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Morphology of *trans*-1, 4-polyisoprene crystallized in thin films

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The development of melt-grown crystalline morphology in thin films of trans-1,4-polyisoprene (TPI) was studied by optical and electron microscopy. The crystalline morphologies observed are explained in terms of thin chainfolded lamellar crystals which would grow (if unrestricted) to a diamond shape. The electron diffraction patterns obtained can be indexed using the unit cells proposed by Fisher [3]. The preferred growth faces for the low melting form crystals (LMF) are the (120) planes and probably the (110) planes for the high melting form crystals (HMF). LMF crystals are exclusive to LMF spherulites and HMF crystals are exclusive to HMF spherulites. At large supercoolings both LMF and HMF spherulites nucleate as bundles of lamellar crystals and grow by extensive, twisting, branching and spawning. LMF spherulites grown at small supercoolings develop as hedrites/axialites, or as splayed groups of large crystals differing in orientation with respect to the electron beam. The frequency of twisting, branching and spawning being minimal at these supercoolings. Row nucleated structures are observed in strained films. They consist of long wavy backbone crystals (5 to 25 nm thick) lying in the direction of strain, overgrown by lamellar crystals (5 to 10 nm thick) oriented at right angles to the strain direction. At some temperatures both LMF and HMF crystals nucleate in the same row. The morphologies observed in thin films are compared with and discussed in terms of the observations made of bulk-grown and solution-grown crystals.

1. Introduction

Gutta percha is a 1,4-chain polymer of isoprene in which the isoprene units have a *trans* configuration in relation to the double bonds. Two crystalline forms of gutta percha (TPI) are generally observed. They are reported to have equilibrium melting temperatures of 87 and 78° C [1]. The low temperature melting crystals (LMF) can be described by an orthorhombic unit cell with $a = 0.785$ nm, $b = 1.90$ nm, $c = 0.472$ nm [2, 3]. Four long-chain molecules pass through this unit cell parallel to the c-axis, with a non planar zig-zag carbon chain. All four molecules are identical consisting of either right- or left-handed molecules [2]. The unit cell has one isoprene unit along its c-axis. While there is agreement on the crystal structure of the LMF crystals, the structure of the high temperature melting crystals (HMF) is a matter of dispute. However, it is clear from the identity periods of drawn structures, in the drawing direction, that the HMF crystal structure must have two isoprene units along the c-axis [2]. Thus it is easily distinguishable from the LMF crystal structure. It is the opinion of the present authors that this structure can be best represented by a monoclinic unit cell as proposed initially by Fisher [3], and later by Takahashi *et al.* [4]. The unit cell due to Fisher has $a = 0.59$ nm, $b = 0.79$ nm and $c = 0.92$ nm, $\alpha = \beta = 90°$ and $\gamma = 94°$. This cell corresponds to the γ-structure proposed by Bunn [2], and has two molecules passing through the cell parallel to the c-axis. The unit cell has been used successfully to index diffraction patterns by several workers [5, 6].

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When TPI is crystallized from the melt and examined between crossed nicols, two types of spherulites are observed [7]. At crystallization temperatures below 35° C, the spherulites display a characteristic Maltese cross, while dendritic type spherulites are observed if crystallization takes place above 45° C. In the intermediate temperature range, both types of spherulites are obtained. The Maltese-cross spherulites have the lower equilibrium melting temperature and contain only LMF crystals [8]. The dendritic spherulites consist of HMF crystals [8]. Some attempts have been made to study the morphology of crystalline TPI by electron microscopy. Keller and Martuscelli [9] succeeded in growing both LMF and HMF single crystals in solution, and showed that the molecules of both crystals were chain-folded. Fischer and Henderson [6], using a replica technique, distinguished branching and twisting lamella crystals in HMF spherulites but only the outlines of LMF spherulites were revealed. Some studies of strain induced crystallization in thin films, have been carried out [10–12]. Machin [10] observed a line structure running in the direction of stress with lateral crystal growth at right angles to the stress direction. He suggested that the central thread was an extended-chain type crystal overgrown by lateral chain-folded crystals. These findings are similar to the earlier results of a detailed study of *cis*-polyisoprene (CPI) carried out by Andrews and co-workers [13–15, 32].

The present investigation is an attempt to study the development of crystalline textures, in strained and unstrained specimens, as a function of temperature and time. This can only be achieved if the crystal growth process can be halted at predetermined times over a range of temperatures. The growth process in thin films of unsaturated polymers can be halted using the technique of staining with osmium tetroxide vapour developed by Andrews [13]. This allows examination of spherulites at all stages of development in the electron microscope and provides thickness contrast when diffraction contrast has disappeared due to melting. The staining does not prevent electron diffraction and dark-field studies being carried out. Studies of this type have been previously carried out on CPI [13–15] and have yielded a great deal more information than the technique of extraction replication or acid-etching from surfaces of completely crystallized bulk polymers. TPI was chosen for the present study as it is an unsaturated polymer and crystallization can be halted using the staining technique. An investigation of TPI also provides an opportunity to examine the development of two types of spherulite of the same polymer in the electron microscope. Electron diffraction from crystals within spherulites can be used to confirm whether a given spherulite contains exclusively LMF or HMF crystals. If a spherulite grows as a physical entity, either LMF or HMF crystals will be exclusive to a given spherulite. However, if a spherulite is not continuous it could contain both LMF and HMF crystals. Studies of the morphology in strained films can also be carried out to determine whether lateral growth on a given central thread is exclusive to HMF or LMF crystals and whether mixtures are possible. This should provide information as to the role and nature of the central crystal. Attempts will be made to explain the optical appearance of the two types of spherulites on the basis of the fine structure observed in the electron microscope, and an attempt will be made to discuss the significance of the results of crystallization in thin films to bulk crystallization.

2. Experimental

2.1. Material

The main material used in this investigation was a commercially purified grade of gutta percha*. Further purification, to remove various resins, was carried out by dissolving 2 g of the polymer in 250 ml of 'Analar' benzene. The solution was filtered and the polymer precipitated by the slow addition of 300 ml of acetone. The resulting polymer was dried in vacuum at 40 to 45° C for 24 h. The dissolution and subsequent extraction of the polymer were conducted in a atmosphere of Argon gas and in subdued light to avoid degradation of the polymer. The resulting polymer had an average viscosity molecular weight $\bar{M}_v$ of 385 000.

2.2. Optical microscopy

These studies were carried out with an optical polarizing microscope equipped with a Mettler (FP2) heating stage. Approximately 0.01 g of sample was pressed between a clean glass microscope slide and a cover slip, separated by aluminium foil 2.5×10^{-5} m thick. Samples were first heated to 90° C for half an hour to ensure that all prexisting nuclei had been removed by melting.

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The specimen was then cooled rapidly to the desired crystallization temperature. The temperature could be measured and automatically controlled to ± 0.1° C.

2.3. Electron microscopy

The method for preparing thin films suitable for crystallization and for the subsequent electron microscope study was essentially that used by Andrews for thin films of CPI [13–15]. The purified polymer was made up into a 1% solution by mass with 'Analar' benzene. The solution was heated to about 65° C and small drops were placed on the surface of grease-free deionized water which had been heated to 5° C above the required crystallization temperature. The solution spreads on the surface leaving a uniform thin film after the benzene has evaporated. Films of about 100 nm thickness were used for the electron microscope study. Circular copper grids were used to collect the films, which were then transferred to a controlled temperature environment for crystallization. Some films were strained prior to crystallization by stretching on the water surface by means of a modified form of draftsman's dividers, similar to those described by Andrews [13]. When crystallization has ocurred for a given time further crystallization was prevented by staining the sample with osmium tetroxide vapour for about 45 sec. Staining with osmium tetroxide vapour also results in thickness contrast in the electron microscope due to differential deposition of osmium atoms; the osmium diffusing much more rapidly into the non-crystalline matrix than into the crystals. The crystals therefore appear light compared to the darker non-crystalline matrix. A more detailed discussion of this contrast will be given in the results section as it is important for a clear understanding of the morphology observed within the thin films.

Electron diffraction studies were carried out mainly to distinguish the different crystal modifications of TPI which occurred within the thin films. To retain electron diffraction patterns or dark-field images for photographic recording, a very low-beam intensity is necessary to avoid specimen damage and loss of crystallinity. The procedure followed was essentially that due to Agar *et al.* [16]. The electron beam is focused on a given area; the beam intensity is then reduced and the microscope set for selected area diffraction. The specimen is then searched in this diffraction condition. When a diffraction pattern is obtained and has been photographed the diffraction area is examined at a higher intensity in transmission. The morphology can then be studied as a result of the thickness contrast due to staining.

3. Results and discussion

3.1. Optical microscope data

When TPI thin films were crystallized isothermally from the melt and viewed under cross-polars in the optical microscope, two forms of spherulites could be distinguished. The first form displayed a characteristic Maltese-cross pattern with the directions of the arms of the cross parallel to the directions of the polarizer and analyser (Fig. 1a). These Maltese-cross spherulites are generally observed at temperatures below 35° C. At higher temperatures, the second form which exhibited a characteristic dendritic pattern (Fig. 1b) was obtained together with Maltese-cross spherulites. The density of the

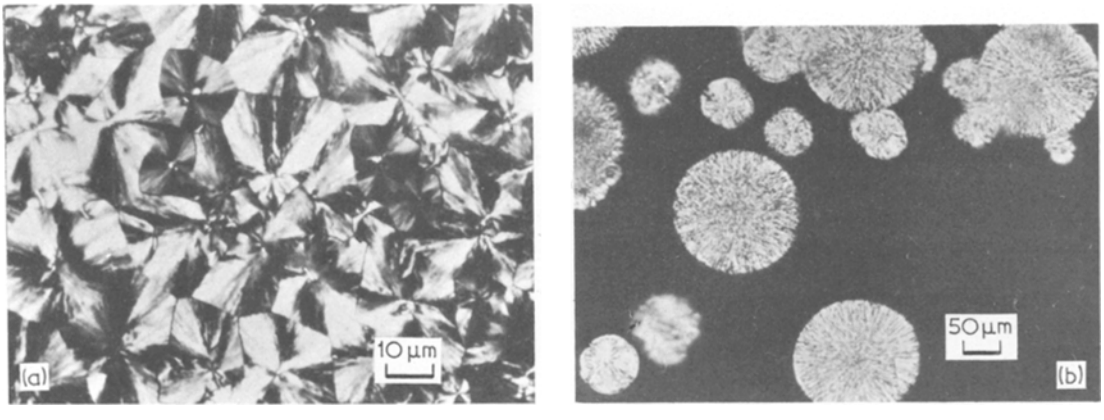


Figure 1 Spherulites as observed between cross-polars in the optical microscope; (a) LMF Crystallized at 30° C, (b) LMF crystallized at 50° C.

Maltese-cross spherulites reduces proportionally as the temperature of crystallization increases and at temperatures close to 60° C, only dendritic spherulites are obtained. When isothermally crystallized films containing both forms of spherulites were heated the Maltese-cross spherulites melted at a lower temperature than the dendritic-type spherulites [17]. Furthermore wide-angle X-ray studies have confirmed that the Maltese-cross spherulites contain LMF crystals and the dendritic spherulites HMF crystals [17]. At a given crystallization temperature (30 to 60° C) the LM F spherulites grow more slowly than the HMF spherulites but have a considerably larger nucleation density.

In addition to these spherulites, crystals of an elliptical shape were obtained at crystallization temperatures above 50° C (Fig. 2a). When the longer axis of the elliptical crystals is at 45° to the directions of the polarizer or analyser, maximum transmission of light is observed (Fig. 2a). When the same field of view is rotated through 45° with the longer axis of the elliptical crystal now in the direction of the polarizer or analyser, almost complete extinction of the birefringence of the crystal is observed (Fig. 2b). Similar elliptical or beam-shaped crystals in gutta percha have been reported by Keller and Waring [18] and Novikova and Trapeznikova [19]. It was suggested that they were single crystals with the molecular axis of the polymer orientated perpendicular to the long axis of the ellipse [19]. Single crystals of the HMF structure showing a similar extinction behaviour have been reported [20, 21]. They are described by Geil [20] as hedrites, having an intermediate structure between single crystals and spherulites. The hedrites can be associated with the axialites grown from solution [20, 22]. In the present investigation, melting temperature determination identifies the elliptical crystals to be of the low melting form. They are of a similar size to the Maltese-cross spherulites formed at the same temperature after the same time (Fig. 2a and b). If the elliptical crystals consist of parallel layers of similarly orientated lamellar crystals the observed birefringence behaviour would result. However, if the lamellar crystals were splayed apart, such that the orientations with respect to an analyser or polariser are regular but different, the resulting birefringence would be close to a Maltese-cross pattern.

3.2. Electron microscope data

3.2.1. Stained thickness contrast and growth of crystals within a thin film

Single crystals grown from dilute solution are platelets a few μm long and of the order of 10 to 20 nm thickness. The molecules have a chain-folded configuration as shown if Fig. 3a. In CPI [14, 15] diamond-shaped crystals with a simple preferred-growth face, e.g. (110), are often observed in thin films. If such a crystal grows in the plane of the film with the molecular axis normal to the film surface a diamond shape outline of the lamellar crystal will be observed when the film is viewed under an electron microscope (Fig. 3a) and the preferred growth angle will be revealed. This orientation of lamellar crystal will be described as 'flat-on' orientation. In this orientation the crystal does not necessarily touch the top or bottom of the film surface as the lamellar thickness is approximately one tenth of the film thickness.

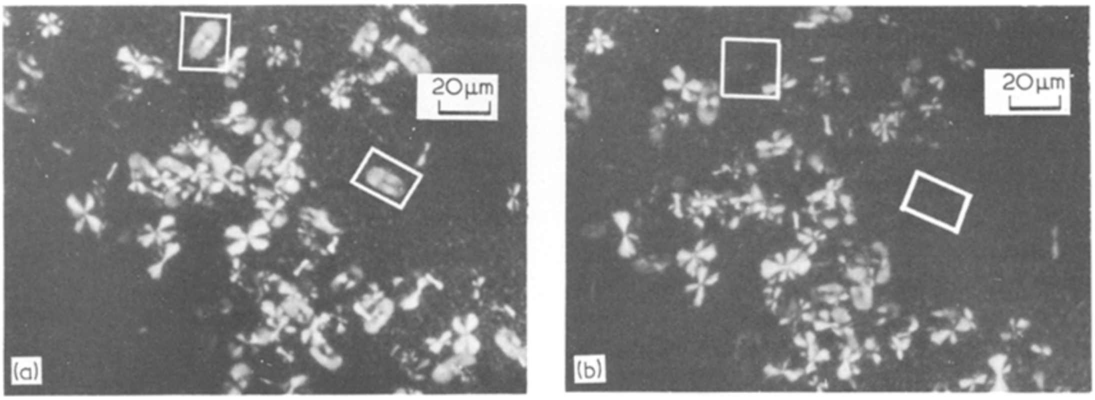


Figure 2 TPI film crystallized at 53° C and observed between cross-polars in the optical microscope. (a) LMF elliptical shaped crystals and small Maltese-cross spherulites. (b) Field of view as in (a) with the specimen rotated through 45°.

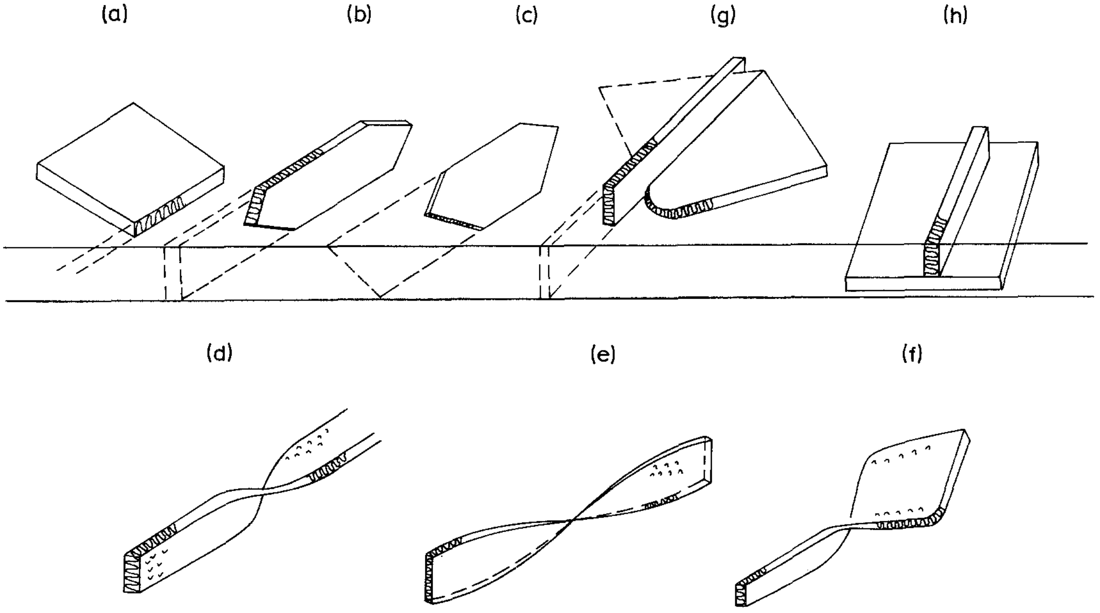


Figure 3 Schematic models showing different orientations of lamellar crystals in a thin film.

However, if the lamellar crystal grows with the molecular axis orientated parallel to the film surface, the resulting morphology will appear as a thin and long lamellar crystal (Fig. 3b). The lamellar crystal with this orientation will be described as 'edge-on' and in general the crystal width will be determined by the film thickness. However, the thickness of the image observed will correspond to the lamellar thickness which is characteristic of a given degree of supercooling. Clearly crystals between these two extremes will also be observed. Crystals growing at an angle to the film surface will result in a projected width which is larger than the film thickness (Fig. 3c). Twisting of a lamellar crystal from a 'flat-on' to 'edge-on' orientation, or vice versa, is also possible. Figs. 3d and e, show a schematic drawing of a half twist and a full twist growth pattern of a lamellar crystal. It is clear that because of the twisting phenomenon during the growth of a crystal, the projected dimension of the crystal when the film is viewed under an electron microscope will vary along the length of the crystal. Following a change of orientation from 'edge-on' to 'flat-on' lateral crystal growth sometimes occurs resulting in a broad diamond shape (Fig. 3f). Clearly the film thickness limits the size that crystals in certain orientations can grow to and hence determines their shape. However, in general, the size of a crystal is determined by the availability of polymer molecules, which must be added to the crystal for growth. Neighbouring lamellar crystals will therefore also impose a size limitation on growing crystals as they effectively subdivide the film with internal surfaces. Parallel groups of crystals growing in an 'edge-on' or 'flat-on' orientation will grow until impeded by crystals growing at an angle to the group. In fact, a crystal in a parallel group will tend to remain parallel during growth as competition for polymer molecules forces it to grow outward, remaining approximately equidistant from its neighbours. Crystals growing in an 'edge-on' orientation will tend to subdivide the film vertically, preventing 'flat-on' growing crystals attaining a full diamond configuration (Fig. 3g). Crystals growing in a 'flat-on' orientation will subdivide the film horizontally and limit the width of 'edge-on' growing crystals (Fig. 3h). Clearly more complex morphologies than those described above will occur, but those described will be sufficient to discuss the electron microscope observations of crystal growth within both spherulites and in orientated structures.

The above discussion assumes that the staining with osmium tetroxide will result in a simple plane projection of crystal shape as our electron microscope image. This requires that the osmium will penetrate the non-crystalline matrix to a depth of at least half a film thickness and that the

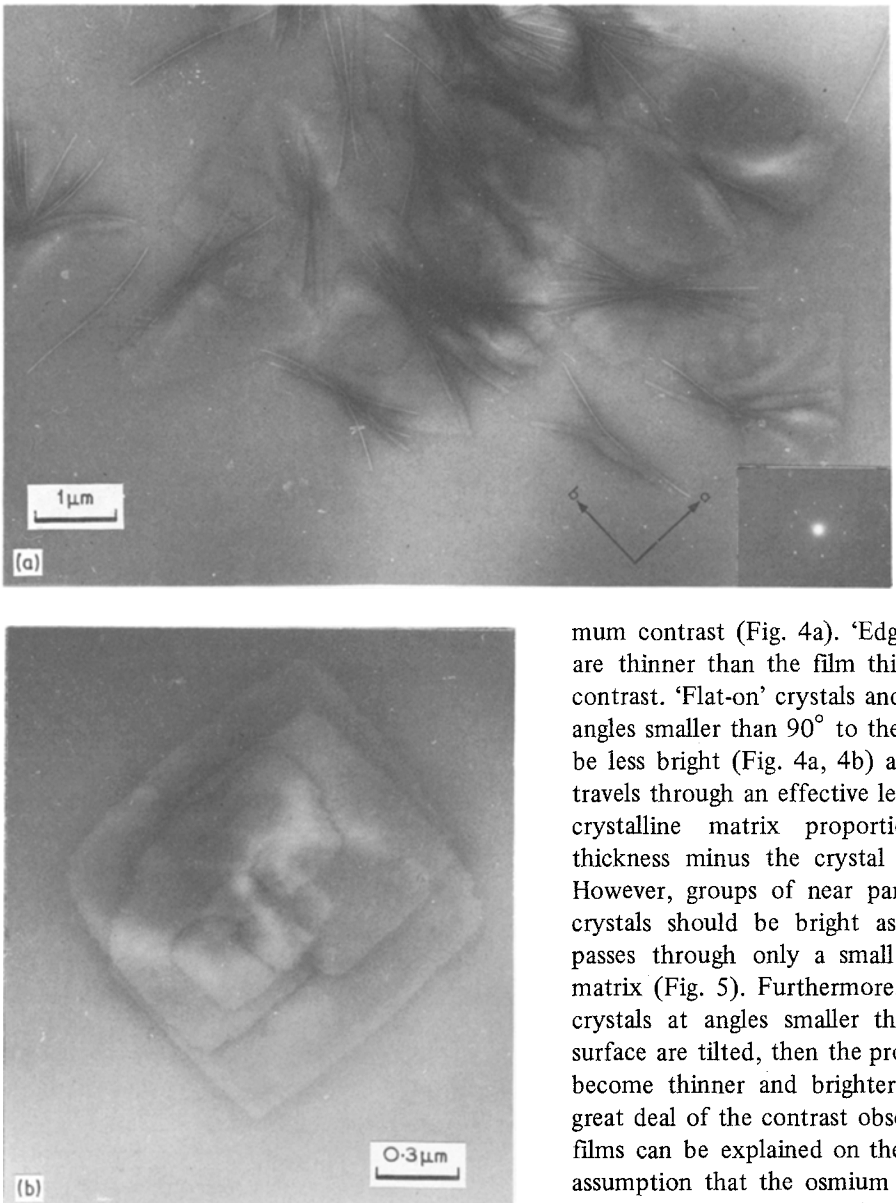


Figure 4 (a) and (b) LMF lamellar crystals in a film crystallized for 3 h 20 min at 56° C.

crystals will absorb a negligible amount of osmium within the staining time. The electron intensity arriving at the photographic plate will depend largely on the thickness of non-crystalline matrix through which the electron beam has passed. This of course assumes that crystal damage as a result of exposure to the electron beam has already taken place and that therefore no diffraction contrast will occur. 'Edge-on' single crystals which touch the film surface should therefore appear bright, compared to the matrix, giving the maximum contrast (Fig. 4a). 'Edge-on' crystals which are thinner than the film thickness will give less contrast. 'Flat-on' crystals and crystals growing at angles smaller than 90° to the film surface should be less bright (Fig. 4a, 4b) as the electron beam travels through an effective length of stained non-crystalline matrix proportional to the film thickness minus the crystal thickness (Fig. 4a). However, groups of near parallel 'flat-on' single crystals should be bright as the electron beam passes through only a small amount of stained matrix (Fig. 5). Furthermore, if films containing crystals at angles smaller than 90° to the film surface are tilted, then the projected image should become thinner and brighter (Fig. 6). Clearly a great deal of the contrast observed in stained thin films can be explained on the basis of the simple assumption that the osmium diffuses mainly into the matrix to a depth of at least half the film thickness. However, in many cases the matrix around a near 'edge-on' crystal appears darker than the matrix at some distance from the crystal, (Fig. 4a). Furthermore, in regions with a high density of 'edge-on' crystals (e.g. centre of spherulites in Figs. 4a, 5, 6) the matrix is often much darker than the matrix containing no crystals. This effect could be explained if there was a tendancy for the osmium to be channelled into the film more rapidly in the region of the matrix/crystal interface than into the unperturbed matrix. Support for this explanation is given by the observations of contrast in strained films. The structure observed consists of parallel rows of near

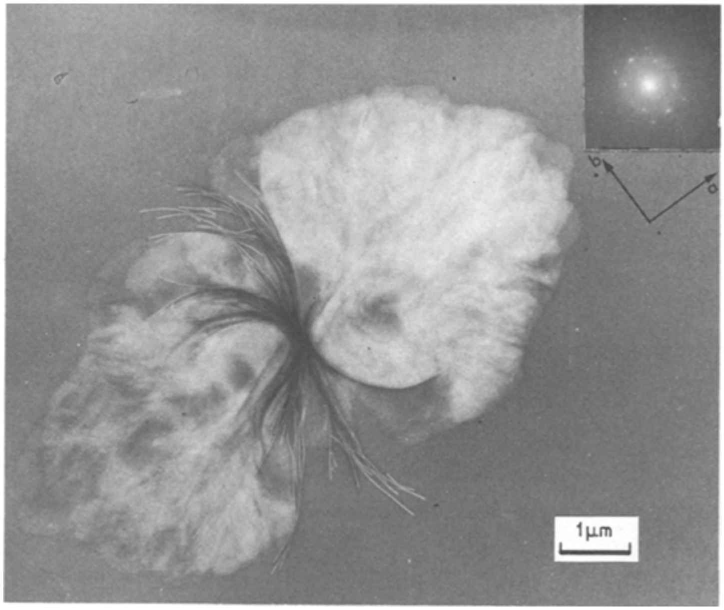


Figure 5 HMF spherulite in a film crystallized for 1 h 57 min at 50.5° C. (× 11 000). Electron diffraction from a crystal at the edge of the spherulite is shown.

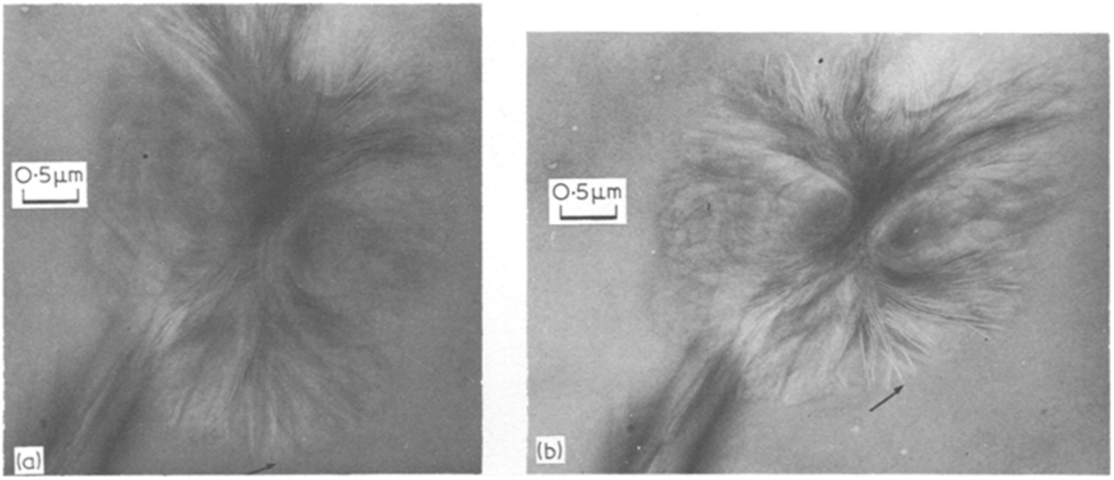


Figure 6 (a) HMF spherulite in a film crystallized for 1 h at 50° C. (× 22 000). (b) shows the same area as in (a) but the specimen has been tilted through 45° with respect to the electron beam. Changes in the crystal thickness and contrast can be seen arrowed.

'edge-on' crystals orientated at right angles to the direction of stretch. The crystals are considerably longer than the film thickness and are assumed therefore to touch both of the film surfaces. It can be seen that the matrix between the crystals is much darker than the crystal free matrix (Fig. 7a). Clearly the osmium has diffused to a greater extent into this region than into the matrix generally. Further support for this explanation is given by the fact that when the crystal density is lower and/or the crystals have not grown to the film surface, little or no darkening effect is observed (Fig. 7b).

3.2.2. Identification of LMF and HMF spherulites in a crystallised film

Crystallization was studied in the temperature range 35 to 56° C. Below 35° C, crystallization is extremely rapid, and above 56° C, occurs only slowly. In this temperature range both LMF and HMF crystals can grow to significant sizes in an acceptable time. Interpretation of the morphologies obtained therefore requires that one is able to distinguish between the two possible modifications. At all temperatures the LMF spherulites grow more slowly than the HMF spherulites but have a higher nucleation density [6, 17]. Further-

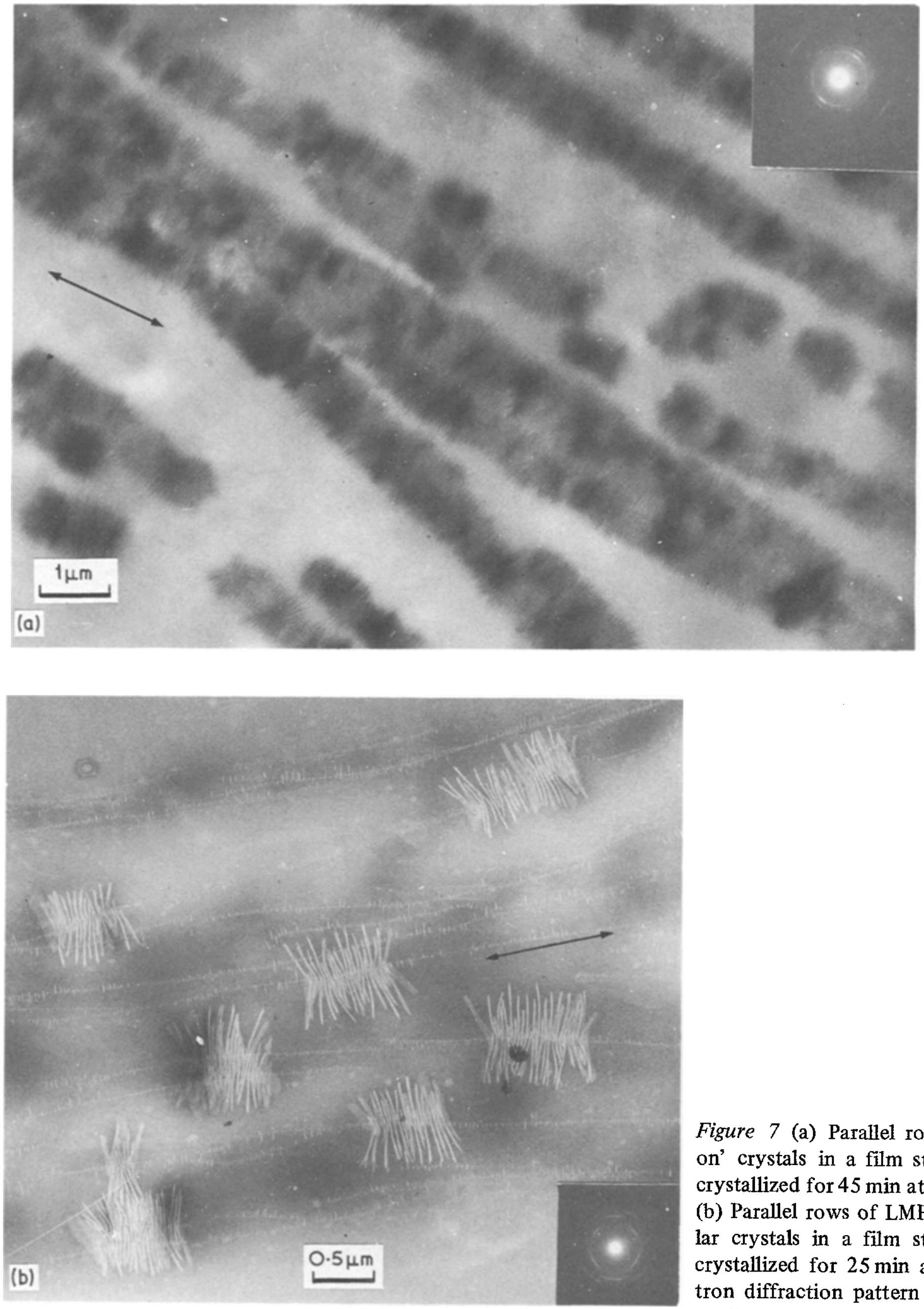


Figure 7 (a) Parallel rows of LMF 'edge on' crystals in a film strained 200% and crystallized for 45 min at 48° C (× 11 000). (b) Parallel rows of LMF and HMF lamellar crystals in a film strained 150% and crystallized for 25 min at 53° C. An electron diffraction pattern from a bundle of HMF crystals is included.

more, at a given crystallization temperature the LMF crystals are growing at a smaller supercooling [1] than the HMF crystals and will always have a greater lamellar thickness [17]. At a given crystallization temperature LMF crystals can therefore be distinguished by their higher nucleation density, smaller length and greater lamellar thickness (Fig. 8). In cases of difficulty, indentification was confirmed by melting out the LMF crystals, prior to staining and observation in the electron microscope, at a temperature above the melting point of the LMF crystal but below the melting point of the HMF crystals. Indentification of spherulites from their electron diffraction patterns was also carried out. Ring patterns are generally obtained which can be indexed, using the unit cell dimensions proposed by Fisher [3] and given earlier. The prominent (120) and (200) reflections are charac-

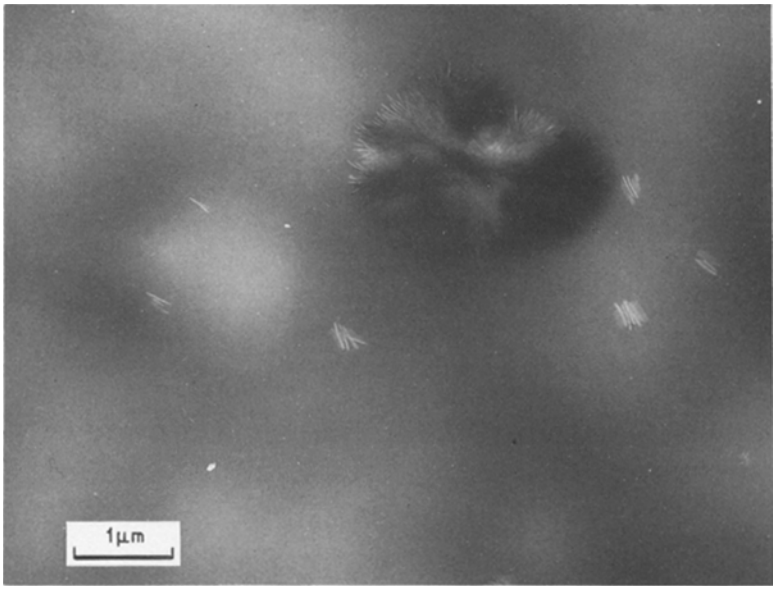


Figure 8 HMF and LMF spherulites in a film crystallized at 56° C for 33 min (× 16 000).

teristic of the LMF crystals (Fig. 9a); whereas the occurrence of the (010) and (110) reflections are distinctly associated with HMF crystals (Fig. 11b). The rings are not continuous as not all crystal orientations are present in the film. A very weak reflection of *d*-spacing 0.60 nm was observed in the electron diffraction pattern of LMF crystals. This was not reported by Fisher [3] and it is suggested to be the (020) reflection with a calculated *d*-spacing 0.594 nm. Electron diffraction experiments were carried out in an attempt to determine whether it was possible for HMF crystals to grow in a LMF spherulite. Films containing LMF spherulites were searched in diffraction but all single crystal diffraction patterns obtained from the edges of spherulites were from LMF crystals. This evidence is by no means conclusive but in the absence of other evidence it must be assumed that a given spherulite contains only crystals of one type i. e. LMF of HMF.

3.2.3. Development of highly branched spherulites at large supercooling

At low crystallization temperatures, less than 40° C, crystallization occurs rapidly and the LMF crystals represent the major fraction of the total crystal population. The nucleation density of LMF spherulites is large, resulting in a small spherulite size. The spherulites consist of highly branched twisting lamellar crystals (Fig. 9a). An electron diffraction pattern from such a spherulite (Fig. 9a) can be indexed using the orthorhombic unit cell proposed by Fisher [3]. When a spherulite is impinged by another spherulite during its growth the boundary of the spherulites was found to consist of interleaved lamellae growing from one spherulite to another (Fig. 9a). In general a lamallar crystal will continue to grow as long as there is crystallizable material in its vicinity unless it impinges on the broad dimension of another crystal. It is possible that a polymer chain may be found simultaneously growing into different lamallae from nominally different spherulites suggesting the existence of interlamellar ties between spherulites [20]. HMF spherulites growing at comparable supercoolings (crystallization temperatures 45 to 56° C) show very similar morphologies to the LMF spherulites described above. They originate as small bundles of lamellae (Fig. 11a) which grow into highly branched spherulites (Fig. 11b). This is shown diagramatically in Fig. 10d. Electron diffraction patterns (Fig. 11b) of these spherulites can be indexed using the monoclinic unit cell proposed by Fisher [3].

The main feature of both HMF and LMF spherulites growing at large supercoolings is the existence of twisting branching lamellae. This can be seen most easily at the edge of a growing spherulite (Fig. 9b). The projected image of a twisting lamellae shows an apparent variation in crystal thickness along its length (Fig. 9b, 3). Keith and Padden [23] suggested that the twisting of

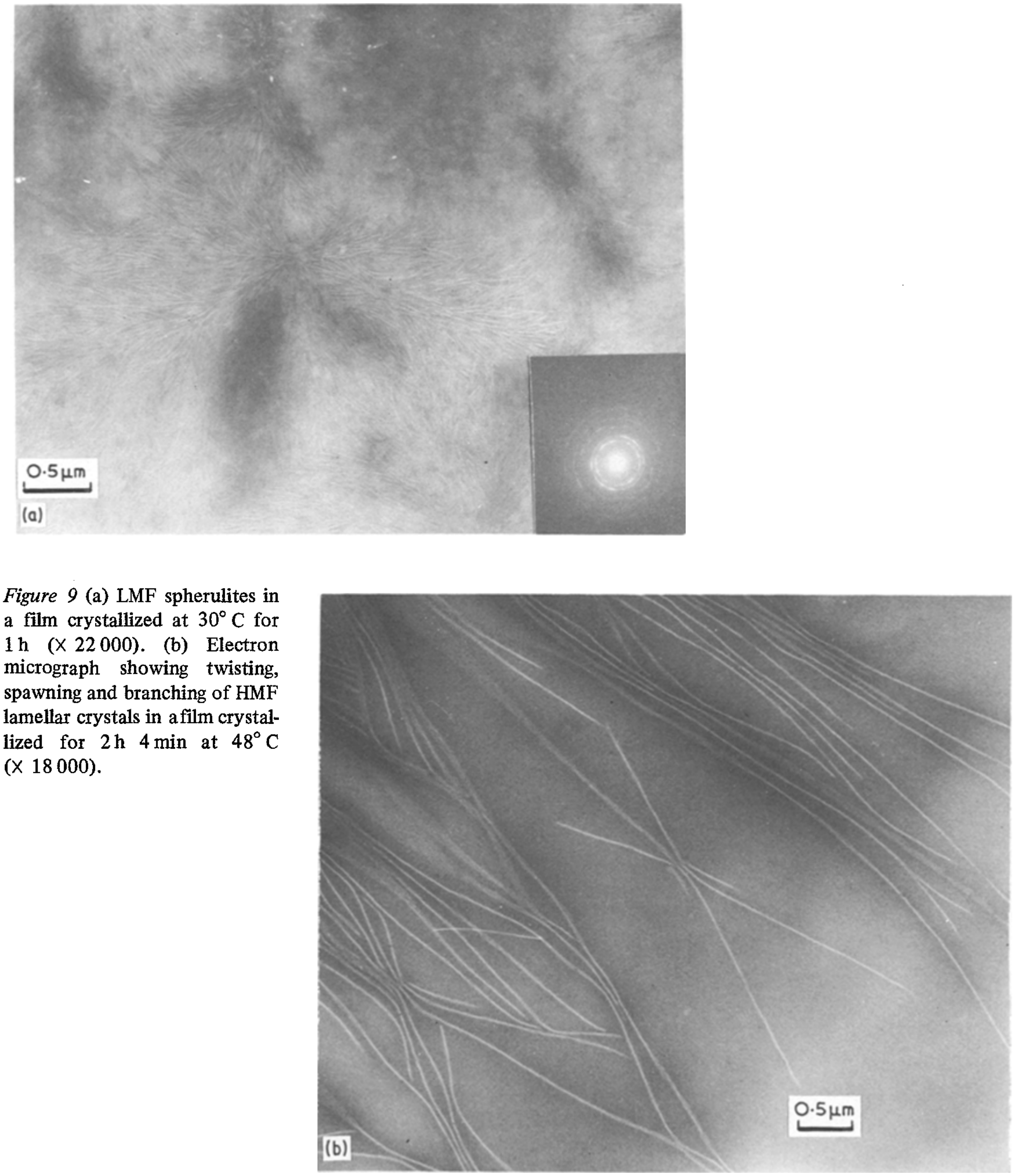


Figure 9 (a) LMF spherulites in a film crystallized at 30° C for 1 h (× 22 000). (b) Electron micrograph showing twisting, spawning and branching of HMF lamellar crystals in a film crystallized for 2 h 4 min at 48° C (× 18 000).

lamellae in a spherulite, may be due to the stress built up on the lateral edges of the lamella. Hoffman and Lauritzen [24] also attributed the origin of twisting to the surface strain accumulated during the formation of the lamella crystals. These mechanisms would imply a functional relationship between the twist frequency and the length of the lammellar crystal, which is not observed in the present case. Owen [15] suggested that the twisting of a lamellar crystal was due to a variation of stress within the CPI thin films. As has been suggested previously, lamellar crystals will grow in a direction determined by the availability of crystallizable material. At rapid growth rates (large supercoolings) they will absorb the molecules which can most easily be removed from the melt. The crystal will grow so as to move towards the molecule as well as the molecule moving to the crystal. This could result in random, full or partial twisting of the lamellar crystals (Fig. 3). Branching

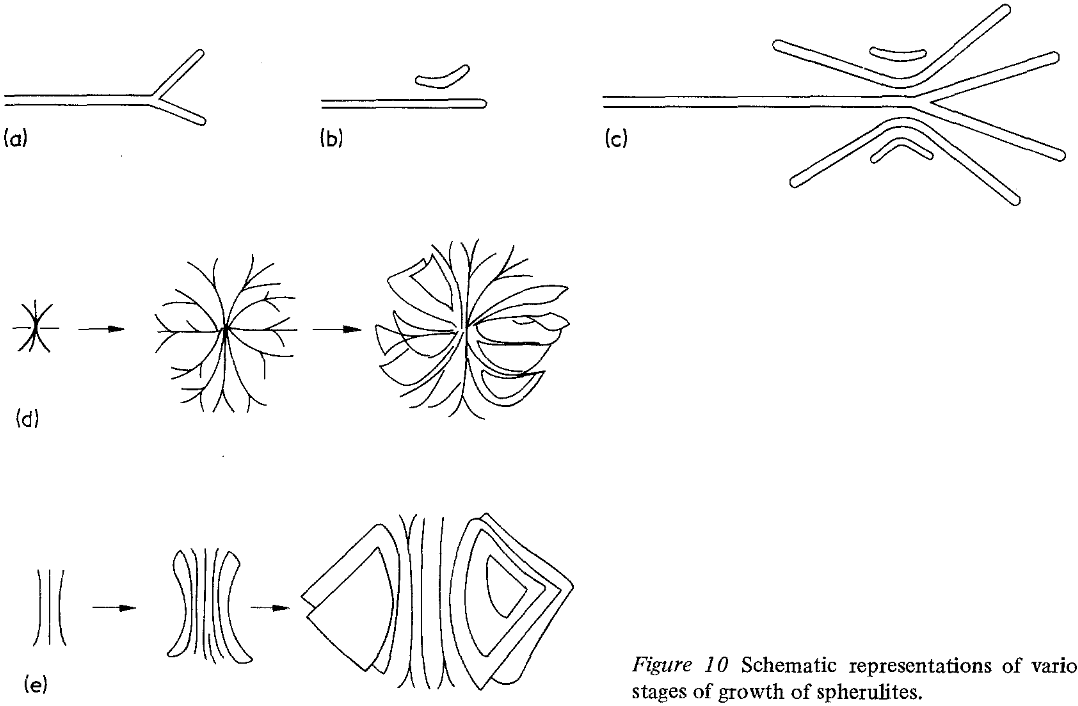


Figure 10 Schematic representations of various stages of growth of spherulites.

of lamellar crystals has been described as a possible space-filling process in the development of a spherulite [24]. In the present investigation it was found that there is also another space-filling mechanism termed 'spawning' when first observed by Owen [15] in CPI thin films. The phenomena of spawning new crystals and branching are shown schematically in Fig. 10a and b. The spawned lamella usually nucleates at a distance of about 4 to 6 nm from the parent lamella and grows steadily away from it (Fig. 10b). A combination of the process of branching and spawning is also shown in Fig. 10c. These features have been observed in LMF and HMF spherulites when growth is relatively rapid (Fig. 9b). Obviously it is easier to observe these phenomena when the crystals are in an 'edge-on' orientation, but there is no reason to suppose that they do not occur with equal frequency when the crystals are in a 'flat-on' orientation (Fig. 5). The frequency of branching increases with the degree of supercooling (i. e. faster growth rate) and may occur as a result of successive multiple nucleation on the growing face of the crystal. The divergence of the branched lamella crystals can be considered the result of the crystals avoiding each other in the search for crystallizable material in the melt. Owen [15] suggested that the molecules which enter or re-enter a parent lamella are partly ordered at some distance from the crystal face as a result of the restriction placed on their mobility by the ordered parent crystal. These molecules result in the formation of another ordered crystal nucleus which will grow as a spawned lammella (Figs. 10c, 9b). The processes are similar to the formation of bi-layer or multi-layer crystals in solution [22, 25], where the new lamella crystals where suggested to nucleate from molecular hairs emerging from the parent crystals. As with branching the frequency of spawning increases with the degree of supercooling (i.e. faster growth rate), and may be the result of increasingly disordered crystal surfaces due to non adjacent re-entry of molecules, the protruding molecules acting as primary nuclei for spawned lamellar crystals.

3.2.4. Development of spherulites containing large unbranched crystals at small supercoolings

In the temperature range 45 to 50° C, LMF sperulites nucleate as either single lamella or bundles of lamellar crystals, (Fig. 4a, 8a). The morphology is similar to that of multi-layer polyethylene solution-grown crystals observed in suspension [26, 27]. A schematic representation of the various stages of growth of these LMF spherulites is given in Fig.

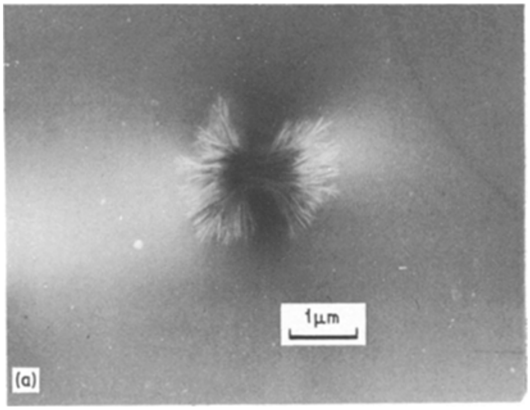
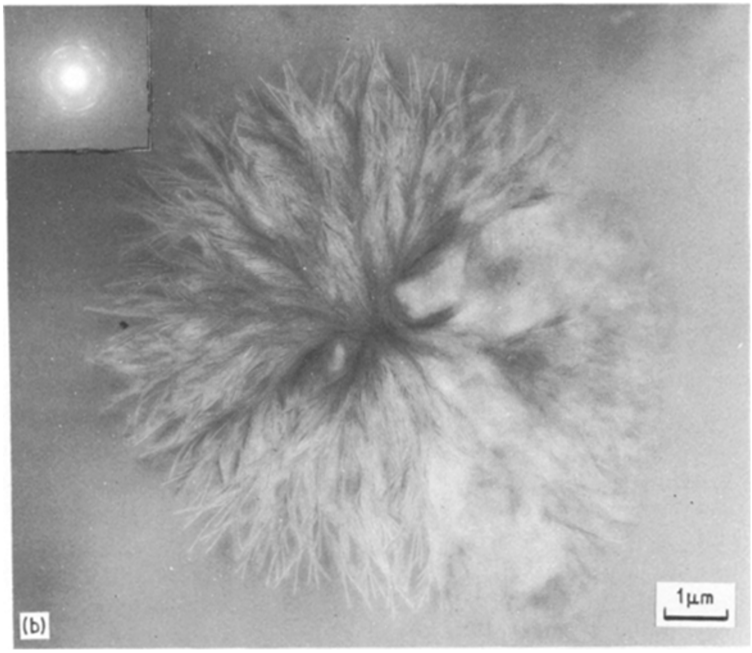


Figure 11 (a) Early stages of HMF spherulite showing spawning and branching of lamellar crystals. Crystallization at 56° C for 30 min. (X 11 000). (b) HMF spherulite in a film crystallized for 41 min at 48° C.



10e. The final form of these structures is a hedrite or axialite. They sometimes give single crystal type electron diffraction patterns (Fig. 4a), but on other occasions give patterns which show that crystals of several orientations are present in the structure. It is thought that some of these structures correspond to the elliptical-shaped crystals observed in the optical microscope (Fig. 2). Structures with crystals of several orientations would result in the Maltese-cross spherulites seen in Fig. 2. In this temperature range very little branching or spawning of crystals is observed and the lamellar crystals grow to a large size. This is not unexpected if the crystals are growing slowly by single nucleation on each growth face and forming surfaces which exhibit near adjacent re-entry of molecules.

3.2.5. The growth face of the LMF and the HMF crystals

Polymer single crystals develop a preferred growth face angle. Kawai and Keller [28] reported that for polyethylene single crystals, the *a* and *b* axes were parallel to the long and short diagonals of the diamond shaped single crystal. Hence, its growth face was deduced to be the {1 1 0} planes [28]. A similar analysis was performed for CPI [15], and polychloroprene crystals [29], in thin films and the growth faces in both cases were deduced to be the {1 1 0} planes. In the analysis of growth rate data, several workers [1, 6, 30] have assumed that for TPI, the growth faces for the LMF and HMF crystals are the {1 2 0} and {1 1 0} planes respectively. The lamellar crystals of LMF and HMF TPI were examined in the present investigation in an

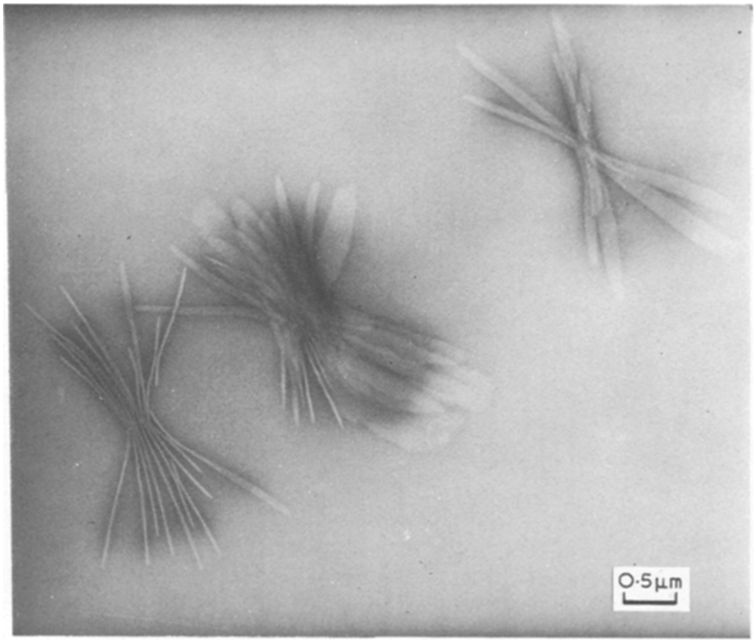


Figure 12 LMF crystals in a film crystallized at 53° C for 3 h.

attempt to confirm these growth faces. Partial or complete diamond shaped LMF crystals are often found at small supercoolings (Fig. 4a and b) and the single crystal electron diffraction patterns obtained (Fig. 4a) have shown that the long and the short diagonals are parallel to the *a* and *b* unit cell axes. Keller and Martuscelli [9] also observed that the maximum crystal length of TPI solution-grown crystals is always along the *a* axis. Thus the smaller of the two angles included by the growth faces (θ) was measured from a large number of specimens and was found to have a mean value of 75° ± 5°. A calculation of angle θ for the (1 1 0) growth planes yields a value of 113° 10′, whereas θ for the (1 2 0) growth planes is 74° 16′. Thus the direction of the *a*- and *b*-axes and the values of the included grown angle θ suggest that the growth face for LMF TPI crystals is more likely to be {1 2 0}. A similar analysis was carried out for the HMF crystals. However, although occasionally single crystal type diffraction patterns are obtained from the edges of spherulites (Fig. 5), diamond shaped crystals are rare and the preferred-face angle θ is not well defined. Confirmation of the orientation of the *a*- and *b*-axes within a crystal is therefore difficult. A mean value of 105° ± 5° has been estimated. A calculation of θ for the (1 1 0) growth planes yields a value of 106° 24′ and 67° 36′ for (1 2 0) growth planes. Thus the probable growth face for the HMF crystal is {1 1 0} as in CPI [15] and polychloroprene [29].

3.2.6. *Crystallization under strain*

The study of strain induced crystallization of TPI was carried out in an elevated temperature range 40 to 56° C to ensure that no crystallization occurs prior to straining of the film. Films were given strains of between 50% and 450%.

Stresses imposed on the film due to surface tension and relaxation of the applied stress lead to uncertainties in the absolute measurement of an individual film strain. However, the relative values of the strains are accurate and it is therefore significant to discuss the results in terms of the experimentally measured film strains.

At low strains, (50%), groups or bundles of lamellar crystals are generally observed (Fig. 13a). The morphology is similar to that of an unstrained film (Fig. 12). However, the lamellae grow in an 'edge-on' orientation and tend to be aligned at right angles to the strain direction. The strain direction is indicated by the direction of the arrows in all the micrographs (Fig. 13a). At the edges of the bundles the crystals tend to splay apart and twist towards a 'flat-on' orientation. Typical row nucleated structures with the lamellar crystals growing perpendicular to the direction of strain are observed at intermediate strains (100% to 250%) (Figs. 13b, 7a). These row nucleated lamellar are similar to those found by Andrews and co-workers [13–15, 32] in CPI. The lamellae are generally straight and grow in the 'edge-on' orientation. Qualitatively, the effect of increasing the strain

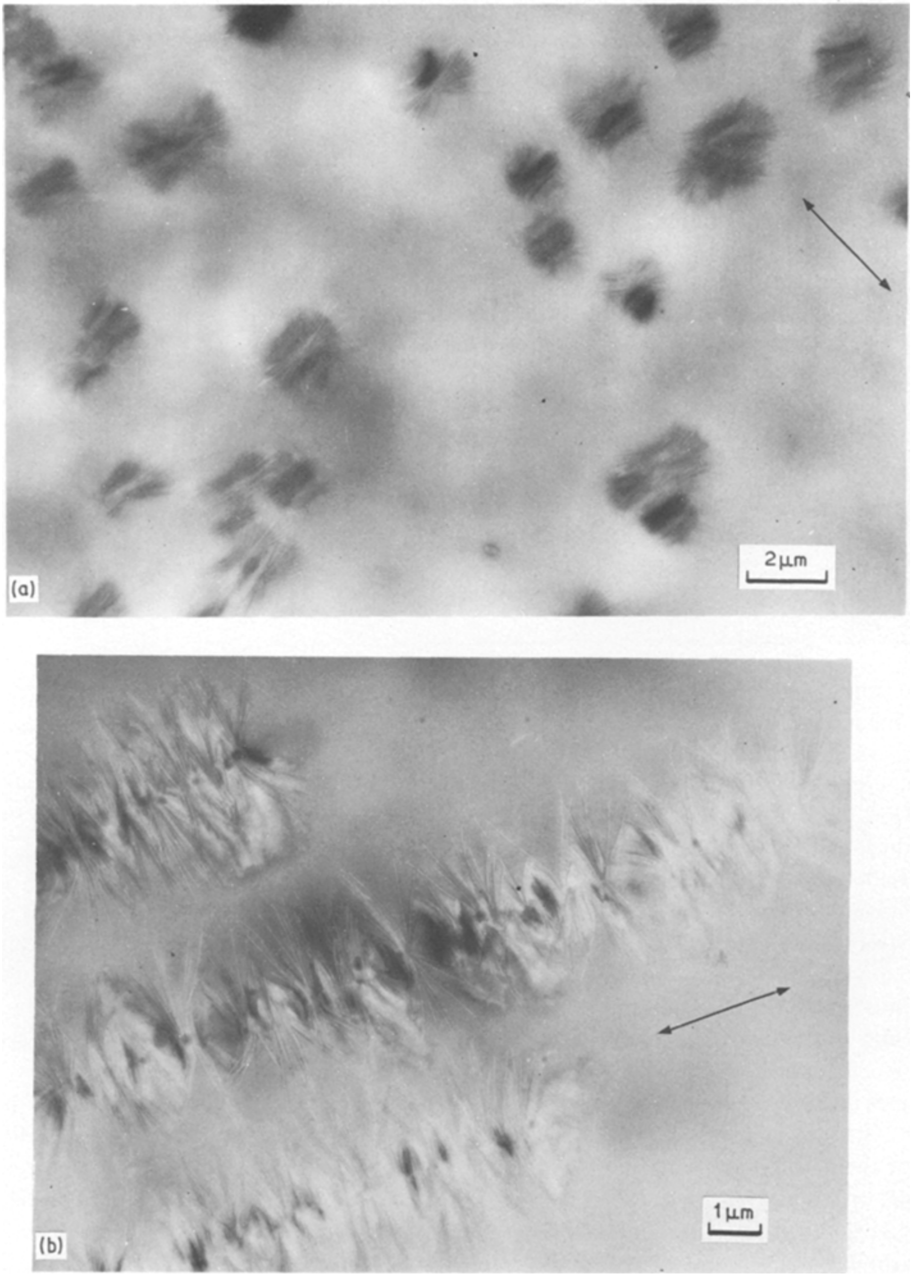


Figure 13 Morphology in strained TPI films. (a) strained 50% and crystallized for 2 h 17 min at 50.5° C. (X 7 600). (b) Strained 100% and crystallized for 41 min at 43° C (X 7 600).

from 100% to 250% is to increase the row nucleation density and to restrict the length to which the lamellae can grow. The lamella crystals are always nucleated close together and are forced to grow parallel to each other in an 'edge-on' orientation as they compete for crystallizable material. A crystal at the end of a row is unrestricted and can splay out to be followed by its neighbours (Fig. 13b). As crystals grow further from the centre of the row, they sometimes cut off the growth path of their neighbours, and they themselves are not restricted to grow at right angles to the strain direction (Fig. 13b). The initially imposed strain is almost certainly relaxed rapidly as the growth rates of the lamellar crystals are found to be independent of strain [15, 17]. The effect of the initially applied

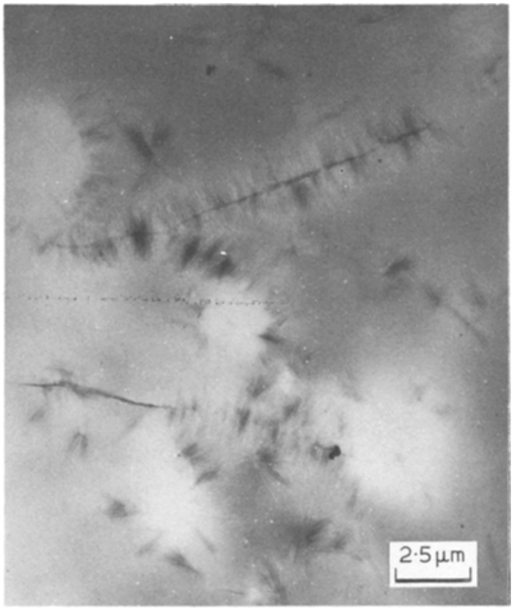
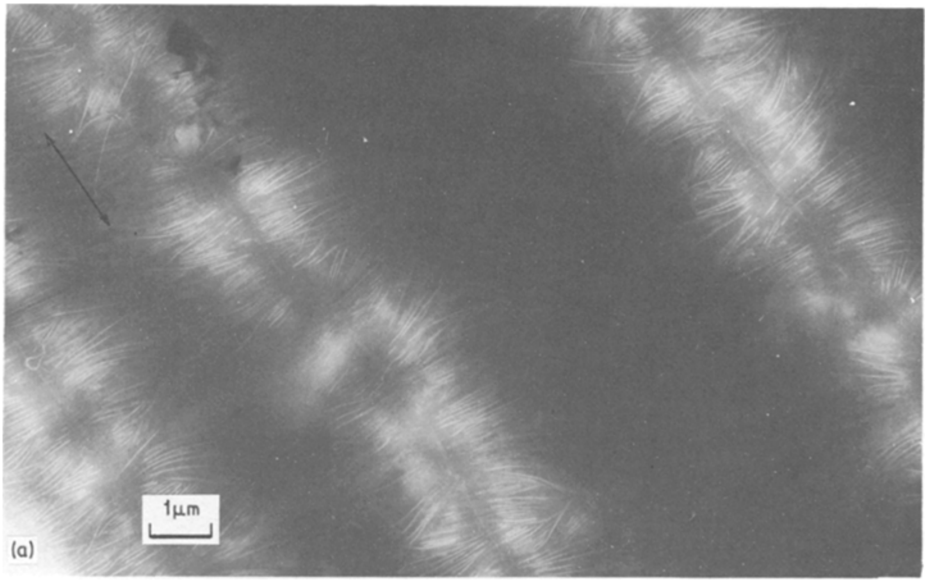


Figure 14 Unstrained film crystallized for 2 h at 50° C. (× 6 400).

strain is to provide row nuclei in the direction of the strain. Even in unstrained films, folds or holes in the film sometimes provide surfaces on which nucleation takes place (Fig. 14). At some temperatures both LMF and HMF lamellar crystals were found to grow from the same rows (Fig. 7b). LMF crystals usually occur predominantly but as the HMF crystals grow more rapidly they are the first to diverge and twist (Fig. 7b.) The HMF and LMF crystals grow in groups and are not interspersed randomly along a row. Electron diffraction patterns (Fig. 7b) from a film strained 150% but crystallized for 1.5 h confirms the longer crystals to be of high melting form. The fact that the HMF crystals occur in groups suggests that they are linked in some way as are crystals within a spherulite. Equatorial arcs of (1 0 1) and (0 2 0) reflec-



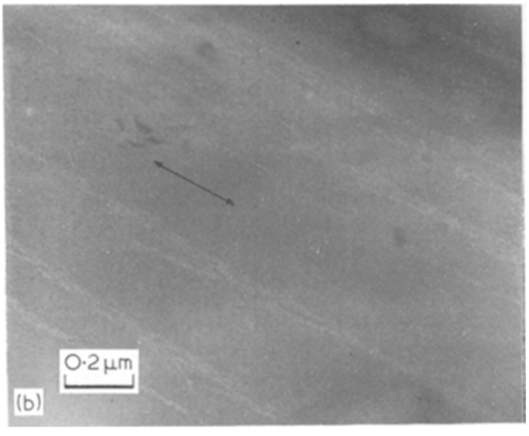


Figure 15 (a) TPI film strained 150% and crystallized for 24 min at 45.5° C. (× 18 000). (b) Isomerized *trans*polyisoprene film (consisting of 10.2% *cis* units) strained 400% prior to crystallization for 20 min at 35° C.

tions are observed from HMF crystals (Fig. 7b). For the LMF crystals, in addition to the equatorial arcs of (1 2 0) and (2 0 0) reflections, a (0 0 2) reflection appears in the meridional position which runs along the direction of strain (Fig. 7a). This indicates that the molecular *c*-axis in a strained film aligns parallel to the straining direction. The identity period of the *c* fibre axis estimated from the (0 0 2) reflection of the LMF crystal was 0.476 ± 0.04 nm. This is close to the value of 0.475 nm reported by Fisher [3]. For the HMF crystal no (0 0 *l*) reflections were detected, thus the *c* fibre axis of the HMF crystals cannot be estimated.

On close examination of the row nucleated structures it is found that there are traces of a central thread running down the rows (Fig. 7b, 15a, 16a). Occasionally this thread is unclear but refocussing usually produces a relatively sharp image. This thread was termed the 'backbone' crystal by Owen [15] when observed in CPI. The central backbone lies in the direction of strain but is often wavy and ribbon-like (Fig. 15a). It appears to be 5 to 25 nm in thickness.

At strains greater than 250% an extremely high density of short lamellar crystals growing at right angles to the direction of strain is observed (Fig. 16a and b). The short lamellar crystals suggest that the backbone crystals must be much closer together than at lower strains. The backbone crystals are however difficult to observe and appear short and wavy (Fig. 16a, 16b). However, if

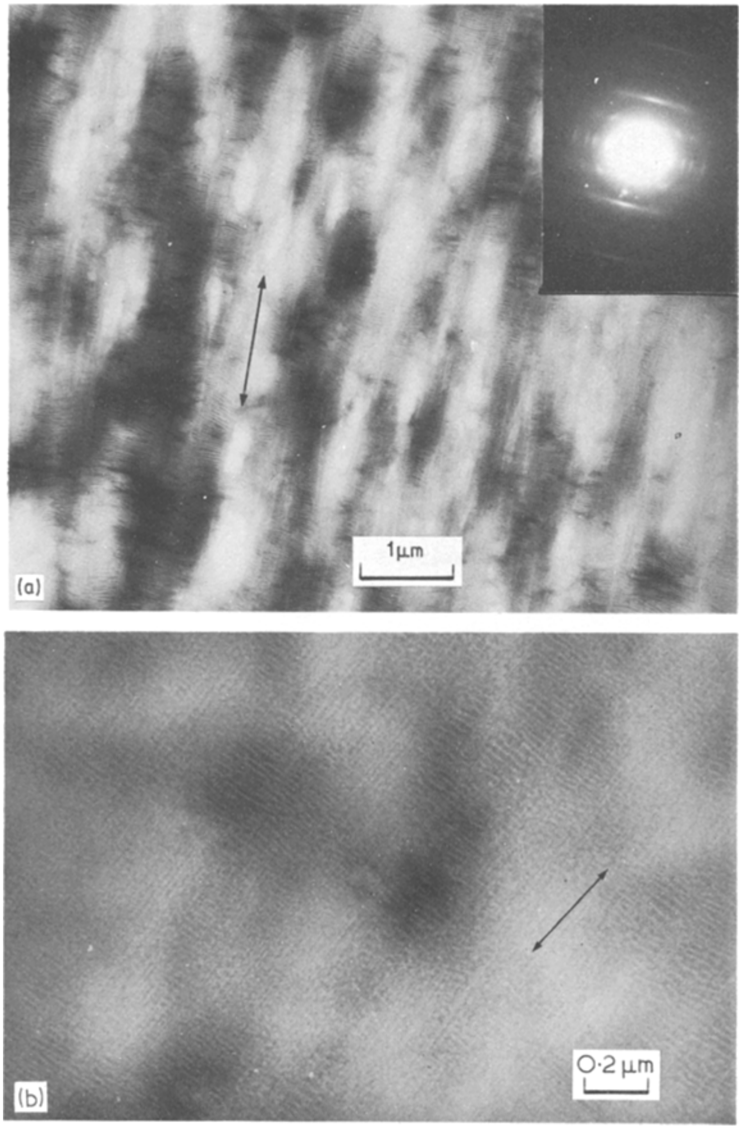


Figure 16 Structure observed in TPI films given large strains prior to crystallization for 3 h 46 min at 50.5° C. (a) 300% strain, (b) 450% strain.

a film of TPI containing 10.2% *cis*-isoprene units on the *trans* chain, is examined long wavy backbone crystals are seen free of lamellar crystal overgrowth (Fig. 15b). The effects of the *cis* units is to decrease the growth rate of the lamellar crystals [17]. It is suggested that the electron micrographs at high strains (Fig. 16a and b), can be explained as a high density of wavy backbone crystals overgrown by a high-density of short lamellar crystals. These structures are similar to the 'shish-kebab' structures of stirring induced crystallization from solution [22, 33]. Both structures probably consisting of extended-chain type crystal backbones overgrown by chain-folded lamellar crystals. It is not clear, in the thin film studies, whether the central backbones form on application of the strain or during the molecular motion occuring during subsequent strain relaxation.

4. Comparison of melt-grown morphologies, bulk crystallization and crystallization from solution

It has been shown that the crystalline morphologies observed in unstrained thin films of TPI can be explained if one assumes the basic crystal units to be thin chainfolded lamellar crystals which would grow (if unrestricted) to a diamond shape. Electron diffraction experiments have shown that the molecules are oriented at right angles to the crystal surfaces. The molecules are parallel to the electron beam in 'side-on' crystals and at right angles to the beam in 'flat-on' crystals. The electron diffraction patterns obtained can be indexed using the unit cells proposed by Fisher [3]. The structure of the crystals can be identified with those grown from solution by Keller and Martuscelli [9]. The preferred-growth faces for LMF crystals are the {1 2 0} planes and probably the {1 1 0} planes for the HMF crystals.

Electron diffraction data from the large single crystals in LMF spherulites suggests that they contain only LMF crystals. Limited electron diffraction data from single crystals at the edge of HMF spherulites suggests that they contain only HMF crystals. These observations have been made in films crystallized at temperatures where both types of spherulites coexist. The results suggest the existence of more than just molecular continuity between crystals within a spherulite. Limited crystalline continuity is probable. HMF spherulites nucleate as bundles of lamellar crystals (Fig. 11a) and grow by extensive twisting, branching, and spawning (Figs. 11b, 6). The frequency of branching and spawning is found to increase as the degree of supercooling increases. It is possible that branching occurs as a result of multiple nucleation on successive growth faces. Spawning may occur as a result of the formation of primary nuclei from cilia near or at a crystal fold surface. The frequency of spawning may increase as adjacent re-entry becomes less common at large supercoolings. These observations are supported by the findings of Fischer and Henderson [6]. They showed HMF spherulites to consist of twisting and branching lamellar crystals, using an etching and replication technique from the surface of bulk samples. The thicknesses of the lamellar crystals in the present thin film study and in the previous study of bulk samples [6] are similar. The appearance of HMF spherulites in thick films with alternating positive and negative birefringence, as observed in the optical microscope (Fig. 1b) is consistent with this model of randomly twisting, branching spawning lamella radiating from a central point. Furthermore the growth rates of spherulites measured in thick films in an optical microscope [1, 6, 17] agree well with the growth rates measured in the electron microscope in thin films [17]. It would seem that the role of the film surface, in thin-film crystallization, is simply to subdivide the volume available for crystallization in much the same way as a growing crystal would. The spherulites grown in a thin film can therefore be considered as a slab section, taken across the diameter of a bulk-grown spherulite. LMF sperullites growing at small supercoolings nucleate as either single lamella or bundles of lamellar crystals (Figs. 4a, 8, 12). The morphology is similar to that of multi-layer polyethylene solution grown crystals observed in suspension [26, 27]. The final form of these structures is either a hedrite/axialite giving a single crystal diffraction pattern or a splayed group of large crystals of differing orientation with respect to the electron beam. The frequency of twisting, branching and spawning is minimal at these supercoolings and large crystals always result. These structures correspond to the hedrites observed in the optical microscope (Fig. 2a and b) and to the small Maltese-cross spherulites grown at small supercoolings (Fig. 2a and b). Fischer and Henderson [6] could reveal only the outlines of LMF spherulites when examining replicas of etched surfaces of bulk samples.

Although the LMF spherulites were grown at lower crystallization temperatures than the HMF spherulites studied the lamellar thicknesses of the crystals in each would be similar as a result of their relative melting temperatures [17]. If the spherulites consisted of splayed groups of large single crystals with little twisting and branching (as found in the present investigations) only the outlines of the spherulites would be revealed. Again it can be seen that the morphologies produced in thin films, thick films and bulk samples are consistent. At large supercoolings (<40° C) LMF spherulites are made up of twisting branching spawning lamellar crystals (Fig. 9a). They are much smaller than their HMF counterparts as a result of a much higher nucleation density. They therefore tend not to develop a full radial symmetry of lamellar crystals. If these LMF spherulites were identical in form to the HMF spherulites one would expect to see LMF spherulites at low supercoolings without Maltese-crosses. Lovering and Wooden [34] do in fact show LMF spherulites crystallized at 40° C without Maltese-crosses. However, in the present investigation Maltese-cross spherulites were observed, even at low supercoolings. It may be that the lower nucleation density of LMF spherulites in thick films in the optical microscope allows the spherulites to grow to a larger size and to assume a configuration resulting in the Maltese-cross pattern. There will of course be no precise temperature when the Maltese-cross pattern will disappear, but the electron microscope results suggest that as the degree of supercooling increases LMF spherulites without Maltese-crosses should be observed in the optical microscope.

Row nucleated structures are observed in strained films. They consist of long wavy backbone crystals (5 to 25 nm thick) lying in the direction of strain, overgrown by lamellar crystals (5 to 10 nm thick), oriented at right angles to the strain direction (Figs. 7b, 15a). The density of backbone crystals increases with strain resulting in much shorter lamellar crystal overgrowths (Fig. 16a). Electron diffraction patterns show the presence of several orders of $\langle 0 0 l \rangle$ layer lines which suggests that the molecular *c* axis lies along the row structures in the strain direction (Fig. 16a). The lamellar crystal overgrowths are mostly LMF crystals but at certain temperatures both LMF and HMF crystals form in the same row, (Fig. 7b). The HMF crystals exist as a group and are not mixed with the LMF crystals. This suggests that there is more than simply a molecular link between these crystals. Limited crystalline continuity is probable. The identity period or the *c* fibre axis estimated from the LMF crystal (002) reflection was 0.476 ± 0.04 nm. This agrees well with the value of 0.475 nm reported by Fisher [3], and with the values estimated from drawn bulk samples of 0.47 nm by Bunn [2]. No $(0 0 l)$ reflections were observed from HMF crystals, partly as a result of the small numbers of crystals present and partly due to the tendency of the crystals to twist and branch. The morphology observed is similar to the structures reported in strained films of CPI [13, 14, 15, 32] and TPI [10]. The morphology also bears a close resemblance to the "shish-kebab" structures of stirring-induced crystallization from solution [22, 33]. The "shish-kebab" backbones are of extended-chain crystal type and are flat ribbons with a width varying from 20 to 30 nm [22]. The images of backbone crystals observed in thin films could be from twisting crystal tapes 5 nm thick and 25 nm wide (Figs. 7b, 15a, 16a). The "shish-kebab" backbones are frequently overgrown by chain-folded lamellar crystals as in the present case.

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