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CHEMISTRY

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THE NATURE OF CRYSTALLINE ELASTIC COPOLYMERS OF ETHYLENE

Recently it has been established that polymers, including elastomers, possessing flexible chains are ordered systems. Even in noncrystallizing rubbers, ribbon-like structures on the order of 1000 Å were found ([1]). Consequently, all physicochemical characteristics of polymers must now be interpreted not only at the molecular level, but also taking into account the existence of supramolecular structures in polymers. Work devoted to studying the relationship between mechanical properties and polymer structure is only now developing. For crystalline polymers it is already known that their mechanical properties are related to the structure and dimensions of supramolecular structures ([2]). But a whole series of questions still remains unclear. Thus, it is generally accepted that crystallization of a polymer leads to a loss of elastic properties (which in a number of cases is indeed justified). However, cases are already known in which even a comparatively high degree of crystallization does not lead to loss of elastic properties, for example chloroprene rubbers ([3]). This gives rise to the suspicion that the loss of elastic properties may be connected not with crystallization itself, but with the emergence of higher supramolecular structures, primarily spherulites. It is possible that the initial stage of crystallization, when well-formed crystalline bundles of chains or fibrils arise in the polymer, may be accompanied by preservation of elastic properties. To clarify these questions it is necessary to observe the picture of the gradual transition from well-formed crystalline spherulitic structures to a possibly more disordered amorphous body.

In the present work, for this purpose, copolymers obtained on the basis of a well-studied crystalline polymer were selected as the object of investigation—statistical copolymers of ethylene and vinyl acetate with various ratios of monomeric units ([4], [5]). With the gradual introduction of a second component into the polyethylene chain, it is possible to trace the entire transition from a purely crystalline to an amorphous body.

Electron-microscopic investigation showed that, in copolymers with a content of vinyl acetate units up to 25 mol. %, no noticeable difference is observed in the electron-microscopic picture from that of pure polyethylene. The crystallographic lattice of copolymers with a content of vinyl acetate units up to 25 mol. % is identical with the lattice of low-density polyethylene. The far reflections disappear, while the values of the interplanar spacings are preserved. A further increase in vinyl acetate units leads to complete amorphization of the samples.

If one takes into account that the relative activity of vinyl acetate in radical copolymerization with ethylene is equal to unity, i.e., the vinyl acetate radical adds with equal ease both its “own” and a “foreign” monomer, then it may be assumed that in the copolymer molecule there will not be a strictly statistical distribution of monomeric units, but, apparently, blocks of 2-3 vinyl acetate units will also be present. It follows from this that

To the article by V. A. Kargin, M. B. Konstantinopolskaya et al., p. 112

Fig. 2. *a* —film of low-density polyethylene; *b* —polyvinyl acetate, leached from an acid solution; *c* —copolymer of ethylene with vinyl acetate containing 10 mol.% vinyl acetate; *d* —the same with 14 mol.% vinyl acetate; *e* —the same with 14 mol.% vinyl acetate at 90°; *f* —the same with 60 mol.% vinyl acetate, obtained at −50°.

the minimum number of methylene units in their sequence at which crystallization can still occur lies within the range 6-10, which agrees well with Flory’ s ideas (⁶).

Table 1

EVA content in copolymer, mol. %	Melting point, °C	Tensile strength, kg/cm^2	Relative elongation, %	Residual elongation, %	EVA content in copolymer, mol. %	Melting point, °C	Tensile strength, kg/cm^2	Relative elongation, %	Residual elongation, %
0	105	90	100	100	13.5	–	–	1200	400
3	100	95	200	–	14	70	90	1300	350
7	90	100	500	–	15	–	–	1300	400
8	–	–	720	300	18	50	70	1300	–
10	80	110	1000	–	25	Soft resin at room temperature	Soft resin at room temperature	Soft resin at room temperature	Soft resin at room temperature

Fig. 1. Graph of crystallinity (a), strength (b), and relative elongation at break (c) as a function of copolymer composition

Figure 1: Fig. 1. Graph of crystallinity (a), strength (b), and relative elongation at break (c) as a function of copolymer composition

However, acetate groups, owing to steric factors, create considerable defectiveness in the crystalline structure of the polymer. At a vinyl acetate content of 25 mol.%, the steric factor becomes predominant and the polymer does not crystallize at all. The results of mechanical tests are given in Table 1.

If the strength and deformation curves are superimposed on the crystallinity curve calculated from X-ray data ([7]), it is seen that the strength maximum occurs at 30% crystallinity of the specimen (Fig. 1). At the same time, it gives relative elongations of 1000% with residual elongations of 400%.

Fig. 1. Graph of crystallinity (*a*), strength (*b*), and relative elongation at break (*c*) as a function of copolymer composition

For a more detailed clarification of the morphological structure of copolymers at different vinyl acetate contents, the processes of structure formation in the copolymers and in their constituent homopolymers were studied by the electron-microscopic method. Films of copolymers obtained on hot water were investigated. The specimens were prepared under identical conditions, i.e., in the temperature interval above the glass-transition temperature and below the melting temperature of the polymer.

Figure 2a (see insert to p. 97) shows a typical microphotograph of low-density polyethylene. Only well-formed spherulitic structures are visible in the field of view. The second polymer—polyvinyl acetate, precipitated from solution in xylene at various temperatures—gives, in the electron microscope, a picture of amorphous spots (Fig. 2b). The introduction of even a small amount of vinyl acetate (up to 5 mol.%) into the main chain of low-density polyethylene changes the electron-microscopic picture. Along with spherulites, less ordered structures of the fibrillar type coexist. Increasing the vinyl acetate content to 10 mol.% leads to the appearance of defective, poorly formed spherulites. The main mass of the substance crystallizes in the form of fibrillar structures and bundles (Fig. 2c). At a vinyl acetate content of up to 14 mol.% in the copolymer film, only remnants of spherulites can be observed, along with the main mass of fibrillar structures (Fig. 2d). Thus, copolymers capable of crystallizing are qualitatively characterized by two types of morphological structures—spherulites and fibrils. However, as the content of vinyl acetate units increases, the quantitative ratio of these structures changes toward an increase in fibrillar formations. In addition, as is evident from the pre-

···the given figures; the spherulites formed in this case decrease in size. At a vinyl acetate unit content of 25 mol.%, only ribbon-like structures, similar to those discovered in rubbers (8), are visible in the electron-microscopic images.

If specimens are applied above the melting temperature of the copolymer, ribbon structures are formed (Fig. 2d). It is clearly seen in the figure that the ribbon-like structures are not homogeneous, but in turn consist of smaller structures oriented perpendicular to the axis of the ribbon. The entire field of view is strewn with similar structures. If, however, specimens of a deliberately amorphous copolymer (60 mol.% vinyl acetate content) are prepared at a temperature below the glass-transition temperature (−50°), then, along with drops of the substance, fibrillar structures arise (Fig. 2e).

The nature of the solvent has practically no effect on the crystallization process of the copolymer.

Let us compare the mechanical characteristics of the copolymers with the electron-microscopic picture. A film of pure polyethylene is hard, has no elasticity, and structurally consists only of spherulitic structures. Already at a vinyl acetate content of 8-10 mol.% reversible deformations appear, although the residual deformations are still considerable. In addition, the copolymer of this composition has maximum strength, which corresponds to the electron-microscopic picture consisting of the remains of spherulites and fibrils. A further increase in the vinyl acetate content to 14 mol.% leads to a sharp increase in reversible deformations, although the residual deformations are still large. The strength decreases somewhat, but remains within the strength limits of pure polyethylene. The structural picture changes toward an increase in fibrillar formations. Consequently, there exists a large range of copolymer compositions (8-20 mol.% vinyl acetate) in which, during crystallization, the higher forms of supramolecular structures characteristic of polyethylene do not arise; instead only primitive structures are obtained, consisting of linear structural formations—bundles and fibrils. Nevertheless, such copolymers, despite the crystallization processes occurring in them, possess elastic properties. It may be assumed that the presence of fibrillar structures, as well as the absence of highly organized supramolecular structures, determines the capacity of the copolymers for reversible deformations. The elastic properties of copolymers of this composition can be explained by the high mobility of the elements of the structures that arise. In addition, the presence of a small number of nuclei of spherulites, along with the main mass of fibrillar structures, creates, as it were, a self-reinforced system of increased strength, in which the role of the reinforcing element is played by the more highly organized structures of the copolymer itself. Thus, the optimal properties of the copolymer lie not in the region of completely amorphous specimens, but in the boundary region of compositions, where the copolymer is still capable of crystallizing but does not form large, perfect structures because of steric factors created by the acetate groups introduced into the polyethylene chain. It may very well be that primitive crystalline structures consisting of linear structural formations—bundles and fibrils—are the most advantageous structural state of the polymer for obtaining optimal properties.

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

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