PHYSICAL CHEMISTRY

V. I. Selikhova, G. S. Markova, Academician V. A. Kargin

1964

SovietRxiv

Abstract

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FORM BIREFRINGENCE IN SPHERULITES AND STRETCHED POLYPROPYLENE FILMS

It is known that in polypropylene, depending on the crystallization conditions, spherulites of several types can be obtained, differing in the magnitude and character of birefringence in the radial direction (^1). The most widespread type of spherulite, obtained by crystallization both from the melt and from a polypropylene solution, is a spherulite with a positive sign and a birefringence strength of about 0.003. For this type of spherulite it has been shown that the direction of the molecular chains makes an angle of 65-71° with the direction of the radial fibril, which is the texture axis (^2). It is not clear how the positive character of the birefringence is achieved when the direction of the molecular chains is close to perpendicular relative to the radius of the spherulite.

In our explanation of this phenomenon we relied on studies of form birefringence in disperse systems ([3,]4). We assumed that the birefringence of a polymer material is composed of two parts: intrinsic birefringence and form birefringence. The first is due to the polymer chains themselves, the second to their aggregates in the form of lamellae or rods. In our case the negative intrinsic birefringence of the chains is overlapped by strong positive form birefringence. On the basis of this assumption, we could expect that, when a spherulite is impregnated with liquids having different refractive indices, the magnitude of the birefringence and its sign would change. However, even after prolonged holding of the film in immersion liquids, no change in the magnitude of the birefringence was observed.

We etched spherulitic films 20 μ thick in silicone oil. After etching, the films were washed with ether and dried. When the film was immersed in silicone oil for 4 min at 145°, the magnitude of the birefringence of the spherulites changed. The magnitude of the birefringence Δ increased from +0.0030 in the initial spherulite to +0.0038 in the dry etched spherulite (the dispersion medium was air with $n = 1$). When liquids with different refractive indices in the interval $n = 1.35$-1.78 were introduced, the curve passes through a minimum $\Delta = -0.0029$ at $n = 1.507$-1.510 (Fig. 1, solid line). Since, according to the theory (^4), at the extremum point the form birefringence disappears, the residual negative birefringence is evidently caused by the chains themselves. It should be noted that the extinction pattern in the spherulites at this time is unusual. The Maltese cross does not have the straight form seen in dry polypropylene spherulites, when the arms of the cross are arranged vertically

Fig. 1. Dependence of the magnitude of birefringence on the refractive index of the impregnating liquids in polypropylene spherulites

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and horizontally (Fig. 2a), but is inclined (Fig. 2b). In all probability, this phenomenon is associated with a deviation (by an angle of 19–25°) of the chains in the fibril of the spherulite from perpendicular orientation.

On the basis of the results obtained, some assumptions can be made concerning the structure of the spherulite. The radial fibril of the spherulite consists of finer structural formations, whose size is smaller than the wavelength of visible light and which therefore cannot be resolved in the optical microscope. These structural formations, in the form of rods or elongated lamellae, are arranged along the radial fibril of the spherulite, which accounts for the positive character of the form birefringence. Polymer material is also present in the spaces between the rods and lamellae; therefore immersion liquids do not penetrate into the fibrils of the spherulite. During etching, the intermediate parts, being built up less densely, dissolve first. As a result, the finest—

cracks in the radial direction.* The immersion liquids penetrate into the radial fibrils, filling the cracks that have arisen and changing the birefringence of the system.

It is also possible to carry out a deeper etching of polypropylene spherulites, using small amounts of silicone oil (the film is only lubricated with oil) at 155–160°. In this case a different dependence of the magnitude of the birefringence on the refractive index of the impregnating liquid is observed (Fig. 1, dashed line). The spherulite etched and washed with ether shows a negative character of birefringence. In immersion liquids the birefringence is positive, with a maximum value of Δ at $n = 1.51$. A linear character of extinction is observed both in dry spherulites and in spherulites impregnated with liquids.

Fig. 1. Dependence of the magnitude of birefringence on the refractive index of the impregnating liquids in polypropylene spherulites.

At present we cannot give an exhaustive explanation of this fact. It is very possible that in this case defective regions of chain aggregates are etched out and numerous cracks are formed in a direction perpendicular to the radius of the spherulite. As a result, strong negative form birefringence arises. It is also beyond doubt that at the point of maximum the value of the positive birefringence cannot be attributed to the intrinsic birefringence of the chains. Let us note that X-ray diffraction patterns of the etched spherulites in all cases showed the same direction of the molecular chains in the radial fibril as in the original spherulites.

We also carried out preliminary experiments on etching, with silicone oil, polypropylene spherulitic films stretched by 500–800%. In the case of weak etching at 145°, the observed dependence of the magnitude of birefringence on the refractive index of the impregnating liquid is a curve with a minimum lying in the region of positive values of Δ, which indicates strong positive intrinsic birefringence. The form birefringence is also positive, but not as significant as in unstretched spherulites. With deeper etching of the stretched film (at 155–160°), a curve was obtained resembling the dashed curve of Fig. 1. Evidently, in this case a considerable negative form birefringence appears, owing to etching of regions of the film located perpendicular to the direction of stretching.

Work on refining the birefringence values in stretched films and on interpreting the results obtained will be continued by us.

Physicochemical Institute
named after L. Ya. Karpov

Received
30 XI 1963

CITED LITERATURE

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* From this point of view the increase in positive birefringence in the dry spherulite after etching is understandable.

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