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ELECTRON-MICROSCOPIC STUDY OF CRYSTALLINE POLYVINYL CHLORIDE

As is known, the morphological forms of crystalline polymers depend on the conditions that affect the kinetics of their formation. The diversity of forms that may be encountered in polymers, depending on the methods of obtaining crystalline preparations and on the nature of the polymer, has been set forth rather fully in works (1-6). However, there are no data in the literature on the morphology of crystalline polyvinyl chloride, since until recently a method for obtaining a highly crystalline product was unknown.

The synthesis of polyvinyl chloride of a high degree of crystallinity made it possible to carry out (7) an electron-diffraction study of this product. The present work presents the first data on an electron-microscopic study* of highly crystalline polyvinyl chloride obtained by the method of free-radical polymerization in aldehyde solutions. The crystalline structure of the polymer studied is confirmed by an electron diffraction pattern containing 20 distinct reflections in the range of interplanar spacings 5.27-1.21 Å. The limiting viscosity number, determined in a cyclohexanone solution at 25° C, was 0.1.

Preparations for the electron-microscopic study were made from solutions of the polymer in cyclohexanone (0.5%). A drop of the solution was applied to the surface of distilled water previously saturated with cyclohexanone. The film formed on the surface was caught on a collodion support. Samples in the amorphized state (the film was dried at room temperature) and in the crystallized state (the film was heated above the glass-transition temperature of the polymer) were subjected to electron-microscopic examination. Heating was carried out at temperatures of 80, 100, and 120° C for different durations. The crystallinity of the heat-treated samples was qualitatively assessed by electron diffraction.

The unheated sample, whose electron diffraction pattern indicated an amorphous state (Fig. 1a, see insert, p. 1325), gives the electron-microscopic picture shown in Fig. 2a, b (see insert, p. 1325). Heating the sample at 100° for as little

as 30 min leads to the appearance of dense formations consisting of parallel ribbons (Fig. 2c). Their appearance is associated with crystallization of the sample, as evidenced by the appearance of sharp lines in the electron diffraction pattern (Fig. 1b). Increasing the duration of heating leads to an increase in the number of these formations, as well as to an increase in their size. The structure of such formations reaches maximum crystallinity, as indicated by an electron diffraction pattern containing a large number of sharp lines (Fig. 1c). It is noteworthy that the ribbon-like formations are arranged predominantly parallel to one another in small groups. In a number of cases the ribbons closely adjoin one another, separating only at the edges. The pointed ends of the ribbons diverge slightly and then bend slightly toward one another.

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* The study was carried out on a TESLA BE-242 M electron microscope.

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Fig. 1. Electron diffraction patterns of polyvinyl chloride films: **a**—unheated specimen; **b**—specimen heated at 100° for 30 min.; **c**—specimen heated at 100° for 4-5 hr.

Fig. 2. Micrographs of polyvinyl chloride films: **a, b**—unheated specimens; **c**—specimen heated at 100° for more than 30 min.; **d**— "pincer-like" formation; **e**—formations in the form of "macropackets" ; **f**—formations in the form of "accordions"; **g**—specimen heated at 120°; **h**—specimen shadowed with chromium; **i, k, l, m**—specimens heated at 80°.

Fig. 3. Micrographs of polyvinyl chloride films: **a, b**—specimens after etching; **c, d**—specimens after fracture of the substrates.

Such formations resemble pincers in their outlines (Fig. 2z). Some formations do not have this pincer-like shape. In this case the arrangement of the ribbons very strongly resembles the scheme of macromolecular packing in a bundle (Fig. 2d). In such a "macrobundle" the parallelism is preserved along its entire length, including the bends; moreover, a reduced density is observed at the bends, which is apparently connected with the known fact of an increase in the defectiveness of the crystalline structure at the sites of bends ([8]). In other cases the ribbons, while retaining parallelism, diverge over a considerable distance, and between them there are formations of the same kind, but having a lower density and somewhat blurred contours (Fig. 2e). In external appearance such a group resembles an elongated accordion.

Heating at 120° does not lead to a noticeable change in morphology as compared with heating at 100°. One may note a greater elongation of the "accordions," and also, sometimes, the absence in them of one of the marginal dense ribbons (Fig. 2zh).

It is very important to note the formations that are encountered rather often

during crystallization in the temperature region above 100°, especially clearly visible when shadowed with chromium (Fig. 2d). They possess a relief, folded structure and resemble an accordion with a parallel arrangement of ribbons. Their difference from the above-mentioned formations consists in the fact that the ribbons lying inside are as dense and distinct as the marginal ones. Such a formation, apparently, can be interpreted, using the terminology of V. A. Kargin and G. L. Slonimskii ([8]), as a petal.

It seemed of interest to investigate the character of the morphological formations during crystallization of the polymer near the glass-transition temperature (80°), which we determined from thermomechanical curves. During crystallization under these conditions, the appearance of more regular crystalline formations with rather sharp boundaries is observed. In Figs. 2i–m the individual phases of the multistage process of formation of such structures are presented.

It is evident that they may have the form either of a more or less perfect triangle (Fig. 2i) or of a rhombus (Fig. 2m), as well as a form intermediate between them (Fig. 2k, l). The background of the micrographs is also noteworthy. On the unheated specimen shadowed with chromium (Fig. 2a, b), two forms of formations are visible: fancifully curved bands and regular circles. Shadowing clearly shows that these formations are in relief, and the round formations have the form of disks. Similar disk-shaped formations are encountered in almost all micrographs, including those of heated specimens. It is seen that all crystalline formations are located within the limits of the disks, only in individual cases protruding slightly beyond them.

For a more detailed study of the character of the morphological forms of crystalline polyvinyl chloride, the surface of crystallized films was etched with dichloroethane. Etching with dichloroethane vapor for 1.5 hours at 30° did not lead to a noticeable change in the morphology of the crystallite formations. Treatment of the preparations with liquid dichloroethane for 1–2 min, followed by drying of the films at room temperature, led the crystallite formations to the appearance shown in Fig. 3a, b (see insert, p. 1325). It is evident that the polymer substance between the marginal ribbons is completely washed out by the solvent, which indicates its less perfect crystalline structure. Of interest is the character of the etching of the ribbons themselves, which after etching reveal a transversely folded structure. Estimating the thickness and length of these transverse formations (300 Å–800 Å, respectively), one may suppose that they are bundles of polymer, and their arrangement in the ribbon fits very well into the mechanism of ribbon formation proposed in work ([8]).

It is interesting to note that after etching the surface of the background, consisting of disks, changed; in this case a fibrous structure appeared. Na-

the observed microfibers, in appearance, resembled the transverse formations mentioned above, from which the ribbons are composed. In all probability, owing to the corresponding kinetic conditions, such formations could not produce more perfect forms (ribbons). Thus, it may be assumed that the total electron

diffraction of well-crystallized polyvinyl chloride is contributed to not only by crystalline formations having the variety of forms noted above, but also by the dense background components revealed by etching.

We also attempted to test the strength of the crystalline formations by rupturing the substrate at the site of their location. This was most conveniently done directly in the electron microscope, subjecting the specimen to strong electron irradiation. Under the action of electrons, the substrate film together with the specimen begins to tear, and from the propagation of the tear around and within the crystalline formation one can judge the relative strength of its various regions. In all cases, when the propagating tear comes right up to a crystallite, it either stops or begins to bend around the crystallite (Fig. 3b, e). In a number of cases, rupture of crystalline formations of the "accordion" type is observed along the lines separating the ribbons.

In conclusion, it may be noted that in films obtained from a solution of crystalline polyvinyl chloride in dichloroethane, no new (as compared with those described) morphological forms were found.

As a result of the investigation, polymorphism has been traced for highly crystalline polyvinyl chloride. A variety of morphological formations has been shown: "macropacks," folded formations, triangles and rhombi common for polymers, as well as disk-like formations constituting the background of the specimens. It has been established that etching of the specimens reveals the transversely folded character of the structure of the ribbons, while rupture of the specimens has revealed the high strength of the crystalline formations.

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CITED LITERATURE

1. V. A. Kargin, N. F. Bakeev et al., *Vysokomolek. soed.*, **2**, No. 8, 1280 (1960).

2. E. Ya. Berestneva, M. B. Konstantinopol' skaya, V. A. Kargin, *Vysokomolek. soed.*, **2**, 1715 (1960).

3. P. V. Kozlov, N. F. Bakeev et al., *Vysokomolek. soed.*, **2**, 421 (1960).

4. Keller, *J. Polymer Sci.*, No. 7, 3 (1959).

5. V. A. Kargin, I. I. Gorina, *DAN*, **139**, 1371 (1961).

6. P. H. Till, *J. Polym. Sci.*, **24**, 301 (1957).

7. D. N. Bort, E. E. Rylov et al., *Zhurn. strukturn. khimii*, **2**, 615 (1961).

8. V. A. Kargin, G. L. Slonimskii, *Introduction to the Physical Chemistry of Polymers*, Moscow, 1960, p. 118.

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