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1958

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Abstract

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PHYSICAL CHEMISTRY

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ON THE FORMATION OF GEOMETRICALLY ORDERED STRUCTURES IN AMORPHOUS POLYMERS

On the basis of experimental data obtained recently by various authors, the assumption has been made that the existing conceptions of the structure of amorphous polymers as chaotically entangled, bent chains do not correspond to the real structure of amorphous polymers. V. A. Kargin, A. I. Kitaigorodskii, and G. L. Slonimskii (^{1}) believe that the molecular arrangement of chains in amorphous polymers can, as a rule, be constructed either from extended chains assembled into bundles or from globules folded back upon themselves. The features of the physical and mechanical properties of amorphous polymers can be readily explained on the basis of such a model.

The existence of molecular bundles formed by the parallel association of extended chains in amorphous polymers was shown, using polyacrylic acid and its salts as examples, in the work (^{2}).

In the present work an electron-microscopic investigation was undertaken of the structure of certain amorphous polymers possessing different structures of their molecular chains. The objects studied were the polymers *Myshyak* (Salvarsan), polyacrylamide, and a copolymer based on methyl methacrylate and methacrylic acid. Thus, polymers containing various polar groups in the chain and, consequently, possessing different intra- and intermolecular interaction forces were investigated.

Specimens for the investigation were prepared by applying a polymer solution to a supporting film, followed by evaporation of the solvent. The concentrations of the solutions were taken in the range from 0.01 to 0.0001%. The investigations were carried out at a direct electron-optical magnification of 18,000–20,000×.

Electron-microscopic investigations showed that Salvarsan, polyacrylamide, and the copolymer based on methyl methacrylate and methacrylic acid form, in dilute solutions, separate secondary aggregates in the form of the molecular bundles mentioned above, of different size and shape. Electron micrographs of such bundles are presented, respectively, in Figs. 1a, 2a, and 3a.

For Salvarsan and polyacrylamide we observe the formation of geometrically regular structures in the form of rectilinearly bounded molecular bundles. The externally regular form of such bundles is noteworthy. Their dimensions are determined, of course, by the magnitude of the molecular weight and by the forces of intermolecular interaction. For Salvarsan, on the basis of the transverse dimensions of the molecular bundles, the dimensions of individual chains, and the distance between them (assuming the densest packing), we find that one bundle consists of 10–50 molecular chains. However, taking into account the fact that we are proceeding from a planar image, and that the bundle naturally has volumetric dimensions, we may suppose at least the square of this number of chains within the bundle.

The data obtained show that a bundle composed of parallel molecular chains retains the flexibility characteristic of individ-

Fig. 1. Salvarsan. 50,000×

Fig. 2. Polyacrylamide. *a* –30,000×; *b* –50,000×

Fig. 3. Copolymer based on methyl methacrylate and methacrylic acid.
a –60,000×; *b* –40,000×

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of an isolated chain. This is evidenced by the fact that, at a certain distance, the bundle loses its rectilinearity in direction, undergoing a coordinated turn through a definite angle. These turns are effected not by a gradual, smooth bending of the bundle, but rather have a "hinged" character. The emergence of such turns can be conceived only as the result of a high degree of order in the arrangement of the molecular chains. Indeed, the process of ordering the chains will lead to the appearance of stresses within the bundle owing to the thermal motion of individual macromolecules. As a result, stresses will accumulate in the bundle, and these will lead to its coordinated turn through a definite angle, according to the all-at-once principle.

It should be noted that the turns of bundles through definite angles, brought about as a result of the appearance of internal stresses, may be the cause of the formation of geometrically regular structures in amorphous polymers. This is the case for the copolymer we studied, based on methyl methacrylate and methacrylic acid. In the case of this copolymer, we observe the formation of geometrically regular polyhedra due to turns of the molecular bundles. It may be thought that the indicated mechanism is the cause of the formation of regular structures in amorphous polymers, also observed for biological systems.

In Figs. 1b, 2b, and 3b are shown microphotographs of the polymers studied, obtained from concentrated solutions. The unfolded secondary structures, whose elements are molecular bundles, indicate that the bundle preserves its individuality at sufficiently high concentrations, where interbundle interaction takes place.

Thus, it has been shown that, in the case of the amorphous polymers studied, there is an ordered arrangement of molecular chains, leading to the formation of rectilinear bundles. The high degree of ordering of the chains in the bundles is also directly indicated by the presence of coordinated turns of the bundles themselves, which have a "hinged" character. Using the example of a copolymer based on methyl methacrylate and methacrylic acid, the possibility of the formation of geometrically regular structures in amorphous polymers through regular turns of bundles was demonstrated.

Thus, the previously formulated supposition that the structure of amorphous polymers should be regarded as a system of ordered molecular bundles has been confirmed.

The authors take this opportunity to express their gratitude to Prof. M. Ya. Kraft and his colleagues for the cellophane kindly supplied by them.

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Received
7 VII 1958

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