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Abstract

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Academician V. A. KARGIN, P. V. KOZLOV, K. BOUKHAL, and N. F. BAKEEV

RECRYSTALLIZATION OF POLYCAPROAMIDE UNDER THE INFLUENCE OF MECHANICAL ACTIONS

Structural studies of recent years have significantly changed our ideas about the structure of crystalline polymers. It has become clear that the crystallization of polymers is accompanied not by the appearance of local orderings of small size, but by the formation of large crystalline structures, which are easily visible in an ordinary microscope and sometimes even with the naked eye. Investigations have shown that such structures arise not only during crystallization from dilute solutions, but also directly in the condensed phase of the polymer. On the other hand, it has become clear that the structure of crystalline polymers in massive blocks closely resembles the well-studied structure of metals. The external similarity, associated with the presence of individual crystalline grains and distinct boundaries of separation, is also confirmed by the similar behavior of both structures under the influence of various actions. Thus, for example, in works [1,2] it was shown that the effect of temperature on the process of formation of the structure of a crystalline polymer in a block is analogous to the phenomenon of hardening and annealing of metals.

In the present communication we shall present results obtained in studying the influence of mechanical actions on the structure of polycaproamide in a block. As the object, polycaproamide was taken, obtained by polymerization of caprolactam in the presence of metallic sodium and acetylcaprolactam [3]. The polymerization was carried out at 195° and the polymer obtained was slowly cooled to room temperature. A block of polycaproamide 7 cm long and 1.5 cm in diameter was immersed in water heated to 60° in order to remove traces of monomer and was kept there for two weeks. The polymer was then dried at 10 mm Hg for 3 months. The molecular weight, determined viscosimetrically, was 14,000. The structure of the polycaproamide was studied in a metallographic microscope of the MIM-8 type. For this purpose the specimens, in the form of the aforementioned blocks, were cooled in liquid nitrogen and a brittle transverse fracture was made. A wedge-shaped notch was first made on the specimen, which facilitated the obtaining of mirror-like fractures. The use of thin blocks and preliminary notches ensured fracture along the boundaries of the structures. This may be judged from Figs. 1, 1, 2, which show photographs of fracture surfaces of polycaproamide. In the photographs, spherulitic structures with distinct

boundaries of separation are visible. Under oblique illumination (Figs. 1, 2) the relief of disk-like spherulites is clearly visible, which undoubtedly indicates displacement of the fracture front along the boundaries of the structures. As is evident from the photographs presented, in a block of polycaproamide, at temperatures below its melting point (at 190-195°), comparatively large spherulites arise during the polymerization process, whose diameter is of the order of tenths of a millimeter.

Mechanical actions on blocks of polycaproamide were carried out by cold rolling on rolls and by impact mechanical actions. For cold rolling, specimens were taken in the form of plates measuring $3 \times 1.5 \times 0.5$ cm. Rolling was carried out on cold rolls for a period of ···

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Fig. 1. **1**—fracture structure of the original polycaproamide in bright field. 200×. **2**—fracture structure of the original polycaproamide under oblique illumination. 200×. **3**—fracture structure of a block of polycaproamide subjected to impact mechanical action. 200×. **4**—fracture structure of a block of polycaproamide after cold rolling. 300×.

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Fig. 2. Glycogen content in the liver at different times of day: **a**—at 8 o' clock, **b**—at 11 o' clock, **c**—at 20 o' clock.

30 min. After rolling, the specimens were subjected to brittle fracture in liquid nitrogen and examined in a metallographic microscope. To carry out impact mechanical treatments, disks 1.5 cm in diameter and 0.5 cm high were cut from a block of polycaproamide. After testing, the specimens were likewise subjected to brittle fracture and examined under the microscope. The results of the investigation are presented in Figs. 1, 3, 4. In Figs. 1, 3 a photograph is given of the structure of polycaproamide after repeated impact deformation (up to 100 times), and in Figs. 1, 4—after cold rolling. In both cases it is evident that, as a result of mechanical treatments, changes occurred in the structure of the specimens studied. These changes are associated with the disappearance of spherulitic structures, characterized by a spherical form, and the appearance of larger pyramidal structures of rhombic form, resembling individual crystals formed during the crystallization of polyamides from dilute solutions ([4]). Upon mild etching of the fracture surfaces with a mixture of tricresol and alcohol, the boundaries separating the structures become more clearly visible; these boundaries also confirm the presence of a rhombic form. Such a process of recrystallization of polycaproamide under the influence of mechanical treatments is very reminiscent of phenomena occurring in metals during cold rolling. Only in the case of polycaproamide, which has a low glass-transition temperature, does this process proceed without subsequent heating of the specimen. This circumstance indicates that the mechanism of such restructuring is not associated

with a diffusional mechanism of rearrangement of the macromolecules forming these structures.

Thus, the preliminary results of the investigation of the influence of mechanical treatments on the structure of polycaproamide undoubtedly indicate the presence of a profound analogy in the behavior and structure of crystalline polymers and metals.

Moscow State University
named after M. V. Lomonosov

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