Reports of the Academy of Sciences of the USSR

M. B. Konstantinopolskaya, Z. Ya. Berestneva,

1963

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1963. Volume 151, No. 5

CHEMISTRY

M. B. Konstantinopolskaya, Z. Ya. Berestneva,
Academician V. A. Kargin

On Fibrillar Single Crystals in a Copolymeric Polyamide

At present the process of structure formation in polymers has been studied rather fully for polyethylene (^{1}) and polystyrene (^{2}). It has been established that crystallization of these polymers proceeds in many stages, i.e., crystals cannot grow by the addition to a nucleus of individual molecules of different length and shape. In the first stage of crystallization, owing to intermolecular interaction during aggregation of molecules, nonequilibrium crystalline formations of regular geometric shape (bundles) arise; these are the basic structural units from which crystals are built. Ultimately, the process of structure formation in polymers is determined by the structure of the macromolecular chains and by the character of the intermolecular interaction between them. It was therefore of interest to follow the process of structure formation in a polyamide, where the forces of intermolecular interaction are of the order of hydrogen bonds. As the object of study, a copolymer of capron and nylon with sebacinamide was chosen. The work was carried out on a JEM-5J electron microscope.

It is known that in regular polyamides plate-like crystals arise rather easily (^{3}). In the case of a copolymer, in the presence of strong intermolecular interaction, the regularity of the chain is disturbed; therefore amorphous specimens are readily obtained and the crystallization process proceeds rather slowly.

When specimens are prepared from a boiling solution of the polyamide in ethyl alcohol, with rapid evaporation of the solvent, films of amorphous structure are obtained. If, however, the specimens are prepared in a desiccator over solvent vapors, which slows the process of its evaporation to several hours, films consisting of spherulites are obtained. In order to regulate the time of solvent evaporation and the temperature of specimen preparation, ethylene glycol, which has a considerably higher boiling point, was chosen as the solvent. The specimens were prepared as follows: a boiling solution of the polyamide in ethylene glycol was deposited on a carbon substrate at various temperatures.

Figure 1a presents crystals of the copolymer obtained at a substrate temperature of 90°. The crystals have a fibrillar structure. In Fig. 1b one ray of a crystal is enlarged. The surfaces of the crystal, consisting of intergrowths of fibrils, are clearly visible. Figure 1c shows a microdiffraction pattern taken from a single crystal of the copolymer. Sometimes large intergrowths of crystals arise on the film (Fig. 2, see insert, p. 1222).

At a substrate temperature of ~100°, well-faceted crystals are not formed. However, in the micrographs crystal nuclei are found, and it is seen how fibrils attach themselves to them; in doing so, the fibrils are oriented with respect to the substrate at different angles (Fig. 3a). A further increase in temperature leads to the appearance of less regular formations of the type of banded structures (Fig. 3b). It should be noted that at all substrate temperatures from room temperature to 180° only fibrillar formations arise; among them, the crystals also have a fibrillar structure.

The influence of temperature on the crystallization of the copolymer can be explained as follows: the nature of the secondary structures that form is determined by the degree of supersaturation of the solution, while the degree of supersaturation of the solution is determined by two factors: the solubility of the polymer as the temperature changes and the rate of evaporation of the solvent at the given temperature. At a substrate temperature of 90°, the evaporation time of the solvent is sufficiently long (~15 min.), and the principal role in the process of structure formation of the copolymer will be played by the rate at which supersaturation of the solution is reached, depending on the solubility of the polymer. Therefore, at a temperature of 90° the crystallization process proceeds to the formation of well-defined crystals.

With an increase in the substrate temperature, the evaporation time of the solvent decreases (~5 min.), which affects the nature of the structures obtained. Well-defined crystals are not encountered, but their individual structural elements are visible.

Thus, in the copolymeric polyamide it has been possible to follow the process of formation of typical fibrillar crystals. Owing to the irregularities present in the chains of the copolymer, the primary structural elements that arise are arranged into fibrils, and the subsequent process of structure formation proceeds by the regular packing of fibrils until single fibrillar crystals arise. It is interesting that in this case there is no formation of lamellar crystals obtained from regularly built polyamides ([3]), since in the copolymer the sequence in the structure of the chain may be disturbed, which affects the construction of the primary structural elements and their subsequent mutual packing.

Thus, using the example of polyolefins, polystyrene, polyamides, and copolymers of polyamides, one can trace all the features of structure formation in polymers as a function of chain structure. In regular polyolefins, lamellar single crystals arise rapidly and easily, but it is difficult to obtain an amorphous polymer. In polystyrene, where there are already considerable irregularities in the chain structure and greater intermolecular interaction, crystallization proceeds slowly, so that it is possible to trace the entire process of structure formation from the appearance of amorphous fibrils to lamellar crystals. In copolymeric polyamide, owing to considerable irregularities in the chain structure and still greater intermolecular interaction, only fibrillar crystals are formed by direct ordering of the fibril. In this case it is not possible to obtain separate planes and lamellar single crystals. In passing to the limiting case—rigid-chain polymers of the cellulose type—because of the low mobility of the structural elements, the process of structure formation does not proceed beyond the appearance of fibrils of amorphous structure.

Physicochemical Institute
named after L. Ya. Karpov

Received
6 V 1963

CITED LITERATURE

1. M. B. Konstantinopolskaya, Z. Ya. Berestneva, V. A. Kargin, *Koll. zhurn.*, **25**, 174 (1963).
2. V. A. Kargin, T. A. Koretskaya, T. A. Bogoevskaya, *DAN*, **149**, No. 2, 370 (1963).
3. D. V. Badanii, P. H. Harris, *J. Polym. Sci.*, **41**, No. 138, 540 (1959).

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