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Abstract

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THE FORMATION OF SECONDARY STRUCTURES OF POLYETHYLENE DIRECTLY IN POLYMERIZATION PROCESSES

Modern views on the structure of polymers in the condensed phase, developed by Kargin and Slonimskii (^{1,2}), have received repeated experimental confirmation. However, in all known cases the study of supramolecular structures was carried out on specimens obtained by transferring the initial polymer through a melt or through a solution. We have obtained confirmation of the structural scheme of a crystalline polymer by tracing secondary structures from the elementary form of supramolecular formations—the bundle—to higher forms arising directly in the process of polymerization.

The object of the study was polyethylene obtained in benzene at 60° and a pressure of 10 atm, using as catalyst partially chlorinated metallic aluminum, according to Radzivanovskii (^{3}), in the form of thin shavings in a mixture with the α-modification of titanium trichloride. A curious feature of the process proceeding under these conditions was that, in the course of the reaction, the polymer grew on the surface of the aluminum as a layer up to 4–5 mm thick. The general appearance of the polymerization product is shown in Fig. 1a (see insert facing p. 782). The internal structure of the reaction product enveloping the aluminum shaving is visible in a longitudinal fracture (Fig. 1b). The photograph shows the fibrous structure of the polymer, the growth of the fibers proceeding independently of one another perpendicular to the surface of the metal (the dark horizontal band in the center). In those cases where fiber growth was not restricted by neighbors, a bush-like character of growth was observed.* A separate fiber, freed by preparation, is shown in Fig. 1c at a magnification of 1350 in polarized light. A distinctly transverse-banded structure with a period of 1.5 μ is clearly visible.

Specimens for electron microscopy were prepared by a specially developed method involving vigorous dispersion of polyethylene fibers in water. After separation of coarse particles, a drop of the suspension was deposited on a collodion substrate and dried at room temperature. In this process, particle forms such as those shown in Fig. 2a were observed. This type of formation is a strip coiled along a helical line, with clearly expressed transverse folding. On more detailed examination (Fig. 2b) it is found that each fold in turn possesses

Fig. 3. Curves of the molecular-weight distribution of polyethylene

Figure 1: Fig. 3. Curves of the molecular-weight distribution of polyethylene

a transverse structure, especially clearly visible at the edges. Estimation of the dimensions of the indicated elements makes it possible to trace the multistage development of the supramolecular structure of the polyethylene obtained.

The thickness of the transverse formations resolved in the electron-microscopic images is 150-250 Å, which corresponds to the probable dimensions of the thickness of a bundle (^{4}). It is clearly seen that the bundles form ribbons, which appear in the photographs (Fig. 2) as transverse folds on the—

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* It is interesting that if the aluminum wire in the catalyst is replaced by a finely dispersed powder, a similar picture is not observed, and in external appearance the polymer obtained is analogous to low-pressure polyethylene obtained in the presence of the catalytic system $Al(C_2H_5)_3 + TiCl_4$.

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Fig. 1. Polyethylene obtained in the presence of the catalytic system α-$TiCl_3 +$ $(Al + HCl)$ at 60° in a benzene medium:
a —general view (5×); *b* —longitudinal fracture of the polymer product (53×); *c* —monofilament isolated from the polymer product (1350×).

Fig. 2. Electron-microscopic photographs of dispersed polyethylene.

strip. The period of bending of the strip corresponds to 3.5–4.5 μ, and this dimension is of the same order as the width of the fold of the monofilament shown in Fig. 1 . The coincidence of these dimensions permits one to suppose that the indicated fragments are identical. Comparison of photographs 1 and 2 leads to the assumption that the strips making up the fiber are in it in a stressed state. After destruction of the fibers during dispersion, the strips straighten somewhat, assuming the form of a helical line. Such a multistage structure fully corresponds to the scheme of the structure of the crystalline phase of polymers proposed by Kargin and Slonimskii in the monograph (^{2}). It is possible that the character of the packing of the polymer chains in the present case is influenced by the force fields of dislocations exposed when aluminum is treated with hydrogen chloride.

Fig. 3. Curves of the molecular-weight distribution of polyethylene

The integral and differential curves of the molecular-weight distribution are shown in Fig. 3. From the data presented it follows that the polyethylene consists mainly of polymer homologues with a number-average molecular weight of the order of 100,000.

The temperature interval of melting, the heat of fusion, and the degree of crystallinity, estimated thermographically, were 121-132°, 35.9 cal/g, and 67%, respectively. The density of the sample studied was 0.955 g/cm^3. The relatively low degree of crystallinity is probably explained by distortions of its lattice caused by numerous bends of the packets.

Analysis of the multistage structure described above, formed directly in the process of polymerization, confirms not only the validity of the scheme of the structure of the crystalline phase of polymers (^{2}), but also the correctness of the earlier suggestion (^{1}) that the appearance of internal stresses should be reflected in the shape of the crystals.

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