CHEMISTRY

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1962

SovietRxiv

Abstract

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CHEMISTRY

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SUPRAMOLECULAR STRUCTURES IN FILMS OF ISOTACTIC POLYPROPYLENE

The present work is devoted to the study of structure-formation processes in isotactic polypropylene. An earlier investigation of the supramolecular structures of isotactic polypropylene arising in a block of polymer during slow cooling from the melt showed that the ordering process in this case can proceed as far as the formation of very large secondary structures of the spherulite type, ranging in size from 40 to 400 μ (^{1}). We studied the supramolecular structures formed in isotactic polypropylene films with thicknesses from 30 to 130 μ. In recent years a number of works have appeared devoted to the study of the crystallization process of polypropylene in thin films (from 5 to 60 μ), in which the ability of polypropylene to readily form spherulitic structures of fairly considerable size is noted (^{2},^{3}). In most works, in order to obtain spherulites, the polymer was melted at temperatures of 250–300° and then crystallized in the temperature range from 120 to 160°. It may be thought that at such high melt temperatures only a very small number of crystallization nuclei remain in the polymer mass, which upon subsequent annealing become centers for the formation of spherulites. In the present work an attempt was made to investigate the process of structure formation in polypropylene as a function of the melt temperature and the cooling rate of the films. We succeeded in realizing a great variety of crystalline structures of isotactic polypropylene, having much in common with the supramolecular structures described for polystyrene (^{4}).

The investigation was carried out on unstabilized polypropylene with $[\eta] = 2.8$, and also on granulated stabilized polypropylene "Moplen" with $[\eta] = 2$ (the intrinsic viscosity was determined in decalin at 120°). The structures formed were examined in polarized light on an MIN-8 microscope and in reflected light on an MIM-8M metallographic microscope and an MBI-6 biological microscope. Samples for the investigation were prepared by the following methods.

1. Polypropylene powder or granules were melted between microscope slides in a thermostat at various temperatures and then slowly cooled to the desired temperature.
2. Polypropylene films were prepared by pressing at various melt temperatures (from 180 to 280°), followed by cooling at different rates (from 2.5° in 10 min to 2.5° in 0.5 min).

Figure 3a and 3b

Figure 1: Figure 3a and 3b

3. Already formed polypropylene films were heated for several hours in a thermostat at various temperatures (from 130 to 180°).

As a result of the investigation, spherulitic structures were also found as the principal morphological forms formed by all methods of obtaining crystalline polypropylene films. Melting the polymer at very high temperatures, of the order of 250-280°, leads to the formation of films consisting entirely only of spherulites. The appearance and sizes of the spherulites can vary greatly depending on the crystallization conditions, from 20 to 400 μ. Two main types of spherulites were found (Figs. 1, 2), which differ only in the defectiveness of their structure.

In those cases in which polypropylene powder or granules are melted—

between cover glasses at temperatures 30-40° above the melting temperature of the polymer, and the melt is then slowly cooled (over 5-6 h) to room temperature, spherulites of the type shown in the micrographs in Fig. 1 are formed. Such spherulites are in most cases two-dimensional and are characterized by a pronounced fibrillar structure. The second type of spherulite is formed when films are pressed at melt temperatures from 230 to 280° (Fig. 2b). Very large three-dimensional spherulites of this type can be obtained if an already formed polypropylene film is heated in a thermostat at 180° for 5-10 min so that the film does not flow, and then the thermostat is cooled

a *b*

Fig. 3. *a* —polypropylene film obtained under the same conditions as in Fig. 2a; reflected light. *b* —large intergrowths of spherulites that arose in a polypropylene film prepared by pressing at 230° and a pressure of 30 kg/cm^2, followed by cooling at a rate of 2.5° per 10 min; polarized light

to 80° over 5-6 h. The sizes of the spherulites can reach 400 μ. In Fig. 2a the boundaries between spherulites are clearly visible. On the surface of such spherulites one can discern the fibrillar character of their constituent elements, but, unlike spherulitic formations of the first type, they are more compact and, evidently, less defective.

The presence of two types of spherulites does not exhaust the variety of crystalline structures formed during the crystallization of isotactic polypropylene in films. In many cases we were able to observe the appearance of large elongated structures—spherulitic intergrowths (Fig. 3). Such formations are obtained together with spherulites of the second type. Their sizes depend on the rate of cooling of the film and may reach many tenths of a millimeter. At the same melt temperature, equal to 230°, the largest intergrowths are formed at a cooling

Fig. 1a

Figure 2: Fig. 1a

Fig. 1b

Figure 3: Fig. 1b

rate of 2.5° per 10 min. With more rapid cooling the width of the intergrowths decreases,

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Fig. 1. Surface of a polypropylene film obtained by melting polypropylene powder between glasses at a melt temperature of 195° with subsequent slow cooling (over 5 h). *a* –reflected light, *b* –polarized light

Fig. 2. *a* –surface of a polypropylene film reheated after formation at 180° for 5 min with subsequent slow cooling (over 5 h); reflected light. *b* –polypropylene spherulites formed in a polypropylene film prepared by pressing at 270° and a pressure of 30 kg/cm^2, followed by cooling over 1 h to 80°; polarized light

Fig. 4. Surface of a polypropylene film prepared by pressing at 200° and a pressure of 30 kg/cm^2 and then heated at 138° for 4 h. *a* –reflected light, *b* –polarized light

1a

1b

2a

2b

4a

4b

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their number increases, they come closer and closer to one another, forming entire regions. Direct observation of the process of the emergence and growth of such structures showed that the process of their formation begins with the appearance of a large number of crystallization nuclei of colloidal dimensions, oriented along straight parallel lines located at different distances from one another (Fig. 3). Subsequently, only transverse growth of such a cluster occurs, in both directions from the line of centers. The width of the spherulitic clusters

Fig. 2a

Figure 4: Fig. 2a

Fig. 2b

Figure 5: Fig. 2b

Fig. 4a

Figure 6: Fig. 4a

depends on the number of lines of nuclei that arise. Exactly such formations, but of much larger dimensions, can be observed on the surface of a polypropylene block and at the sites of inclusions of air bubbles during crystallization in the bulk of the polymer substance from the melt. Apparently, supermolecular structures of the cluster type are formed when the temperature of the melt is not high enough to melt a large number of crystallization centers, and the fluctuation swarms existing in the melt become centers for the formation of clusters.

Changing the melt temperature and the cooling rate of the film substantially affects the character of the structures formed. At melt temperatures of about 180-200° and subsequent rapid cooling (over 20-30 min.) to room temperature, large spherulites and clusters do not form in the films. In many cases the structure of the film simply does not become manifest. However, after heating such films at 135-140° for 1-6 hours, the film structure begins to be clearly visible in the form of entangled fibrillar formations (Fig. 4). Apparently, at melt temperatures only slightly exceeding the melting temperature of the polymer, a large number of unmelted fluctuation swarms exist in the melt. During subsequent cooling, intra-swarm crystallization takes place, accompanied by the formation of a new phase and, consequently, by the appearance of interfaces. But with rapid cooling of the melt, further complication of the crystalline structure does not have time to occur for purely kinetic reasons. As a result, a finely crystalline structure of the type of crystallized swarms is fixed in the film. It may be thought that upon subsequent heating of the films at 135-140° there arises considerable molecular mobility of polypropylene ([5]), promoting recrystallization of the existing structures. However, the presence of a large number of crystalline centers determines the formation of only small aggregates of fibrous structure, which often have a preferential orientation. Apparently, the aggregates that arise are analogous to the clusters of spherulites (Fig. 3), whose growth is arrested at the first stages of formation.

Thus, during the crystallization of isotactic polypropylene in thin films, depending on the crystallization conditions, it is possible to realize a great variety of morphological forms of crystalline structures, differing in the character of their

Fig. 4b

Figure 7: Fig. 4b

supermolecular packing. Undoubtedly, such diversity of crystalline forms must be reflected in the mechanical properties of the polymer material. Consideration of the features of the mechanical behavior of different morphological forms in isotactic polypropylene will be the subject of another communication.

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Received18 VI 1962

CITED LITERATURE

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