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Physical Chemistry

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1961

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Abstract

Full Text

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Investigation of Secondary Structures Formed in Capron Fibers

It is known that the properties of fibers and articles made from them can change substantially during use as a result of a number of processes taking place in the polymers themselves. One of the processes leading to deterioration of the physicomechanical properties of fibers is the formation of secondary structures. Naturally, in order to prevent or reduce the intensity of such phenomena, it is necessary to know the mechanism of these processes. Despite the importance of this problem, the formation of secondary structures has been little studied.

In the literature, the crystallization processes of various polyamides from dilute solutions have been investigated in the greatest detail, and the formation of secondary structures has been established ([1],[2]). During slow crystallization, various forms of secondary structures were formed, from spherulitic formations to individual crystals. Of great interest is the study of the conditions for the formation of secondary structures during crystallization of polyamides in the condensed phase. The present work is devoted to this question.

Objects of the Investigation and Experimental Procedure

As objects of investigation we used capron monofilaments (approximately 1 mm thick), drawn fivefold. Such a monofilament is convenient because it makes it possible to follow secondary structures arising in different layers of the fiber, from the surface to its center, in the transverse direction.

The recrystallization process in the fiber was carried out by annealing; preliminary measures were taken to prevent shrinkage of the fiber and oxidation of the object during heat treatment. Annealing was carried out at 205° (the melting temperature of capron is 215°). At this temperature the specimens were held for 1–1.5 hours and then slowly cooled to room temperature. In all, the recrystallization process was carried out over 10 hours.

To study secondary structures during recrystallization of the fiber, the method of ultrathin sections was used. Sections from different regions of the fiber were obtained by a procedure developed by us on a Söstrand Ultra-microtome LKB-Producter. Sections were obtained both from recrystallized oriented capron fibers and from the initial, unrecrystallized but oriented monofilaments. To make sure that the structure of the specimens being sectioned did not change

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Fig. 1

Figure 1: Fig. 1

appreciably during cutting, sections were obtained at different positions of the cutting edge of the knife relative to the fiber axis. For example, longitudinal sections were obtained in two ways: 1) the fiber axis was positioned perpendicular to the knife edge, the knife in this case moving parallel to the fiber axis; 2) the fiber axis was positioned parallel to the knife edge, which advanced onto the specimen as if from the side.

Ultrathin sections about 200 Å thick were studied with a UEMB-100 electron microscope. From the micrographs obtained it was established that the appearance of longitudinal sections obtained by the two methods indicated above is the same.

Experimental data and their discussion

In studying sections of the original oriented capron fiber, we found that in the oriented fiber there apparently exist only small secondary structural formations. The large structural formations present in capron fiber are destroyed during its orientation.

Fig. 1. *a* —large flat spherulites of capron from longitudinal sections; *b* — elementary microfibrils encountered in transverse sections of the fiber

Figure 1a presents a micrograph of a longitudinal section from the surface layer of the fiber. During recrystallization, large spherulitic formations are produced; they do not have a spherical shape. In studying transverse sections of the surface layer of the fiber, individual bundles were found. This may serve as evidence for the formation, in the surface layers of the recrystallized fiber, of flatter spherulites. In sections obtained from the inner layers of the fiber, both in the longitudinal and in the transverse direction, more perfect crystalline formations are observed. In Figs. 1b, 2, and 3, micrographs of sections of recrystallized capron fiber are presented, from which it is evident that diverse forms of secondary structures are formed at the expense of elementary microfibrils. The microdiffraction data obtained by us from these specimens make it possible to suppose the following process: first, crystalline microfibrils are formed, the minimum dimensions of which reach about 100 Å in width and several microns in length. Then branching of the elementary microfibril is observed, with the formation of individual bundles and complex spherulitic structures, up to the occurrence of separate, well-bounded crystals. The dimensions of these secondary structures, even for the same forms of structural formations, may be different. The interaction existing between several growing crystalline nuclei and the presence of various kinds of structural defects in the solid polymer specimen are probably the principal reasons why the secondary structures, even for one and the same form, have unequal dimensions.

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Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

We were also able to observe, during recrystallization of the specimens, the appearance of more complex structural formations, which have dimensions of tens of microns. These secondary structures apparently form as a result of the arrangement of elementary crystalline microfibrils in a definite

Fig. 2. Transverse sections of secondary structures of kapron consisting of microfibrils

order. Figure 2 shows microphotographs of transverse sections of such structural formations. In transverse sections of recrystallized specimens of kapron fiber, lamellar crystals are often observed

Fig. 3. Crystalline formations of kapron from transverse sections. *a* –lamellar crystals, *b* –aggregates of crystals

(Fig. 3*a*); sometimes these lamellar crystals, joining with one another, form large crystalline aggregates. It seems to us that the lamellar crystals also arise at the expense of crystalline microfibrils. In some cases we found that, alongside the lamellar crystals, there are also microfibrils arranged in a disordered manner. Apparently, they are formed when the lamellar crystals are destroyed by the action of the knife during the cutting process. In sections obtained both in the longitudinal and in the transverse directions of the oriented recrystallized fiber, clearly bounded individual crystals are visible. In some cases we found aggregates of such crystals (Fig. 3*b*).

The circumstance that protruding microfibrils are noticeable on many of the crystalline formations we observed compels us to suppose a microfibrillar structure for these crystals.

On the basis of a careful study of microphotographs of sections of oriented recrystallized fiber, we established that during recrys-

crystallization, first, a very strong coarsening of the secondary structures occurs in comparison with those observed in the original oriented fiber. Such coarsening of the secondary structural formations is well confirmed by data known from the literature ([3]). Second, during recrystallization of kapron fiber, new secondary structures of various shapes are formed. Apparently, this is connected with the fact that they arise under different conditions than in solution, namely, in the condensed state. It is clearly apparent from the microphotographs that all forms of secondary structural formations have sharp boundaries, just as is known in the case of metal crystals. It may be assumed that, in the polymer, disordered,

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looser regions are located between the well-ordered crystalline formations. We did not observe a continuous transition from crystalline formations to the loose, disordered region.

In an electron-microscopic study of the forms of secondary structures arising during recrystallization of oriented kapron fiber, we established that all secondary structural formations exist in the crystalline regions of the polymer under investigation. These regions have anisodiametric forms, with diameters ranging from 1 to 10 μ. In the microphotographs the boundaries of these anisodiametric regions are clearly visible. Evidently, the partially crystalline polymeric kapron fiber consists of these regions, "macrofibrils." In the intervals between these crystalline macrofibrils there exist loose, disordered regions—the amorphous phase of the polymer. These amorphous regions are, as it were, a binding–supporting medium for the crystalline macrofibrils.

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Received
12 VI 1961

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