DENDRITIC MECHANISM OF FORMATION OF LARGE CRYSTALLINE STRUCTURES IN ISOTACTIC POLYPROPYLENE

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Abstract

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DENDRITIC MECHANISM OF FORMATION OF LARGE CRYSTALLINE STRUCTURES IN ISOTACTIC POLYPROPYLENE

It is known that crystallization of a number of polymers from dilute solutions leads to the formation of plate-type crystals (^{1}). Chain molecules in such crystals have a folded configuration and are arranged perpendicular to the plane of the plate. Recently, in crystallizing isotactic polypropylene from dilute solutions, we obtained crystals of another type, which, in contrast to those named above, had not a planar but a fibrillar structure (fibril diameter of the order of 100 Å) (^{2a}). On the basis of the behavior of fibrillar crystals in the course of deformation (^{2b}), as well as electron-microscopic data on the genesis of individual fibrils with a diameter of the order of 100 Å (^{2v}), it was suggested that crystals of this type are built not from folded polypropylene molecules, but from aggregates of straightened chain bundles with a diameter of the order of 20 Å, by their spiral bending during packing.

In the present work a new type of fibrillar polypropylene crystals is described, built of fibrils with a diameter of the order of 20 Å, in which the molecular chains have a straightened configuration and are arranged along the fibrils.

Two samples were chosen as objects: isotactic powdery unstabilized polypropylene with $[\eta] = 2.8$ and a melting temperature of 165°, and granulated stabilized "Moplen" polypropylene with $[\eta] = 2$ and a melting temperature of 175° (the intrinsic viscosity was determined in decalin at 120°).

The operation for preparing the crystals was as follows: a 0.01% solution of polypropylene in decalin was heated to boiling and quickly transferred to a thermostated cabinet, in which a temperature of 90° was maintained. At this temperature the solution was kept for 3–5 hr.; then drops of it were placed on electron-microscope grids with a carbon film support, located in the same thermostat. After evaporation of the solvent, the grids were removed from the cabinet, the specimen was shadowed with Pt/Pd and examined in a JEM-5G electron microscope.

Results and discussion.

It is known that, in the case of low-molecular-weight substances, rapid evaporation of the solvent from the surface of a drop of solution creates favorable conditions for dendritic growth of crystals ([3,4]). As a rule, it begins from peripheral regions, spreading into the depth of the drop in the direction of the most protruding point of the crystal, and is accompanied by numerous morphological variations.

Examination in the electron microscope of polypropylene samples obtained by the method described above showed that dendrites are also formed in the case of isotactic polypropylene. They grow by lateral branching of the main dendritic trunk, which in this case is a single-stranded fibril with a diameter of 10–20 Å, as well as a ribbon consisting of several fibrils. Depending on the method of branching, dendrites can be divided into two main types. Structures of the first type begin to grow from the edges of the window of the electron-microscope grid and are highly elongated, branched crystals (Fig. 1a). Within this type of crystal, by varying the solvent-evaporation temperature (90–94°), a set of polypropylene dendritic structures was obtained that differ in the frequency of lateral branching, the length of the lateral fibrils, their flexibility, and their ability to aggregate into ribbons.

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Fig. 1. *a* –branched dendrite, *b* –fibrillar rhombic skeleton

Fig. 2. *a* –overgrowth of skeletons in rhombic planes, *b* –simplest bundle-like formations

Fig. 3. *a* –thickening of fibrils in the process of volumetric dendrite growth, *b* –spherulite-like dendrite

Dendrites of the second type can be observed mainly in the central regions of the window of the electron-microscope grid. In contrast to crystals of the first type (Fig. 1a), they develop in such a way that a definite ratio is maintained between the growth rates of the main dendritic trunk and its lateral branches, as a result of which rhombic fibrillar frameworks are formed (Fig. 1b). These frameworks are subsequently capable of being filled in to form rhombic planes (Fig. 2a).

The polypropylene fibrillar dendrites obtained (Figs. 1a, 1b, 2a) possess a number of interesting features, of which we shall first note the following: first, they are all two-dimensional structures and, second, they are built of the finest fibrils, the diameter of which, determined from the shadow of the deposited metal, lies within the range 10–20 Å. On the basis of the morphological features of the structures obtained and the small transverse dimensions of the fibrils composing these structures, one may think that we are dealing with a new type of polymer crystals which, unlike the known structures (of polyethylene, polyoxymethylene, and other polymers [1]) with a folded structure of the macromolecular chain, are built of straightened macromolecules arranged along the fibrils. Electron-microscopic data show that crystals of this type are formed from bundles of straightened molecules (2-5 molecules), which in the micrographs appear as short fibrils 10-20 Å in diameter. If the process of structure formation of polypropylene is carried out at high solvent-evaporation temperatures, of the order of 100° and above, dendritic crystals do not grow; instead, short fibrils 10-20 Å in diameter, as well as the simplest formations consisting of aggregates of a few fibrils, are present on the substrate (Fig. 2b). With a gradual lowering of the solvent-evaporation temperature to 90°, one can observe that a fibril 10-20 Å in diameter is preserved and acts as a structural element in the formation of a fibrillar dendritic crystal. This, in particular, can be seen in Fig. 1a, in which, simultaneously with the grown dendrite, separate fibril bundles are present between its lateral branches. The high resolution of the electron-microscopic images makes it possible to observe directly the mode of packing of the structural elements during dendritic crystallization. It consists in their being fitted one after another and side by side, which proceeds without a change in the configuration of the fibril bundles themselves. As a result, the growing fibrils retain the diameter of the primary structural element, i.e., 10-20 Å, and consequently also the straightened configuration of the molecular chains. Such a mode of packing of fibril bundles is apparently also retained in the case of the volume growth of dendrites. This assumption is based on electron-microscopic data that make it possible to trace the transition of two-dimensional fibrillar dendrites into bulk crystals of complex structure. Figures 3 and 4 show crystals whose growth begins with the formation of a flat fibrillar framework of rhombic shape (Fig. 1b). Experiments have shown that the development of such frameworks into the bulk can proceed in many ways and lead to a great variety of structures. These are, first of all, spherulite-like dendrites (Figs. 3b, 4b). As can be seen in Fig. 3b, they are formed in the case where several dendritic frameworks at once, similar to the structures shown in Fig. 1b, develop from the center of the crystal. In this case the growing dendrites are turned relative to one another in such a way that, as a result, a number of more or less radially directed branches diverge from the center, and cry-

became similar to a spherulite. By superposition of the growing dendritic branches on one another and their interweaving, as shown in Fig. 3a, the crystal thickens. Under conditions of unhindered development, such structures grow strongly, forming in the peripheral regions a flat fibrillar network resembling a cobweb (Fig. 3b). On these crystals, which combine both three-dimensional and flat regions, it proved possible to trace clearly the transition of a two-dimensional structure into a three-dimensional one and, in connection with this, the change in the transverse dimensions of the growing fibrils. At the edges of the crystal the fibrils have a diameter of 10-20 Å. As one approaches the center, one can observe their ever-increasing aggregation into ribbons and superposition on one another (Fig. 3a), accompanied by thickening of the fibrils up to 100 Å and more. In the central regions of the structure, the phenomenon of superposition

Fig. 4. a—rhombic fibrillar crystal; b—spherulite-like dendrite

Figure 1: Fig. 4. a—rhombic fibrillar crystal; b—spherulite-like dendrite

and interlacing takes place not only at the level of individual fibrils 10–20 Å in diameter, but also at the level of fibrillar ribbons, thickened fibrils, and even dendritic branches (Fig. 3b, center of the crystal). This circumstance leads to a substantial complication of the dendritic crystal, in which it is no longer possible to resolve the fine fibrillar-lamellar structure. If several such dendrites grow side by side, they interfere with one another and develop mainly in three dimensions, up to the formation of true spherulites (Fig. 4b), which under an optical microscope appear as spherical particles up to 10–15 μ in size.

Fig. 4. *a*—rhombic fibrillar crystal; *b*—spherulite-like dendrite

Dendrites of another type are shown in Fig. 4a. They are formed, apparently, from flat rhombic skeletons (Fig. 1b) by being superposed on one another in such a way that the branches of one dendrite are located above the branches of another. In this process, a certain ratio of growth rates in two mutually perpendicular directions is maintained, which determines the rhombic faceting of the three-dimensional crystal. It has been found that these dendrites, too, are capable of growing into structures of the spherulitic type.

Thus, these observations show that spherulitic forms of polymer crystals can be formed, along with other mechanisms (5, 6), also by a dendritic mechanism.

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