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SUPER-MOLECULAR STRUCTURE OF DILUTE SOLUTIONS OF HIGH MOLECULAR WEIGHT POLYMERS WHICH LEAD TO REDUCED TURBULENT FRICTION

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Data are obtained which indicate a relationship between the viscoelastic properties of dilute solutions of high molecular weight polymers and their super-molecular network structures. The changes in structure are determined which result as the concentration and molecular weight of the polymer are increased.

Dilute solutions of linear high molecular weight polymers with their unusual hydrodynamic and physical-chemical properties have long attracted the attention of investigators. The reduction of turbulent friction, increase of the resistance to filtration, the suppression of the breakup of jets, and the flocculating effect of extremely small polymer additions are all effects which have not only theoretical interest but also considerable applied value. The progress in understanding the special features of dilute polymer solutions is closely related to the development of modern concepts of the structural features of these liquids. However, it is precisely on this basic question that no unified opinion has been developed up to now.

A point of view is widely encountered in polymer science according to which the polymer chains in dilute solutions are molecularly dispersed. In this sense a dilute solution is taken to mean a solution in which there is no overlapping of the macromolecular tangles, which in the case when the limit exists $[\eta]_0 = \lim\limits_{c\to 0,\ \dot{\gamma}\to 0} (\eta-\eta_s)/(c\eta_s)$, (which is termed the characteristic viscosity) results in the condition $c[\eta]_0 < 1$ being satisfied. Consistent experimental information exists in favor of the molecular dispersity of dilute solutions for polymeric materials with molecular weights $M \leqslant 10^5$. In this connection it is sufficient to recall the classical results of H. Staudinger and W. Carothers and other authors, who determined the molecular weights of polymers by basically different methods: chemical (titration of the end groups), and physical (cryoscopy, ebullioscopy, osmometry) [1]. These experiments led to comparable data, and indicated not only the existence of polymers with molecular weights exceeding 10^4, but also the molecular dispersity of these materials in solution. It was possible to advance these results by still another order of magnitude with respect to M after the development of the light-scattering method by Debye. The use of light scattering and osmometry for measuring the molecular weights of polymers reaching values as high as 10^5 led to the same numerical values, which inidcates, in particular, the correctness of the concepts of the molecular state of subdivision of such polymers in dilute solutions [2].

The successes in proving the separateness and discreteness of macromolecules with $M \leqslant 10^5$ in dilute solutions led to the unfounded confidence that this discreteness is retained for dilute solutions of macromolecules with larger molecular weights also, i.e., for the solutions for which the series of effects listed above are characteristic. In particular, this confidence is related to the attempts which have been made to explain many of the hydrodynamic features of the behavior of liquids with small polymeric additions on the basis of considering the interactions of single macromolecules with the flows. The point of view being discussed here has become particularly popular among theoreticians as a result of the tempting possibilities it provides for simplifying calculations.

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However, no factual data exist which show that solutions of high molecular weight polymers ($M > 10^5$) are necessarily true solutions even when the condition of diluteness ($c[\eta_0] < 1$) is satisfied. In addition, in favor of this enough evidence has accumulated even from the early years of the establishment of polymer science that macromolecules of large molecular weights associate in solutions.

Various experiments indicate the existence of super-molecular formations which arise in dilute solutions as a result of physical attraction forces between the long polymer chains. Association of the macromolecules has been proposed for explaining the differences (which are sometimes very considerable) which are observed in the measured molecular weights on changing the solvent or the temperature of the solution (see [4], for instance). Analogous interpretations were required by light scattering experiments, which in the case of high molecular weight polymers gave values of M which exceeded the real values by several orders of magnitude [5]. The presence of super-molecular structures in dilute polymers solutions, which causes the turbulent drag reduction effect, is discussed in [6, 7]. Investigations of the viscoelastic properties of solutions of high molecular weight polymers have led to results which differ importantly (especially at small concentrations) from the predictions of the theories which assume the discreteness of the macromolecules [8]. These data also suggest that because of the tendency of the long macromolecules to associate, their complete segregation in solution appears to be possible only at extremely small concentrations which are several orders of magnitude smaller for $M \geqslant 10^6$ than the calculated concentration for the occurrence of overlapping of the macromolecular tangles, $c = 1/[\eta]_0$.

A concept of the detailed structure is given by electron and optical microscopy of samples prepared from the solutions being investigated. The observations show that under certain conditions in the dilute solutions of high molecular weight polymers there are continuous three-dimensional networks, the elements of which are long fibrils [9-14]. In the solutions of some polymers the fibrils consist of many macromolecules and have thicknesses sufficient that they can easily be observed by optical means without requiring resource to the use of electron microscopy.

The purpose of the work which we have carried out was the further investigation by optical microscopy of the structures of dilute polymer solutions which show special hydrodynamic behavior. Particular attention has been paid to aqueous solutions of polyethylene oxide (EPO), since their elastic properties have been well investigated for various molecular weights and concentrations [8], so that it would be possibel to explain the relationship between the structure and the elastic properties. Experiments were also carried out with solutions of EPO in isopropanol and of polyisobutylene in hexane.

The investigation and photography of the samples were carried out on a NU2IE optical microscope (K. Zeiss, German Democratic Republic). A VUP-4 vacuum station was used in the preparation of the samples.

The samples were prepared by means of removing the solvent from droplets of solution placed on a cover glass. Two well-known methods of removing the solvent under vacuum were used: with preliminary freezing of the droplets by liquid nitrogen (so-called lyophilic drying), and without preliminary freezing (rapid drying) [15].

In order to carry out the rapid drying procedure the cover glass with the droplets of solution was placed in the vacuum chamber of the VUP-4 apparatus. When the vacuum was drawn, the droplets very rapidly froze as a result of the intense evaporation. By using a thermocouple it was shown that by freezing the solution in the process of sublimation it was possible to self-cool the solution to —35°C. At such temperatures the sublimation of the solvent occurred quite rapidly. After the freezing of the droplets was complete the drying was continued for about 20 minutes more to ensure the complete removal of the solvent.

When the method of rapid drying is used there is the danger of obtaining an inadequate picture of the structure of the solution as a result of the crystallization of water in the process of the slow cooling during evaporation and the consequent increase in concentration. For this reason, the method of lyophilic drying was also used in addition to the method of rapid drying. In this case, the cover glass with the liquid droplets was submerged in liquid nitrogen before being placed in the vacuum chamber. According to the estimates made in [16], under these conditions the rate of cooling of the droplets exceeds 100°C/second. With such rapid cooling, vitrification of the solvent obviously occurs; if crystallization of ice also occurs the crystals are able to grow only to a small size not exceeding 1 μm. The cover

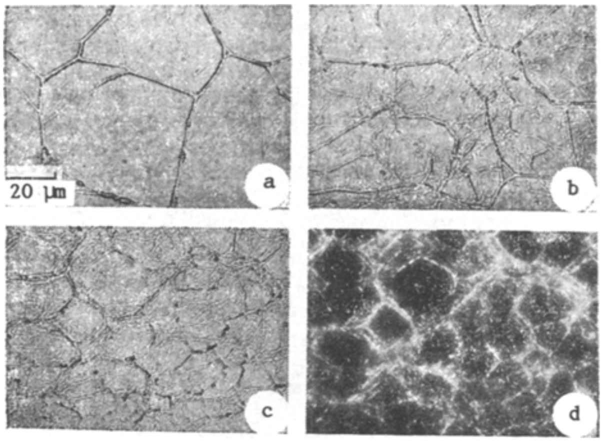

Fig. 1. Fibrillar network structure of aqueous solutions of PEO, $[\eta]_0$ = 2500 (using the method of rapid drying): a): $c = 5\cdot10^{-6}$; b): $c = 2.5\cdot10^{-5}$; c) and d): $c = 10^{-4}$; a), b), c): full-light photographs; d): with crossed polarizers.

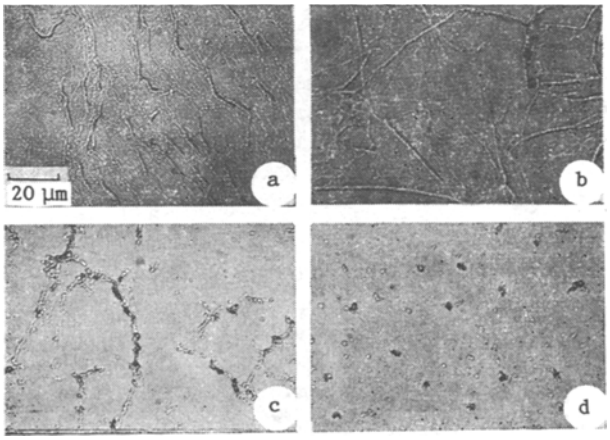

Fig. 2. Changes in the super-molecular structure of aqueous solutions of PEO, $c = 10^{-5}$, as the molecular weight of the polymer varies (using the method of lyophilic drying): a): $[\eta]_0$ = 4500; b): 2500; c): 450; and d): 90.

glass was then mounted in liquid nitrogen within the cavity of a container with a mesh cover specially made of copper. The container was then rapidly transferred onto a microscope stage cooled by liquid nitrogen in the vacuum changer of the VUP-4 apparatus, the vacuum pump was switched on, and the liquid nitrogen was then evaporated from the cavity of the container, after which the sublimation of the frozen solvent began. The VUP-4 apparatus made it possible to carry out vacuum treatments down to 1-0.1 mPa.

The sublimation of the aqueous solutions of PEO was carried out at a temperature of −80°C. At this temperature it was not possible for ice crystals of large dimensions to arise in the process of vitrification and recrystallization. It is highly improbably that ice crystals are formed at all. A period of 8-10 hours was required for the complete removal of the water from the droplets. After the sublimation was complete the samples were slowly warmed to room temperature under vacuum. They were then removed for examination under the microscope.

A study of the samples under the microscope led to the conclusion that in dilute solutions of high molecular weight polymers a network-type super-molecular structure exists. The elements of this network are fibrils consisting of many macromolecules. On increasing the concentration the density of the network increases, though as a rule the thicknesses of the

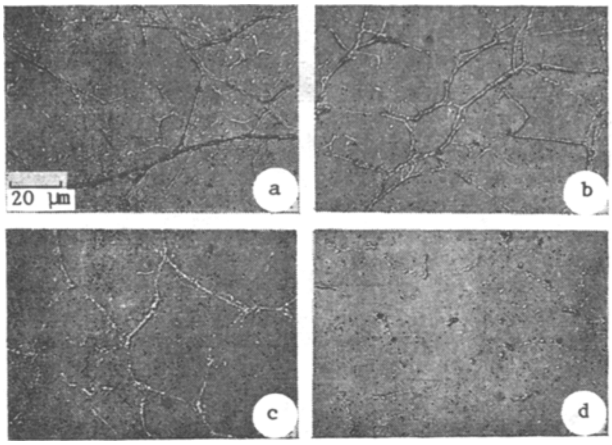

Fig. 3. Changes in the super-molecular structure of an aqueous solution of PEO, $c = 10^{-5}$, $[\eta]_0 = 2500$, as degradation occurs during flow (using the rapid drying method): drag reduction is 52% (a), 35% (b), 5% (c), and 0% (d).

fibrils vary very little. Figure 1 shows photographs of samples obtained from aqueous solutions of PEO of various concentrations. In all the photographs the fibril thickness is of the order of 1 μm, which is in agreement with the results of [12, 13]. The size of the cell in the network and the lengths of the individual fibrils decreases as the polymer concentration increases.

The polymeric material in the fibrils exists in an oriented state. This is indicated by the birefringence of the fibrils (Fig. 1d). On rotating the microscope stage with the sample the brightnesses of the various fibrils change. Depending on the orientation of the fibril, it can be clearly seen against the dark field, or can be completely blacked out. It can be concluded that the macromolecules in the fibrils are arranged in parallel and are oriented along the axis of the fibril. Thus, the fibrils represent liquid-crystal domains which in the three-dimensional network make up one of the parts of the bicontinuum which is the solution.

The photomicrographs in Fig. 2 were made with samples obtained by the method of sublimation drying of aqueous solutions containing at a single concentration ($c = 10^{-5}$) PEO polymer homologs of various molecular weights. It can be seen that at a small molecular weight ($[\eta]_0 = 90$) the association of the macromolecules does not lead to the formation of a continuous network, though it occurs. A fibrillar network is observed in the solution having $[\eta]_0 = 450$. The network becomes thicker with further growth of the molecular weight. The occurrence of the network and the increase of its thickness are in good agreement with the occurrence and increase of the elastic properties of the aqueous PEO solutions as the molecular weight of the dissolved polymer increases [8]. Thus, the limiting value of the characteristic viscosity beginning with which a measurable characteristic time and viscosity anomalies occur in dilute aqueous PEO solutions and the drag reduction effect begins lies at about 300, while with constant concentration and increasing molecular weight the elastic properties of the solution increase.

Solutions of high molecular weight polymers degrade during flow. Their viscoelastic properties gradually disappear as a result of the destruction of the macromolecules, leading to a decrease of their molecular weight. It can therefore be expected that in the course of degradation of the solution the thickness of the network structure will decrease. This does occur in fact.

The photomicrographs in Fig. 3 correspond to samples from PEO solutions gradually degrading in a rotating apparatus with coaxial cylinders which was described in more detail in [17]. The inside radius of the rotor (the outer cylinder) of this apparatus was 7.0 cm. The experiments were carried out with the rotor turning at 2000 r.p.m. at room temperature. The value of the drag reduction effect was determined, from which it was possible to judge the degree of destruction.

The photomicrographs which have been made correspond to various values of the drag reduction effect: the first (Fig. 3a) was made with a fresh solution, while the last (Fig. 3d) corresponds to a solution which had been so much degraded during flow that the drag reduction effect had completely disappeared. It can be seen that as the degree of degradation increased the thickness of the network decreased. Ultimately, the continuity of the network disappears.

The observation of samples prepared from dilute solutions of high molecular weight PEO in isopropanol and of high molecular weight isobutylene (type P-200) in hexane, both of which showed drag reducing effects, showed that these solutions also have fibrillar network structures.

Reservations can be found in the literature in connection with the interpretation of observations of samples of polymer solutions [14, 18]. Fears are expressed that the network structure is not connected with the actual structure of the solution, but arises in the process of preparation as a result of the stratification of the supercooled solution and the displacement of the polymer molecules to the boundaries of the crystals of solvent which are formed during freezing. The experiments which have been carried out show that there is no basis for these fears. If it is assumed that the observed network structure arises as a result of displacement of the polymer to the boundaries of crystals, then in this case the nature of the sample must depend on the conditions under which it was prepared. However, the network structure has been observed in samples prepared both by rapid drying and also by sublimation drying, in which case the samples obtained by the different methods from the same solution differ little (compare Fig. 2b with Fig. 3a). There is good correlation between the viscoelastic properties of the solutions and the natures of the structures which are observed, which would hardly be the case if the network arose only in the preparation of the sample. In addition, the fibrillar network structure is also observed in the case of solutions of PEO is isopropanol, where the solvent vitrifies during rapid cooling [19]. All of this suggests that the picture which is observed corresponds to the real structure of the polymer solution.

The fact that the picture which can be observed adequately represents the real structure of the polymer solution is indicated by the following experiment. A drop of an aqueous PEO solution ($[\eta]_0 = 4500$, $c = 4 \cdot 10^{-5}$) was placed between the touching tips of a tweezer. The tips were then freed, which led to the droplet being drawn out into a liquid thread. Simultaneously, the ends of the tips with the thread being formed were submerged in liquid nitrogen. The frozen thread was placed on a cover glass and was transferred under liquid nitrogen onto the stage of the VUP-4 apparatus, after which sublimation drying was carried out. This procedure made it possible to determine the network structure in deformed form. The investigation of this structure under the microscope showed that as a result of the stretching of the liquid the overwhelming majority of the fibrils in the thread are oriented along its axis. This would not be the case of the network arose during the freezing as a result of the displacement of the polymer into the intercrystalline zones.

The liquid-crystalline fibrillar network structure of a solution of a high molecular weight polymer is an equilibrium fluctuating super-molecular structure. It is the cause of the special behavior of these solutions. The considerable elastic properties connected with this structure lead to unusual hydrodynamic phenomena: the turbulent drag reduction and filtration anomalies. The flocculating capability is explained by the occurrence of fibrillar bridges between solid particles [20]. The birefringence of flows which is characteristic of solutions of high molecular weight polymers is also obviously connected with the fibrillar network structure. In fact, as shown by the last experiment, the fibrils are oriented along the flow in elongational flows, and since the macromolecules in them are likewise oriented, an orientation of the macromolecules with the flow occurs, which leads to the birefringence. Evidence in favor of this interpretation is provided by the fact that birefringence in a flow and drag reduction both disappear if the molecular weight of the polymer becomes less than some critical value [21].

NOTATION

c, mass concentration; $\dot{\gamma}$, shear rate; η, viscosity of solution; η_s, viscosity of solvent; $[\eta]_0$, characteristic viscosity; M, molecular weight.

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