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Characterization of superheatable flow-induced polymer crystals by optical microscopy

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Crystallization from an oriented melt produces superheatable fibrous crystalline structures contained in a matrix of polymer which melts normally. A polarizing optical microscope fitted with a well-controlled heated specimen stage can detect very small amounts of superheatable oriented material, and the form and distribution of these crystals may be observed directly. The presence of even smaller amounts of organized material at high temperature may be inferred from its effect on the recrystallization of the specimen. Superheatable crystals are often produced by crystallization during flow, and sometimes unintentionally in processing. Hot-stage optical microscopy is shown to be a rapid and highly sensitive technique for detecting such structures.

1. Introduction

A general and distinctive property of polymers is the wide range of melting temperatures obtained from a single sample. The observed melting temperature can vary considerably, depending on the previous history of the sample. In particular, the fibrous crystals of polyethylene produced by stirring a supercooled solution [1, 2] and generally called shish-kebabs contain material which melts at temperatures considerably higher than normal [3-6]. Extensive studies of this behaviour have been carried out, primarily by differential scanning calorimetry (DSC) but also by optical microscopy and infra-red spectroscopy [5] and dilatometry [7]. It is difficult to summarize the experimental results of these papers partly because of the wide range of different materials used. However, at the moment our primary concern is optical microscopy. The polarizing optical microscope, when fitted with compensators, measures the local direction and degree of orientation of the index ellipsoid. In most polymers this means the orientation of the chain axis. The microscope does not distinguish between extended and folded chain crystals nor between crystals and oriented molten material. Pennings and van der Mark [5] reported that by 130 to 133°C some part of the material had melted, producing an isotropic matrix full of strongly birefringent fibres. The fibrils, several microns in diameter, remained birefringent up to 190°C on heating at 10°C min^{-1}. This was for a low molecular weight material, Marlex 6050 (M_n 8 × 10^3, M_w 9 × 10^5). With Hostalen GUR (M_n 10^5, M_w 1.5 × 10^6) the birefringence did not disappear until, at 220°C, the polymer degraded. On similar samples, X-ray diffraction and infrared spectroscopy could detect no crystalline structure above 140°C. Although in a number of cases an endothermic peak was found at 180°C, the main melting peak on the DSC ended at about 150°C, for heating rates of 10°C min^{-1} or less.

Oriented crystallization of bulk polymer has also been studied in depth, and it has been shown that structures analogous to shish-kebabs are produced, with lamellar crystals growing out perpendicularly from a line nucleus [8, 9]. More recently, highly oriented polyethylene has been prepared in this laboratory by crystallization during flow, either in a capillary rheometer, a method intensively studied by Southern and Porter [10], or in an apparatus designed to produce elongational flow [11], a condition necessary for the formation of shish-kebabs [2, 12]. When these oriented materials are heated, a point is reached where that part of the material which has crystallized normally melts. We now find that the structure and microscopic appearance of the bulk material becomes the same as that of the partially melted shish-kebab mats described by Pennings and van der Mark [5]. Using the great sensitivity of the optical method for detecting persistent birefringence, it has been possible to detect very small amounts of fibrous crystals in bulk crystallized samples which had been subjected to much less severe strain. Even pressing a pellet into a thin film at 20° C above the melting point is sufficient.

2. Experimental details

A Zeiss Ultraphot microscope fitted with a Mettler FP52 temperature controlled specimen stage was used for all the experiments. The temperature control was calibrated by observing the melting points of phenacetin (134.5° C) and benzanilide (163° C) and found to be correct to 0.2° C at these temperatures.

Specimens for optical microscopy are normally immersed in fluid to reduce reflection from their surfaces. All immersion fluids tried, including silicone oil, had a detectable effect on polyethylene, reducing the temperatures at which disordering transitions occurred. Specimens were therefore observed dry, except for a few which were embedded in epoxy resin.

3. Specimen preparation

3.1. Extruded specimens

Extruded specimens of linear polethylene were prepared (a) in an Instron capillary rheometer at 131.5° C and a plunger speed of 1 mm min^{-1} using Rigidex 9, or (b) in a jet extrusion apparatus designed by Mackley and Keller [11] to produce extensional flow and thus oriented crystallization. Two different polyethylenes of the same melt flow index were used in this device. One was an experimental polymer, type GM48/2400, kindly supplied by Dr T. Cunningham of ICI Ltd, and the other was Marlex 6002. Both extrusion machines produce long fibres, and for the optical microscope pieces of fibre were embedded in epoxy resin and sections were cut with a microtome, parallel to the fibre axis.

3.2. Thin film specimens

Thin film specimens were prepared from a variety of materials simply by melting a little of the commercial product between two glass slides on a Kofler hot bench and pressing and shearing the slides to give a film less than 100 μm thick. The film was quenched in water and then separated easily from the glass slides.

3.3. Solution crystallized specimens

Solution crystallized specimens were prepared to provide a comparatively well understood composite consisting of the same material in oriented and unoriented crystal forms. Shish-kebab crystals of Marlex 6002 were grown from a 0.5% solution in xylene, by stirring with a cylindrical stirrer at 1400 rpm and 100° C, or with an ordinary glass encapsulated magnetic stirring rod during slow cooling from 130° C. Normally repeated washing with fresh hot solvent is required to separate the fibrous crystals from the overgrowths of normal lamellar crystals. In this case the desired end product was an intimate mixture of the two, so there was no washing. Instead the precipitated mass was removed from the mother liquor, spread out and partially disentangled, then placed between filter papers under a heavy weight and vacuum dried. The resulting sheets could be used directly in the microscope.

4. Observations

4.1. Extruded specimens

Fig. 1 shows a section cut from the capillary rheometer specimen described in (a) of Section 3.1. At room temperature there is a strong overall birefringence and little clear fine structure. On heating to 133° C (Fig. 1a) the overall birefringence is weakened, and a fibrous structure parallel to the extrusion direction of the rheometer begins to appear. Individual strongly birefringent fibres become distinct as the temperature is raised further, and the appearance of the specimen changes little between 135 and 140° C (Fig. 1b). There is little retraction on heating to this temperature and the original appearance returns on cooling. When similar specimens are heated at 1° C min^{-1} the birefringence of the fibres weakens and they finally disappear at 151.5° C. If the specimen is then cooled, recrystallization re-forms the fibres in their original positions and the rest of the material crystallizes more slowly. As an example Fig. 1c shows the fibres which remain strongly birefringent at 142° C in one area of the section and Fig. 1d shows recrystallization making these fibres larger and making others visible. To suppress this memory effect the specimen has to be kept for a few minutes at 165° C or higher. The bright spots in Fig. 1c and d are birefringent impurity particles and seem to be associated with the strongest persistent birefringence. The recrystallized material in Fig. 1d does not have

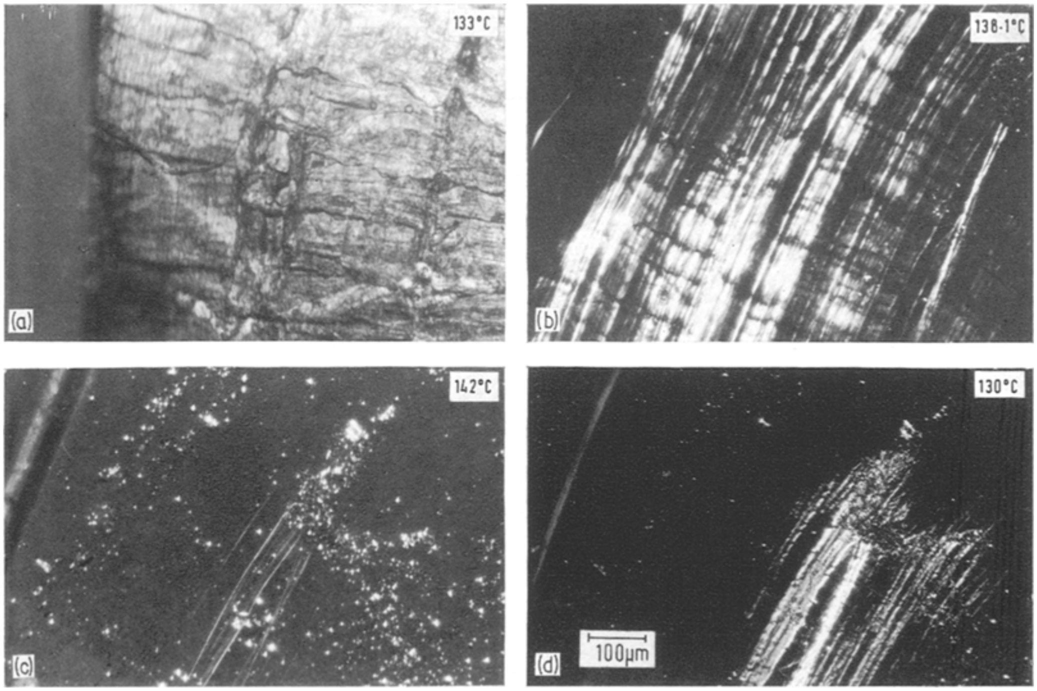

Figure 1 Optical micrographs taken with crossed polars of a thin section of polyethylene crystallized in a capillary rheometer. (a) At 133° C, there is little change from room temperature; (b) at 138° C, a great change has occurred. The specimen now consists of birefringent rods in an isotropic matrix; (c) at 142°C, some rods persist; (d) at 130°C, after cooling from 142° C, rapid recrystallization occurs on the rods which persisted.

an unusually high melting point or persistence of birefringence. If the specimens were heated again this material would melt quickly, leaving only those fibres in Fig. 1c, which have persisted from the original preparation.

DSC melting traces from pieces of the same preparation are given in Fig. 2. The three curves refer to samples from different parts of the capillary. Two show a normal melting peak (B and C) and two a peak at a higher temperature (A and B). The micrographs in Fig. 1 come from specimens corresponding to curve (A) of Fig. 2, where the high temperature melting peak is largest. Where this peak is smaller, there is less persistent birefringence in the optical microscope. Even in curve (A), the melting is complete at 140° C, when there is still a considerable amount of persistent birefringence.

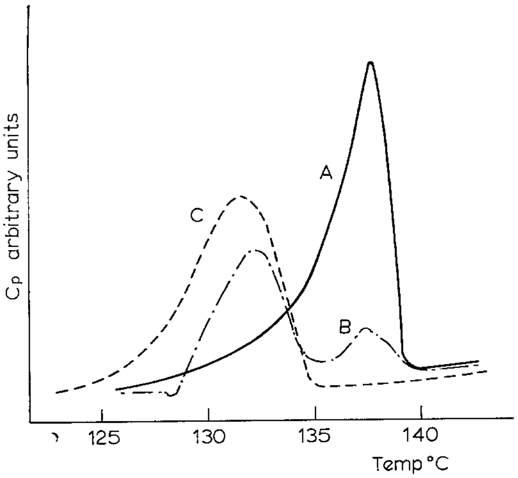

Figure 2 DSC traces of polyethylene crystallized in a capillary rheometer. (A) A sample taken from the preparation and region used for Fig. 1. Melting appears to be over at 140°C. (B) and (C) specimens from the same preparation as in Fig. 1, but from different parts of the capillary, where the polymer is less well oriented.

Fig. 3 is a sequence of micrographs taken during the heating, at about 3°C min^{-1} of the specimen of polyethylene type GM48/2400 crystallized in a jet extrusion apparatus ((b) Section 3.1). At room temperature (Fig. 3a), the section already appears fibrous. At 120° C (Fig. 3b), there has been a slight change of shape, the regions of strongest birefringence have altered, and it has become apparent that some of

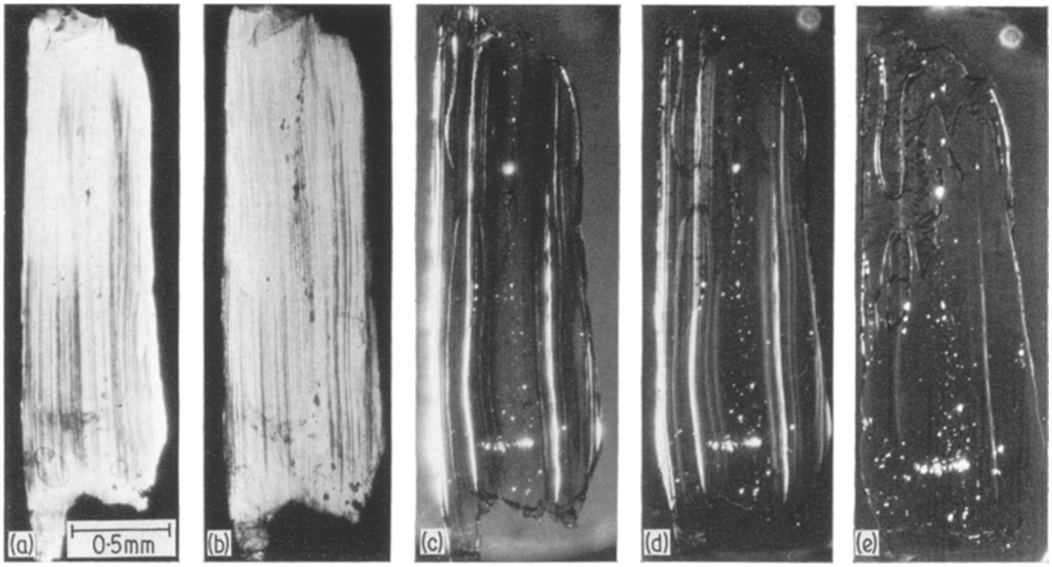

Figure 3 Optical micrographs taken with crossed polars during the heating of a thin section of polyethylene crystallized in a jet extrusion apparatus. (a) At 20° C, a fibrous appearance, highly birefringent; (b) at 120° C, the appearance has changed in detail only; (c) at 134° C, drastic change, most of the material has melted; (d) at 143° C, little further change; (e) at 166° C, the birefringent lines have weakened, but persist.

the fine structure is due to the sectioning knife. At 128° C the material softens and flows to wet the glass slide and cover slip. There is a much greater change at 132 to 133° C. The knife marks disappear, much of the material becomes transparent and parallel bundles of distinct fibres appear (Fig. 3c). There is some slight compensation of positive birefringence in the vertical direction of this picture, so that the small fibres are extinguished and appear darker than the isotropic matrix. The structure changes little on further heating except that the fibres fade and the smaller ones disappear (Fig. 3d and e). Only the strongest is still visible at 180° C and this becomes fuzzy and indistinct, finally vanishing at 189° C. On cooling to 126° C, crystal growth occurs first along the tracks of the most persistent birefringence, but in a discontinuous manner as though the original line nucleus has begun to break up. A DSC trace of the same specimen heated at 10° C min^{-1} is shown in Fig. 4 curve A. Superimposed on it with an arbitrary vertical displacement is a trace of a pressed sheet of the same material (curve B). This thick, pressed sheet had little strain history, and showed no persistent birefringence in the optical microscope. A small high-temperature shoulder is visible in curve A, ending at 150° C. The vertical scale of the curves has been expanded to make this clear, and the main melting peaks are off scale, but they were identical. The area of the high temperature shoulder is about 0.2% of the area of the main peak. Another specimen heated at 10° C min^{-1} in the microscope, with no interruption for photography, underwent the same changes of appearance shown in Fig. 3. At this heating rate the sudden melting occurred at 134° C instead of 132 to 133° C, and the last trace of birefringence persisted to 204° C.

A different starting material, Marlex 6002, in the same apparatus produced a sample where visible fibrils persisted only to 147° C, on heating at 3° C min^{-1}. A temperature of 160° C was enough to destroy most of the "memory" of the fibres, although their effect on recrystallization could still be clearly detected after 90 min at 160° C. At higher temperatures, flow of the molten specimen obscured the effect. When a similar section was restrained by embedding in epoxy resin, the fibres were visible to a slightly higher temperature (150° C), and the position of the fibres was clear on recrystallization after 1 h at 163° C.

4.2. Thin film specimens

The original observation was accidental and

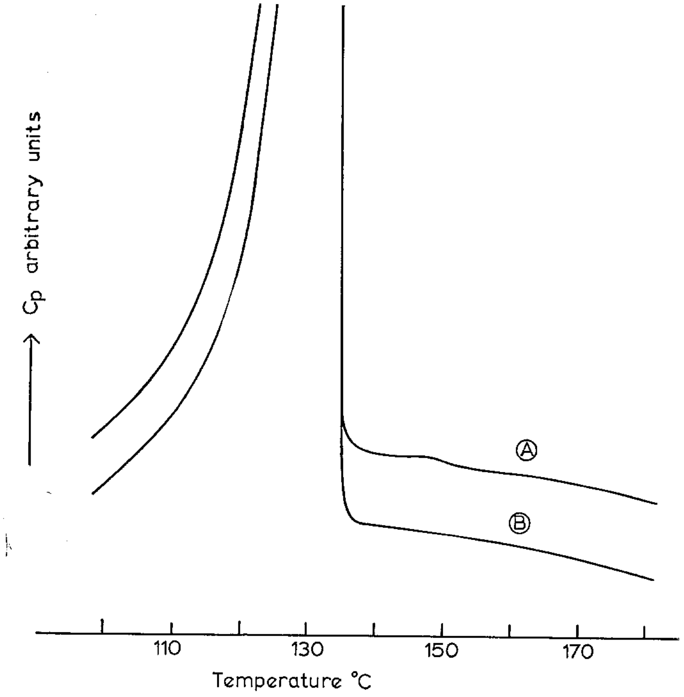

Figure 4 (A) DSC trace of the preparation used in Fig. 3, with a high melting "tail" up to 150°C. (B) DSC trace of the same material but sample taken from thick, pressed sheet. Melting is complete at 138°C.

surprising. Thin films of polyethylene prepared (for other purposes) by hot-pressing appeared isotropic when cold, but when they were heated to a few degrees above their melting point, then cooled and recrystallized slowly, the first crystallization was in the form of strongly birefringent fibres. These fibres often outlined the flow pattern of the hot-pressing. They were lost from view on further crystallization, hidden by the much greater amount of spherulitic crystallization. When the specimen was heated again, the spherulitic matrix melted first, and then the fibres, but only because the fibres had started crystallization at a higher temperature. However, at the centre of the fibre was a very much fainter fibril, which remained birefringent to a much higher temperature. The concentration of this superheatable material was so low in these specimens that the fibrous structures were very difficult to find when the specimen was heated directly to a high temperature. It was usually necessary to use the recrystallization behaviour described, and the large birefringent rods which appeared, as markers. The crystallization behaviour was the same, i.e. large rods appeared, when freshly pressed film was crystallized slowly in the hot stage. Thus the quenching and remelting process described is not essential, but merely a convenient way of handling the samples.

Fig. 5 shows a thin film of Marlex 6002 pressed at 170°C which was cycled between 127°C and a higher temperature, holding at the high temperature for 2 min and increasing it by 2°C each cycle. In Fig. 5a, at 142°C, faint birefringent lines extend between two impurity particles. The lines were still visible up to 152°C. Fig. 5b, c and d were taken after 2 min at 127°C, and after cooling down from 142, 162 and 172°C. The amount of recrystallized material is less in Fig. 5c and much less in Fig. 5d, where the surfaces of the impurity particles no longer nucleate crystal growth.

4.3. Solution crystallized specimens

The appearance of a solution crystallized composite prepared from Marlex 6002 by stirring during slow cooling is shown in Fig. 6. The specimen is opaque at room temperature (Fig. 6a), because of scattering from the voids between the crystals. At 129°C, the lamellar crystals begin to melt and birefringent regions appear (Fig. 6b). At 134°C (Fig. 6c and d), there are clearly distinguishable strongly birefringent rods in an isotropic melt. Heated at 3°C min^{-1} they fade, disappearing at 155°C. After melting at 168°C for 5 min, there is some preferential recrystallization in rod form, but degradation is quite severe. Because of the previous report that

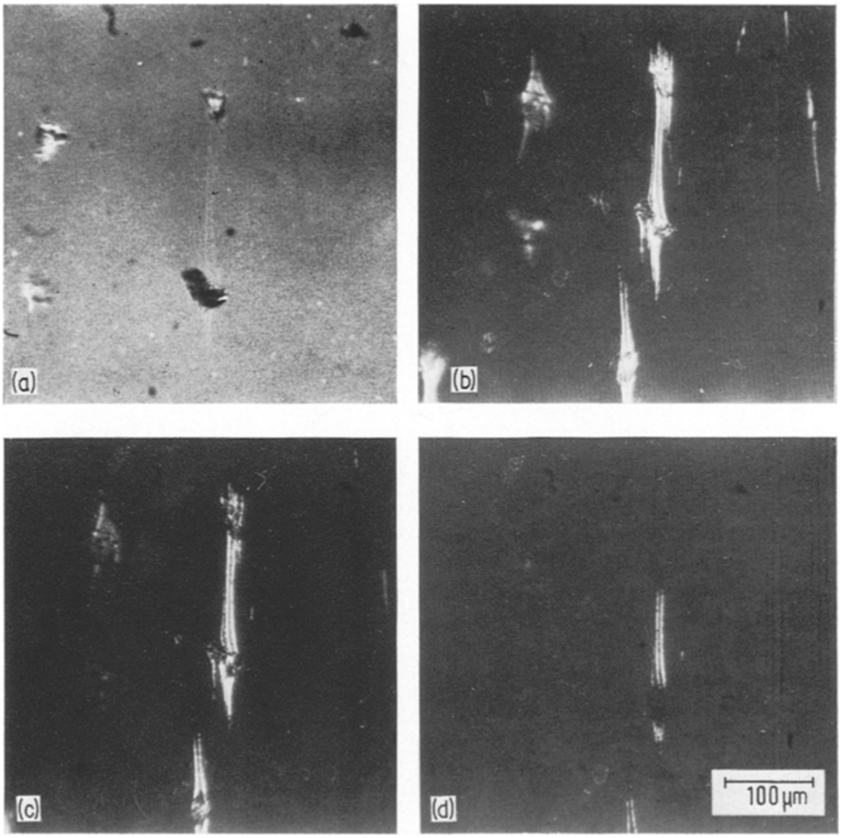

Figure 5 Optical micrographs taken with crossed polars of polyethylene pressed to a thin film at 170° C, then quenched. (a) At 142° C birefringent lines are clearly visible; (b) 2 min after cooling to 127° C from 142° C; (c) 2 min after cooling to 127° C from 162° C, recrystallization behaviour is only slightly affected by heating to162° C; (d) 2 min after cooling to 127° C from 172° C, recrystallization occurs only on the sites of lines visible at 142° C.

birefringence persisted in this type of specimen up to 190° C [5] a mat of crystals was embedded in epoxy resin, in a vacuum to ensure penetration between the fibres. In this case the material was very closely constrained, and protected from the air. The specimen never became completely transparent, but it was clear enough to detect the birefringence, and this changed only slightly between 134 and 210° C. Specimens prepared by isothermal crystallization on a cylindrical stirrer at 100° C produced a mat containing too high a proportion of superheatable material to distinguish the individual fibrils very easily. Nevertheless, the structure was basically similar, and the birefringence persisted up to 156° C.

4.4. Other materials

The experiments described above all used high density polyethylene, the most commonly used material in this field of study. A quick survey of other crystalline polymers was made using thin film specimens, to see if row-nucleated crystals with superheatable birefringent nuclei were produced. Many were produced in polypropylene and isotactic polystyrene, and some were produced in polyoxymethylene and polyethylene–polypropylene co-polymers (up to 18% PP). None were produced in low density polyethylene or polyoxyethylene (mol wt 60 000). The method could not be applied to Nylon 6, as too high temperatures were required, or to poly-4-methyl pentene-l which has too low a birefringence. Both polypropylene and isotactic polystyrene were different from polyethylene in that the orientational effects of hot-pressing could be seen at room temperature. Polystyrene samples were pressed at 250° C quickly cooled to 190° C and crystallized there for a few minutes,

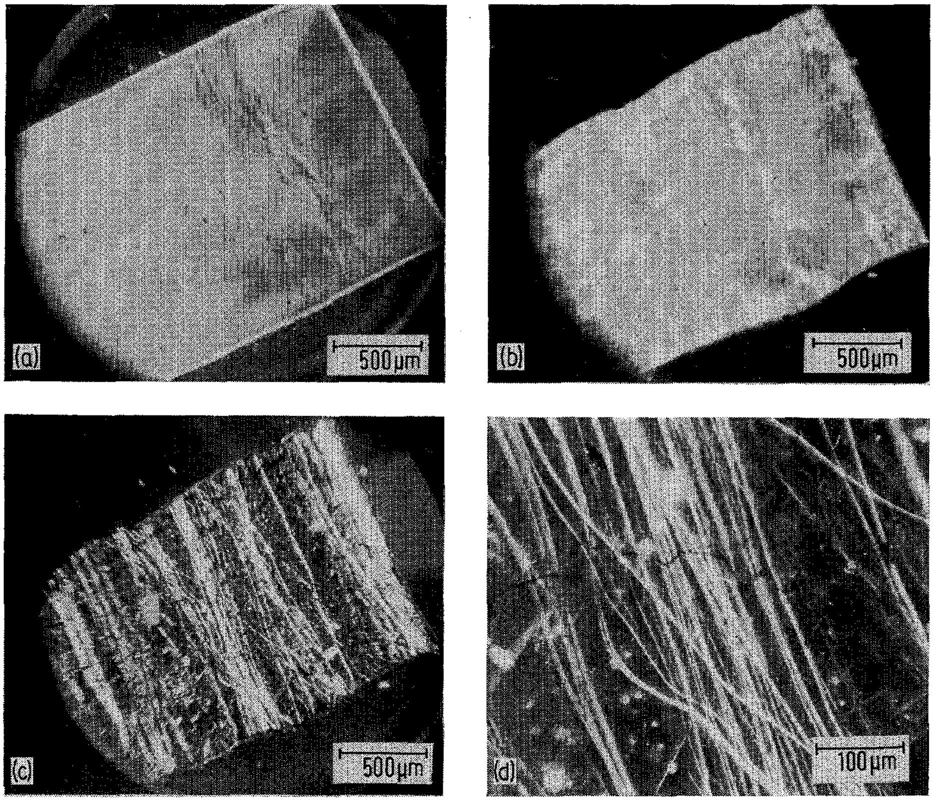

Figure 6 Optical micrographs taken with crossed polars of polyethylene crystallized from stirred solution during slow cooling. (a) Opaque at room temperature; (b) at 129° C, becoming transparent; (c) at 134° C, a transparent matrix containing birefringent rods; (d) higher magnification of (c).

then quenched. Crystalline rods grow on the line nuclei at 190°, but spherulitic growth is slow to start, and polystyrene can be quenched without further crystallization, so that on quenching, the birefringent rods are embedded in a transparent glassy matrix [13]. Polypropylene needed no such special treatment, Fig. 7a shows a polypropylene film at room temperature which had been pressed at 190°C, and immediately quenched in water. The lines of birefringent sheaves on a central thread look just like giant shish-kebabs. They are clearly visible because they consist of the highly birefringent hexagonal crystal form, such as makes up type III spherulites, whereas the matrix is monoclinic, the more stable crystal form that gives type I and II spherulites [14]. Close examination at higher magnification shows that the central thread nucleates growth everywhere along its length but where the thread seems to stand out alone, the overgrowth is monoclinic. On heating the sample, all the oriented structures disappear at about 150°C, the melting point of the hexagonal crystal form. Continuing to heat, the monoclinic form melts at 168°C, but a faint ghost of the birefringence remains. Faint birefringent lines on the site of nucleating threads can sometimes be seen and persist for longer than the other features, but only up to 174°C. The sample in Fig. 7 was heated to 170°C, when no features remained visible, then cooled quickly to 140°C. Fig. 7b shows the appearance after 2 min recrystallization at that temperature. Strong lines appear on the sites of central threads and others become visible.

5. Discussion

5.1. Experimental results

The first salient point to note is that by the present application of the hot stage in the manner described, it has become possible to identify fibrous components within the texture of a crystalline bulk polymer by direct visual observation. Such fibrous components result from oriented crystallization occurring under a

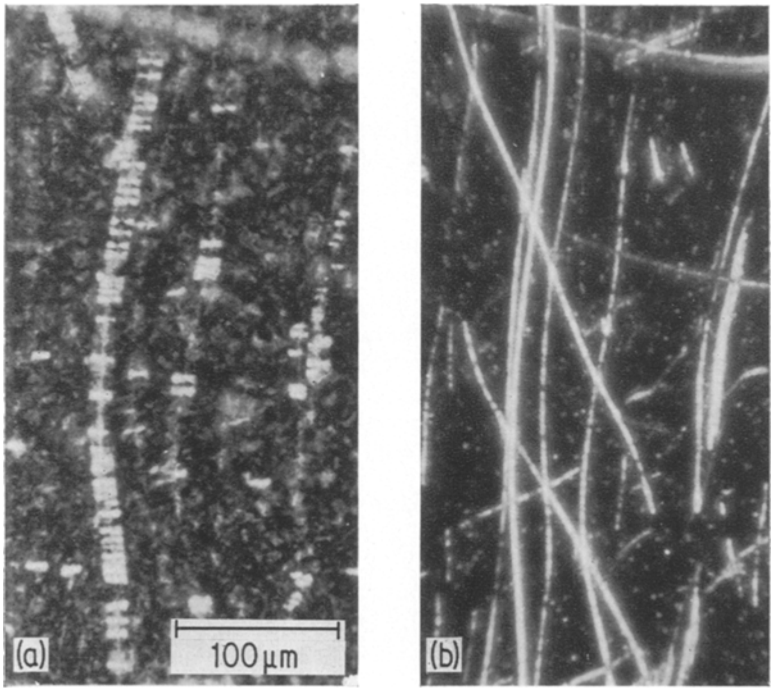

Figure 7 Optical micrographs taken with crossed polars of polypropylene pressed to a thin film at 190°C and then quenched. (a) Room temperature, row nucleation clearly visible; (b) melted at 170°C, then held at 140°C for 2 min, recrystallization occurs on the sites of row nucleation.

variety of circumstances. We now find that the crystals formed from oriented polymer have a basic similarity whatever the method of production. The highly oriented bulk-crystallized material may appear largely homogeneous when cold, but on heating, distinct birefringent fibres appear. These fibres are of very similar appearance, size and stability to fibrous crystals produced by stirring a solution, when they are embedded in normal molten material. The persistence of orientation and, therefore, birefringence at high temperatures, depends on the viscosity of the melt [5] and the structure which is relaxing to isotropy; the degree of extension and entanglement of molecular chains and the oriented volume seem reasonable variables. Varying the molecular weight will affect both the viscosity of the melt and the oriented structure produced. The effect observed, that higher molecular weights are slower to randomize, can be explained by viscosity alone. When very different preparation methods are applied to the same polymer, the decay of orientation on heating is similar for all the preparations, as the birefringence disappears at about the same temperature. Thus similar structures must be produced. But when different polymers are used, they give very different results even when the viscosities (melt flow indices) were identical.

The presence of small amounts of highly persistent orientation in ordinary bulk samples with some strain history is new information, although row-nucleated crystals have been seen in sheared isotactic polystyrene [13] and in sheared polybutene-l [15]. In the latter case, the crystallization process was observed in an optical microscope during steady shear. Row nucleation was associated with solid particles in the melt, either impurities or growing spherulites. In the present observations, fibrous crystals have been observed to form in a variety of circumstances, and they are sometimes associated with visible impurity particles (Figs. 1c and 5). When a growing spherulite was the cause of nucleation extending along the flow direction [15], the explanation could be fragments of growing lamellae being broken off and carried away. It is clear from Fig. 4c that the superheatable nucleating material does not form on the surface of the impurity particle itself. It appears that the particle acts by affecting the flow to produce a local extensional flow field, and this produces orientation and extension of the molecules [12]. The flow in each case produces the abnormal persistently birefringent structures, since the recrystallization experiments show that although strongly birefringent large fibrous crystals can be produced by nucleation on the persistent fibres, this recrystallized material melts normally.

5.2. Experimental technique

The sensitivity of the optical microscope as a detector of birefringent material depends on the spatial concentration and on the recognizable form of the material. In the present favourable case, the long fibres are easily detected and are distinguishable from birefringent impurities even when the fibres are very small. When the hot stage is in position, the resolution of the microscope is limited by the small numerical aperture of long working distance objectives. Unless special objectives are available the limit will be 1 to 2 μm. If a birefringent object is smaller than this, only the retardation is measured, so there is no distinction between a very small object of high birefringence and a larger, weaker one. If the object is larger than the resolution limit, its birefringence can be estimated assuming some symmetry, in this case assuming the fibres are cylindrical. Measurements of several large rods indicates a birefringence of 0.01 (at 134°C) compared with the maximum theoretical birefringence of 0.06. A cylinder of birefringence 0.01 would still be detectable down to a diameter of 0.3 μm. A single rod of resolvable diameter, 1.5 μm, and of arbitrary length 50 μm in each field of view would mean a concentration of only 10 ppm. Thus a concentration of 0.1% could be measured to 10% precision from one photomicrograph, ignoring the size distribution of the fibres. However, this is not the real virtue of the optical method, it is rather that many fields of view can be scanned rapidly, by focusing at different levels in the specimen, and by moving the specimen, to get an immediate impression of the distribution of the material of interest.

In the past it was the DSC method which served to detect high melting components within the composite texture of a crystalline polymer. Usually it had to be inferred from separate morphological work, if and when such a component corresponded to fibrous crystals. The present hot-stage technique now provides a morphological method which enables a direct visual identification of the high melting component which is also detected and measured by the DSC. In this respect the two techniques are appropriately complementary. Nevertheless, for quantitative work there are differences as regards the concentration range of the fibrous units where each technique is most usefully employed. Generally, if the DSC gives a high melting peak sufficiently large for quantitative work, the microscope image will be difficult to interpret at those temperatures because of the large amount of overlapping birefringent material. When the DSC peak is becoming difficult to distinguish, the sensitivity of the microscope comes into its own, and individual structures are easily resolved. In conclusion, the optical microscope with hot stage has proved itself an extremely valuable tool for the analysis of strain-induced crystallization in polymers.

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