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1957

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Abstract

Full Text

CHEMISTRY

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COMPARATIVE STUDY OF THE ORDER ARISING IN POLYMERS DURING THEIR CRYSTALLIZATION OR ORIENTATION OF CHAIN MOLECULES

The structure of chain polymer molecules, consisting of identical molecular groupings arranged more or less regularly, sets polymer systems apart as a special group. In contrast to low-molecular compounds, for which the principal source of order is the spatial arrangement of the atomic groupings of the substance under investigation, in polymer systems a high degree of order apparently may also be a consequence of the mutual arrangement of chain polymer molecules. As a result, in polymeric substances order may be attained not only in the process of polymer crystallization, but also through the mutual orientation of chain molecules, irrespective of whether crystallization processes occur in this case or whether crystallization is absent. If one considers the degree of crystallinity of a polymer proceeding only from the geometry of the order present in the specimen, without separating the elements of order, then one may commit the error—unfortunately still widespread—whereby the sharp scattering patterns obtained for a number of plant fibers have been explained by a number of authors as necessarily indicating the crystalline state of the polymer.

Fig. 1. Curves of the distribution of intensity with angle for crystalline and amorphous polytrifluorochloroethylene

In our opinion, it is necessary to distinguish between the elements of order created by the mutual arrangement of chains and the order arising during crystallization. This can be tested in two ways: by studying crystallizing polymers by direct structural methods at temperatures above and below the melting temperatures of crystalline polymers, or by examining -

considering the structure of highly oriented specimens while preserving an unchanged orientation of the polymer under study during its melting and crystal-

Fig. 2. Curves of angular distribution of intensity for crystalline and amorphous terilene

Figure 2: Fig. 2. Curves of angular distribution of intensity for crystalline and amorphous terilene

lization.

The study of crystalline polymers at temperatures above and below the melting temperatures of their crystals was carried out by us jointly with Ermolina, using terilene and polytrifluorochloroethylene as examples. In this investigation it was shown by the electron-diffraction method that the interference patterns obtained from specimens at temperatures above and below the melting temperatures of their crystals have much in common. The coincidence of the principal maxima on the curves of angular distribution of the intensity of coherent scattering for both polymers makes it possible to consider that the polymers studied by us are ordered systems even in the amorphous state. Indeed, in constructing the radial-distribution curves we found that the first maxima on the curves correspond to distances between atoms in the polymer molecule and are a consequence of the regular structure of chain molecules. The last maxima for both polymers studied corresponded to the mutual arrangement of the polymer molecules (Figs. 1 and 2).

Fig. 2. Curves of the angular distribution of intensity for crystalline and amorphous terilene

Thus, for the two polymers studied, we noted that their order in the amorphous state is close to that in the crystalline state, differing in the latter case only by additional elements of order. It is evident that the appearance of order in the mutual arrangement of chains in a polymer already occurs in the amorphous state. In the process of crystallization, additional bonds arise without a substantial change in the order in the arrangement of the polymer chains.

It is considerably more difficult to carry out an experiment for a comparative structural study of oriented polymers that are in the amorphous and crystalline states but that retain the same degree of orientation. In this case it is necessary to prevent the flow of the polymer at high temperatures by creating a sparse but stable structural network, to orient the polymer at a comparatively low temperature, at which the polymer has comparatively high tensile strength, which will make it possible to apply a large force for the orientation of the polymer chains. Then the oriented specimen must be fixed and heated to the melting temperature of the crystals without rupture of the specimen under the influence of the stresses arising in it.

The present investigation was devoted to a comparative study of the order arising in polymers in the process of orientation of molecular chains. In formulating the work, we were interested in finding such conditions under which, in one and the same polymer, it would be possible to preserve an unchanged orientation of the polymer chains when the phase state of the polymer was changed.

Experimental Part

A comparison of the elements of order arising during crystallization of a polymer and during orientation of molecular chains was carried out by us using polyethylene and gutta-percha as examples, by direct structural methods. X-ray-

a b

Fig. 3. Electron diffraction patterns of an oriented polyethylene specimen: *a*—before irradiation; *b*—after irradiation

a b

Fig. 4. Electron diffraction patterns of an oriented specimen of vulcanized gutta-percha:
a—at 20°; *b*—at 70°

The X-ray diffraction patterns were obtained with copper K_α radiation at 38 kV and 14 mA; the electron diffraction patterns were obtained on an EM-4 electron diffractograph at 40 kV.

Films of low-pressure polyethylene, 100–150 μ thick, were obtained by hot pressing. Strips no more than 3 mm wide were stretched to the limit and irradiated with fast electrons using a 200 kV linear accelerator and a current of 20 μA. Polyethylene films 0.01–0.05 μ thick were obtained from a hot xylene solution on the surface of hot glycerin, stretched on special frames, and irradiated with fast electrons in vacuum, likewise using a linear accelerator, or directly in the electron diffractograph.

The required irradiation dose was monitored by simultaneously irradiating unstretched and stretched specimens until complete amorphization of the unstretched polyethylene films. We established that, in the course of irradiation of unstretched polyethylene films, or of stretched films whose ends were not fixed during irradiation, destruction of the crystals occurs and irreversible processes of polymer amorphization take place. When stretched specimens with a fixed degree of extension are irradiated, the interference patterns are characterized by the preservation of a number of reflections. Figure 3 shows electron diffraction patterns obtained for stretched polyethylene films, both initial and irradiated with fast electrons. A similarity was established between the interference patterns for a number of reflections for polyethylene specimens in the crystalline and amorphous states. Thus, it was found possible to separate the reflections of the interference pattern that arise as a result of orientation of the polymer chains, and to determine what part of this pattern is due to simple uniaxial orientation of the polymer chain molecules and what part to the appearance of a more rigorous order during crystallization.

We then carried out experiments with specimens of gutta-percha. Thin gutta-percha films (0.02–0.05 μ thick) were obtained from a solution in a gasolinebenzene mixture on the surface of water. The films were picked up on special frames and vulcanized at room temperature in vapors of sulfur monochloride for 2–5 min, in order to create a sparse but stable network preventing the flow of polymer chains at high temperature.

The films were then stretched by $\sim 150\%$, transferred onto diaphragms with a collodion substrate, and heated directly in the electron diffractograph to temperatures exceeding the melting temperature of the crystals. Figure 4 shows electron diffraction patterns obtained from stretched vulcanized gutta-percha films at 20 and 70°. The interference patterns from molten gutta-percha specimens retain a number of reflections. This interference pattern is a consequence of the orientation of the chain molecules of gutta-percha.

On the basis of the experimental material obtained, in our opinion it has been shown with sufficient reliability that mutual ordering of polymer molecules can arise already in the amorphous state of the polymer. This ordered state is apparently a necessary, although not sufficient, condition for subsequent crystallization.

In addition, the experimental material obtained confirms the possibility of separating the order that arises in a polymer upon orientation of the polymer molecules and upon crystallization. During crystallization of polymers, an additional order arises in the system, but its share is small in comparison with the ordering in oriented specimens.

Physical-Chemical Institute named after L. Ya. Karpov

Received
15 VII 1957

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