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# Study of polyethylene spherulites using scanning electron microscopy

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A detailed scanning electron microscopy study has been made of spherulites in melt-crystallized polyethylene. In particular, unetched, ion etched, nitric acid etched and plastically deformed polyethylene samples have been examined. It appears that the spherulites visible on the surface of these samples consist of lamellae which possess alternate right- and left-handed partial twists. It is quite possible that enough material was removed from the surfaces of the samples by ion etching that the spherulites visible on etched samples could be representative of bulk samples. While questions remain both about the half twist model and about the current full twist model, the half twist model deserves consideration as an alternate model for spherulite structure.

## 1. Introduction

While polymer spherulites have been known since 1945 [1], their fine structure and the arrangement of the crystallites within them is still something of a mystery. With the discovery of folded chain crystals of polyethylene grown from dilute solution [2], it was proposed [3] that the fibrous texture of polyethylene spherulites in the optical microscope could be reconciled with the radial *b*-axis orientation and tangential chains [1] if the spherulites were arrays of long ribbon-like single crystals radiating outward from the centre. The concentric rings seen in many polyethylene spherulites in the polarizing microscope, due to periodic variations in the refractive index along the spherulite radius, were explained by allowing the optically uniaxial ribbons to be helically twisted along their length.

Immediate support for this model came from analysis and computer simulation of the complex extinction patterns observed in the polarizing microscope when large thin spherulite sections were tilted [4-7]. Of particular importance was the observation that the bands appeared to move uniformly in and out as thin spherulite sections were tilted in the polarizing microscope [4]. Fujiwara [8] also found a 180° rotation of the unit cell around the *b*-axis in each band of large, thin spherulite sections, using X-ray diffraction with a beam whose diameter was $\frac{1}{4}$ of the band width. Subsequent attempts to verify the nature of the twist, particularly in bulk samples did not yield straightforward results. Transmission electron micrographs of solution cast thin films of polyethylene showed wiggly ribbons that seemed to be twisted [9], but the difficulties of deciphering large numbers of overlapping lamellae precluded unambiguous interpretation. Keller and Sawada [10] examined the debris from fuming nitric acid degradation of bulk samples and found twisted fragments up to one band period (one half twist) long. Likewise, electron microscopy of replicas of spherulite surfaces [11] revealed densely packed lamellae but did not conclusively show the nature of the twist. Also, in some of the replicas the lamellae did not appear to twist at all. Some branched polyethylene spherulites which had nucleated on the surface of the sample had lamellae which appeared to have alternating half twists rather than full twists [12].

However, while the full helical twist model seems to be reasonably consistent with most of the experimental evidence, it has one serious

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drawback; such lamellae cannot be packed closely enough together to fill space well [13]. The authors have recently demonstrated this problem and presented scanning electron micrographs of ion etched linear polyethylene spherulites which showed lamellae which instead appeared to have a series of alternating partial twists [14]. Such lamellae fit together neatly to fill space well, and they still produce the rings observed in the polarizing microscope. It is the purpose of this paper to offer additional evidence to support this half twist model, based on careful scanning electron microscope observation of unetched, ion etched, fuming nitric acid etched, and drawn spherulites.

## 2. Experimental

Samples were prepared from whole Marlex 6015 linear polyethylene ($M_n = 7500$; $M_w = 153000$) as received. For all experiments except the $HNO_3$ degradation, discs approximately 1 cm in diameter and 0.5 to 1 mm thick were prepared by melting one Marlex pellet on a glass slide on a hot plate and manually flattening the melt by quickly pressing it with another slide covered with aluminium foil. The disc was then crystallized with an air surface by setting the slide on which it was melted on a mound of crushed ice or a cool table top. The samples for nitric acid etching were prepared from several pellets by the same technique, producing squares 1 cm across and 2 to 3 mm thick. Spherulites nucleated on the air surfaces of the samples and ranged from 20 to 50 μm in diameter with band spacings on the order of 2 μm. Due to the sensitivity of the band spacing to crystallization temperature, this varied somewhat from sample to sample.

Some preliminary observations were made on discs crystallized as above but with the top surface still in contact with a slide covered with shiny aluminium foil. This produced a surface which was quite smooth and featureless on initial SEM examination. Initial attempts to grow smooth-surfaced samples between glass surfaces produced samples with a layer of extremely densely nucleated spherulites on the surface [15]. The removal of the glass, however, disturbed the surface. On the other hand, the shiny foil nucleated fewer spherulites permitting them to grow to sizes intermediate between those of the glass and air surfaces. The foil did not stick to the polyethylene surface to damage it upon removal.

Some of the sample discs were examined in the scanning electron microscope (SEM) without further treatment. To produce the necessary conducting surfaces, the samples were vapour-coated with a layer of a 60% Au-40% Pd alloy a few hundred angstroms in thickness. Examination was with 20 kV electrons at beam currents of 200 μA. The sharpest image was generally obtained in the secondary emission mode. The electron beam was usually at 45° to the surface for maximum contrast, though observations were also made at other angles.

Another group of samples was etched in an Ion Micro Milling Instrument (IMMI), manufactured by Commonwealth Scientific Corporation. The samples on SEM stubs were mounted on a slowly rotating stage inclined at 13 to 15° to a beam of argon ions accelerated through a potential of 6 kV. Some samples etched at 3 kV also yielded satisfactory though less clear results. The low angle of incidence resulted in slow, gentle etching for the surfaces of samples etched at higher angles of incidence appeared ragged and disturbed in comparison to those etched for much longer periods of time at 15° to the beam with the same beam current. Specimen heating was reduced to what appeared to be minimal amounts by using the very low beam current of 15 to 30 μA over an area of approximately 1 cm$^2$. After etch times of up to 17 h, only a few per cent of the material appeared to have been removed. The difficulties of such accurate measurement of specimen thickness precluded determination of etch rates. However, some bulk removal seemed to have taken place as evidenced by the fact that many spherulites were visible as sections other than the nearly diametral ones of the surface. Also, some of the glue on the stubs around the edges of the specimens had been very visibly removed after etch times of several hours. For example, a layer of glue (silver conductive paint) approximately 1 mm thick on one sample was almost totally removed after 5 h at 6 kV, 15 to 18 μA, and 15° angle of incidence. After etching, the samples were coated as above with the Au-Pd alloy before examination.

The samples for fuming nitric acid degradation were digested by the method of Palmer and Cobbold [16] for 4 h. This produced a layer of etched material on the surface which could then be coated and examined in the SEM.

For the drawing experiments, dumbbell-shaped specimens 1 cm in length were cut from sample discs. Some were Au-Pd coated without being mounted on SEM stubs, and then the coated samples were drawn on a tensile stage in the SEM. This permitted direct observation of spherulites drawn up to 50%. However, as the spherulites approached the neck in the sample, the tiny cracks which had been forming in the brittle coating grew severe enough to obscure the structures beneath. For this reason some of the samples were drawn from 100 to 400% in the tensile stage outside the microscope to produce a neck, removed from the jaws, and glued to SEM stubs for coating and examination. The relaxation which occurred before examination did not appear to change the structures under observation significantly. To verify this, a few samples were drawn, coated and then redrawn to their original length or longer. The differences between these drawn spherulites and the undrawn ones appeared to be somewhat more extreme, but they were not qualitatively different from the changes in spherulites that were not redrawn after coating.

## 3. Results and discussion

SEM contrast for a coated specimen depends solely on the topography of the surface. Anything that enhances this will enhance the visibility of features in the microscope. The various sample treatments all depended on this fact.

When unetched samples with air surfaces were first placed under the electron beam, the spherulites were clearly visible as featureless round regions that appeared to be slightly mounded. However, the differences in topography caused by the fine lamellar details were small enough that the contrast (and, therefore, the visibility) were poor. However, after times ranging from a few seconds to a few minutes under the beam, depending on the sample and the magnification being used, the features could be seen to rise gently above the original level of the surface. The spherulites themselves expanded upward, heightening their original slightly rounded shape. The bands became visible and the individual lamellae became more clearly defined with respect to their neighbours. This is in agreement with the work of Grubb and Keller [17], which came to the attention of the authors after the present work had been completed. The same features appeared on the surfaces that were grown against the aluminium foil, though on initial examination no trace at all of the spherulitic structure could be seen. Similar contrast development in transmission and scanning electron microscopy of microtomed slices of polyethylene has been observed by Dlugosz and Keller [9].

Observation of this phenomenon with a television monitor which provided a continuous picture (as opposed to the normal raster scan of one frame per second), showed conclusively that the features that developed were not artifacts. They rose smoothly and continuously from the features that were present before irradiation. None of them were depressions such as those observed in some spherulites by Grubb and Keller [17]. This is easily explained by the fact that Grubb and Keller used films thin enough for transmission electron microscopy, while the spherulites under investigation here were on the surface of discs 0.5 mm or more in thickness. The portions below the surface spherulites would prevent them from sinking below the surface. Only the areas directly exposed to the beam developed improved contrast. The topography development seemed to be permanent, for samples examined two months or more after the initial observation still had square areas of heightened contrast where the previous scans had been.

The contrast development process can be followed in Fig. 1a to d, a series of micrographs of a sample crystallized against aluminium foil. Particular attention should be paid to the accidental tweezer scratch running across the centre of each picture. It can be seen to have periodic white striations across it in the first picture. After six raster sweeps of 40 sec each, a faint spherulitic structure can be seen. After twelve sweeps, the white markings in the scratch are revealed as portions of the band structure of the spherulite which were mechanically displaced to provide the surface relief necessary for SEM contrast. After twenty raster sweeps the sample has reached maximum contrast, with the scratch barely discernible. The conclusion, then, is that both mechanical scraping at room temperature and the effect of the electron beam revealed the same structures. The following facts all argue against the heat of the beam being sufficient to cause any melting or annealing phenomenon: (a) the speed of the development, (b) the agreement between band spacings observed optically and in the SEM, (c) the smooth continuous development of the features from those initially visible on the surface, and (d) the fact that structures developed slowly at low magnifications and beam intensities appear to be identical (except for slightly less surface relief) with those developed rapidly at higher magnifications and

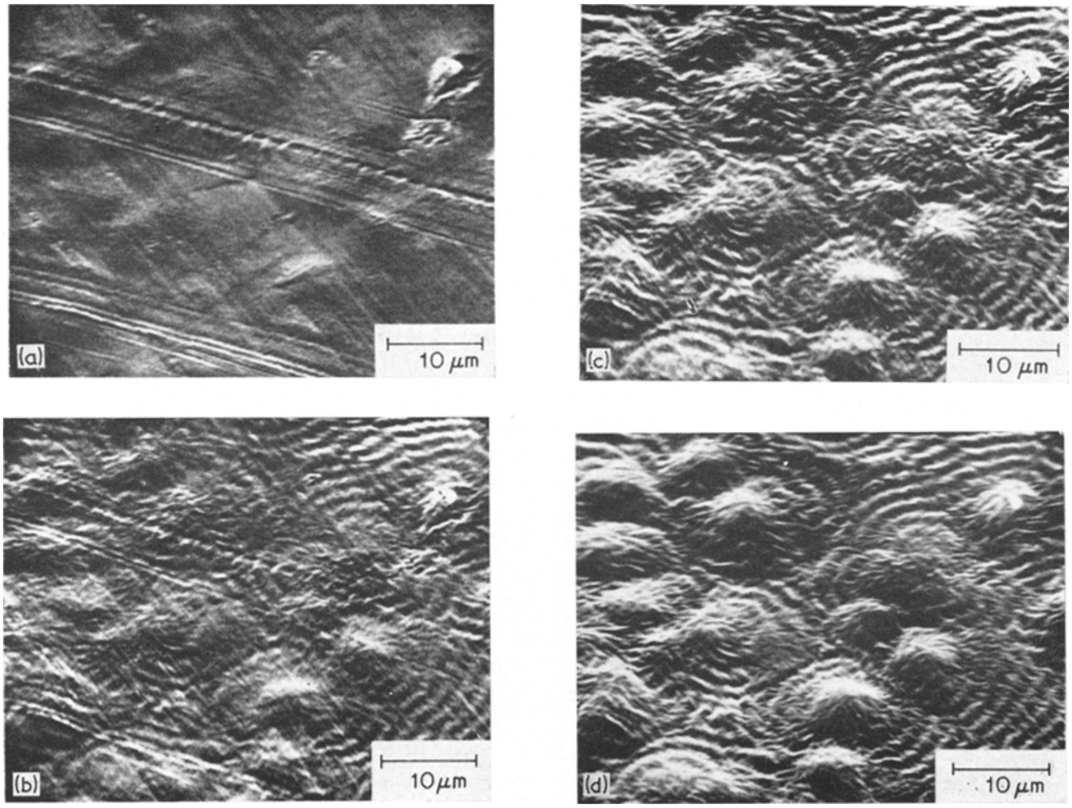

*Figure 1* (a) Scanning electron micrograph of surface of polyethylene crystallized against aluminium foil upon immediate observation in the SEM. Angle that electron beam makes with specimen surface is 45°. (b) Same area as that in Fig. 1a but after six raster sweeps of 40 sec each across the area of view in the SEM. (c) Same area after twelve raster sweeps across the area of view. (d) Same area after twenty raster sweeps across the area of view.

beam intensities. The model of Grubb and Keller [17] appears to give a reasonable explanation for most of the features observed here. There does, however, appear to be another factor, possibly residual surface stresses from the crystallization process, in operation. The heat of the beam could be sufficient to permit local plastic deformation of the surface in response to such stresses. This is strongly suggested by the fact that surfaces crystallized under the foil-covered slides developed contrast in a few seconds that required a minute or more for air surfaces at the same magnification, scan speed, beam voltage and current, and coating thickness.

The appearance of the unetched spherulites is shown in Figs. 2 and 3. The spherulites are made up of lamellae which appear as densely packed white wiggly lines. A number of them take the form of sine waves that can be followed for as many as two bands or at least for one entire band. Since the white lines are of the order of 500Å in width, they must be the edges of the ribbon-like lamellae. They could, however, be the edges of stacks of thinner lamellae, but this

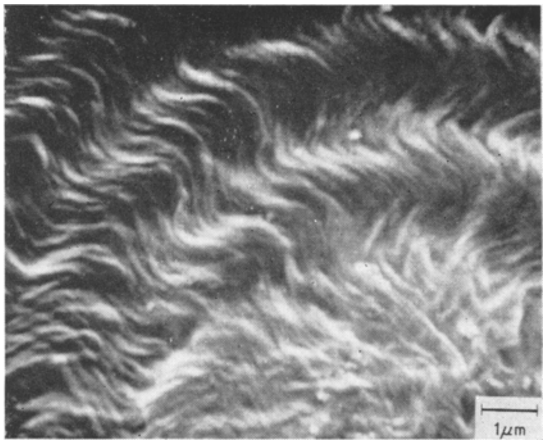

*Figure 2* Detail of a polyethylene spherulite on a surface grown against aluminium foil showing sinusoidal edges of lamellae. The electron beam makes an angle of 70° with the surface.

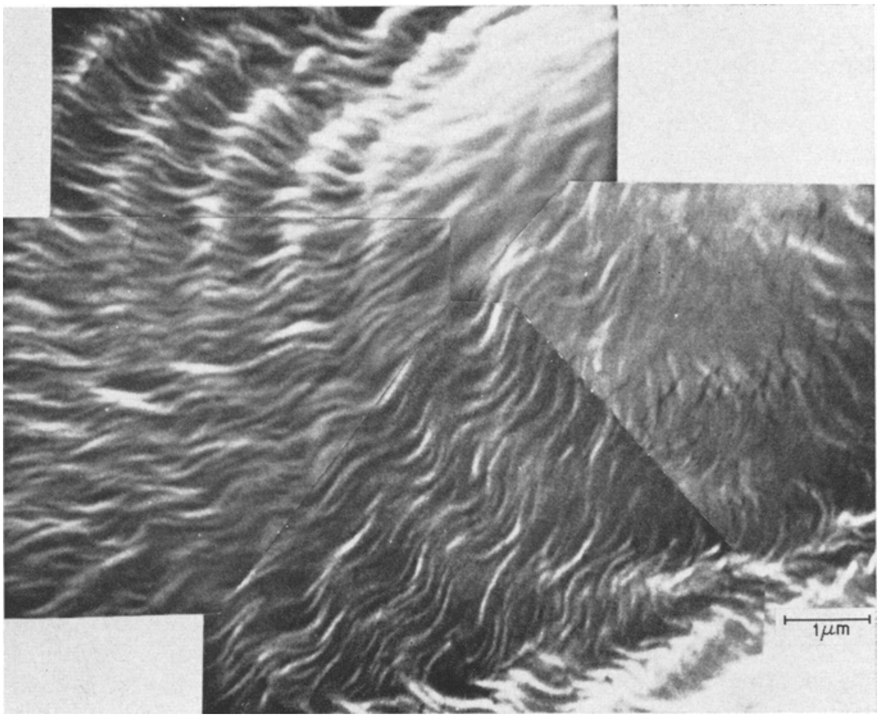

*Figure 3* Detail of a polyethylene spherulite on an air surface showing sinusoidal lamella edges. The electron beam is at an angle of 55° to the specimen.

would have little effect on the conclusions to be drawn. The dense packing and edge continuity are incompatible with helically twisted lamellae as will be demonstrated below. On the other hand lamellae with alternating right- and left-handed partial twists would be expected to have continuous edges in the form of sine waves.

Surface etching produced structures identical to those in unetched samples, but the half twisted nature of the lamellae was revealed even more clearly. The individual crystalline lamellae were quite plainly visible, apparently because of preferential removal of the disordered material between them. Fuming nitric acid is known [10] to attack the fold surfaces, tie molecules and other disordered material while leaving the crystalline portion relatively untouched. The ion etching also appears to remove the disordered material preferentially (though not exclusively by any means) as evidenced by the similarity in appearance of samples prepared by each method. However, it is interesting to note that samples etched by both methods also showed some additional contrast development under the beam that was superimposed upon the surface relief produced by the etching.

Fig. 4 shows the surface of a sample which was etched in fuming nitric acid. The edges of the lamellae are particularly visible across the valleys where they are continuous. On the other hand, the valleys are where the edges of fully twisted lamellae would be expected to disappear. This

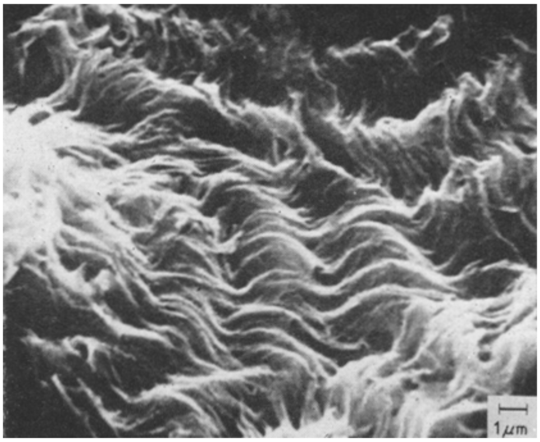

*Figure 4* Scanning electron micrograph of a spherulite which was etched for 4 h in fuming nitric acid. The electron beam is at an angle of 55° to the specimen.

micrograph does, however, suggest a point which is substantiated by the other micrographs, that the lamellae probably do not extend continuously from the centre to the edge of the spherulites. Instead, they are probably only a few band widths in length. Similar observations on solution-grown spherulites have been made by Heber [18]. These spherulites were initially flat when observed in the SEM. The mounded topography which is superimposed on the relief from the nitric acid etching developed under the beam.

Figs. 5 and 6 are micrographs of ion etched samples. Fig. 5, a sample etched at 6 kV for 4 h, shows the remarkable clarity that is available with this technique. Many of the lamellae can be followed for two or more bands. Again, most of the mounded topography developed under the beam from initially etched but flat spherulites. However, in some of the most heavily etched samples the spherulites were already slightly raised before exposure to the electron beam. This was noticed only in the samples etched at 3 kV and suggests that the ions may have been destroying some of the crystallinity of the lamellae in much the same way as an electron beam [19]. It is also possible that the surface may have been heated enough to deform slightly in response to possible surface stresses, as outlined below.

Fig. 6, a micrograph of a portion of a spherulite etched at 6 kV for 4 h, represents the most convincing evidence to date for the existence of half twisted lamellae. Several of the ribbons are continuously visible for two band periods. Several cracks are visible in the alloy coating. These appear to have formed as the ridges expanded outward, creating tensile stresses in the brittle coating. The irregular region in the lower right-hand corner of the picture is a portion of another spherulite. The lamella marked with the letters can be seen to be nearly vertical at point A, to dip over at B, and to rise again to C. While this spherulite shows the partial twist most clearly, it does seem to be typical of other diametral sections of spherulites in this and other specimens.

The characteristics of lamellae with full and alternating partial twists are shown in Fig. 7. The figures are photographs of groups of copper strips twisted to resemble lamellae with full and partial twists. The strips were painted black with

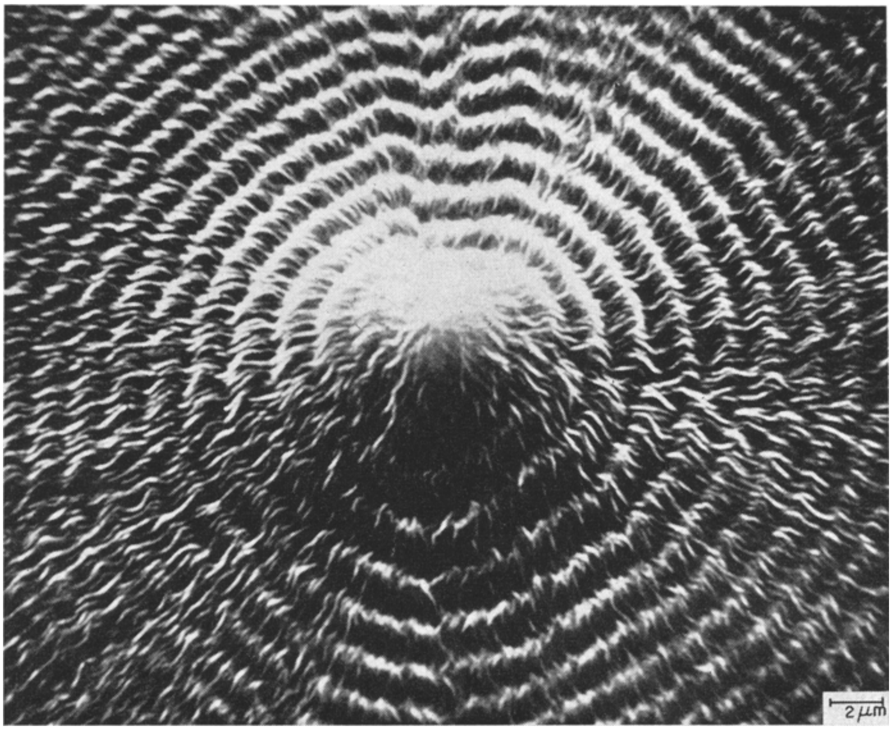

*Figure 5* Scanning electron micrograph of an ion etched spherulite. The electron beam is at 55° to the specimen.

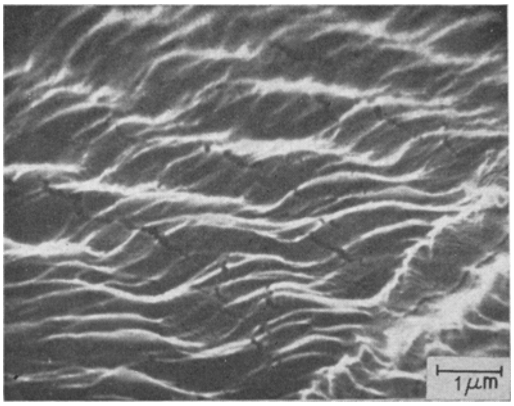

*Figure 6* Scanning electron micrograph of a portion of an ion etched spherulite showing continuous lamella edges. The centre of the spherulite is off of the left hand side of the picture.

white edges for clarity. Fig. 7b is a set of fully twisted ribbons. The white edges are never continuous, for they all disappear once during each twist cycle. Furthermore, the ribbons cannot be packed any more closely together than the width of one of them, another fact that is incompatible with the present observations.

In contrast to this, the partially twisted lamellae in Fig. 7a are completely consistent with the micrographs. The continuous edges of the lamellae, the sinusoidal shapes of the edges, and the dense packing can all be accounted for.

Having established a self-consistent model for spherulite structure, it was next decided to test this model further in observations of the tensile deformation of unetched spherulites. Fig. 8 is a montage of scanning electron micrographs showing an area above the neck, where the spherulite seems to be strained around 50%. The sample was coated after being drawn. The spherulite deformed homogeneously [20] into an ellipsoid with the long axis along the draw direction. The individual lamellae have also deformed with the spherulite. Although some of the contrast was developed under the beam, much of it came from the drawing process outside of the microscope. Similar development of topography in drawn compression moulded samples which had initially smooth surfaces was observed by Geil [11]. Ridges and valleys are visible in previously unirradiated drawn samples immediately upon insertion into the microscope, an observation which is not explained by the model of Grubb and Keller.

The expected effects of plastic strain on spherulite morphology are illustrated schematically in Fig. 9. In particular, Fig. 9a shows the unstrained spherulite whose lamella edges are sinusoidal. Fig. 9b shows the effect of a vertical tensile stress which gives rise to a plastic strain. As the spherulite itself becomes ellipsoidal, the lamellae within it must lengthen and shorten along the major and minor axes. This has happened in the spherulite in Fig. 8. This straightening out of the lamellae is even more graphically illustrated in Fig. 10, which is a portion of a spherulite which was coated and then drawn somewhere under 50% on the tensile stage in the microscope. In this picture the visibility of the continuity of the lamellae edges from band to band is particularly striking.

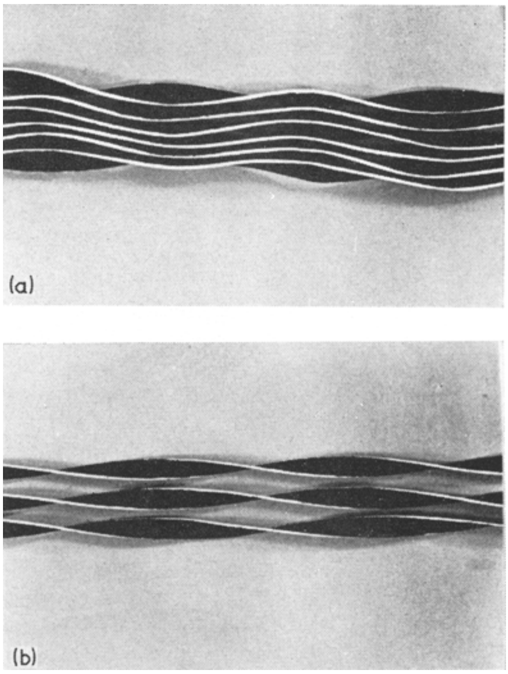

*Figure 7* (a) Packing arrangement of lamellae possessing alternating partial twists. (b) Packing arrangement of fully twisted ribbons.

The lamellae perpendicular to the draw direction present a more complicated problem. Twinning [21] can make the lamellae shorter and wider, as is needed to increase the sine wave amplitude. However, since this can only account for a 15% contraction along the original *b*-axis, further shortening must come by bending of the neutral axis of the lamella (the original *b*-axis) either by buckling of the lamella or by slip across the axis.

Finally, Fig. 11 is a micrograph of a spherulite

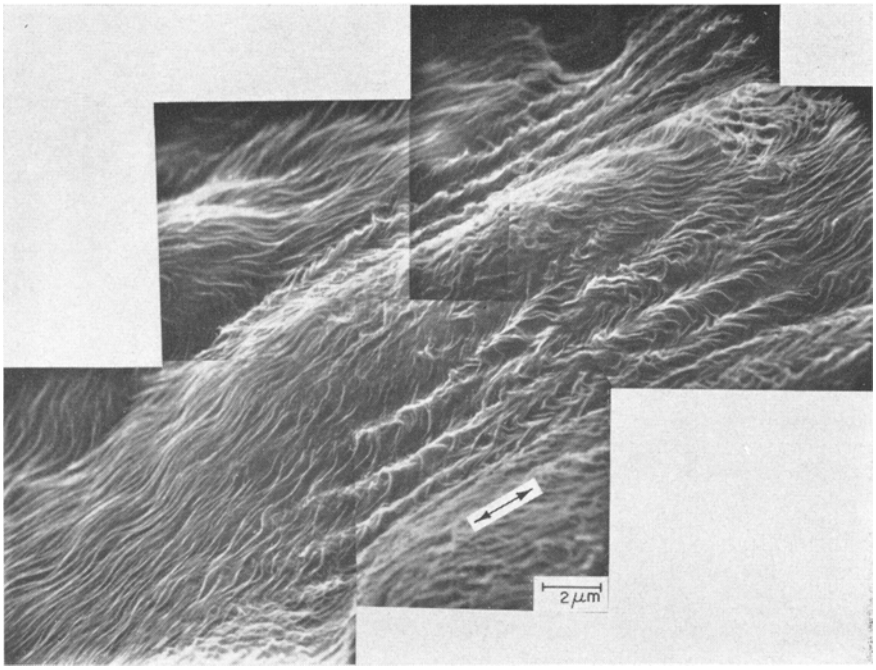

*Figure 8* Montage of scanning electron micrographs showing a spherulite drawn to approximately 50% elongation. The electron beam makes a 55° angle with the specimen surface. The arrow indicates the tilt axis and the tension direction.

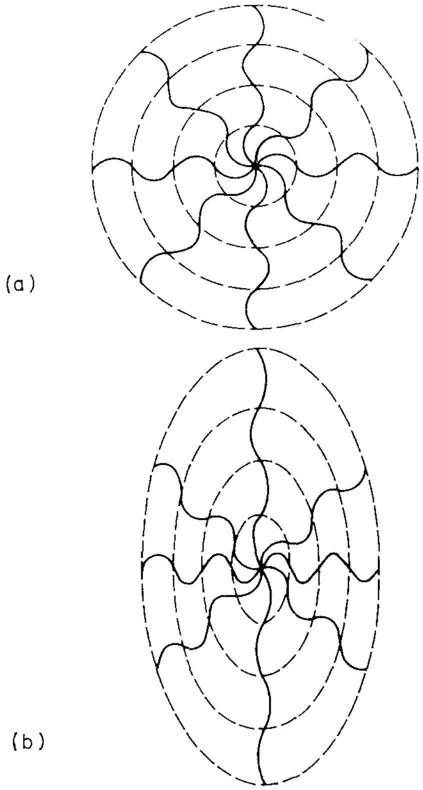

*Figure 9* Schematic illustration of a spherulite with sinusoidal edges of lamellae. (a) Undeformed; (b) drawn.

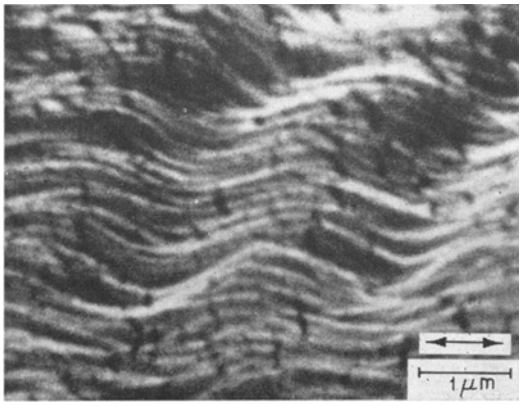

*Figure 10* Scanning electron micrograph of a spherulite drawn to under 40% after coating, illustrating that the lamellar edges straighten along the draw direction.

which was drawn before coating and seems to have an elongation of under 50%. The changes in the sine waves, as in Fig. 9, are clearly visible here.

Several questions still remain, however, about the present observations. The first is the reason for the twist itself. It has been suggested [22] that the driving force for a twist is the surface energy associated with a fold surface that is bulkier than the well-ordered interior of the crystalline lamella.

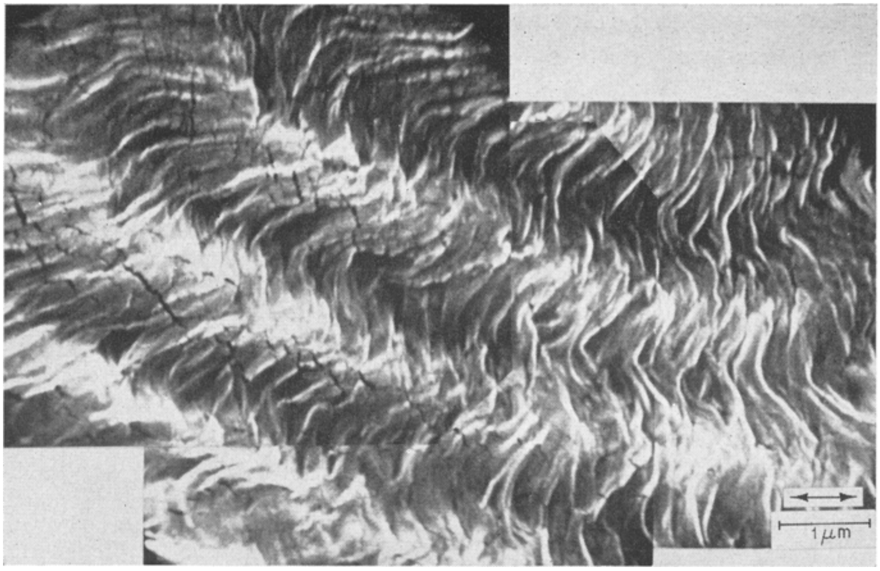

*Figure 11* Montage of micrographs showing one quadrant of a spherulite drawn under 50% along the indicated direction. The electron beam makes an angle of approximately 70° to the surface.

A twist would increase the surface-to-volume ratio allowing the surface layer to fit more easily on the lamella. A screw dislocation model has also been formulated for the twist [23]. Either proposed twist model is compatible with the above results.

A simple model based essentially on a restatement of the packing arguments can be suggested as the reason for the twist reversal. One can imagine the situation illustrated schematically in Fig. 12a. The tips of three closely spaced parallel lamellae extend outward into the melt and grow by addition of new material at their ends. In Fig. 12b new molecules are laid down on the tip in such a way that each layer is rotated slightly for whatever reasons in relation to the previous one. This, of course, would result in continuously twisted lamellae if each lamella were isolated from its neighbours. However, if the growing lamellae are close enough together, they will reach a stage (Fig. 12c) where contact with their neighbours would prevent further twisting in the original direction. The lamellae would then have to reverse the sense of the twist as growth continued (Fig. 12d).

A second question concerns the terraced nature of the bands in the spherulite after exposure to the electron or ion beam and after drawing. One possible model for the deformation uses the following reasoning: the portions of the lamellae which are normal to the surface are reasonably free to expand outward by slipping past one another. In the portions where the lamellae are parallel to the surface, however, the easy direction of slip is also parallel to the surface rather than out from it. This would produce the constraint for terracing or the formation of ridges and valleys along these regions. The hill and valley formation by either process could also be aided if the lamellae were not oriented precisely so that their average *a*-axis orientation was perpendicular to the surface, but if instead they all leaned slightly in one direction. Examination of many of the micrographs suggests that this could be the case.

The model of Grubb and Keller [17] does seem to provide a reasonable explanation for the basic topography development under the electron beam. An explanation is still needed, however, for (a) the fact that contrast development is so much faster on the surfaces crystallized against aluminium foil than on the air surfaces, and (b) the appearance of ridges and valleys on drawn, unirradiated spherulites. One can speculate that the surface may be locally plastically deforming in response to applied stress or to surface stress either remaining from the crystallization process or caused by differential thermal expansion between the surface and the cooler interior. For the undrawn samples such deformation could be made possible by localized beam heating and would in no way preclude the

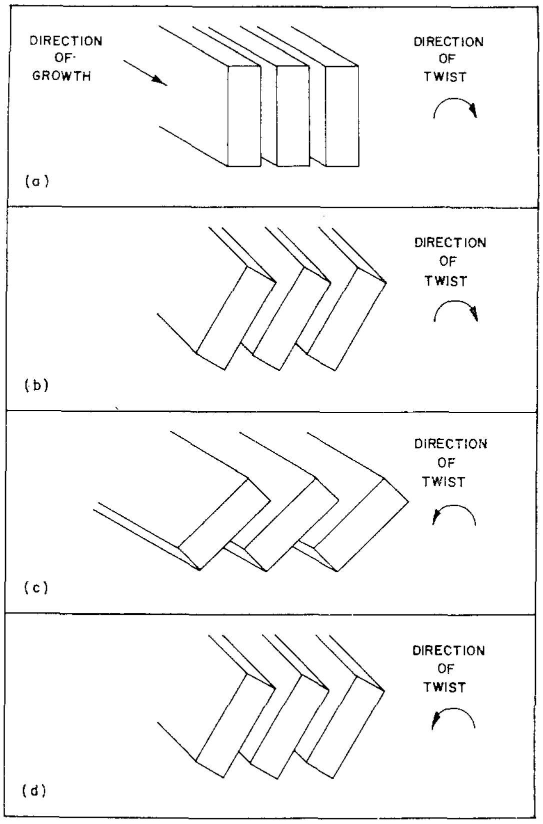

*Figure 12* Schematic diagram of a possible mechanism for the formation of an oscillating twist rather than a full twist during crystallization. (a) Closely spaced lamellae extend out into melt. (b) The lamellae twist during growth. (c) The lamellae have twisted so far that they are in contact with their neighbours, requiring that the direction of twist be reversed. (d) Growth continues with the reversed twist.

possible additional operation of the Grubb and Keller process. The features seemed to rise faster and further in etched samples than they did in unetched ones. This lends support to the contention that ion etching (and $HNO_3$ etching) preferentially removes the disordered material, including the tie molecules, between the lamellae. The tie molecules in unetched material provide a constraint against the lamellae expanding freely or slipping against each other that does not appear to be as powerful in the etched samples. Also, it is difficult to determine for sure whether the cracks extend through the coating into the polymer. Since they occur predominantly in etched samples, it seems possible that they do extend, at least in some places, into the polymer and that the removal of the disordered material could have made cracking of the brittle lamellae possible. However, since in some places the polymer is visible in the crack, it is more likely that the increased cracking in the etched samples is due to the greater magnitude of the surface relief development.

The final and most important question concerns whether the spherulites under observation here are indeed representative of the bulk material, or whether some surface phenomenon may cause half twists in spherulites which nucleated on the surface while full twists exist in the interior. This question cannot be answered conclusively at present. If the twisted fragments reported by Keller and Sawada [10] are pieces of fully twisted lamellae, rather than half twisted ones, then the original question of space filling again appears, and even though generation of a spherically symmetrical aggregate appears to be easier with fully twisted lamellae than with partially twisted ones, the formation of spherulites from the half twisted lamellae would probably be analogous to the formation of spherulites in polymers such as polypropylene, whose lamellae are flat [24]. The ion etching experiments carried out thus far have removed only small amounts of material. The etched samples had evidences of sections other than the diametral ones seen in unetched samples, though it is still possible that insufficient material was removed to get below the surface spherulites. The removal of 100 μm or more of glue around the specimen, however, does suggest that the surface layer may have been removed, and that diametral sections visible after etching for several hours are not necessarily surface nucleated spherulites. Even the replicas of spherulites which nucleated below the surfaces of films, which have been cited as evidence for the full twist model [11], still show lamellae of indeterminate twist which are extremely close together, supporting the half twist model. Further work on heavily etched specimens and fracture surfaces is necessary to answer this question.

The partial twist model presented here is not without its problems. The evidence of nitric acid degradation [10], X-ray diffraction from thin sections [8] and in particular polarized light microscopy of thin sections [4-7] suggests quite strongly that the ribbons do indeed have full twists. In particular, if a planar array of partially twisted ribbons radiating from a common centre (a model for a spherulite diametral section) were tilted, the bands would not be expected to move in and out in phase with each other. Instead, they would split up into pairs of rings moving in opposite directions. The answer to this problem may be tied in with the questions of how representative the diametral sections actually are of spherical bulk spherulites and whether the addition of more material above and below the diameter to create a sphere would affect the extinction patterns. Also, in such thin films the spherulites usually nucleate on either surface of the film [11], making them subject to possible surface effects. The answers to these important questions would shed much light on the problems of spherulite structure.

Another question about the partial twist model is that the lamellae would not have spiral symmetry. The result of this would be that not all diametral sections of one spherulite would have the same lamellar structure. There would be one direction of view where incomplete extinction would be seen (the amount of extinction depending on the angle of each partial twist) and another where less than maximum birefringence would appear. Spherulites have been observed with less than the maximum birefringence predicted from fibre studies [11], but to the authors' knowledge incomplete extinction has not been observed.

Finally, the processes of SEM contrast development and ion etching are not completely understood. While the correspondence of the structures seen in the SEM before and after etching with those observed optically makes it unlikely that actual surface melting has occurred, some annealing or other phenomenon would not be out of the question. Further work on the ion etching process itself is presently under way, particularly on the question of how much of the surface is being removed.

## 4. Summary and conclusions

When examined in the SEM, spherulites of melt-crystallized polyethylene exhibit time-dependent contrast. This appears as surface relief and occurs in unetched and ion- or nitric acid-etched samples. The proposal of Grubb and Keller [17] can explain the basic beam-induced topography development, but an additional process such as surface plastic deformation in response to local stresses can also be proposed. A process such as this is needed to explain the fact that samples crystallized against aluminium foil develop contrast many times faster than those with air surfaces.

Enhanced contrast can be obtained by ion etching of the specimen surface, due probably to more rapid attack of the disordered interlamellar material than of the lamellae themselves. This is supported by subsidiary studies involving fuming nitric acid etching of surface spherulites. It appears likely that some bulk removal of the surface material has occurred after ion etching, so that spherulites seen as diametral sections in ion etched material would not have nucleated on the surface.

The individual spherulites show concentric bands which appear to be due to alternating right- and left-handed partial twists of each lamella in the spherulite. Not only is this twist configuration consistent with most existing experimental observations, but it also satisfies the space filling requirements for a spherulite. Observations of spherulites plastically deformed in tension also suggest the half twist model, at least for the surface spherulites.

It is not the purpose of this paper to present the partial twist configuration as an established model. Questions remain both about it and about the full helical twist model. In particular the evidence of polarizing optics in favour of the full twist model cannot be ignored. It is hoped, however, that the evidence presented here will reopen fruitful inquiry into the nature of spherulite structure.

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