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Abstract

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STRUCTURE FORMATION IN CRYSTALLINE POLYSTYRENE

Recently it has become evident that many properties of crystalline polymers depend on their supramolecular structure ($^{1-3}$). By changing the supramolecular structure, one can obtain a polymer possessing different mechanical properties. The objective of the present work was to study the processes of structure formation in crystalline isotactic polystyrene. First of all, the conditions for the formation of supramolecular structures were clarified. For this purpose, the influence of the temperature and time of crystallization on the character and rate of formation of secondary structures was studied.

The object of the investigation was crystalline polystyrene purified by the method described in (^{4}). After purification the polymer was melted on a slide glass, placed in a thermostat, where it was kept for from 10 to 60 min at temperatures from 110 to 215°C. A systematic study of the structure-formation process was carried out at temperatures of 120, 145, and 175°C. These temperatures are the most convenient for studying the structure-formation process, since below 120° crystallization proceeds too slowly, while above 175° the structures that have formed are partially destroyed. The structure formation occurring in the crystalline polymer was observed in polarized light at magnifications from 200 to 600 times. The objects were photographed with a Zenit camera mounted on an MIN-8 microscope.

Figure 1 shows photographs of the supramolecular structures of polystyrene that form during its crystallization for 30 min at temperatures of 120 and 145° and for 15 min at 175°C. From the experimental data presented it is evident that the process of structure formation in polystyrene is a complex process and does not always end with the formation of spherulites.

During the crystallization of polystyrene, along with spherulites, more complex structural forms may be produced. In the optical microscope, formations in the form of "ribbons" or, possibly, "rods" are clearly visible; their dimensions range in length from 25 to 500μ and in width (coinciding with the width of the spherulites formed under the same conditions) from 1 to 120μ (Fig. 2). Subsequently these elongated formations, closely adjoining one another, create plates. The formation of such structures is observed at all the indicated temperatures and proceeds by one and the same mechanism, but at different rates. These differences in the rate of the process lead to the formation of ribbons and plates of different sizes. Variations in the sizes of the supramolecular formations are associated with the fact that the rate of growth of spherulite-like particles, which serve as the initial units in the construction of complex structures, depends on temperature. The spherulite-like particles united into "ribbons" do not lose the ability to grow in width; however (Figs. 1-3, see insert, p. 584) the width of the ribbon in all cases practically coincides with the diameter of the separate spherulite-like particles formed under the same temperature and time conditions; its length, however, is determined by the number of spherulite-like particles participating in its construction.

The influence of temperature on the dimensions and character of supramolecular structures makes it possible to elucidate the mechanism of their formation.

When considering the dimensions of the ribbons formed at 120, 145, and 175° and at identical crystallization durations (Fig. 1), it was found that

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Fig. 1. Secondary structures of isotactic polystyrene formed at different temperatures and different crystallization times: *a* –120°; 30 min., *b* –145°; 30 min., *c* –175°; 15 min. 200×

Fig. 2. Microphotograph of a "ribbon," 200×

Fig. 3. Effect of crystallization duration on the dimensions of secondary structures: *a* –15 min.; *b* –45 min. (crystallization temperature 145°, 200×); *c* –15 min.; *d* –60 min. (crystallization temperature 175°, 600×)

the widest ribbons are obtained at 175°, and the narrowest at 120°; moreover, at this temperature the spherulite-like particles are so small and imperfect that they cannot be resolved at a magnification of 200 times. The ratio of the ribbon length to its width makes it possible to estimate the number of spherulite-like particles entering into it. This ratio depends on temperature and reaches its greatest value at a temperature of 145°.

Let us now consider the influence of the duration of crystallization of polystyrene on the dimensions of the secondary structures. Fig. 3 gives microphotographs of polystyrene specimens whose crystallization took place at 145° for 15 and 45 min and at a temperature of 175° for 15 and 60 min. From the photographs presented it is evident that the duration of crystallization has the same effect on the character and dimensions of the supramolecular formations as does temperature. The longer the crystallization time, the wider the ribbons that form and the smaller the ratio of their length to their width.

Thus, in studying structure formation in crystalline polystyrene, we have come to the conclusion that, during the crystallization of polystyrene and the formation of supramolecular structures, two processes should be distinguished: the growth of spherulite-like particles and their aggregation. In those cases where the number of growth centers is not very large and they do not interfere with one another, crystallization proceeds to the formation of regular spherulites. This is observed at high temperatures and is seen most distinctly at long crystallization times. At low temperatures, when the rate of spherulite growth is small but the number of growth centers of spherulite-like particles is large, their aggregation into ribbons occurs (Fig. 1a). The spherulite-like particles that have combined into ribbons continue their growth only in the transverse directions, as a result of which the width and, possibly, the thickness of the ribbon increase until the ribbons, having closed with one another, form plates, which stops their further growth. The ribbons in the plates themselves may be arranged in a very ordered manner, but their positions in plates superposed on one another do not coincide (Fig. 1b, c).

Thus, our investigations of the microscopic structure of crystalline polystyrene have shown that the formation and disappearance of macrostructures in the crystalline polymer, occurring in the interval 110–215°, leads, depending on the temperature and duration of the crystallization process, to the predominance either of separate, chaotically arranged spherulites or of ribbons consisting of spherulite-like "particles" capable, in their further growth, of packing into plates. One or another ratio of the processes of growth of spherulite-like particles and their aggregation is the cause of the differences in the secondary structures that form. Therefore, in crystalline polystyrene there coexists an enormous number of different types of supramolecular structures that determine the mechanical properties of the polymer.

The investigation carried out opens a route to obtaining systems with a prescribed structure, in which particular supramolecular formations predominate. The emergence of such structures revives interest in true colloidal processes developing in polymer systems. The role of the independent structural unit in this case is played not by individual polymer molecules or bundles, but by spherulite-like formations, whose dimensions correspond to the dimensions of colloidal particles.

The structure formed as a result of aggregation of such particles must have much in common with the structure that arises in the formation of gels or jellies in typical colloidal systems.

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