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Abstract

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MORPHOLOGY OF THE SUPRAMOLECULAR STRUCTURE OF POLYFORMALDEHYDE

The problem of the relationship between the physicomechanical properties of polymers and the nature of their supramolecular structures has now acquired especially great importance. For many types of crystallizing polymers, a variety of morphological forms of supramolecular structures has been found and, in many cases, their decisive influence on the formation of the physicomechanical properties of polymers. In this respect polyformaldehyde has as yet been little studied. It is known that polyformaldehyde is capable of crystallizing readily owing to the high regularity of its macromolecules (1). The parameters of its unit cell and the conformation of the polymer chains have been determined by X-ray diffraction (2, 3). In polarized light, Maltese crosses were found in films of polyformaldehyde obtained from the melt; these changed depending on the conditions under which the melt was cooled (4). There are no other indications in the literature of a more detailed study of the morphology of the secondary structures of polyformaldehyde.

The present work is devoted to a microscopic study of the types of secondary structures arising from the melt of polyformaldehyde. The initial polymer, in the form of a finely dispersed powder, was applied to glass heated to the melting temperature of the polymer (180°). To avoid thermal destruction, the melt obtained was rapidly cooled to 160° and held at this temperature for 2 hours, and then again slowly cooled to room temperature. The samples obtained by this procedure were examined in a MIM-8M metallographic microscope in reflected light. In a similar way, for various samples of polyformaldehyde, a study was made of the morphology of secondary structures arising in layers of different thicknesses—from hundredths of a millimeter to several millimeters. In the latter case, the conditions for two-dimensional directed growth of the secondary structures were already excluded.

Microscopic study of the samples obtained by cooling the melt showed the unusually high ability of polyformaldehyde to form a great variety of types of secondary structures.

In Fig. 1 (top) are shown photomicrographs of one of the samples of polyformaldehyde obtained by slow cooling of a thin layer, not exceeding hundredths

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

of a millimeter, of the melt of a highly dispersed powder. In this case, very characteristic forms of flat polyformaldehyde crystals with multiaxial symmetry were observed, resembling the icy patterns of water crystals. Owing to the nonuniform influx of substance to the individual elements of the crystal during its growth, we observed a great variety of crystal forms while the equality of the angles between its elements was preserved.

As the thickness of the layer of melt increased (Fig. 1, bottom) to tenths of a millimeter, other forms of secondary structures were found in samples of the same type: all the structures possess a clearly expressed fibrillar structure, as well as distinct and geometrically regular boundaries of separation.

The sizes of such formations are large and range from 50–70 μ to 150–200 μ in diameter. All the types of structures observed by us, from extremely

To the article by I. M. Abramova et al., p. 1047

Fig. 1

Fig. 2

Fig. 3

densely packed polygonal forms to structures with spherical symmetry had a clearly visible three-dimensional character under the microscope. This fact indicates that in this case crystallization of the polymer proceeds not under conditions of two-dimensional directionality of structural growth, but in the bulk.

We observed that, with an increase in the thickness of the melt layer, i.e., in the transition from thin films to the bulk of the polymer, the regularity of the geometric form is gradually distorted and the clear boundary between individual formations disappears (Fig. 2). In thicker layers of the solidified melt, only individual spherulites of fibrous structure could be distinguished, bordering one another by a fringe of fibrils of the peripheral regions, without clear and regular boundaries of separation (Fig. 3, left). It could be assumed that precisely such should be the supramolecular structure of polyformaldehyde blocks obtained under identical conditions. This assumption was confirmed when it proved

Fig. 3

Figure 3: Fig. 3

possible to obtain an etching pattern from the surface of polyformaldehyde in a block (Fig. 3, right).

In microscopic examination of polyformaldehyde specimens with other intrinsic viscosities, both structures of the type described above and structures of a somewhat different character were found. After 3-4 months of storage of some polyformaldehyde specimens under laboratory conditions, a noticeable increase in their melting temperature was observed; at the same time, the character of the supramolecular structures also changed somewhat. In this case, a great variety of forms of secondary formations was no longer observed.

Thus, rich morphological forms of secondary structures of polyformaldehyde, arising in the process of slow cooling of the melt, have been discovered for the first time. It has been shown that polyformaldehyde is capable of crystallizing readily and of giving a great variety of types of supramolecular structures of varying degrees of perfection, which is undoubtedly connected with the high regularity and flexibility of the polymer macromolecules. It has been found that, under certain conditions, polyformaldehyde has the ability to form structures of the highest orders—crystals—the growth of which apparently proceeds by a mechanism close to the crystallization of low-molecular-weight substances.

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Fig. 1. Micrographs of a thin layer of cooled polyformaldehyde melt; layer thickness: top—hundredths of a millimeter (200×), bottom—tenths of a millimeter (500×)

Fig. 2. Micrographs of a thick layer of cooled polyformaldehyde melt (500×)

Fig. 3. Micrographs of the surface of polyformaldehyde in the bulk: (500×); left —the specimen was obtained by cooling the melt; right—a polymer block etched with sulfuric acid.

Note: Figure translations are in progress. See original paper for figures.