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On chlorosulphonation and the electron microscopy of polyethylene

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It is shown that chlorosulphonation is a major aid to the electron microscopy of polyethylene for various samples which had mostly been crystallized at high pressures and included at least a proportion of the so-called chain-extended form. It is confirmed that sheets of excess electron density are produced at lamellar surfaces, but also including lateral surfaces. This is due primarily to the incorporation of chlorine and sulphur rather than to added uranium. The time to achieve an overall reaction varies sensitively with morphology, decreasing as the number of diffusion channels increases. Crystallinity is gradually lost, but sufficient crystals remain when a sample has become uniform, and in their initial orientations, for diffraction studies to be possible. The technique has been used to demonstrate that, during melt crystallization, the thickness of one lamella changes in response to altered growth conditions. This is direct confirmation that lamellar thickness is determined by secondary nucleation at the growth front. The tapered profile of a growing lamella previously observed in thick crystals of various polymers has been observed for chain-folded polyethylene lamellae, providing further evidence that this is a general feature of melt growth.

1. Introduction

A major difficulty in investigating structure–property relationships of cyrstalline polymers has always been the absence of an adequate method of characterizing the lamellar texture of bulk material. While in principle one ought to be able to prepare consecutive sections, examine these and so build up a three-dimensional picture, as is commonly done in biology, in practice even if one obtained the sections they were not generally stable in the beam of an electron microscope and detailed examination was impossible. For polyethylene this is no longer the case.

After chlorosulphonation and soaking in uranyl acetate, it has been found that polyethylene becomes stained, is easier to section and, above all, is stable in the electron beam, permitting direct observations of fine structure in unprecedented detail [1–5]. We have begun to use the technique to investigate polyethylene in the so-called chain-extended form, i.e. polyethylene which at high pressures has passed through the disordered hexagonal structure without subsequent melting [6]. Such samples have many advantages for evaluating the new technique and we report here on its mechanism, application, limitations and potential. We confirm, first, that the staining produces sheets of high electron density at crystal surfaces by showing that the image varies in the appropriate way for tilted specimens. It is then possible to identify all the main features in a single photograph of a particular section provided that this is of a thickness commensurate with that of the constituent lamellae; for sections appreciably thinner or thicker than this value identification is much more difficult. Secondly we show that the electron-dense regions in the image are formed by chlorosulphonation rather than the subsequent addition of heavy metal cations. This is due to crosslinking, which causes a higher peak to appear in the melting endotherm as reaction proceeds. It follows that the morphology observed has been transformed from that initially present although this causes no immediate difficulties in interpretation and, indeed, details are recorded which have not been observed previously. At the same time,

while crosslinking stabilizes most samples, those which are potentially brittle do not always benefit to a sufficient degree and remain difficult to examine. Thirdly, it is shown that the degree of staining is insensitive to variations in interlammelar conditions; contrast appears, as so often, to be primarily a question of accessibility, and side-surfaces are observed to be stained as well as the large lamellar surfaces. It has also proved possible to obtain over 100 serial sections of an entire sample with this technique which, quite clearly, represents a major advance in morphological characterization.

2. Materials and techniques

The experimental work in this study can be divided into three main parts: (i) preparation and crystallization of polyethylenes in the required form, (ii) staining samples with chlorosulphonic acid and, in some cases, uranyl acetate as well, (iii) analysis of the stained materials by electron microscopy of their sections and differential scanning calorimetry of larger pieces.

The polyethylenes used were high-density linear products, the main ones being Hifax 1900 (Hercules Powder Company Ltd.) with a high molecular weight $>10^6$ and a sharp, lower molecular weight fraction called LM6, with* $\bar{M}_n = 3.3 \times 10^4$, $\bar{M}_w = 4.8 \times 10^4$, extracted in this laboratory from Rigidex 140–60 (BP Chemicals Ltd.). Recrystallization at high pressures was usually achieved by cooling at 0.5 K min^{-1} from the melt at either 2.30 or 4.95 kbar in the piston and cylinder press [7]. In addition some samples from related work [8] with the diamond-anvil cell [9], which allows crystals to be observed while growing at high pressures, were studied. Those described here were of LM6 grown from the melt initially at ~3 kbar; the pressure falls during crystallization as the system approximates to constant volume conditons [9]. The samples in this way are very small (0.5 mm diameter, 25 μm thick) so that for comparison, and measurement of other properties, larger samples of the same fraction were crystallized under isobaric conditions in the piston and cylinder press.

Staining was achieved by submerging pieces of the polyethylene weighing 5 to 10 mg in chlorosulphonic acid at 60° C in sealed containers for several hours. Afterwards, samples were washed with acetone at its freezing point, and then distilled water. Unless stated to the contrary they were also soaked in a 1% aqueous solution of uranyl acetate for at least 3 h.

An entire LM6 sample crystallized in the diamond-anvil cell, was stained for 45 min at 60° C. When dry it was embedded in Araldite (Ciba Geigy embedding Araldite CY212) to facilitate handling during the sectioning procedure. Sections nominally 200 nm thick, were cut using a Bright Instrument Co. Ltd. rotary retracting microtome 5030, equipped with a 45° glass knife. The Araldite block was clamped directly and the sections mounted on electron microscope grids as they were cut. Hifax samples prepared in the piston and cylinder were large enough to be handled readily without embedding. They were held rigidly in Tryco-m-bed, (Aerosol Marketing and Chemical Co. Ltd.) which freezes the sample to the mounting block at sub-zero temperatures. The knife was cooled to approximately −20° C.

Electron microscopy of the sections was carried out at 100 kV. using a Phillips EM301 electron microscope equipped with a rotary goniometer stage enabling sections to be tilted through ±60° about any axis. Among other advantages, this allowed stereo pairs of photographs to be taken.

Differential scanning calorimetry of unstained and stained samples was carried out with a Perkin Elmer DSCIB Differential Scanning Calorimeter, using samples of approximately 2 mg at a scanning rate of 8 K min^{-1}. The Hifax crystallized at 4.95 kbar showed a single high melting peak before staining and following previous usage [7], is described as having a chain-extended texture. The other samples, Hifax crystallized at 2.30 kbar and LM6 crystallized at 2.87 kbar, both had two distinct melting peaks at atmospheric pressure, corresponding to separate initial crystallizations as the disordered hexagonal and orthorhombic phases. These we term mixed samples.

It became apparent early in the study of the stained polyethylenes that the amount of penetration by the acid was very dependent on the length of treatment. A systematic investigation of this effect was carried out on Hifax after various treatments using samples a little larger than 1 mm cube and weighing ~2 mg. Treatment with chlorosulphonic acid at 60° C varied between 3 and 27 h; treatment at room temperatures produced similar results but after considerably longer times.

* $\bar{M}_w$ = weight average molecular weight.
$\bar{M}_n$ = number average molecular weight.

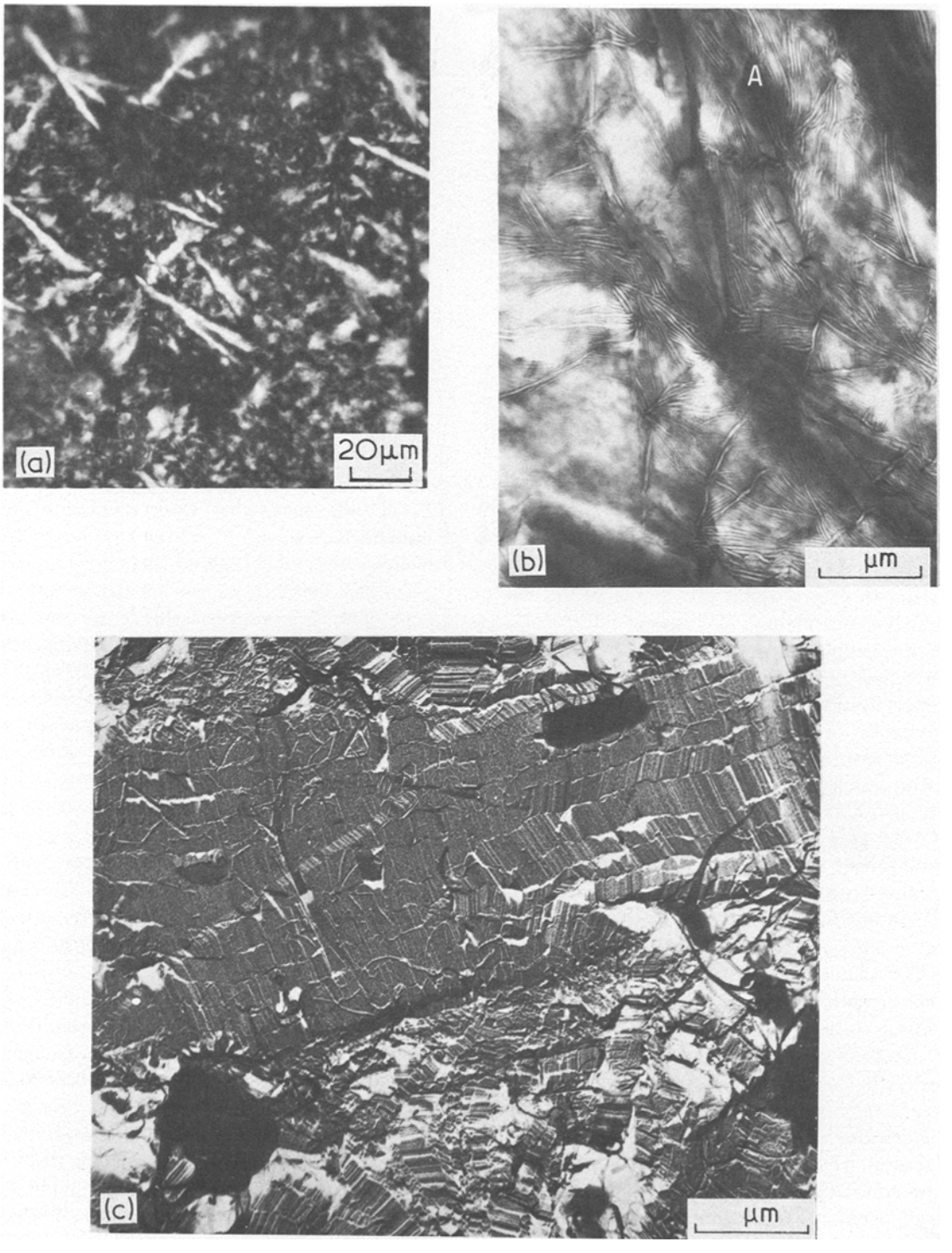

Figure 1 The morphology of LM6 fraction following crystallization in the diamond-anvil cell: (a) viewed optically between crossed polars and (b) a stained section in the electron microscope. (c) a fracture surface replica of a similar sample crystallized at 2.87 kbar in the piston and cylinder apparatus.

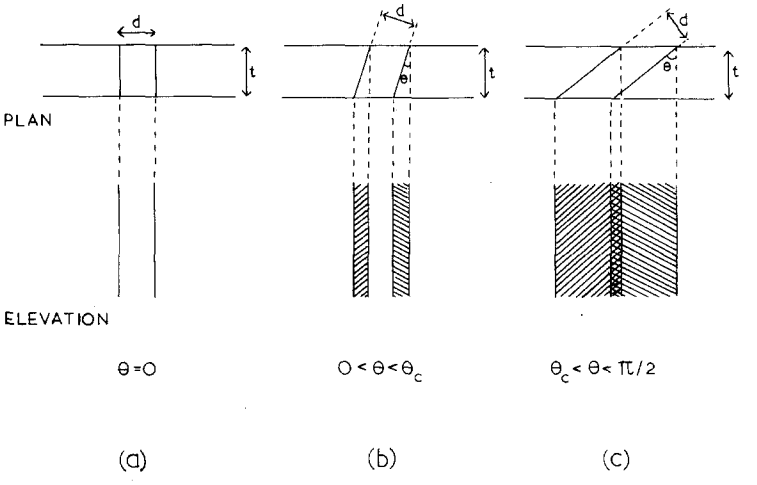

Figure 2 Diagrammatic representation of the variation in the image of a lamella, thickness d, in a section, thickness t, with the angle θ between their two normals.

3. Results and discussion

3.1. Images of tilted lamellae

A staining and sectioning technique is expected to show a random view of polymer morphology, subject to qualification only as to the location of the stain. In general terms this is true of the chlorosulphonation method as illustrated in Fig. 1a and b for a sample whose crystals had previously been watched growing from the melt at ~3 kbar in the diamond-anvil cell [8]. Fig. 1a shows the entire thickness of the sample (~25 μm) in transmission between crossed polars while Fig. 1b is of a section after staining. The similarity in texture is evident, though both forms of lamellae are resolved in Fig. 1b but only the thicker population in Fig. 1a. By comparison in Fig. 1c a fracture surface of a larger sample with only 50 wt% of thick lamellae shows these almost exclusively, a conclusion which has been inferred from previous work [10, 11]. The chlorosulphonation method, therefore, reveals a more representative morphology than is identifiable in fracture surfaces.

According to de Korosy and Zeigerson [1], polyethylene lamellae are stained or their large surfaces on chlorosulphonation. If this is true, one anticipates parallel sheets of excess electron-density which should have the behaviour illustrated in Fig. 2. When a lamella is rotated about an axis parallel to its length in the section, as is the lamella indicated in Fig. 3, the surface contrast always broadens as expected (Figs. 2b and 3b). The anticipated overlap which should start at a tilt angle θ_c producing a central dark band (Figs. 2c and 3c and d) is not often well resolved, however. This appears to be mainly because there is a strong line of contrast where the lamellar surface meets the cut surface of the section, possibly due to some relaxation, and this dominates what will otherwise be the rather weak contrast of the stained regions when not viewed edge on. In certain samples, notably those of Hifax polyethylene, the lamellar morphology also appears to be more complicated than a planar sheet, and this also detracts from the expected contrast. Nevertheless, the broadening of stage b (see Fig. 2) which is observed to vary as it should with sin θ, confirms that there are sheets of excess electron density at the basal surfaces of stained lamellae.

Knowledge of the change in contrast with tilting (which has been checked over $\pm 60^\circ$ of tilt for particular specimens) now allows the identification of all the main features in a single electron micrograph as is demonstrated in Fig. 4. These are assignable by inspection but have all been checked by appropriate tilting and the viewing of stereo pairs.

Region A is clearly a hole penetrating the whole section thickness. B is one end of a crack in the stained polyethylene, which has propagated since sectioning. The material close to C has been rolled up and distorted. Not all light regions are necessarily holes, however. For example at D, lamellae clearly pass through a light area showing that it is not a hole. Light areas of this nature could be due to a thin area in the section but are most likely to result from lamellae lying parallel to the section. These need not have their stained surfaces in this particular section but, even if one or both surfaces were included, the thickness of electron dense surfaces would be a small fraction of the specimen thickness, so that there would be high transmission and low contrast. The lamella E, has its normal

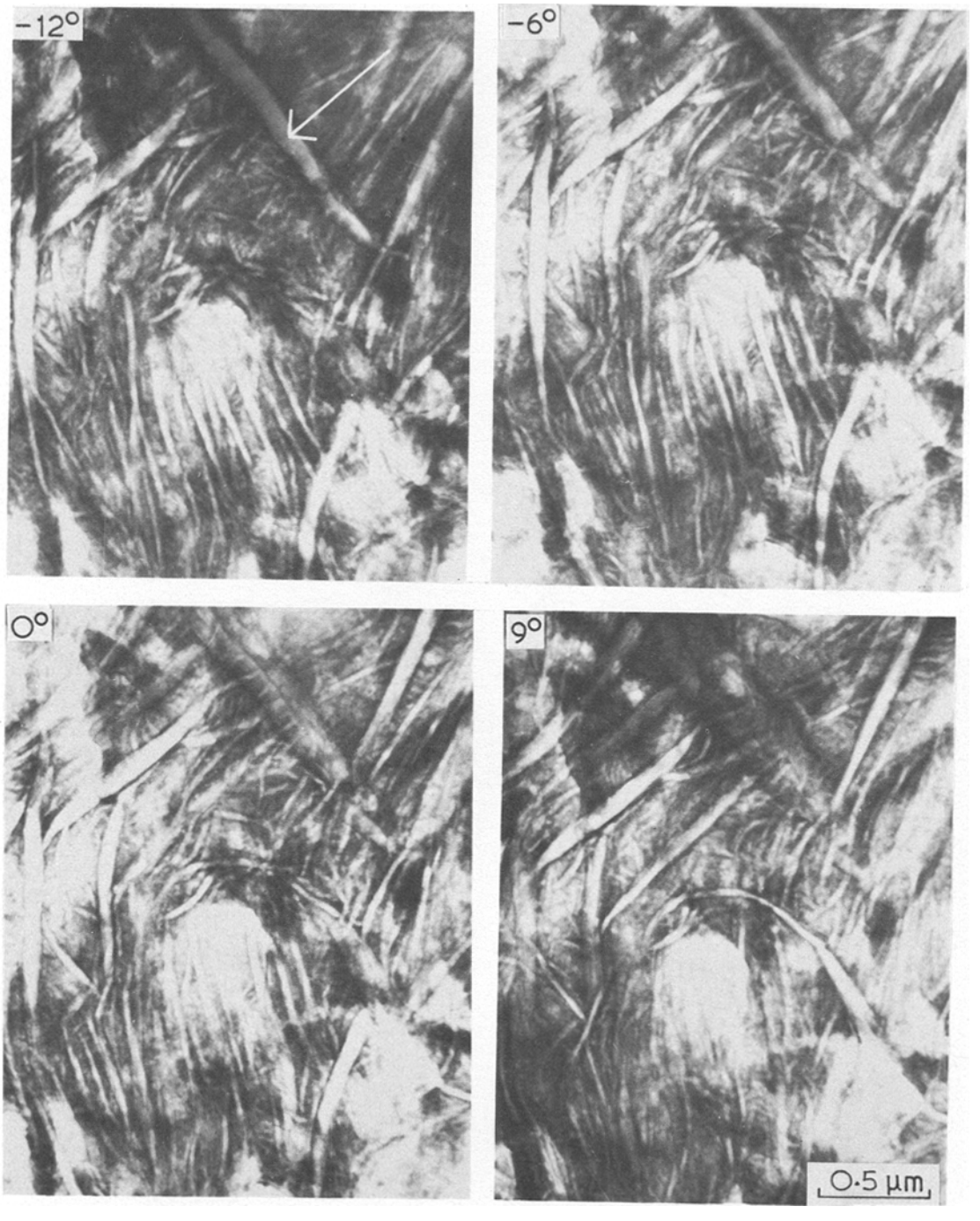

Figure 3 A sequence of electron micrographs, taken at the indicated tilt angles, of a stained section of mixed Hifax. The arrowed lamella illustrates the changes drawn in Fig. 2; the tilt axis is along its length.

lying at approximately 30° to the section surface, that is $\theta \sim 30°$ in Fig. 2b. A point of note here is that the lamella bridges the end of the crack, B, which can be seen to extend further than is readily observed without the use of stereo pairs. A large lamella tilted at some angle greater than 45° is observable at F. G and H, on the other hand mark lamellae lying virtually perpendicular to the section surface (i.e. parallel to the direction of the electron beam, as the section is untilted in this

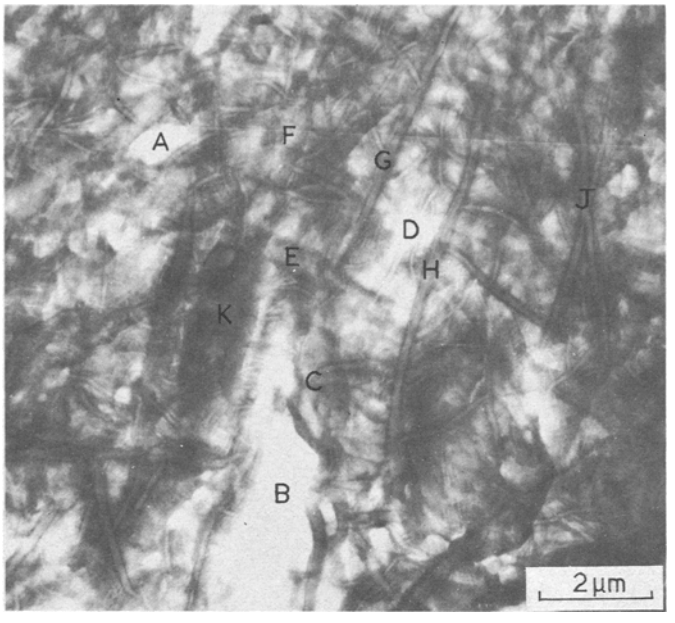

Figure 4 The identification of particular features, described in the text, in a stained sample of chain-extended Hifax.

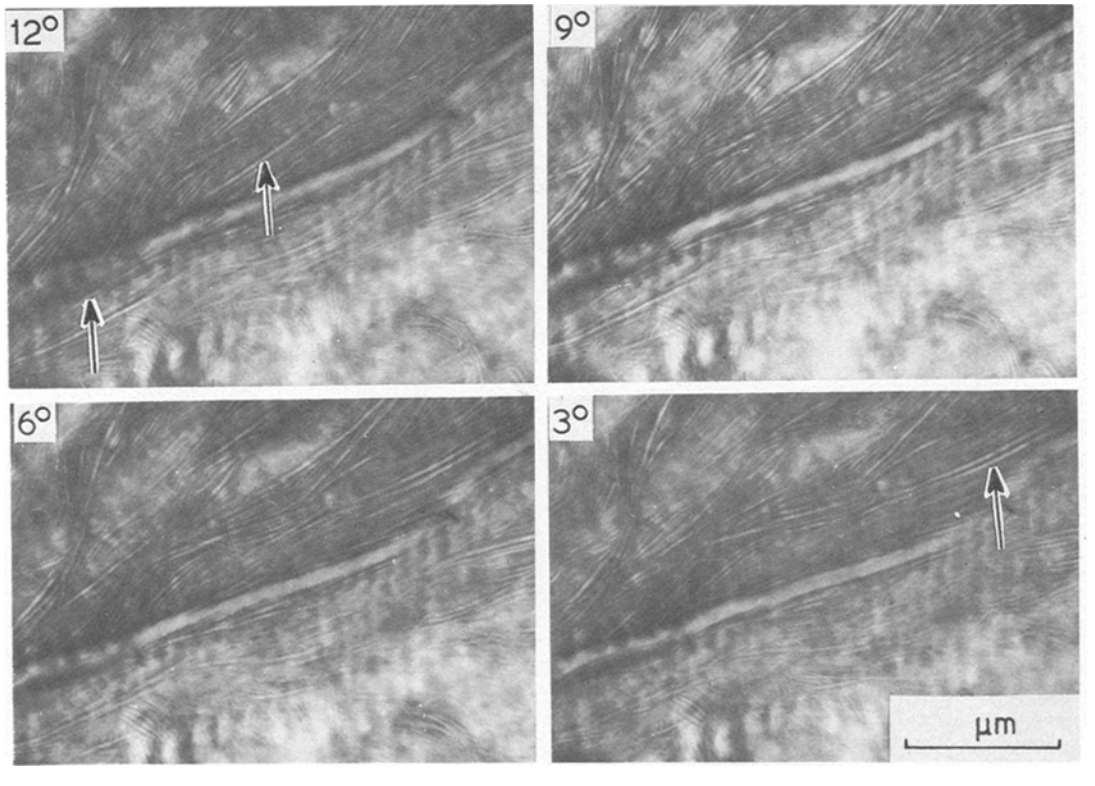

Figure 5 A series of electron mircographs showing how thin lamellae are identifiable for a much smaller angular range than are thick ones. Those arrowed disappear within the sequence of tilts about an axis approximately parallel to the length of the thick lamella. This effect is liable to bias the interpretation of images unless allowed for.

figure). Structure within the lamellar thickness is readily discernible in both G and H, the interpretation of which is beyond the scope of this paper. At J there appears to be the outer edge of a lamella, with a second lamella at a different orientation lying at a different level in the section. Finally a dark region, such as K, contains features which can generally be identified, as in this case, at higher magnifications.

Such identification is only possible, however, if the section and lamellar thicknesses are commensurate. For example, the specimen of Fig. 5 contained lamellae of two thicknesses, but while a thick lamella can easily be seen over the whole range of tilts, the thinner ones are only identifiable over a narrow range of orientations. This is because of overlapping in the images of adjacent lamellae which occurs at a smaller angle, the thicker the section (Fig. 2). In a similar way, in a section much thinner than lamellae are thick, the width of the stained surfaces is reduced and it is correspondingly harder to associate the two related surfaces and to assess the degree of tilt. There is also a greater chance of not including a lamella's surface in the cut section. Evidently, therefore, for ease of interpretation of lamellar detail one should match the specimen and lamellar thicknesses. Having done this one can then identify the nature of all areas in a photograph and not merely those where lamellae happen to be edge on.

3.2. The origin of contrast

Knowing that chlorosulphonation stains the surfaces of polyethylene lamellae, one is interested in the specificity of staining; i.e. to what extent differences in surface condition are shown up. In practice, there is no apparent alteration of contrast whether there are folds or chain-ends in the basal surfaces. Thus in Fig. 1b, the thick lamellae will contain molecules approximately once-folded and probably with end-groups excluded; the same molecules must be folded several times to fit into the thin lamellae of the same sample and yet no difference in the width of the stained interfaces, or their contrast, is evident. However, when one examines deformed specimens the total staining is much increased, and one has too much absorption if the section thickness is maintained. At first sight it should be an easy matter to reduce blackening by replacing uranium by atoms of low atomic number, but this is not so.

Fig. 6 shows two specimens of the same sample which were chlorosulphonated indentically but

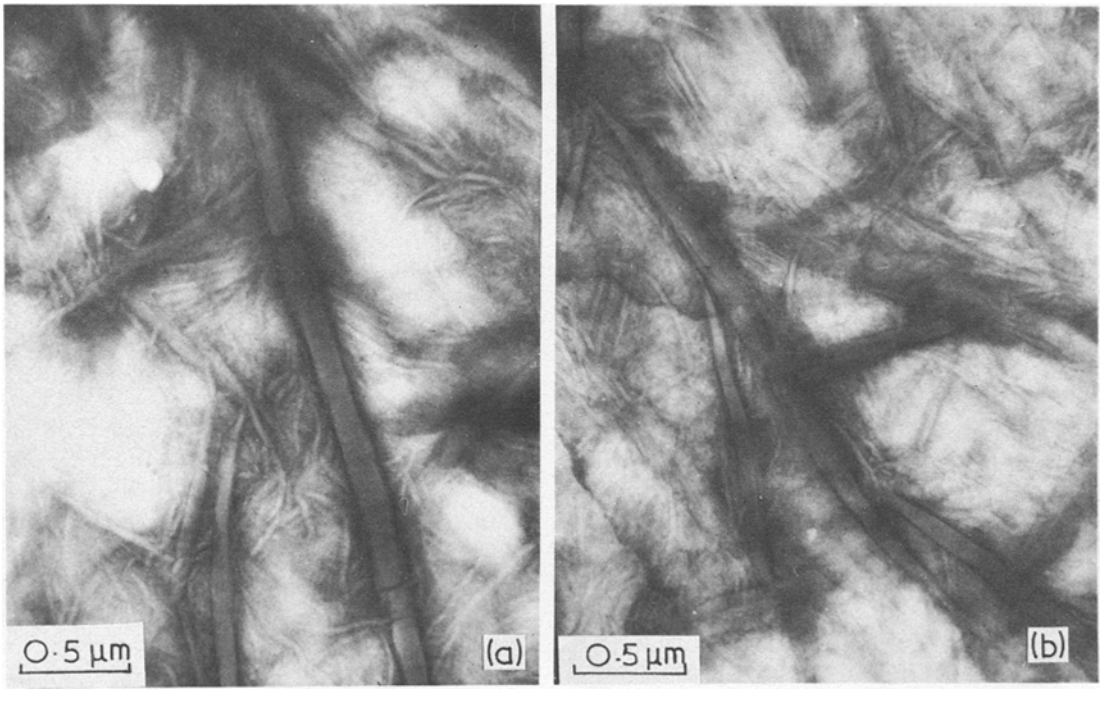

Figure 6 A comparison of contrast in the same stained sample of mixed Hifax, with (a) and without (b) the addition of uranyl acetate.

only one of which (that of Fig. 6a) was then treated with uranyl acetate. Although electron microscopic contrast after the chlorosulphonation step has been reported previously [1], it is still surprising that there is no obvious difference in Fig. 6 after the addition of uranium. That contrast is primarily due to the incorporation of chlorine, and sulphur, rather than uranium, in the sample has, however, been confirmed directly by energy dispersive analysis of X-rays (EDAX) of our samples through the courtesy of Pye Unicam Ltd.

The only difference clearly associated with the addition of uranyl acetate is that the staining contrast becomes stable; without uranium it generally fades. This may be a consequence of metal ions being incorporated in crosslinks in a similar way to proposed [12] mechanisms of curing a commercial chlorosulphonated polyethylene. The addition of uranyl acetate to chlorosulphonated polyethylene had no detectable effect on the melting endotherm.

3.3. Time-dependence of staining

During chlorosulphonation samples turned black. This is rather curious because commercial chlorosulphonated polyethylenes are white [12], but may well be due to the acid charring the sample. The blackening proceeds inwards from the surface and many hours are needed for a sample to become homogeneous; this is also evident from the melting endotherms.

Fig. 7 shows, for samples of chain-extended Hifax, how the melting endotherm alters for increased time in chlorosulphonic acid at 60° C. A second melting peak, due to the blackened regions and approximately 15 K above the original, soon appears and grows at the expense of the first. Concomitantly, the crystallinity falls continuously with time; after 27 h, the reduction is approximately 50%. By then a sample has become homogeneous but still contains crystals which, according to X-ray photographs of drawn samples, still have essentially their original orientations. Diffraction studies are possible, therefore, although the much-raised melting point shows that crystals have been affected by the chlorosulphonation.

The reason for the increased melting point is not yet entirely clear. It is surely related to crosslinking and, at first sight, could be a converse of the effect documented by Illers [13] whereby etching of the surface layers of chain-extended polyethylene crystals by nitric acid removes super-

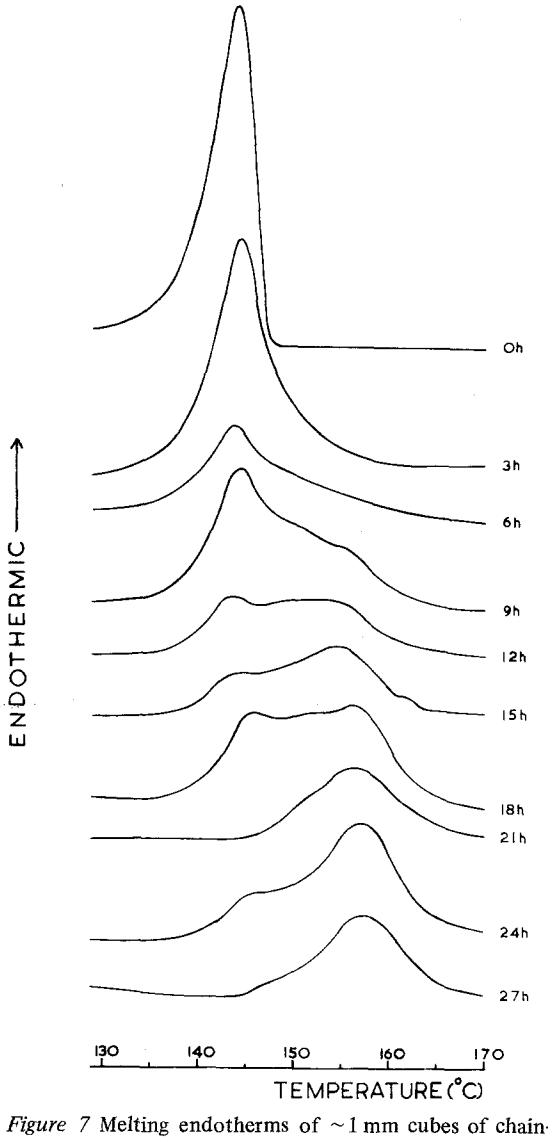

Figure 7 Melting endotherms of ~1 mm cubes of chain-extended Hifax after chlorosulphonation at 60° C for the stated times.

heating. The matter is more complicated, however, with marked differences apparent between various chainfolded polyethylenes, and remains under investigation.

Similar melting experiments have been carried out on various other polyethylenes. Normal chip of the commerical polymer Rigidex 9 (BP Chemicals Ltd.) lost its crystallinity completely after 18 h cholorosulphonation at 60° C, as did a mixed Hifax sample containing equal weights of chain-extended and chain-folded lamellae, both populations losing crystallinity at the same rate. For drawn chain-extended Hifax, however, 6 h in the acid at 60° C was sufficient to destroy all crystallinity.

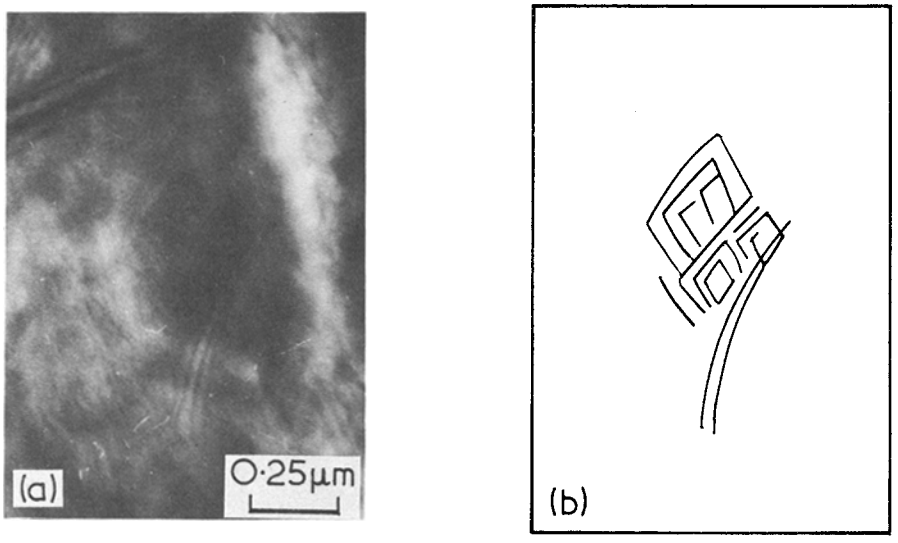

Figure 8 (a) Growth pyramid with lateral surfaces stained, in a section of LM6 fraction, (b) location of pyramid.

It is evident from these results and from the slow progress of blackening through a sample that the degree of reaction is limited by diffusion, presumably of the acid itself, though conceivably some reaction product could be involved. The relative times to complete reaction are in decreasing order of the number of diffusion channels. For melt-crystallized polyethylene these are expected to be the basal or fold surfaces whose number increases inversely with crystal thickness; chain-folded samples should, therefore, become chlorosulphonated before those containing thick, chain-extended lamellae. It is also clear that reaction does not depend appreciably upon surface condition. Some of the evidence has already been cited, but the point is also established directly by Fig. 8. Here, despite low contrast, there is unmistakably a growth pyramid (in a mixed polyethylene sample) with the side surfaces of the terraces, which alone are edge-on, in strongest contrast. It follows that, in a given sample, reaction should not generally discriminate between lamellae or different lamellar populations so that the observation that in a mixed sample, thick chain-extended lamellae react at the same rate as chain-folded, at a rate faster than in a wholly chain-extended environment is to be anticipated. In particular, however, it could conceivably happen that the nature or long range of the surfaces of the thick layers could promote diffusion so that, temporarily, only this population would be stained. On one occasion we saw such an effect, but have been unable to repeat the observation. Turning to drawn, chain-extended samples, however, the deformation evidently creates additional diffusion channels so that the observations of very rapid reaction and much more extensive staining (to be discussed in a separate publication) fit into the same pattern. The pertinent conclusion is, therefore, that the time and temperature of treatment need to be ajdusted to the samples used to ensure homogeneity and that crystals remain for possible diffraction studies. A third factor may concern mechanical stability. Much of the usefulness of this technique is due to the unprecedented stability given to polyethylene sections in the electron beam. Many of our specimens, however, are brittle and do not all attain sufficient stability when treated. In certain cases, prolonged treatment seems to ameliorate matters; in others one still needs to rely on the rapid working techniques used for diffraction microscopy of polymers to benefit from the stained contrast.

3.4. Fine-structural detail

Finally in Fig. 9 we show some of the early benefits this technique has brought to our work. Fig. 9a is of mixed Hifax sample which crystallized in both orthorhombic and high-pressure hexagonal phases. It is noteworthy, however, that the thick lamellae formed via the hexagonal phase have, in certain cases, continued to grow as thin orthorhombic lamellae. The same lamella, therefore, grows at two very different thicknesses corre-

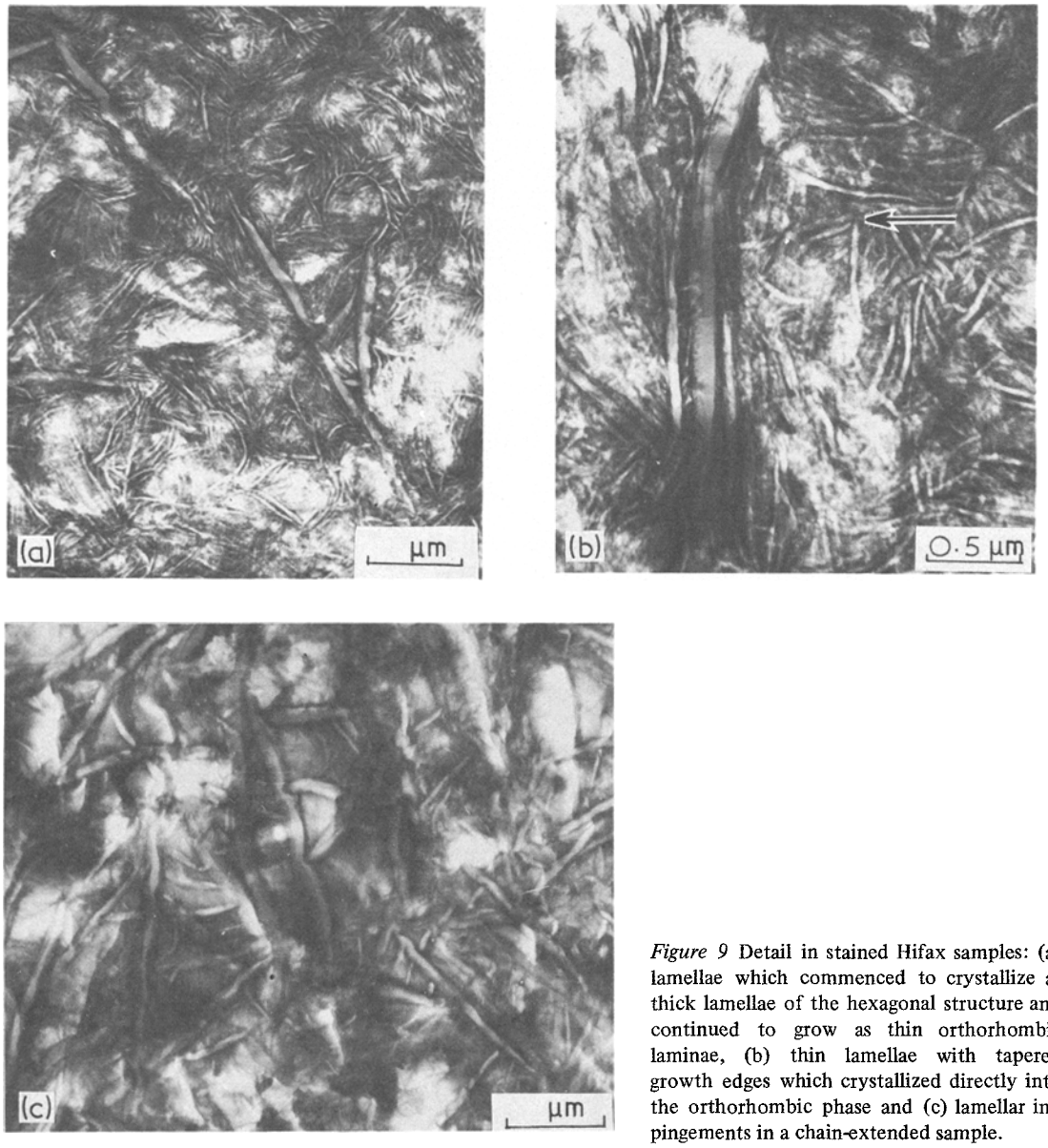

Figure 9 Detail in stained Hifax samples: (a) lamellae which commenced to crystallize as thick lamellae of the hexagonal structure and continued to grow as thin orthorhombic laminae, (b) thin lamellae with tapered growth edges which crystallized directly into the orthorhombic phase and (c) lamellar impingements in a chain-extended sample.

sponding to the changed growth conditions. This is the first direct demonstration that lamellar thickness in melt growth is determined by secondary nucleation at the growth front and is comparable with similar phenomena found in solution growth [14].

There is a difference between the two cases in that, whereas the change in thickness for solution growth is sharp (within the resolution of the electron microcope), this is not the case for melt growth. Here the tapering profile associated with crystallization of polyethylene into the high-pressure hexagonal phase [6] is frozen into the lamella. For a long time, in papers from this laboratory, it has been argued that this tapered profile is probably a general feature of polymeric crystallization from the melt [6]. In Fig. 9b there are several cases where chain-folded lamellae grown in the orthorhombic phase clearly taper towards their growing edge. This is important in itself and also because it is strong experimental support for regarding the high-pressure crystallization of polyethylene, where phenomena are easier to study because of the large crystal size, as a model for crystalline polymers in general.

When lamellae impinge, their profiles tend to

become rounder [10, 15]. Fig. 9c shows detail of several impingements demonstrating the advantage brought by sectioning to the study of features only occasionally revealed in fracture surfaces. Similarly in Fig. 1b the large lamella A has evidently sheared under the stresses of crystallization but it is unlikely that this would have been identified in a fracture surface. Allied to this, consecutive sections can be prepared. For example, an entire polyethylene sample from the diamond-anvil cell in which individual lamellae were watched growing from the melt at high pressures has been sliced, after staining, into 125 serial sections. Evidently the chlorosulphonation technqiue is a major advance which seems destined to add very considerably to our knowledge of the morphology of polyethylene samples.

4. Conclusions

The main conclusions of this paper are:

(1) Chlorosulphonic acid produces sheets of excess electron-density at all surfaces of polyethylene lamellae; this is primarily due to incorporation of chlorine and sulphur rather than to added uranium.

(2) The time to achieve an overall reaction varies sensitively with morphology, decreasing as the number of diffusion channels increases. Crystallinity is gradually lost during reaction but sufficient crystals remain when a sample has become uniform, and in their initial orientations, for diffraction studies to be possible.

(3) Observations of changes in lamellar thickness with changed growth conditions confirm directly that this parameter is determined by secondary nucleation at the growth front.

(4) The tapered profiles of growing lamellae previously identified for crystallization of polyethylene into the disordered hexagonal phase at high pressure and in PTFE have now been observed for chain-folded lamellae crystallized in the orthorhombic phase. The phenomenon thus appears to be general to polymeric crystallization from the melt.

(5) The chlorosulphonation technique brings added contrast plus unprecedented detail and beam stability to polyethylene specimens as well as facilitating systematic sectioning. It is a major contribution to the tools of morphological research.

Note added in proof

A hitherto unremarked feature of chlorosulphonated polyethylenes is that lamellar thicknesses can be substantially lower, by factors approaching two, than values for the untreated polymer given by other techniques (D. C. Bassett and A. M. Hodge, submitted to Proc. Roy. Soc. A).

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