KINETIC CONDITIONS FOR THE FORCED TRANSITION OF MACROMOLECULES OF AN ACRYLONITRILE COPOLYMER INTO THE UNCOILED STATE

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It is well known that during the spinning process fibers pass through a stage of the action of a lengthwise hydrodynamic field. This takes place both in the pre-spinneret region and also during orientation stretch. As a result of such action, the macromolecules go over into an uncoiled oriented state, which also ensures a high strength for the article obtained. Although a large number of experimental and theoretical works have been devoted to questions about increasing the strength of polymeric fibers [1], the critical conditions for transition of micromolecules into the uncoiled state as a function of the molecular weight of the chain, the concentration of the solution, and solution temperature, etc., have been insufficiently studied.

In the present article, we examine conditions for the uncoiling of the macromolecules of a ternary copolymer based on acrylonitrile, methacrylic acid, and acrylic acid (AN:MA:AA) in an aqueous sodium thiocyanate solution under the action of a hydrodynamic field which is close to lengthwise, as a function of the concentration of the solution. Such a field was generated by the procedure suggested by Keller [2] in the gap between coaxial capillaries. We note that the ternary statistical AN:MA:AA copolymer is a typical representative of the materials which are used in the technology of Nitron fibers. These fibers have a high similarity to wool, with a low thermal conductivity, a high elasticity, and easy dyeability [3, 4].

As the object of study, we used an AN:MA:AA copolymer containing 4.5% by wt. of methacrylic acid and 3% by wt. of acrylic acid. We investigated the behavior of the macromolecules in an aqueous solution of sodium thiocyanate at a sodium thiocyanate concentration of 51.5% by wt. and with a polymer concentration in the solution of 1 • 10^{-2} g/cm^2. According to the data of [5], a solution of AN:MA:AA whose polymer concentration is 0.05-0.06 g/cm^3 is technologically suitable for fiber preparation.

The mean molecular weight M of the polymer was determined on the basis of measurements of its intrinsic viscosity [η] in dimethylformamide solution (containing 0.25% by wt. of added lithium chloride) and this proved to be equal to 454 cm/g. Calculations by the formula [η] = 7.24 • 10^{-2} M^{0.66} [5] gave M = 560,000.

In investigating the action of a lengthwise hydrodynamic field on the solution, we used a set-up analogous to that described in [6]. The set-up was modified so that there was the opportunity to work with solutions whose viscosity approached that of technological solutions. All elements of the assembly were made of stainless steel. The solution was forced through capillaries, creating a pressure in the space between the capillaries which exceeded atmospheric pressure. The flow viscosity gradient g in the main direction of flow of the solution was calculated by the following formula

\[ g = \frac{2Q}{\pi r l}, \]

where Q is the flow rate of liquid through one capillary in 1/sec; r = 0.05 cm — it is the radius of the capillary; l = 0.2 cm is the distance between the end surfaces of the capillaries.

The critical velocity gradient \( g_{cr} \) corresponding to the start of intensive uncoiling of the macromolecules was defined as the gradient at which the appearance of an optically anisotropic string was clearly recorded between the capillaries.

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Fig. 1. Dependence of reduced birefringence index \( \Delta n/\Delta n_\infty \) on velocity gradient \( g \) for solutions of the acrylonitrile copolymer of various concentrations (in g/cm\(^3\)): 1) 1 \times 10^{-3}; 2) 2 \times 10^{-3}; 3) 5 \times 10^{-3}; 4) 1 \times 10^{-2}; 5) 2 \times 10^{-2}; 6) 5 \times 10^{-2}.

The mean degree of uncoiling of the macromolecules which was attained in the hydrodynamic field \( \beta = \langle h^2 \rangle^{1/2}/L \) was estimated on the basis of the refractive indices \( \Delta n \) of the optically anisotropic region of the solution, considering that at large degrees of uncoiling \( \beta^2 = \Delta n/\Delta n_\infty \). Here \( \langle h^2 \rangle \) is the mean square of the distance between the chain ends, \( L \) is its contour length, and \( \Delta n_\infty \) is the limit in possible birefringence for the concentration of solution used. The value of \( \Delta n_\infty \) can be calculated by the formula of Peterlin [7]

\[
\Delta n_\infty = \frac{2n(n^2+2)^2}{9n} (\alpha_1 - \alpha_2) N',
\]

where \( n \) is the mean refractive index of the solution; \( (\alpha_1 - \alpha_2) \) is the difference in polarizability of the chain segment, caused both by its inherent optical anisotropy and also by the microform effect; \( N' = C/M_N N_A \) is the number of segments in a unit volume of the solution; \( C \) and \( \rho \) are the concentration and density of the solution; \( M_N \) is the weight of the segment; and \( N_A \) is Avogadro's number.

The values of \( (\alpha_1 - \alpha_2) \) and of \( M_N \) for the AN:MA:AA copolymer in aqueous solution are unknown. This fact required us to carry out an estimate of \( (\alpha_1 - \alpha_2) \) by the birefringence method in a shear stream. We used an optical set-up with an penumbra compensator, as described in [8]. As a result of the measurements, it was found that the value of \( (\alpha_1 - \alpha_2) \) for the investigated copolymer coincides with that obtained for pure PAN in solution, where the birefringence figure for the polymer and the solvent are the same. It should be noted that in view of the closeness of the birefringence figures for the polymer and the solvent, the contribution of the microform effect to the value of \( (\alpha_1 - \alpha_2) \) is only slight. The coincidence of the values of \( (\alpha_1 - \alpha_2) \) for PAN and the AN:MA:AA copolymer is connected with the small content of units in the micromolecule which differ from PAN, and this also causes only a small difference in both the optical and also the confirmational characteristics of the macromolecules of these polymers. This permits one in calculations of \( \Delta n \) to use the values of \( (\alpha_1 - \alpha_2) \) and of \( M_N \), which have been obtained for PAN and which have the values, respectively, of \( 23 \times 10^{-25} \) cm\(^3\) and 673 g/mole.

Results of studies of the action of a hydrodynamic field on the macromolecules of the AN:MA:AA copolymer are shown in Fig. 1 in the form of a dependence of the reduced birefringence index \( \Delta n/\Delta n_\infty \) on the velocity gradient \( g \). It is evident that the lower the concentration of the solution, the higher are the values of \( \Delta n/\Delta n_\infty \). For a solution whose concentration is \( 1 \times 10^{-3} \) g/cm\(^3\), the \( \Delta n/\Delta n_\infty \) ratio attains 0.75, to which corresponds a degree of uncoiling of 0.9. At a concentration of \( 5 \times 10^{-2} \) g/cm\(^3\), the maximum attained value of \( \Delta n/\Delta n_\infty \) is 0.1, which corresponds to a degree of uncoiling of 0.3. These data indicate a strong deformational action on the copolymer chains by a hydrodynamic field which is close to lengthwise.

The decrease in maximum \( \Delta n/\Delta n_\infty \) value with increase in concentration of the copolymer in solution may be explained by an effect of partially uncoiled chains on the structure of the hydrodynamic field itself. This effect may be displayed in deviations from lengthwise flow, which should also lead to the less efficient uncoiling of the macromolecules. Another possible explanation is the formation of a network of adhesions in the solution which does not have time to break up during the limited time of action of the field on the solution. The data of [7] are an indirect argument in favor of the correctness of such assumptions. Here, it was shown that in dimethylformamide solutions, the chains of PAN and of the AN:MA:AA copolymer have closely