STRUCTURE FORMATION IN A CROSSLINKED POLYETHYLENE MELT CRYSTALLIZING UNDER UNIAXIAL TENSION


The formation of supermolecular structure has been investigated in the case of medium-pressure polyethylene film subjected to a dose of 30 Mrad of n, γ radiation. The melt, pre-stretched at 160°C to various degrees of elongation α, was crystallized at constant temperature. The results are interpreted on the basis of an analysis of the effect of the mechanical field on the growth kinetics and the orientation relative to the direction of extension of the individual crystallites; the first factor determines the shape and the second the sign of the spherulite.

The forming of fibers and films from polymer melts at moderate drawdown ratios leads to the development of spherulites flattened relative to the direction of extension [1-4]. As a rule, the flattening of the spherulites increases and their mean size decreases with increase in drawdown. At least two spherulite flattening mechanisms can be distinguished [5]. The first reduces to the existence in the fiber of two considerably different temperatures gradients – longitudinal and transverse. The longitudinal gradient is usually several orders lower than the transverse gradient [6], which in accordance with the inversely proportional dependence of the spherulite growth rate on the degree of supercooling may lead to the growth of nonspherical spherulites [5]. A second factor responsible for the growth of flattened spherulites may be the actual mechanical field of the longitudinal velocity gradient that develops in the presence of drawdown. This gradient tends to suppress the growth of folded crystals whose molecular axes are normal to the direction of extension of the melt [7]. Since the radial growth of a spherulite takes place at the expense of the formation on the surface of the growing nucleus of folded crystals with tangential chain orientation [8], this mechanism leads to the slowing of spherulite growth in the direction of extension, i.e., to the formation of spherulites flattened relative to that direction.

Naturally, one mechanism does not exclude the other and under actual conditions they probably both contribute to the distortion of the spherulite. However, it is important to determine the relative importance of the two mechanisms under various conditions. This was the object of the experiments described below, in which specimens placed in uniaxial tension were crystallized under isothermal conditions.

Specimens of medium-pressure polyethylene (MPPE), whose properties are described in [2], were prepared as follows. Film 500-μ thick, obtained by extrusion through a flat die [2], was subjected to a total dose of 30 Mrad of n, γ radiation. This, already crosslinked, film was remelted under slight pressure at a temperature of 190°C and cooled in water at 20°C; specimens with working dimensions of 5 × 10 mm were cut from this film, and marks were made on their surface at intervals of 0.5 mm. Then the specimens, secured in the tensioning device, were placed in an oil bath at T1 = 160°C, where after soaking for 5 min they were stretched manually and transferred in the fixed stretched state to a water bath at a certain temperature T2 < Tm, where crystallization took place. The relative elongation α was determined from the distance between marks on the crystallized specimen.
The structure of the film thus obtained was investigated microscopically and from the diffraction of polarized light in a MIN-8 microscope in accordance with a technique proposed by one of the authors [9]. The polarized-light diffraction patterns [10] make it possible to determine the average size R and estimate the shape (for example, the flattening $\lambda_1$) of the spherulites. Typical patterns for small, moderate, and large degrees of preliminary elongation of the melt are presented in Fig. 1. The results of calculating the dimensions and estimating the shape of the spherulites in film obtained by crystallization at $T_2 = 5$ and $100^\circ C$ from a melt stretched to various $\alpha$ at $T_1 = 160^\circ C$ are given in Fig. 2.

A qualitative consideration of the changes in the diffraction pattern (see Fig. 1) as $\alpha$ increases shows that at small and medium $\alpha$ the spherulites are flattened relative to the direction of extension, but at sufficiently large $\alpha$ there is a transition from flattened spherulites to individual scattering elements, whose greatest dimension coincides with the action of the tensile load. As follows from Fig. 1c, the diffraction patterns for these structures are similar to those for the flattened spherulites, but rotated through $\pi/2$ (compare Fig. 1b and c). Polarizing-microscope observations show [11] that on those elongation intervals,