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Morphological Verification of "Row Nucleation" in Isotactic Polystyrene; Evidence for Single Crystals Within the Bulk

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In order to detect the sites responsible for crystal nucleation under stress, isotactic polystyrene was crystallised in the stretched state so as to give isolated "row nucleated" column structures within an amorphous matrix. Sections were cut both longitudinally and transversely to the stretch direction. A central line discontinuity could be seen in all columns in agreement with expectation from "row nucleation". Electron diffraction patterns from column portions contained by transverse sections identified such portions as single crystals, a rather exceptional demonstration of true single crystals within the bulk interior. While the origin of the contrast in the electron micrographs of longitudinal sections is problematical, that in the transverse sections conforms to observations and deductions made in work on solution grown polyethylene crystals [11].

1. Introduction

The texture of a polymer crystallised under stress is well established at least in its basic features [1-3]. It consists of columns parallel to the stress direction where the columns themselves consist of lamellae which grow transversely with respect to the column axis. In the much studied case of polyethylene, if the stress is low the lamellae may twist as they do in spherulites while at higher stresses they have their basal planes all parallel so that the chain axis within them is aligned along the stress direction [1]. This morphology is due to the "row nucleation" of lamellae [4]. Accordingly, the nucleation centres from which the lamellae emanate are closely spaced along lines parallel to the stress direction. By current ideas and by analogies with crystallisation from stirred solutions [5] these lines of nuclei should correspond to filaments with the molecules aligned in the filament axis. It is these filaments which are considered as the primary products of stress induced crystallisation.

Evidence for the above model is essentially of two types. In the first place electron microscopy on thin films [1, 3] and in some instances surface replicas of massive samples [e.g. 6] and secondly X-ray diffraction on massive specimens [2]. In the electron microscope work the columns of transversely growing lamellae are clearly defined but the identification of the central thread as a representative structure element presents some difficulty (conspicuous threads have nevertheless been demonstrated recently, after completion of the present work, in surface replicas [7]). On the other hand, the nucleating stage of the crystallisation has been clearly established by recent X-ray work on massive samples [2]. In accordance with expectations, a highly oriented fibre pattern appeared first in the course of crystallisation and under appropriate circumstances this was followed by the development of a distinctly different diffraction pattern corresponding to the transversely growing lamellar arrangement. The highly oriented fibre pattern clearly corresponds to the nucleating phase. While it is consistent with this phase having a filamentous character it does not provide direct evidence on the morphology. The present work was undertaken to obtain such evidence.

2. Thin Films

In order to achieve this objective we wanted to be able to interrupt the columnar crystallisation at any stage within a massive specimen, so as to obtain columns in isolation, and then cut ultramicrotome sections along preselected directions. For this purpose the polymer has to be quenchable in a glassy state, a requirement not satisfied by polyethylene. A suitable model substance proved to be isotactic polystyrene. Preliminary work on thin films by Machin [8] revealed that isotactic polystyrene can be obtained in a row nucleated form. Fig. 1 is an illustration from that earlier work. The columnar crystallisation is self evident. Closer inspection reveals that the lamellae are like polygonal (apparently hexagonal) umbrellas, or, in places, S-shaped layers. These are the counterparts of the well-established hollow pyramids and "chair" crystals in polyethylene [9]. The central thread, however, if present, could not be identified presumably because of the dense lamellar overgrowth.

It is to be noted that in polystyrene the lamellae are never twisted, not even if crystallised under low stress. This may be associated with the fact that in contrast to polyethylene, where the lamellae are ribbon shaped, hence prone to twist, in polystyrene they are concentrically stacked hexagons where twisting along the lateral growth directions is not readily envisaged. Indeed to our knowledge banded spherulites, which are the optical consequences of twisted lamellae, have not been observed in isotactic polystyrene even when crystallised in the absence of stress. For this reason the nucleating fibrils and the nucleated lamellae would both have the same lattice orientation, with the chains parallel to the stress direction. Consequently the two phases cannot be distinguished by X-ray diffraction.

3. Massive Samples

3.1. Sample Preparation and Optical Microscopy

For the present experiments on massive samples amorphous isotactic polystyrene was first irradiated with a dose of 300 Mrads of γ rays. Small blocks were then drawn in an oil bath at 120°C to 200 to 400% elongation and kept clamped in the drawn state (they were still amorphous when examined by X-rays after cooling to room temperature). The clamped samples were subsequently annealed at 170°C when cyrstallisation occurred. This could be interrupted at the desired stage by cooling to room temperature. Sections were then cut both perpendicular and parallel to the stretch direction for examination with the optical and electron microscope. Longitudinal sections prepared for optical microscopy revealed birefringent structures in a non-birefringent medium (fig. 2). These structures have the characteristic appearance of row nucleated columns of lamellae. The observed negative birefringence with respect to the column axis is consistent with the polystyrene chains being oriented along this direction.

In what follows the electron microscopy of suitably thin sections will be described in greater detail.

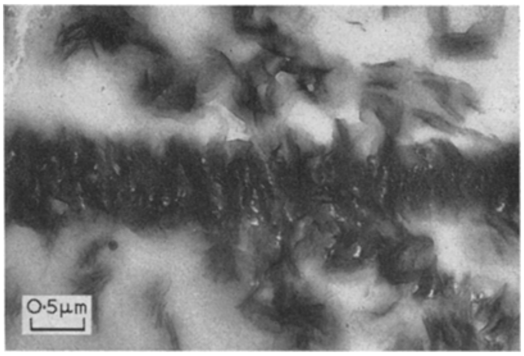

Figure 1 Thin film of isotactic polystyrene partially crystallised under stress and quenched (etched with chloroform). Transmission electron micrograph (from Machin [8]).

Figure 2 Longitudinal section of isotactic polystyrene crystallised in the stretched state. Photomicrograph, crossed polaroids.

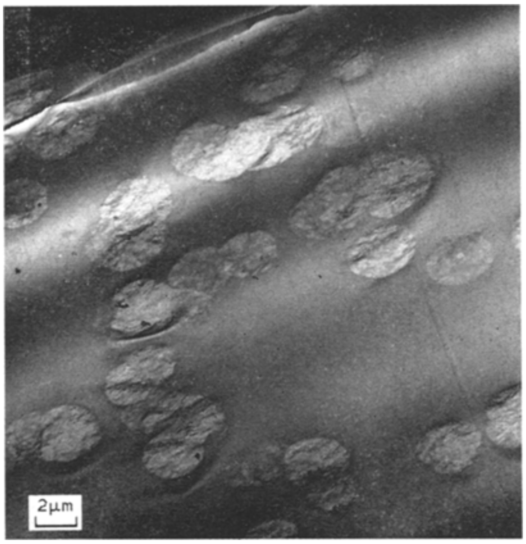

Figure 3 Transverse section of isotactic polystyrene crystallised in the stretched state. Electron micrograph.

3.2. Electron Microscopy

3.2.1. Transverse sections

These were cut perpendicular to the stress direction as exactly as possible. The micrographs (fig. 3) revealed oval or slightly polygonalised inclusions in a structureless matrix. We interpret these as the columns (in fig. 2) seen in cross section. (The oval shape is due to the compression caused by the knife.) Electron diffraction patterns could be obtained from individual ovals and they gave single crystal diffraction patterns with slightly arced spots (fig. 4). With the aid of the diffraction rings produced by the metal evaporated on the section for calibration purposes the visible sets of hexagonally arranged reflections were found to be 11.2, 6.5 and 5.6Å and hence were identified with the 110, 300 and 220 reflections of polystyrene [10] respectively (see fig. 5). Accordingly, each oval in fig. 3 is a polystyrene single crystal. The outermost pair of polymer reflections displaying two-fold symmetry were identified as {211}. Such {hkl} reflections are not expected to be visible if the crystals are seen exactly along the chain axis which in fact is implied by the hexagonal arrangement of the {hk0} reflections. We suggest that these reflections are from small inclined regions of the crystals in particular from crystal edges bent so as to bring the {211} planes in reflecting position. This is consistent with the fact that the intensity of that pair of the {220} reflections which lie along the assumed tilt axis is higher than the intensity from the other four of the set of six, and also with numerous indications from thin film electron micrographs where the layer edges can often be seen bent.

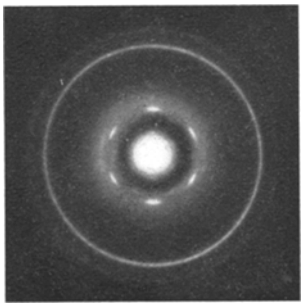

Figure 4 Electron diffraction pattern given by one of the ovals in fig. 3. The rings are due to gold with which the section was coated for calibration. Centre is printed more strongly (Fig. 3 and all the other electron micrographs are unshadowed.)

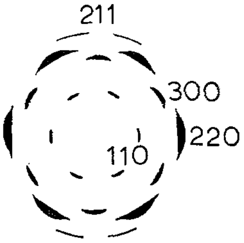

Figure 5 Sketch of polystyrene diffraction pattern in fig. 4 to aid identification of reflections.

It is to be noted that to our knowledge this is the first instance that a genuine isolated single crystal identified both morphologically and by its diffraction pattern has been obtained within the interior of a massive sample of a crystalline polymer. As apparent, this was achieved by growing them in the row-nucleated form where a transverse section will contain such crystals with a high probability and this in the most informative "flat on" view.

The lighter contrast of the ovals in fig. 3 requires further comments. The contrast remains when the specimens have ceased to diffract, and there is no metal coating, so the effect must be due to mass thickness differences. As cut the sections are of uniform thickness, and the crystal density is slightly greater than the amorphous density. This would lead to a contrast opposite to that observed. However, stereoscopic microscopy shows that the sections do change after being cut. Fig. 6 is a stereo-pair where each "oval" stands

Figure 6 Transverse section of isotactic polystyrene crystallised in the stretched state. Electron micrograph, stereo pair to show elevation of lighter oval region.

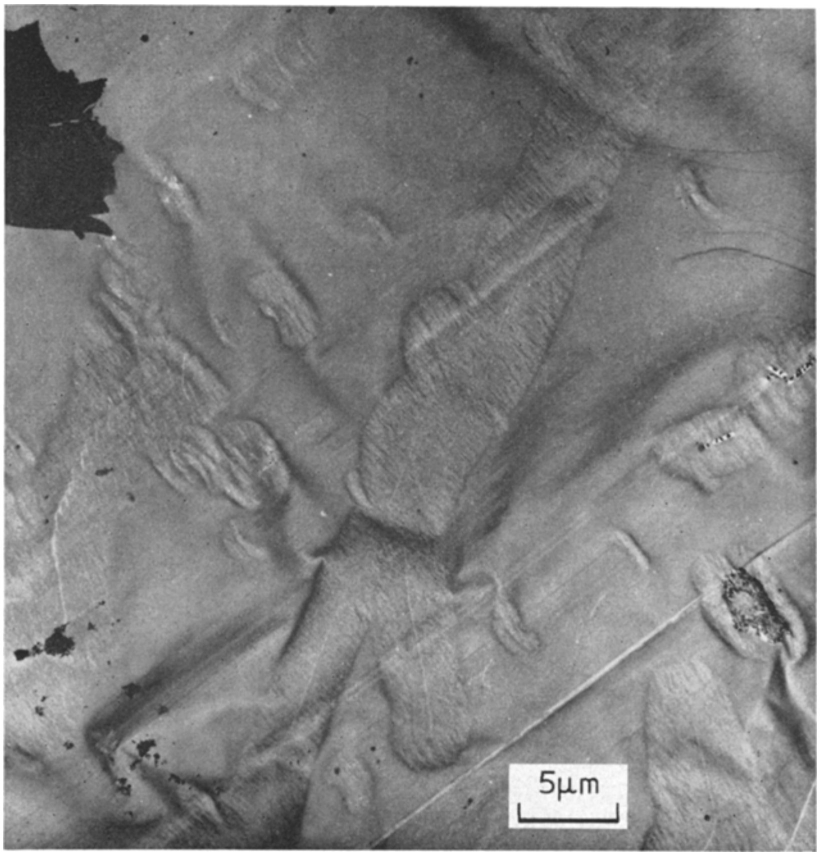

Figure 7 Longitudinal section of isotactic polystyrene crystallised in the stretched state. Electron micrograph.

out as a rough cone, of semi-angle 60 to 80°. The contrast of the ovals and their departure from the plane were both enhanced by exposure to the electron beam. Micrographs taken at the lowest possible radiation dose still showed the effects, but a considerable amount of radiation was used in the specimen preparation. Thus in the beam the ovals increase in area by becoming non-planar, and reduce in mass thickness. From the diffraction evidence of fig. 4, the ovals are single crystals in the "flat on" orientation. This is equivalent to the effects described in the preceding paper [11], where polyethylene single crystals mounted on a deformable substrate expand laterally and become thinner as a result of irradiation. In this case the amorphous matrix is less deformable and the crystalline region is thus forced out of the plane of the specimen.

3.2.2. Longitudinal sections

These were most informative when cut with the section plane at an angle of about 30° to the stretch direction, as this increases the probability that a section will contain a column and that such a column is sampled across its central region. The columns were always distinguishable from the amorphous surroundings (fig. 7). Without exception they all contained a distinct central line about 500Å thick which terminated before reaching the column ends. This proves that these lines are not accidental markings but intrinsic constituents of the columns themselves. This point is further supported by the fact that these central lines change direction or bifurcate just as the corresponding columns do (fig. 7).

The details, however, create problems which cannot be resolved from the evidence available. The first of these concerns the shape of the central discontinuity. If the column is circularly symmetric and the cutting plane is inclined at 30° to its axis, a central thread should appear for only a short length of the column, as the section passes through the centre. Serial sectioning and more accurate knowledge of section thickness would be required for further evaluation. The second problem is the origin of the contrast of these crystalline structures in the electron microscope. Fig. 8 contains a region where the columns were poorly aligned, and two columns cross. The central line is bright, where it is parallel to the cutting direction, but dark where it is perpendicular to it, a feature which was consistently observed. Clearly the origin of contrast in the different morphological forms in different orientations, also as related to the cutting direction, would need to be studied along the lines of the preceding paper [11]. This is imperative if the rational interpretation of crystalline self structure in bulk polymers is going to be pursued. In spite of these difficulties the micrographs reveal structural features which certainly do exist.

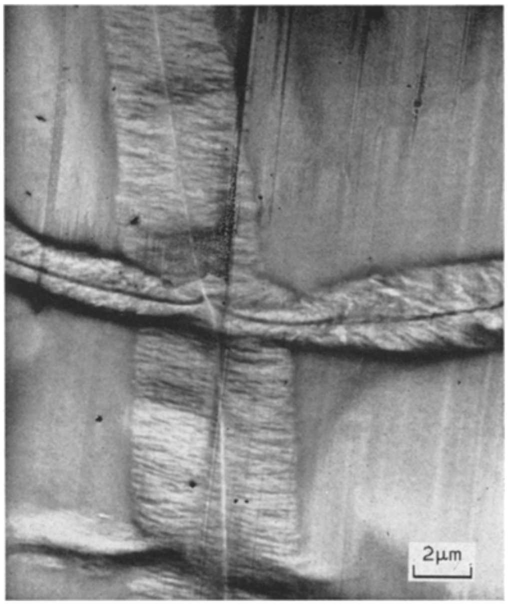

Figure 8 Longitudinal section of isotactic polystyrene crystallised in the stretched state. Electron micrographs showing rows along two directions.

4. Conclusions

The existence of a central filament within columnar crystals resulting from crystallisation under stress within bulk samples has been visually demonstrated. Even if the origin of the contrast by which it is seen is not understood the observation itself is consistent with the existing model of a "row nucleated" two stage crystallisation postulated in previous works. In addition, the transverse sections revealed single crystals identified visually and by electron diffraction, a rather exceptional demonstration of the existence of isolated crystals within the interior of an otherwise undisturbed, melt crystallised bulk polymer.

Acknowledgement

We wish to acknowledge the contribution to this subject by Dr M. J. Hill (formerly Machin) mentioned in the text. Her early work on this subject was the starting point of the present investigation.

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