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Abstract

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CHEMISTRY

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ON THE FORMATION OF LARGE MICROSCOPIC STRUCTURES IN CRYSTALLINE POLYPROPYLENE

In the majority of works published at the present time, the study of the crystallization process of polymeric substances has been carried out either in dilute solutions or in thin films, where the two-dimensional character of the film could not but affect the nature of the structures formed. Of greatest interest, however, is apparently the study of crystalline forms arising directly in the bulk of the polymeric substance, which is of great importance for the processes of formation and processing of polymer materials. Work in this direction has been conducted chiefly along the lines of electron-microscopic investigation of the fine structure of fracture surfaces of crystalline polymers (1–4), and only very recently have indications appeared of the existence, in the mass of a polymeric substance, of secondary structures of microscopic dimensions, revealed in the process of etching a section of a polymer block with poor solvents (5,6).

The present work is devoted to the study of microscopic structures of isotactic polypropylene that arise in the mass of the polymeric substance during slow cooling from the melt. The investigation was carried out on polypropylene samples with a molecular weight of about 100,000. The molten polymer was slowly cooled (at a rate of 0.07 deg/min) to the desired temperature, at which it was then held for 6 hours. The surface of the brittle fracture, obtained by impact deformation of the sample at the temperature of liquid nitrogen, was studied. The investigation was carried out on a metallographic microscope of the MIM-8M type.

As a result of the investigation we have shown for the first time that the process of crystallization in the condensed phase of a polymer can proceed to the formation of very large (40–200 μ in diameter) spherically symmetric structures of the spherulite type, possessing sharply expressed phase boundaries (Figs. 1 and 2). Thus, upon cooling the molten polymer mass, the ordering process, in a relatively short time, manages to reach the formation of perfect crystalline structures. This is impossible to imagine if the polymer melt is regarded as a

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

system of randomly entangled chains. It is evident that already in the molten polymer there must exist a certain preliminary order in the arrangement of the molecular chains, and that during cooling only the completion of this order takes place, ending with the formation of the crystalline phase.

The fact that such large spherulites are formed during the crystallization of a polymer under conditions of high viscosity and, consequently, low mobility of the chains is new evidence for the bundle theory of the structure of polymers, first proposed by V. A. Kargin, G. L. Slonimskii, and A. I. Kitaigorodskii ([7]). According to this theory, polymers in the crystalline and even in the amorphous state are regarded as well-ordered systems, constructed either of globules or of extended chains gathered into bundles ([8]). The crystallization process begins with the crystallization of the bundle, while the formation of the crystalline structure is the last stage of chain ordering. The most perfect crystalline form is

single crystals. But most often the process of crystallization in polymers does not have time to proceed to the formation of single crystals, but stops at the formation of less perfect secondary structures—spherulites. The formation of spherulites is preferable from a kinetic point of view, since this process requires minimal rearrangement of the sluggishly mobile structure of the crystalline polymer. On the basis of the present work, we see that

Fig. 1. Microphotograph of the fracture surface of a polypropylene block crystallized under slow cooling (over 24 hours) from the melt from 180 to 100°

Fig. 2. Microstructure of the tear surface of a polypropylene block crystallized under rapid cooling (over 2 hours) from the melt from 180 to 100°, followed by holding at this temperature for 6 hours.

crystallization in the condensed phase of a polymer can lead to the formation of very large spherulites.

It should, however, be noted that during crystallization of polypropylene in a block, alongside large spherulitic structures, in many cases at various crystallization temperatures we were able to observe very large (over 200 μ) regularly bounded formations that do not possess the radially symmetric form of spherulites and that in outward appearance resemble single crystals (Fig. 3). The results of the investigation of such structures will be the subject of subsequent communications.

Fig. 3

Figure 3: Fig. 3

To determine the influence of the crystallization temperature on the structure of the spherulites formed, the process of crystallization of polypropylene was studied over a wide temperature range. The following regularities were observed:

1. Depending on the crystallization temperature, changes are observed in the sizes of the spherulites. In the temperature range 130–140° there form spherulites whose diameter reaches values on the order of 40–100 μ. The sizes of spherulites obtained at crystallization temperatures in the region of 100° have diameters of 160–220 μ. As can be seen from Figs. 1b and 2, the spherulites possess sharply expressed boundaries of separation.

Fig. 3. Microstructure of the fracture surface of a polypropylene block quenched from the melt in liquid nitrogen. Large formations of the type of single crystals are visible

2. The crystallization temperature also influences the structure of the spherulites. Those obtained at temperatures above 100° possess a lamellar structure. On going to temperatures below 100°, the lamellar character of the structural elements of the spherulites changes to a fibrillar one, up to complete degeneration of the spherulitic formations into a system of entangled fibrils.

The crystalline structure of a polymer substance apparently has a great influence on the character of fracture of the polymer material. In brittle fracture of a polypropylene block in the presence of large formations, fracture possibly proceeds along the boundaries of crystalline grains. An increase in the size of the spherulites should in this case be accompanied by a considerable increase in the brittleness of the material. Indeed, polypropylene specimens in which the spherulites reach values on the order of 200 μ are destroyed much more readily than blocks containing finer crystalline formations. But in many cases, under impact deformation, destruction of the spherulite itself also occurs, and then the lamellar character of the elements of its structure is revealed.

Thus, we have shown that the process of crystallization of isotactic polypropylene in the condensed phase can proceed to the formation of very large spherulites and even single crystals, and that the sizes and character of the structural elements of the spherulites change with changes in the crystallization temperature. Undoubtedly, such crystalline formations have a substantial influence on the properties of the polymer material.

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