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On the crystal texture of linear polyaryls (PEEK, PEK and PPS)

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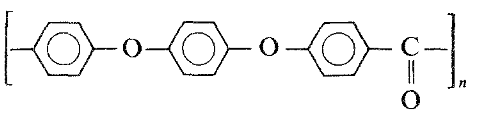
Three linear polyaryls, polyetheretherketone (PEEK) polyetherketone (PEK) and polyphenylenesulphide (PPS) have been examined regarding crystal morphologies as obtained from solutions and molecular orientation in melt grown spherulites, the latter involving also experiments on the carbon fibre containing polymer. In addition to the individual features observed in solution grown crystals agreeing with those being reported concurrently from elsewhere, the present coordinated results on three polymers underline the common crystallization behaviour and texture for this family of polymers. These common features comprise the existence of lamellae as symptomatic of chain folding, acicular shapes indicative of uniaxial growth (*b* being the growth direction in all three cases), and irregular crystal edges. The sheaf development of these crystals then leads readily to a postulated radial *b*-axis orientation in spherulites, confirmed directly in melt crystallized samples possessing transcrystalline textures induced by nucleating carbon fibres. Observations on the effect of carbon fibres drew our attention to the combined influence of the crystal nucleating effect and separation distance of these fibres on the resulting crystal texture of the polymer matrix: varying the relative magnitude of the two effects, can even reverse the overall crystal orientation in the sample. Such considerations should be pertinent to crystal texture development in composites with crystallizable thermoplastic matrices in general.

1. Introduction

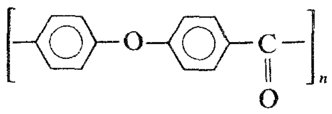
1.1. Scope

The main objective of the work underlying the present paper was to investigate morphology of PEEK (polyphenyletheretherketone, Structure A,



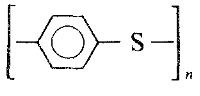
(A)

[1]) a comparatively recent polymer of currently developing technological significance. To broaden the base of the investigation two further chemically similar polymers were included, namely PEK (polyphenyletherketone, Structure B,



(B)

[1]) and PPS (polyphenylenesulphide, Structure C,



(C)

[2]).

The underlying common chemical features, namely phenyl groups along the main chain, coupled through oxygen, ketone and/or sulphur will be apparent from the formulae. The similarity of the chemistry is matched by similarities in the crystallography (see below) and, most importantly for us, by the crystallization behaviour. Regarding the latter, all three polymers crystallize slowly, at least as compared to other regular polymers containing no aromatic groups (as e.g. polyethylene or polymethylene oxide) and the resulting fully crystallized samples have a comparatively low crystallinity (less than 70%, usually below 50%). This raises a long outstanding issue in crystallinity studies; namely how is the large amorphous content to be visualized in the context of the morphology in a fully crystallized sample, which must contain two phases, amorphous and crystalline, where the crystalline material is, presumably, lamellar. (By "fully crystallized" we mean that crystallization has proceeded as far as it can under the conditions of crystallization. In terms of the usual spherulitic crystallization this corresponds to complete impingement of spherulites without intervening untransformed amorphous non-spherulitic regions.)

The first objective was to examine whether lamellar crystals from solution were obtainable or not, and, if so, to examine their external morphology and the relation of this morphology to the crystal structure by means of electron diffraction. At the time when this investigation was undertaken the subject area was still completely undocumented. Since then, solution grown lamellar single crystals of PEEK have been reported by Lovinger and Davis [3]. Our own work on

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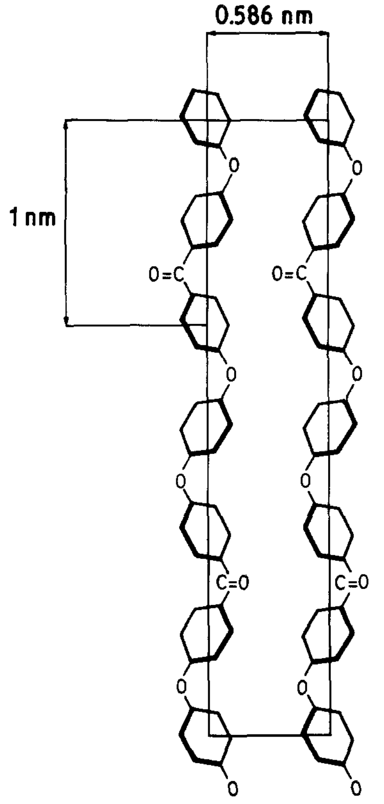


Figure 1 The 1 0 0 plane of the PEEK unit cell.

PEEK, pursued independently at the time, has led to similar results yet with certain differences which will be briefly reported together with the corresponding new documentation for PEK and PPS. The observed multilayer morphologies of solution grown crystals have then led naturally to certain suppositions regarding the anticipated crystal orientation in spherulites. We have been able to verify these suppositions on melt crystallized spherulitic samples of all three polymers by utilizing the nucleating effect of carbon fibres embedded in thin films of the polymers.

These observations on carbon fibre induced orientation effects drew our attention to the technologically important carbon fibre composites. It has for instance already been reported in the literature that when the commercially available PEEK-carbon fibre composite APC-2 (made by ICI, Wilton) is crystallized by slowly cooling from the melt, the crystals in the PEEK matrix exhibit a slight orientation relative to the carbon fibres [4]. Our present observations lead us to inferences regarding possible matrix morphologies which are relevant to this type of composite and to thermoplastic fibre composites in general.

1.2. Crystal structure and crystallization behaviour

The crystal structure of all three polymers is known to be orthorhombic with two molecules traversing each unit cell, the unit cell extending over two phenyl groups in the chain direction. This conventionally is designated the c-axis. As such these polymers are very similar in crystal structure to polyphenyleneoxide (PPO) [5]. In the cases of PEK, PPS and PPO the c-axis dimension corresponds to the crystallographic repeat unit, although the crystallographic repeat unit in PEEK extends over six phenyl units. However, it is convenient to adopt a similar unit cell for all these materials. The (1 0 0) plane of PEEK is shown in Fig. 1. The other polymer structures can be derived from this by suitable replacement of ether and ketone linkages with the appropriate groups. In each case there is rotation of the aromatic units relative to the (1 0 0) plane; adjacent phenyl units along each chain are rotated by a constant amount but in the opposite sense. Table I shows the cell dimensions for all four polymers reported in references [1, 2, 5]; slight variations have been published in the case of PEEK and PEK [6–9]. The cell dimensions of PPO are shown for the sake of completeness.

TABLE I Characteristics of materials used. Unit cell parameters (a, b, c), glass transitions (T_g) and melting points (T_m).

	Unit cell dimensions (nm)			T_g (°C)	T_m (°C)
	a	b	c		
PEEK	0.775	0.586	1.00	144	345
PEK	0.763	0.596	1.00	154	367
PPS	0.867	0.561	1.026	92	295
PPO	0.807	0.554	0.972	85	285

It is well known that thermal transitions in these materials occur at exceptionally high temperatures when compared with aliphatic polymers, no doubt because of the restricted chain mobility imposed by the presence of main chain phenyl groups. The effect of this can be seen from Table I, where values of the glass transition temperatures (T_g) and the melting points for these polymers are listed. The data pertaining to PEK, PPS and PPO were obtained from references [1], [2] and [5], respectively.

2. Experimental details

2.1. Materials

Samples of PEEK and PEK were supplied by ICI Petrochemicals and Plastics Division (Wilton). The PPS used was obtained from the Phillips Chemical Company. Low molecular weight PEEK and PEK were used for the preparation of solution grown crystals and melt crystallized thin films containing carbon fibres. The incorporation of carbon fibres into the films was found to produce orientation effects within the polymer. High modulus (Type I) fibres (Hercules HMS4) and high strength (Type II) fibres (supplied by Fothergill Engineered Fabrics Ltd) were used. The fibres supplied by Fothergill Engineered Fabrics Ltd, Littleborough were known to have been coated with a thin layer of epoxy resin; the surface treatment of the other fibres was unknown beyond the fact that they were not epoxy coated. In both cases the fibres were approximately 7 to 8 μm in diameter.

2.2. Specimen preparation

2.2.1. Solution grown crystals

Crystals of the polymers were obtained by crystallization from solutions in hot organic liquids. The polymers used are of a highly insoluble nature and therefore the available solvents were limited to liquids of highly polar character heated to high temperatures. Benzophenone was found to be a suitable solvent for both PEEK and PEK, which dissolved at approximately 260° C and in the boiling liquid respectively.

Cooling from the dissolution temperatures to lower temperatures resulted in crystallization of the polymers. Benzophenone itself is a solid at room temperature (melting point approximately 48° C) and thus to facilitate subsequent specimen preparation, once the crystal suspension had been allowed to cool to ambient temperature, the benzophenone was exchanged with acetone, which dissolves benzophenone while leaving the polymer crystals unaffected.

Crystals of the third polymer, PPS, were prepared from solutions in α-chloronapthalene, where the dissolution temperature is approximately 230° C. Subsequent crystallization was allowed to occur at approximately 187° C. The polymer precipitate was then hot filtered and washed in hot solvent before the suspension was cooled to ambient temperature. α-chloronapthalene is liquid at room temperature and therefore a solvent exchange was unnecessary.

2.2.2. Melt crystallization

Thin films of each polymer incorporating the chosen type of carbon fibre were produced by heating small amounts of polymer and fibre on microscope slides. When the polymer was molten, films were pressed or smeared between cover-slips and the slides. For our purposes it was desirable that large spherulites should be produced. Therefore, where choices of polymer preparations were available, those which possessed a low density of crystal nuclei were selected. In general, the formation of large spherulites is encouraged by prolonged heating of the melt well above the melting point. This tends to achieve complete melting of persisting microscopic crystalline regions which otherwise will act as nucleating seeds during subsequent crystallization. If all such seeds are eliminated then the number of potential nucleation sites is decreased and the spherulites will grow to a larger size than would otherwise be the case. However, this technique cannot be applied to PPS because it rapidly alters molecular structure, above the melting point of approximately 295° C by means of crosslinking and chain extension [10]. PPS was therefore only kept above its melting point for a short time prior to crystallization.

The films were all crystallized isothermally at low supercoolings, which also favours the growth of large spherulites. At the end of the isothermal crystallization periods the films were either quenched or rapidly cooled. Later the films were removed from the microscope slides and cover-slips; it was found that detachment was facilitated by soaking in acetone.

2.3. Method of investigation

2.3.1. Solution grown crystals

Crystals of the three polymers were prepared for transmission electron microscopy (TEM) and electron diffraction by depositing small amounts of the crystal suspensions on carbon film supported by TEM copper grids. The solvents were allowed to evaporate and the crystals obliquely shadowed with platinum–palladium alloy to enhance contrast. A Philips 301 transmission electron microscope operating at an accelerating voltage of 100 kV was used for bright field microscopy and electron diffraction.

2.3.2. Thin films containing carbon fibre

The melt crystallized thin films were examined optically by polarized light transmission microscopy. Photomicrographs were taken using an Ultraphot II microscope equipped with a 35 mm camera. Using a first order sensitive tint plate the signs of birefringence of spherulites of all three polymers were determined.

In some cases locally oriented regions of polymer were observed optically, the nature of the orientation being described in a later section of this paper. Selected area wide angle X-ray diffraction (WAXD) patterns from such areas were obtained. In the majority of cases this was achieved using a camera with a 200 μm diameter defining aperture. This camera was also equipped with a telescope and a specimen holder capable of lateral motion, thereby allowing reasonably precise specimen alignment. In one case the area of interest was selected by cutting it out of the film under a microscope and mounting it in the path of a large beam.

In some cases selected area small angle X-ray scattering (SAXS) patterns were also obtained from approximately the same areas as the WAXD patterns using the SERC Synchrotron Radiation Source (SRS) at Daresbury. Again a camera allowing accurate specimen area selection and possessing a 200 μm diameter defining aperture was employed. The intensity of X-ray scattering in the low angle range from a 200 μm diameter area of the polymers used is low and the use of the high energy SRS therefore greatly reduced the necessary exposure times.

All of the X-ray studies, apart from the SAXS work with synchrotron radiation, were undertaken with nickel filtered CuK_α radiation. In every case our patterns were recorded on film using flat plates.

3. Results and discussion

3.1. Solution grown crystals

From inspection of electron micrographs shown in Figs 2a to c it is at once apparent that there are features common to crystals of all the three polymers. In all cases the polymers have crystallized from solution in elongated, multilayered, sheaf-like lamellae possessing rough edges, rather than as isolated single crystals.

The basic underlying feature is a recognizable layer-morphology, the layers being elongated lath or spear shaped with jagged edges (Fig. 2d). This in itself, as also recognized by Lovinger and Davis [3], is suggestive of chain folded crystallization. The jaggedness discloses a fibrosity, the layers splitting or cleaving along the lath or spear direction which clearly corresponds to the direction of growth. This in turn suggests that the fold plane is parallel to the long dimension, hence growth direction, of the crystal in analogy with other systems displaying this kind of growth habit [11].

As in all analogous polymer structure studies, information on molecular and lattice orientation is required to be related to the lamellar morphology; this

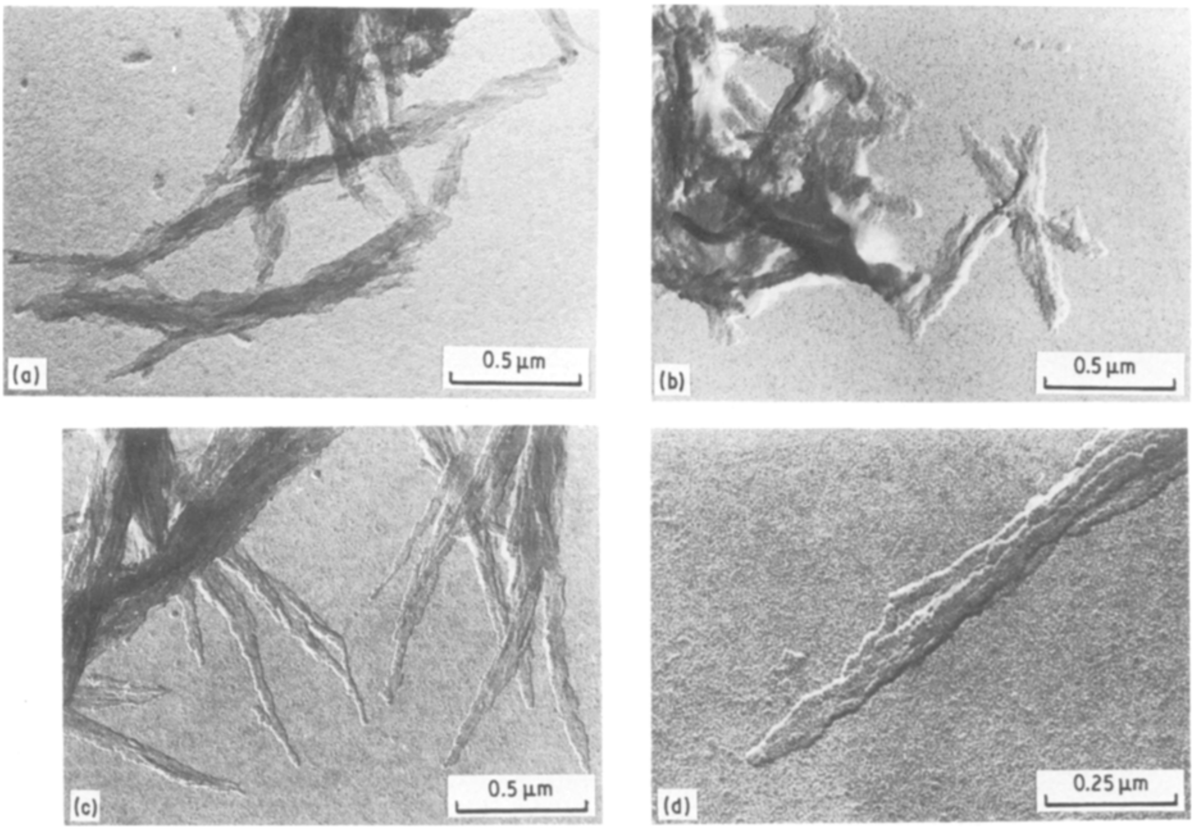
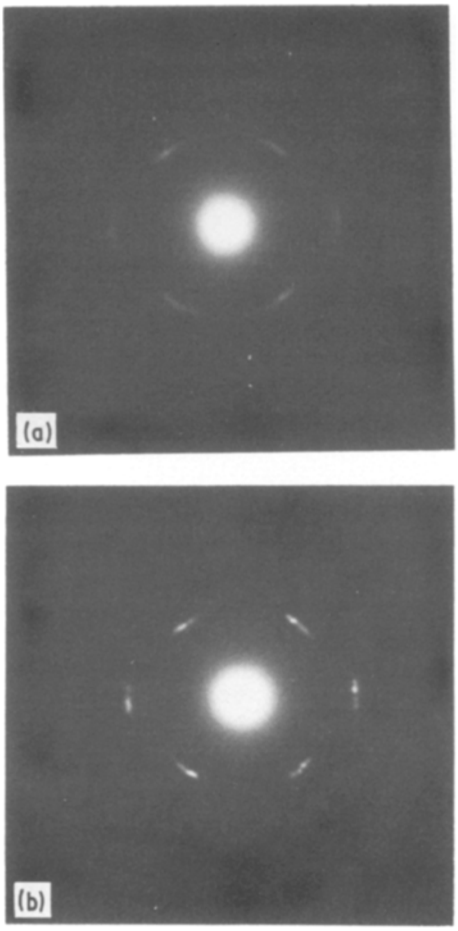


Figure 2 Electron micrographs of solution grown crystals. (a) PEEK grown in a 1% solution in benzophenone at approximately 222° C. (b) PEK grown in a 0.02% solution in benzophenone, (c) and (d) PPS grown in a 0.25% solution in α-chloronapthalene at approximately 187° C.

information, as is well known, can be obtained from electron diffraction. Diffraction patterns of single layers could be obtained from the tips and edges of the sheaves where individual layers are seen flat on. Figs 3a to c show these types of diffraction patterns for PEEK, PEK and PPS, respectively.

According to the crystal structures established in melt crystallized specimens the reflections are all $h\,k\,0$ (see below), and their mutual disposition is consistent with a c-axis projection in all three polymers, supported further by the absence of visible $h\,k\,l$ reflections. The argument in favour of chain folding then follows along the familiar lines.

In detail, the diffraction patterns of all three polymers consisted of the principal $h\,k\,0$ reflections visible,



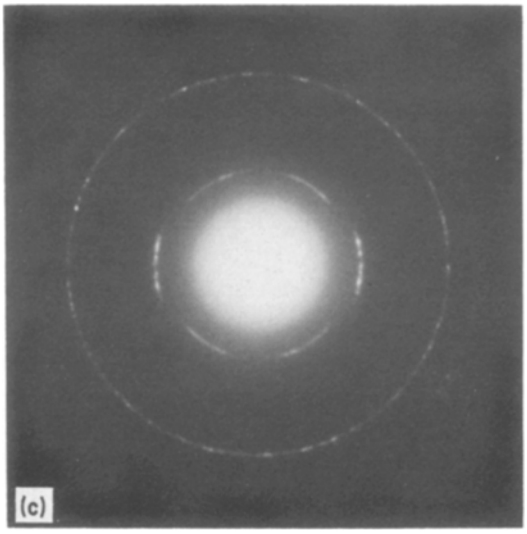


Figure 3 Electron diffraction patterns from peripheries of crystal sheaves. Sheaf direction vertical (a) PEEK (b) PEK (c) PPS. In each case 2 0 0 is horizontal and the other visible reflections are 1 1 0. In the negative of Fig. 3c the 0 2 0 reflections are clearly visible. Fig. 3c also shows diffraction from Pt/Pd shadow.

1 1 0, 2 0 0 and 0 2 0, the latter very weak and sometimes only visible on the negative.

In addition to the *c* (molecular) axis being perpendicular to the layers the diffraction patterns also disclosed that the long crystal (lath) dimension is always along *b* which, by the above morphological argument, could also be the fold plane direction.

So far the above corresponds to the findings by Lovinger and Davis [3] on PEEK, now extended also to PEK and PPS. The above authors also refer to 2 1 0 reflections in PEEK. 2 1 0 is a forbidden reflection for all three unit cells, as are all *h k* 0, with $(h + k)$ odd [7, 9 and 2]. We only saw this reflection in the best diffraction patterns of PPS where it is extremely weak and we therefore expect other intrinsically more intense *h k* 0 reflections (e.g. 1 3 0) to be more noticeable first. Yet, whenever *h k l* reflections were also present from areas in nearby sheaf interiors (see below) the strong 2 1 1 reflection appeared at a position very close to the expected 2 1 0 in a purely *c*-axis diffraction pattern. (0.308 nm (for 2 1 1) against 0.323 nm (for 2 1 0) in the case of PEEK). In fact, unless special precautions were taken in the area selection, 2 1 1 reflections were difficult to avoid. We think therefore that it is likely that the 2 1 0 referred to in [3] was in fact 2 1 1.

When extending the electron diffraction to the multilayer portion of the aggregates further features emerge: (i) the preferential *b*-direction parallel to the direction of maximum crystal elongation in individual layers is preserved as that corresponding to the sheaf direction. Thus 0 2 0 (where visible) is centred along the sheaf direction and 2 0 0 is always found along the direction perpendicular to it (Fig. 4) (ii) The reflections become increasingly disoriented (arced) to varying extent (iii) *h k l* reflections keep appearing progressively when moving towards the sheaf interior. Prominent amongst these is the 2 1 1 already mentioned. At the same time higher order *h k* 0 reflections may also appear. The appearance of 0 4 0 in PPS is clearly a consequence of the relative intensification of 0 *k* 0 reflections while others (see Fig. 4) are likely to be the consequence of the larger areas being selected with increasing contribution from the now more numerous *c*-axis oriented crystals which, in view of their thinness, give a comparatively large contribution to the diffraction patterns.

The interpretation of the aforementioned effects, relating single layer orientation to orientation within the sheaf interior with one common invariant-crystal direction, can proceed along well established lines, as first introduced in analogous studies on nylons [11]. The procedure is to consider progressive stages of randomization around the crystallographic axis corresponding to the sheaf axis, which is the *b*-axis, as identified in the present work. This provides for all stages of development between the single crystal and a fibre orientation with *b* as the fibre axis. A paper by Kumar *et al.* [12] published during the latter stages of preparation of the present paper gives evidence that '*b*' is radial in PEEK spherulites; this conclusion having also been reached by Lovinger and Davis [3, 13].

By past precedent these findings should provide a link between solution grown crystals and melt grown spherulites. Morphologically, the sheaves develop into spherulites with the elongated fibrous units becoming the radial growth units in the spherulites. Thus the direction of growth in the spherulites should be the same as the direction of maximum crystal elongation, i.e. *b*. Finally, the plane normals of the lamellar constituents of the sheaves should become tangential in the spherulites. The present examination of solution crystallized specimens hence provides clear indications to the expected direction of growth in melt crystallized spherulites. This we shall verify in a later section of this paper.

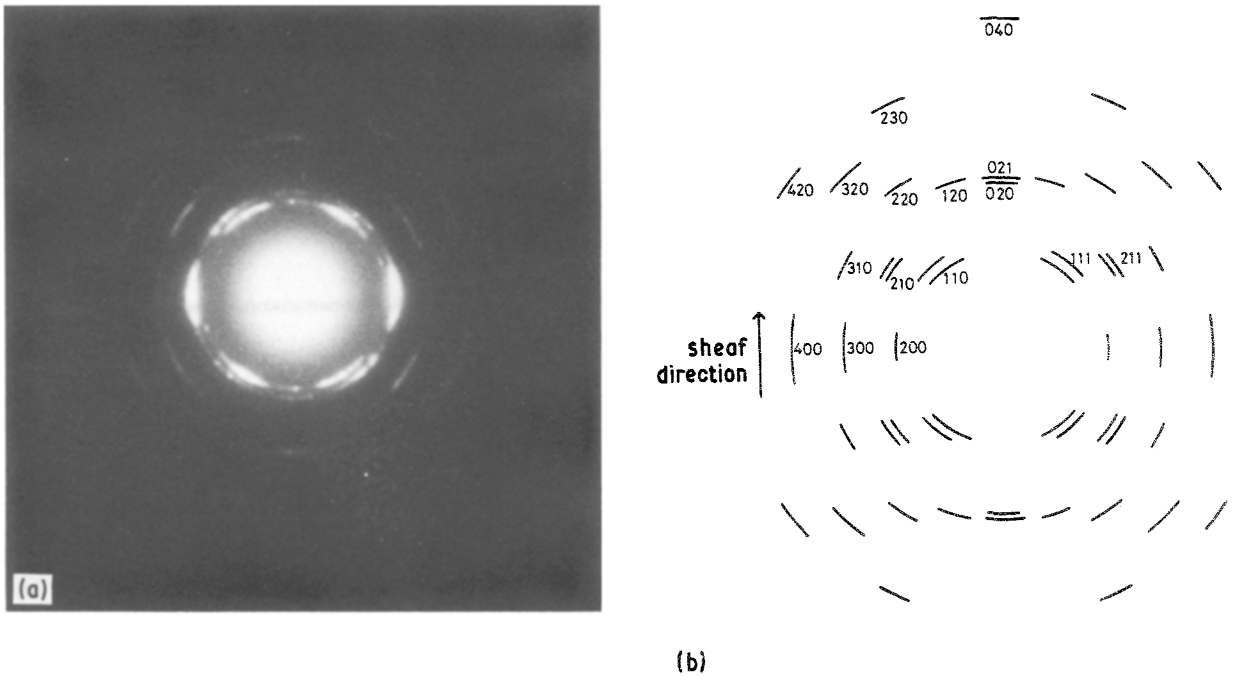


Figure 4 (a) Electron diffraction pattern and (b) sketch showing all the reflections from multilayer portion of PPS crystal aggregate. Sheaf direction vertical. Note the presence of *h k l* reflections, particularly 2 1 1 and 1 1 1.

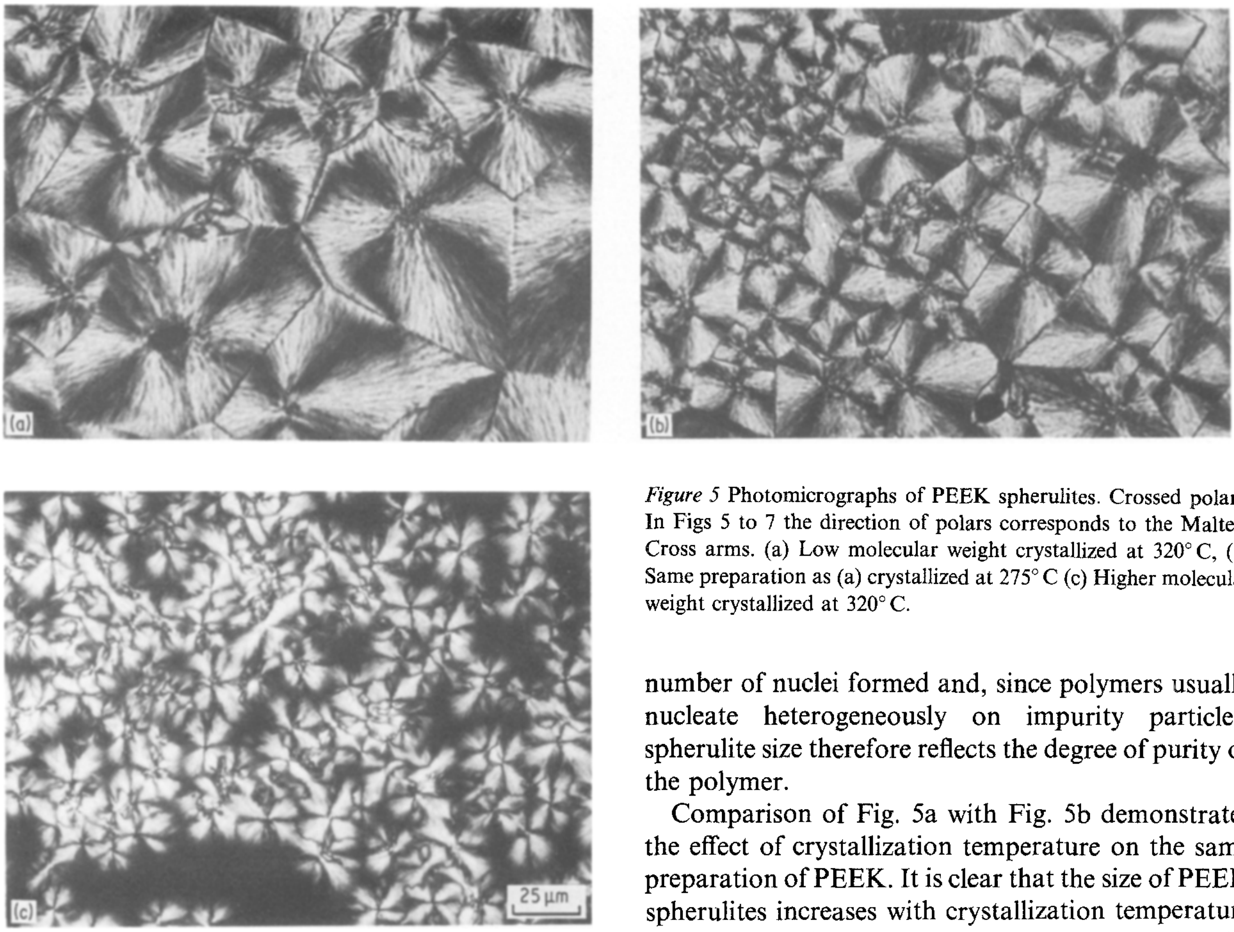


Figure 5 Photomicrographs of PEEK spherulites. Crossed polars. In Figs 5 to 7 the direction of polars corresponds to the Maltese Cross arms. (a) Low molecular weight crystallized at 320° C, (b) Same preparation as (a) crystallized at 275° C (c) Higher molecular weight crystallized at 320° C.

3.2. Melt crystallization

3.2.1. General

Fig. 5 shows how the spherulite size in a fully crystallized film can vary with preparation of the same polymer. Two preparations of PEEK subjected to the same thermal history and crystallized at 320° C are compared in Figs 5a and c, where clearly the final spherulites in Fig. 5a are larger than in Fig. 5c. In general, the size of spherulites is governed by the number of nuclei formed and, since polymers usually nucleate heterogeneously on impurity particles, spherulite size therefore reflects the degree of purity of the polymer.

Comparison of Fig. 5a with Fig. 5b demonstrates the effect of crystallization temperature on the same preparation of PEEK. It is clear that the size of PEEK spherulites increases with crystallization temperature where the nucleation rate is low compared with the growth rate. This is in agreement with findings by Blundell and Osborn [14] and Kumar *et al.* [12].

Figs 6 and 7 also show spherulites in films of PEK and PPS. It may be seen that all the three materials display a speckled appearance interpreted as an indication of incipient banding.

Examination of the films using a first order sensitive tint plate showed that all three materials displayed negative birefringence, i.e. the direction of highest refractive index hence the molecular axis is tangential. We did not observe any instances of positively

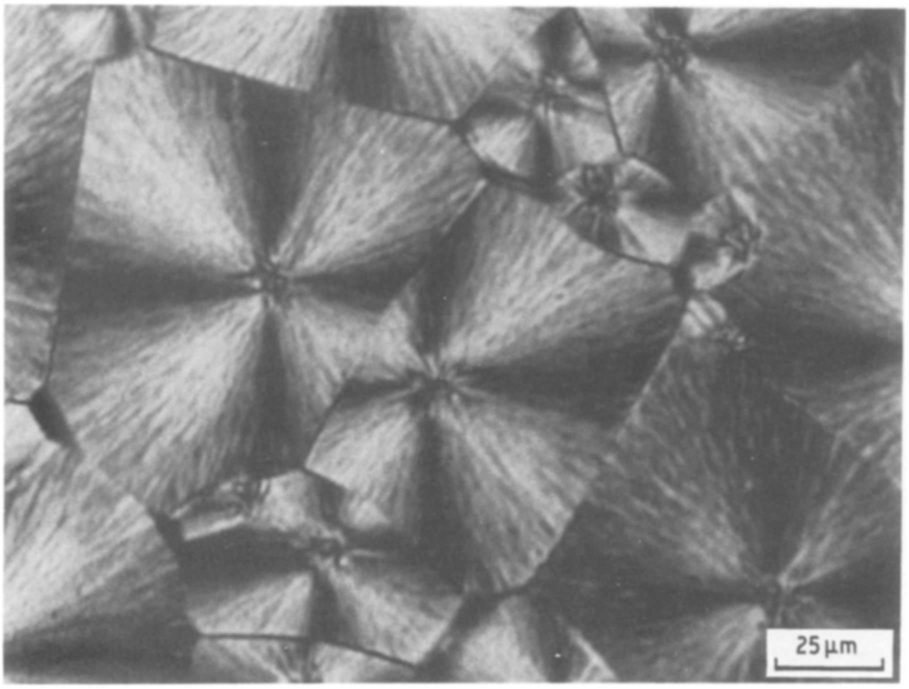


Figure 6 Photomicrograph of PEK spherulites. Crossed polars. Crystallized at 350° C.

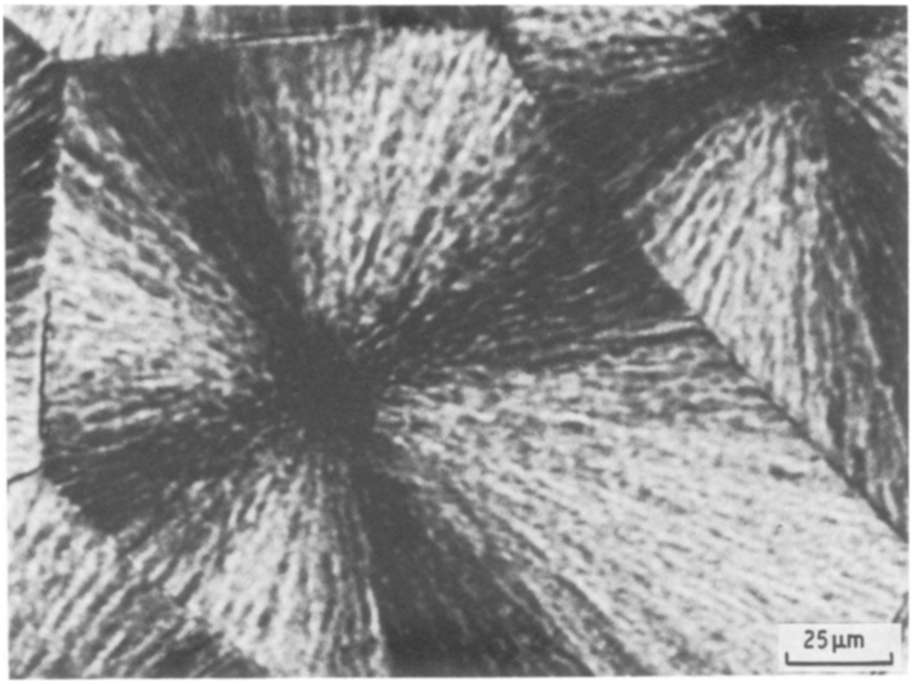


Figure 7 Photomicrograph of PPS spherulites. Crossed polars. Crystallized at 265° C.

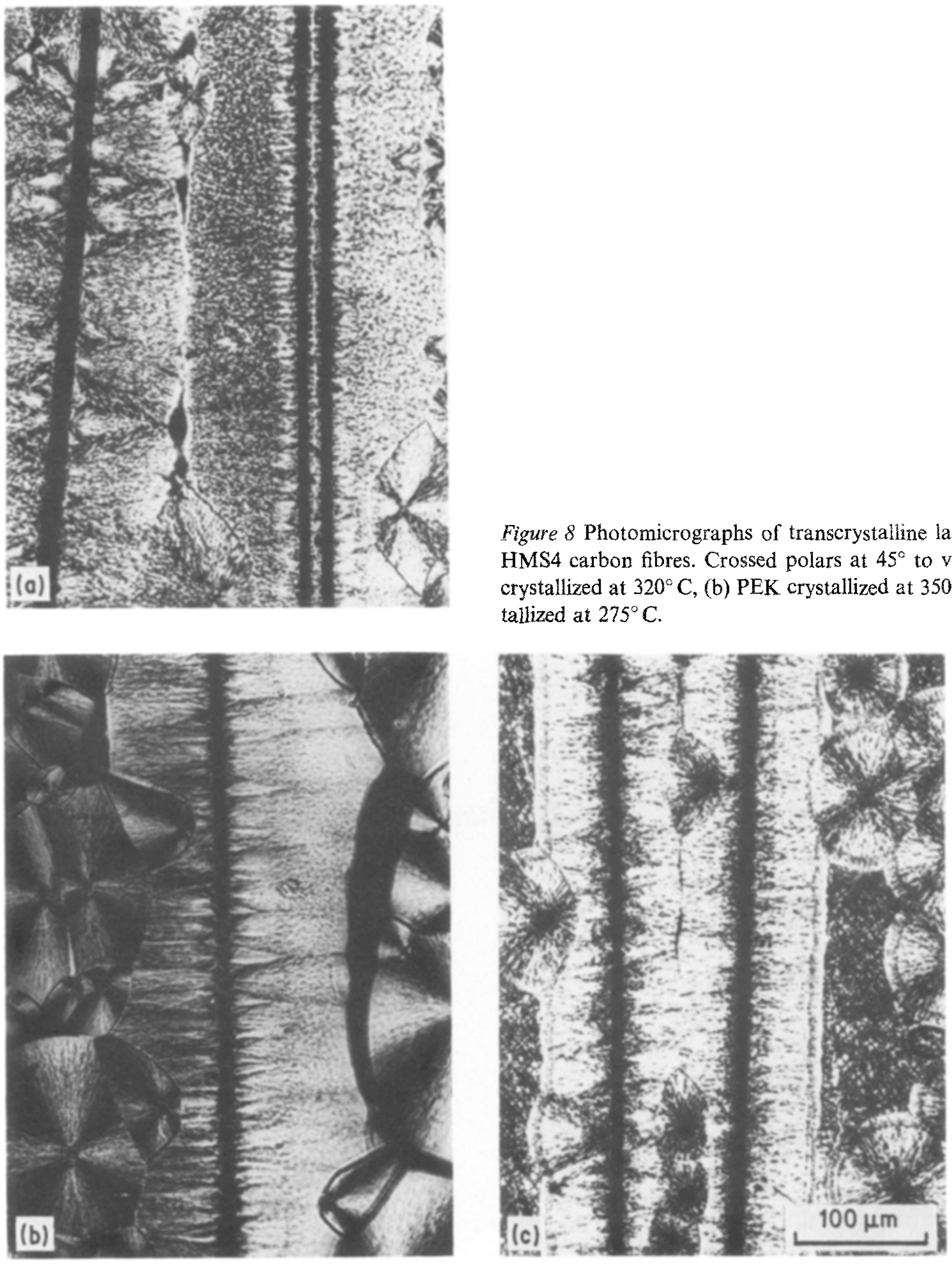


Figure 8 Photomicrographs of transcrystalline layers on Hercules HMS4 carbon fibres. Crossed polars at 45° to vertical (a) PEEK crystallized at 320° C, (b) PEK crystallized at 350° C, (c) PPS crystallized at 275° C.

birefringent spherulites such as has been reported on work on earlier preparations of PEEK [14].

From this brief description it thus appears that the crystallization behaviour of these aromatic backbone polymers is similar to that of more widely studied aliphatic crystallizable polymers, such as polyethylene.

Fig. 8 shows large transcrystalline layers (tcl) of all three polymers formed on Hercules HMS4 carbon fibres. Clearly these fibres nucleated growth of all three polymers extremely well. In some cases tcls nucleated on adjacent fibres were found to impinge, so that virtually all the inter-fibre matrix consisted of tcls Figs 8a and c. Transcrystallinity itself is a widely known phenomenon caused by preferential nucleation on the surface of a substrate compared with nucleation in the bulk. Nucleation occurs at closely spaced surface sites, and thus subsequent growth parallel to the substrate from the nucleation sites can only proceed until spherulites emanating from adjacent nuclei impinge. However, growth normal to the substrate may advance unhindered until the growing front impinges either on spherulites nucleated in the bulk or on a tcl formed on a neighbouring surface. Under such circumstances extended regions will result with spherulite radii lying all parallel and oriented normal to the nucleating surface in two dimensions, as in thin films, or all lying in parallel planes in thicker samples. In either case this preferential orientation of spherulite radii imparts overall orientation to macroscopic regions, if not to the whole, of the sample. Detection and evaluation of such orientation, in the knowledge of the underlying polarizing optical texture, provides a method of determining the growth direction of spherulites while avoiding the need to resort to the technique of microbeam X-ray diffraction.

In the case of the thin films prepared in this study it seemed that the exact sites of nucleation sometimes lay on the upper or lower surfaces of the carbon fibres when viewed through the microscope slides. Although the fibres may not actually have been in contact with the slide or the coverslip (the film thickness being

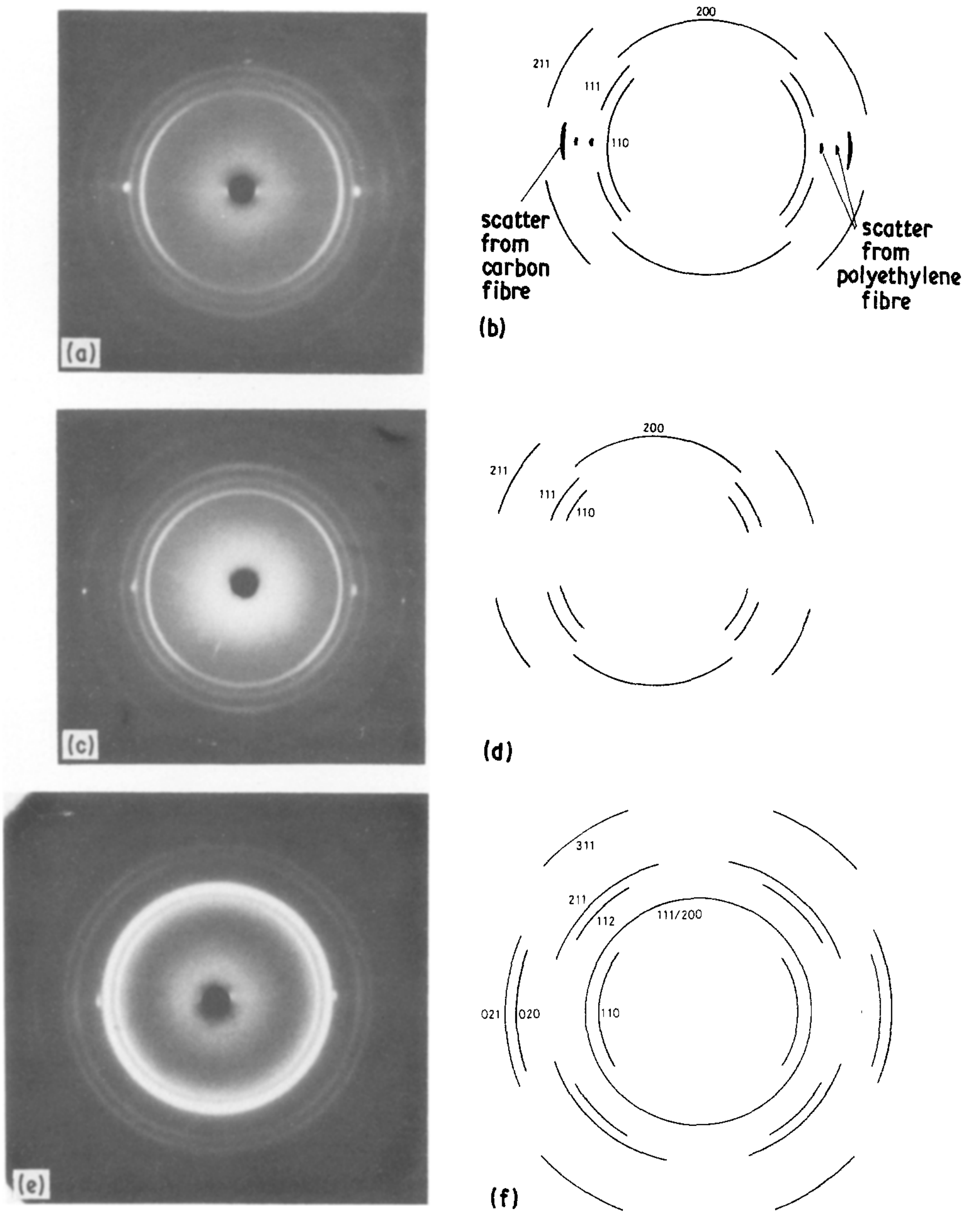


Figure 9 WAXD patterns and sketches of transcrystalline layers shown in Fig. 8. The carbon fibre direction is vertical. The sharp equatorial spots are from a polyethylene fibre used as a direction calibrant. (a) and (b) PEEK, (c) and (d) PEK, (e) and (f) PPS. The arcs on these sketches correspond to the intensity maxima only.

greater than the fibre diameter), these sites could have been the places of enhanced shear in the melt during pressing with a contributory effect of enhancing nucleation.

Fig. 8c shows two sizes of PPS spherulites, the larger of which are characteristic of the isothermal crystallization at 275° C, while the smaller ones are characteristic of the subsequent cooling process. In Fig. 8a there is some evidence of quenched uncrystallized material between transcrystalline layers but otherwise full spherulite crystallization seems to have been achieved isothermally throughout the sample.

Fig. 9 illustrates some selected area WAXD diffraction patterns from regions shown in Fig. 8 with accompanying sketches to show weaker reflections which are not expected to reproduce well in the prints. The carbon fibre direction is vertical. The orientation effects are weak, but a common pattern emerges, although this can be best understood by looking at different reflections in the different polymers. In PEEK and PEK the 2 0 0 reflections are arced along the carbon fibre direction, the 0 2 0 reflections are not visible, but the positions of the other reflections (1 1 0, 2 1 1, etc.) are consistent with 0 2 0 along the equator. In PPS (Fig. 9e) the 0 2 0 is visible and is strongly arced on the equator. In PPS the 2 0 0 reflection has a very similar spacing to the 1 1 1 and both are strong. The second arc from the centre in Fig. 9e is a composite of these two reflections and cannot be used to judge the maximum of either unambiguously. While texture patterns cannot be uniquely determined from the maxima of a few reflections only, the above patterns are consistent with sheaves growing along '*b*' in all three cases (as observed in the electron microscope) normal to the carbon fibres and otherwise randomly oriented around the direction of crystal growth.

In all three polymers the final overall degree of orientation is expected to be weak due to the cylindrical averaging around two mutually perpendicular directions, as a result of which much of the disorientation in the pattern would be intrinsic to the texture.

In view of the known transcrystalline morphology the crystal orientation within spherulites should be identified as consisting of radial, cylindrically symmetrical texture elements with *b* as the "fibre" axis aligned along the spherulite radii. This method of assignment is supported by the whole background of past micro X-ray diffraction studies on spherulites and by works on transcrystalline and equivalent structures formed by other polymers. The above assignment is also fully consistent with the observed negative birefringence of the spherulites and, of course, with the generally accepted morphological picture of lamellae growing out radially, which links it naturally to our own electron microscopy.

Complementary SAXS patterns obtained from the tcls of PEEK and PEK are shown in Figs 10a and b, respectively. In the case of PEEK (Fig. 10a) there is diffuse scattering concentrated on the meridian (with respect to the carbon fibre) corresponding to a spacing of approximately 20 nm (without Lorentzian correction); similar SAXS measurements are reported in [12, 14]. Such scattering is interpreted as arising from the internal lamellar morphology of the transcrystalline layers. The location of the peaks is entirely consistent with the lamellar structure, where the lamellae are, on average, oriented parallel to the growth direction hence the inferred spherulite radii.

The same interpretation applies to the pattern from PEK but with a long spacing of approximately 16 nm (without Lorentzian correction). Fig. 10b also shows equatorial scattering in the form of streaks. Such equatorial streaking is characteristic of carbon fibre alone. Its presence or absence is likely to depend on whether a sufficient amount of fibre lies in the path of the beam. Some equatorial scattering from the carbon fibres is also apparent on the WAXD patterns (Fig. 9) and is labelled on Fig. 9b.

3.2.2. A second form of constrained growth

In the above case of transcrystalline structures the high density of nucleation sites along the fibre presents constraints to spherulitic development. It has, however, become apparent in the course of the present study that another form of constrained growth may also arise in such composites. Such effects have so far been recognized only in localized areas under the polarizing microscope, with identifiable consequences for the corresponding diffraction patterns. We found these effects sufficiently important to present here. Firstly because they may, under certain circumstances extend over the whole macroscopic sample, and secondly, because in combination with the case of transcrystallinity, they point to a wider principle concerning the effect of the filler component on the

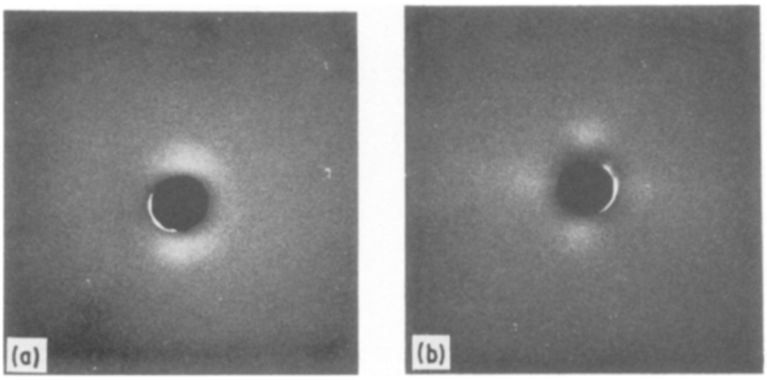


Figure 10 SAXS patterns from transcrystalline layers shown in Fig. 8. (a) PEEK, (b) PEK. The carbon fibre direction is vertical.

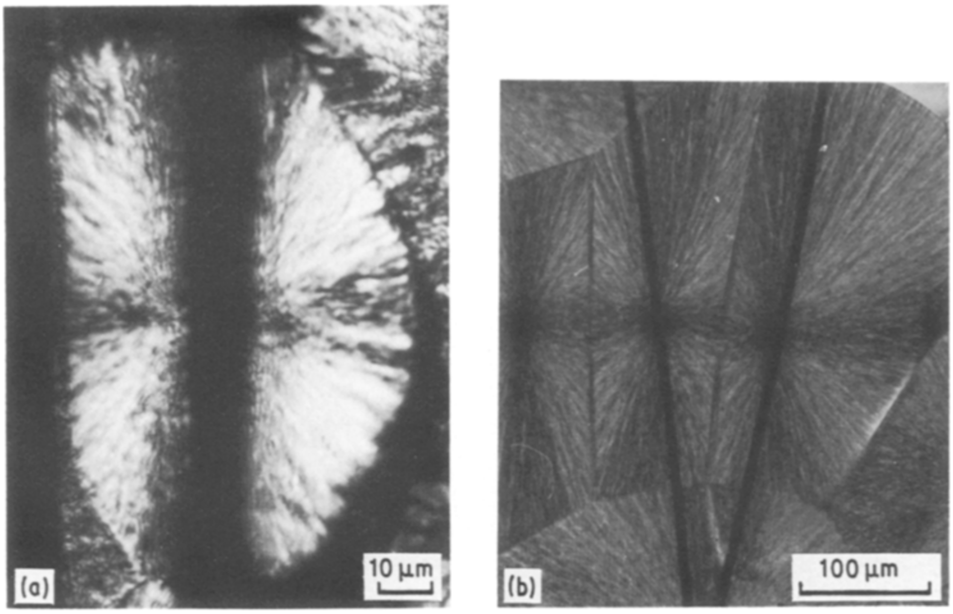


Figure 11 Photomicrographs of spherulites oriented parallel to Type II epoxy coated fibres. (a) PEEK crystallized at 320° C, (b) PPS crystallized at 250° C. Crossed polars. Polar directions vertical and horizontal.

crystal texture of the polymeric matrix in composites containing thermoplastic polymers. The additional constraints are caused by the carbon fibres themselves where, in contrast to the case of transcrystallinity, they have little or no crystal nucleating effect on the matrix. This is the situation with the epoxy coated carbon fibres used for the experiments below.

The recognition of the alternative constraints to spherulitic growth arose from photomicrographs such as Fig. 11 (a), PEEK and (b) PPS. Here we see spherulites of elongated shapes, the direction of elongation being parallel to the carbon fibre direction. It is apparent that the effect is due to constrained growth rather than deformation of spherulites already grown, the close adjacency of the carbon fibres stunting growth perpendicular to the fibres while allowing it parallel to them, provided the growth is not arrested by other spherulites. If the fibres themselves have little or no nucleating effect, such spherulites will only arise at distances which are large compared with the fibre separation and elongated spherulites such as in Fig. 11 will result. Note that the overall direction of elongation is perpendicular to that arising from transcrystallinity, which should be reflected in the diffraction patterns. This we set out to test in what follows.

An area such as shown in Fig. 11 was selected under the optical microscope. This was cut out and then mounted on a layer of "Durafix" adhesive over the guard aperture of a suitable WAXD camera, where the beam size was large compared with the specimen area. Fig. 12 is the diffraction pattern obtained from part of the area of PPS shown in Fig. 11b. While orientation effects are weak there is distinctly greater

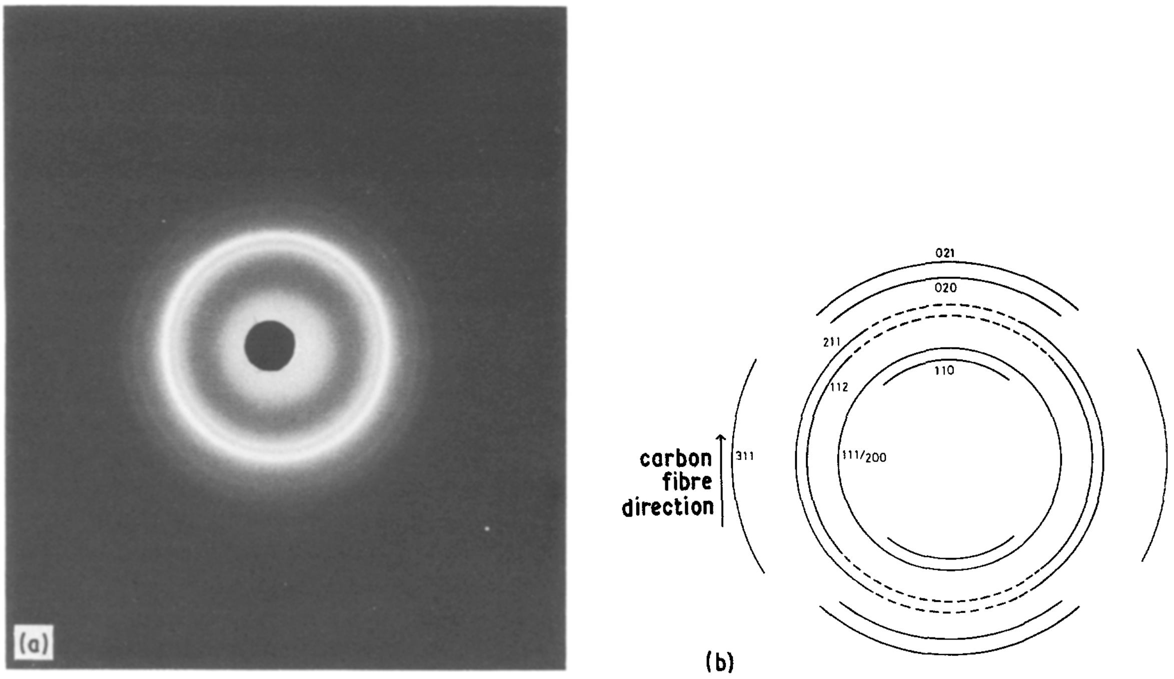


Figure 12 WAXD pattern and sketch of area of PPS shown in Fig. 11b. The carbon fibre direction is vertical.

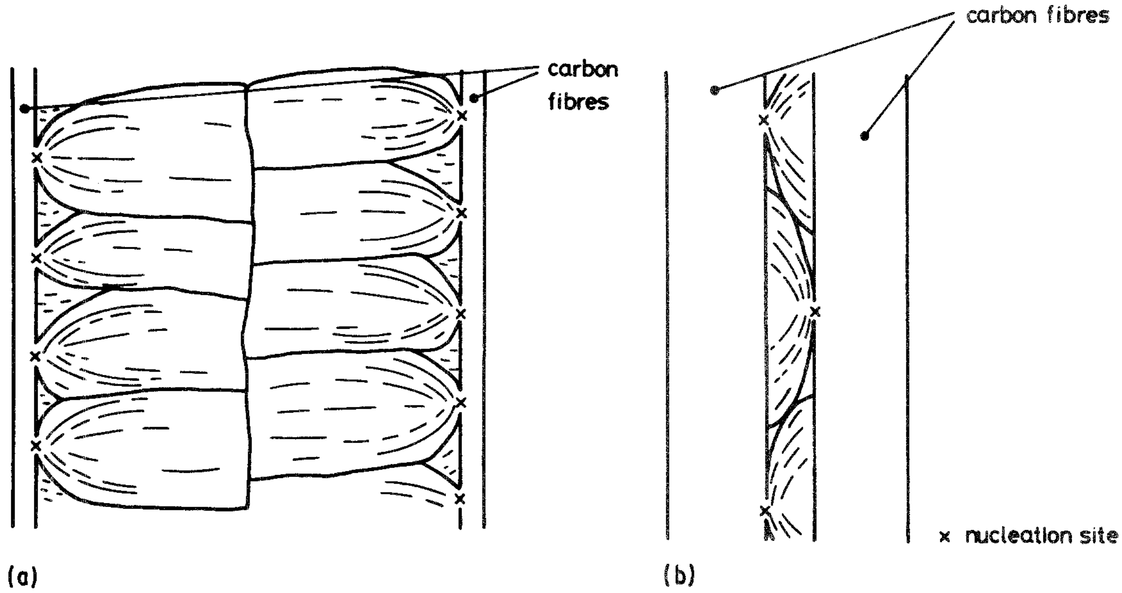


Figure 13 Diagrammatic representation of the two possible spherulite morphologies resulting from constrained growth in thermoplastic composites. The nucleation density on the fibres is the same in each diagram.

intensity on the meridian with respect to the carbon fibre direction for the (0 2 0) (0 2 1) and (1 1 0) reflections. This corresponds to a 90° rotation as compared to the transcrystalline sample (Fig. 9e), as was anticipated from the optical micrographs.

Clearly the orientation effects are weak, but this is the necessary consequence of the inherently greater divergence of the spherulitic radii than in the transcrystalline samples, which in turn, from our argument, should be related to the fact that the constraints, inducing unidirectional spherulitic growth, were not as stringent in our conditions of sample preparation. Further samples, where such constrained growth extends over the full macroscopic sample, would have been desirable for a more conspicuous demonstration of the effect.

Fig. 13 shows, diagrammatically, the two morphologies which we find in the carbon filled PEEK, PEK and PPS samples. Where the carbon fibres are far apart and have a high nucleating density transcrystalline layers grow out with *b*, the crystal growth direction, at right angles to the carbon fibre direction (Fig. 13a). In other samples, where the carbon fibres are close, or have little or no nucleating effect, the growth of the spherulites is limited by the proximity of the carbon fibres; extended growth along *b* is only possible along directions more closely parallel to the fibres (Fig. 13b). It was essential that the epoxy coated carbon fibres (poor nucleation) were all placed close enough to give the constrained spherulitic texture. The appropriate combination of crystal nucleation and fibre spacing would be required to enhance the effects. We are inclined to believe that the slight orientation effects reported to occur in the commercially available PEEK/carbon fibre composite "APC-2" [4] may have originated in the mechanism depicted in Fig. 13b.

It is to be noted that the scheme is all based on existing morphological knowledge and no new postulate is involved. Possibly the simplest way of looking at it is to consider the spreading of Huygens wavefronts from fixed sources which are the crystallization nuclei. The rest follows from the number and from the disposition of these nuclei relative to the particulate components (in this case carbon fibres) of the composite. It follows, a fortiori, that the scheme in question is not confined to the PEEK, PEK, PPS systems which, as the main subjects of the present work, happened to be the materials on which these, in retrospect fairly obvious, generalizations were recognized.

While the present studies are confined to structure aspects, it will be apparent that they should be of consequence also to properties: e.g. the mechanical behaviour should be significantly different in textures such as Figs 8a and 11a. Here we can provide at least one pointer in the form of Fig. 14 which displays preferential fracture along the line (or surface) where two transcrystalline growth fronts meet. The reason why such a boundary should represent sites of

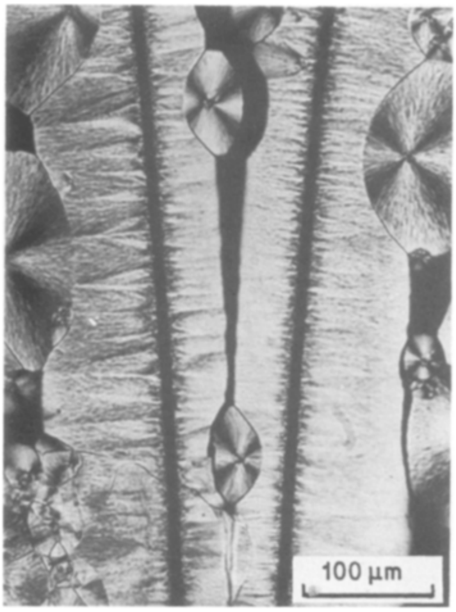


Figure 14 Photomicrograph showing cracking between PEK transcrystalline layers formed on Hercules HMS4 carbon fibres. Crossed polars at 45° C to vertical.

structural weakness is intuitively obvious. It will be equally obvious that such considerations should be pertinent to composite design.

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