollen fiber, as was indicated in [1], and the degree of swelling increases with improvement of the solvent (i.e., with decrease in χ).

From the second equation of (13) we obtain

$$M(\varkappa) = \sum_{k=1}^{y} \nu_k \ln \frac{\nu_k}{g_k - \nu_k} \approx -\varphi_1 - \chi(1 - \varphi_1)^2.$$

It is easy to see that a unique solution $\varkappa = \varkappa_0$ of this equation exists if

$$\varphi_1 + \chi(1 - \varphi_1)^2 < -\min\{M(\varkappa)\} =$$
$$= -M(0) = \ln(z - 1).$$

This condition is actually the condition for existence of the initial solution at zero τ. At large χ, which corresponds to poor solvents, there is a critical concentration of the solution φ_{10}, so that when $\varphi_1 > \varphi_{10}$ the solution cannot exist.

The critical value of the tensile stress $\tau_0 = \varkappa_0 h^{-1} kT$, i.e., it is proportional to the temperature. It is easy to convert from τ_0 to the critical values of the tensile stress or longitudinal velocity gradient: $p_0 = \sigma^{-1}\tau_0(\nabla\nu)_0 = \eta^{-1}p_0$, where η is the longitudinal (Trouton) viscosity of the polymer solution.

In the model under consideration thermodynamic equilibrium between the solution and mesophase is possible only because stretching of the polymer molecules reduces the number of possible configurations and thus reduces entroyp of the solution. There is a parallel increase in the free energy of the solution (7). The model under consideration involves isoenergetic stretching of the polymer molecules, so that precipitation of a solid polymer from a solution is a typical entropy effect. A more thorough treatment will necessitate consideration of retardation of the internal rotation of the segments through our introducing some rigidity characteristics of the molecule. These characteristics could have a wide range of values [3]. It is possible also phase is accompanied by the suppression of several internal degrees of freedom of the molecules. Consideration of the latter effect will presumably lead to lower values of the critical quantitites (see the analysis of the effect of torsional vibrations of the segments on the melting point of a crystalline polymer in [3]).

We note also that all the arguments relate to the possibility of formation of a solid phase during stretching of a solution, but not to the actual occurrence of this process in a specific control period. In concentrated solutions the mobility of the polymer molecules can be too low, while in dilute solutions the distance between the polymer molecules can be too great, to lead to appreciable expression of solvent from the solution during the experiment. Analysis of the conditions of thermodynamic equilibrium is obviously inadequate for investigation of this question and it will be necessary to consider the kinetics of transition between different states.

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