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Abstract

Full Text

PHYSICAL CHEMISTRY

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ON THE DEPENDENCE OF THE CONFORMATION OF A POLYMER CHAIN IN SOLUTION ON THE CONCENTRATION OF THE SOLUTION

(Presented by Academician V. A. Kargin on 20 VI 1961)

In studying the properties of solutions of polymethacrylic acid over a wide range of temperatures and concentrations, we established that, on passing from dilute to concentrated solutions, a change occurs in the sign of the temperature dependence of viscosity ^(1,2). The mechanism of this phenomenon, associated with changes in chain conformation, is considered in the present work.

Using a Shvedov-type rotational viscometer, we investigated the shear dependence of the viscosity of aqueous solutions of polymethacrylic acid (viscometric molecular weight 330 000) at concentrations of 6, 9, and 12% and at temperatures of 20–65°. The most significant results are presented in Fig. 1. The data obtained indicate that, over a wide range of shear rates, the viscosities of 6% solutions at 20° are higher than at 50°, whereas, beginning with a concentration of 9%, the viscosities have a greater value at the higher temperature. A similar increase in the viscosity of polymer solutions in poor solvents upon heating has also been observed earlier for aqueous gelatin solutions ^(3,4) and benzene solutions of butyl rubber ^(5,6), and was explained by the unfolding of macromolecular chains occurring upon heating. It is natural to suppose that, in the case of polymethacrylic acid as well, the increase in viscosity upon heating in a concentrated solution is also associated with the unfolding of chains owing to the rupture of intramolecular bonds and with the strengthening of the interaction of the unfolded chains with one another. This supposition is also supported by the data shown in Fig. 1 on the sharp increase in viscosity when a certain value of the shear rate is reached. For a 9% solution, the sharp increase in viscosity occurs at a shear rate of 6.3 sec⁻¹ at a temperature of 50°, and for a 12% solution—at a lower shear rate already at 20°. This phenomenon, discovered by Kachalsky ⁽⁹⁾ and called negative thixotropy, can be explained only by the unfolding of chains under the action of shear stresses. It is significant, as we have established, that the phenomenon of negative thixotropy has both a lower and an upper temperature limit within which it manifests itself. If, for a 9% solution, the phenomenon of negative thixotropy does not appear at temperatures above 60°, then for a 12% solution it is no longer observed even at

Fig. 1

Figure 1: Fig. 1

50°. Apparently, the upper temperature limit up to which negative thixotropy can appear is determined by the gelation temperature⁽⁶⁾. Obviously, at the gelation temperature the chains are already sufficiently unfolded, so that no additional unfolding under the influence of shear stresses takes place.

In studying gelation in solutions of polymethacrylic acid earlier^(1,2), we proceeded from the assumption that the increase in viscosity and structure formation occurring as a result of decreased solubility upon heating are associated with additional coiling of macromolecules and with strengthening

interactions between them. In light of the data we have now obtained, we believe that gel formation is also determined rather by the interaction of chains unfolding upon heating. Indeed, on transition to a concentrated solution the ratio between the number of intra- and intermolecular bonds changes; as a result, transition to more extended conformations upon deterioration of the solvent may prove thermodynamically more favorable. Although straightening of the chains leads to a decrease in their entropy, it can be compensated by a significant change in heat content due to the fact that, in the interaction in the case of extended chains, a considerably larger number of carboxyl groups can take part.

Fig. 1

The ideas set forth are consistent with the data of Harman and Patat⁽⁷⁾, who observed a sharp decrease in the solubility of dextran in water under prolonged action of shear stresses, associated with unfolding of the chains and strengthening of the intermolecular interaction between them. Transition to more extended conformations of polyacrylic acid molecules with increasing solution concentration was also observed in the work of Kargin, Bakeev, and Pshezhetsky⁽¹⁰⁾, which likewise confirms our proposition concerning the unfolding of chains in more concentrated solutions.

Thus, it follows from the foregoing that the conformation of a polymer molecule in solution depends not only on the nature of the polymer, the solvent, and temperature, but also on the concentration of the solution.

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