On quantitative permanganic etching

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(Received 31 December 1985)

Permanganic etching exposes lamellae within a variety of crystalline polymers. It is frequently observed that certain lamellar populations and other regions are removed preferentially by the etchant. This selectivity has been studied quantitatively by using 5 μm sections of a linear polyethylene that had been crystallized to form two populations, one of which contained lamellae roughly half as thick and molecules half as long as the other. Changes in the melting endotherm of sections with the time of etching and the related mass losses have been studied in relation to electron microscopy and molecular-mass data of polymer extracted from the sample with xylene. It was found that in sections cut at 20°C, the lower melting population suffered substantially greater deformation, but this could be limited by cutting at lower temperatures. The changes undergone by cold-cut sections were linear with etching time and revealed preferential removal of the thinner lamellae at a rate of 3.3 Å s^{-1}, compared to 1.6 Å s^{-1} for the other population. It was also found that if sections were annealed at a temperature between the two melting peaks, a treatment giving similar populations to the original but with sectioning damage healed, then linear etching continued at a rate of 1.7 Å s^{-1}, but now with little or no discrimination between the two populations.

It is concluded that when differential permanganic etching is observed it is not necessarily, at least in this case, an intrinsic property related to lamellar thickness or molecular mass, but reflects a secondary effect, namely the different responses of elements of physical texture to stresses imposed during sample preparation. Conversely these findings illustrate very well that the systematic spatial variation of texture imposed on a polymer by crystallization results in a corresponding systematic and local variation of properties.

(Keywords: permanganic etching; spherulites; polyethylene; electron microscopy; microstructure)

INTRODUCTION

It is arguably the case that the central problem in polymer materials science remains the characterization of physical microstructure and the elucidation of its effect on properties. This knowledge is essential to a fundamental, analytical approach to understanding polymers, but a detailed knowledge of spherulitic and other organization within melt-crystallized polymers is only beginning to become available. That this situation should have persisted so long is due partly to the complexity of the materials and partly to technical difficulties in their examination. A major obstacle has been the inability to image specimens at high resolution with the electron microscope. One knows that there is substantial texture in crystalline polymers below the resolution of the optical microscope and for nearly thirty years attempts have been made by using a wide variety of techniques to relate this to presumed lamellar structures whose precise arrangement must strongly affect mechanical and other properties. It is only recently, however, that it has become possible to use transmission electron microscopy to study actual lamellar organization representative of the interior morphology of melt-crystallized polymers. Chlorosulphonation of polyethylene[1] and permanganic etching[2,3] of various polyolefins and other polymers offer alternative and complementary means of studying polymer lamellae and their organization within spherulites and other textural entities. Both these techniques confirm not only that crystalline polymers, even when of only moderate crystallinity, are profusely lamellar, but also show that there is a hierarchy of lamellae with a systematic spatial distribution through a sample[4]. Permanganic etching offers additional information on differences between different components of the morphology through differential etching. It has been appreciated from the introduction of this technique that etching could be differential between many regions, revealing various differences, including those of polymeric components in blends, lamellar thickness and related segregation, as well as deformed regions representing differences of order[2]. This paper is the first that attempts to quantify the physical and molecular differences underlying such differential etching.

The basic approach attempted is to determine the progressive changes with etching time in the melting endotherms of thin sections cut from a sample and relate these, on the one hand, to electron microscopy of etched samples and, on the other, to the lengths of molecules removed. The combination should, in principle, provide information on what is removed from where and when.

In this first paper, we report results on a sample of linear polyethylene containing two lamellar populations. It is demonstrated that etching differentiates strongly between the two populations, which differ both in molecular mass and in lamellar thickness. The observed data are consistent with two steady-state processes removing material from lamellar edges at rates of angstrom per second, approximately inversely proportional to the thickness of the respective lamellae. Further work has shown, however, that within the limits of error the discrimination is due to neither lamellar thickness nor molecular length *per se*, but reflects rather a secondary consequence of the selective response of the morphology to deformation in the preparation of sections. It is shown

0032-3861/86/081163-07$03.00

that the lower melting population of lamellae suffers greater damage during sectioning and is then etched at a greater rate. If this damage is removed by appropriate annealing treatments then there is little or no difference in etching rate for the two populations. This would be consistent with the rate-controlling step being molecular scission at fold surfaces.

EXPERIMENTAL

Preliminary experiments began by studying the linear polyethylene homopolymer Sclair 2907 crystallized at temperatures of 118°C and above. It was soon found, however, that the large spherulites within such samples were responsible for a noticeable inherent variability in the melting endotherms between different sections. This tended to compromise the desired detection of changes, due to differential etching, in the lower portion of the melting endotherm. It was, therefore, decided to facilitate the experiment first by examining a more typical, highly nucleated polyethylene, and secondly by crystallizing it in two stages to give two crystal populations and a bimodal melting endotherm. The work described in this paper concerns the linear polyethylene Rigidex 140–60 (BP Chemicals Ltd), which was crystallized sealed in glass tubes under diffusion pump vacuum (*ca.* 10 mPa) at 128°C for 3 h and then quenched.

Melting endotherms of this material and of 5 μm thick sections cut from it with a glass knife under the varying conditions to be described were measured by differential scanning calorimetry (d.s.c.). A scanning rate of 10 K min^{-1} was used in a Perkin–Elmer DSC2C instrument. Calibration was against the melting point of high-purity indium.

A number of thin sections was etched in a 0.7% w/v solution of potassium permanganate in a 2:1 mixture of concentrated sulphuric and dry orthophosphoric acids, for various times at room temperature (nominally 20°C)[3]. Washing procedures were as described previously[2]. The bulk material and some of the sections were replicated by either of two methods leading to shadowed carbon replicas, which were examined by transmission electron microscopy. The replication method used for bulk material was a standard two-stage or indirect process using cellulose acetate. For etched sections a direct method was preferred in which the sample itself was carboned and shadowed, and then backed with cellulose acetate; subsequently the sample was dissolved away in xylene followed by the backing film. In all cases the photographic illustrations resulting have been presented on the page to try to give the correct impression of relief, i.e. of lamellae standing proud in the etched surface.

The extent of fractional crystallization in the sample was determined by selectively extracting the material causing the lower peak in the melting endotherm. A temperature of 105°C and xylene as solvent was suitable for this purpose. The molecular masses both of the extracted (i.e. lower peak) and residual (upper peak) material were measured by gel permeation chromatography (g.p.c.) with orthodichlorobenzene used as solvent. The interfold lengths of the two populations could be obtained by g.p.c. on degraded samples that had been digested for 3 days at 60°C in fuming nitric acid, following established procedures[5]. We are indebted for all g.p.c. measurements to the PSCC at RAPRA. These figures are consistent with those estimated from their melting points using the correlation measured previously[6].

RESULTS

The melting endotherm of the bulk polyethylene sample is curve A in *Figure 1a*. This is in agreement with previous work using this grade of polymer and the same crystallization temperature[6]. It was shown then that the upper of the two peaks comes from polymer crystallized isothermally at 128°C, the lower from material crystallized subsequently on cooling. In the present case the area ratio of the quenched peak (at 130.3 ± 0.5°C) to the isothermal peak (at 135.5 ± 0.2°C) is 2.6 ± 0.2 for bulk material. The respective average molecular masses are $\bar{M}_m = 4.3 \times 10^4$, $\bar{M}_n = 1.1 \times 10^4$ for the quenched population and $\bar{M}_m = 9.3 \times 10^4$, $\bar{M}_n = 3.2 \times 10^4$ for that crystallized isothermally. The corresponding average interfold lengths were 160 and 320 Å respectively. If one assumes a chain inclination to lamellar normals of 34.4° (refs. 7 and 8), these figures are equivalent to average lamellar thicknesses of 132 and 264 Å.

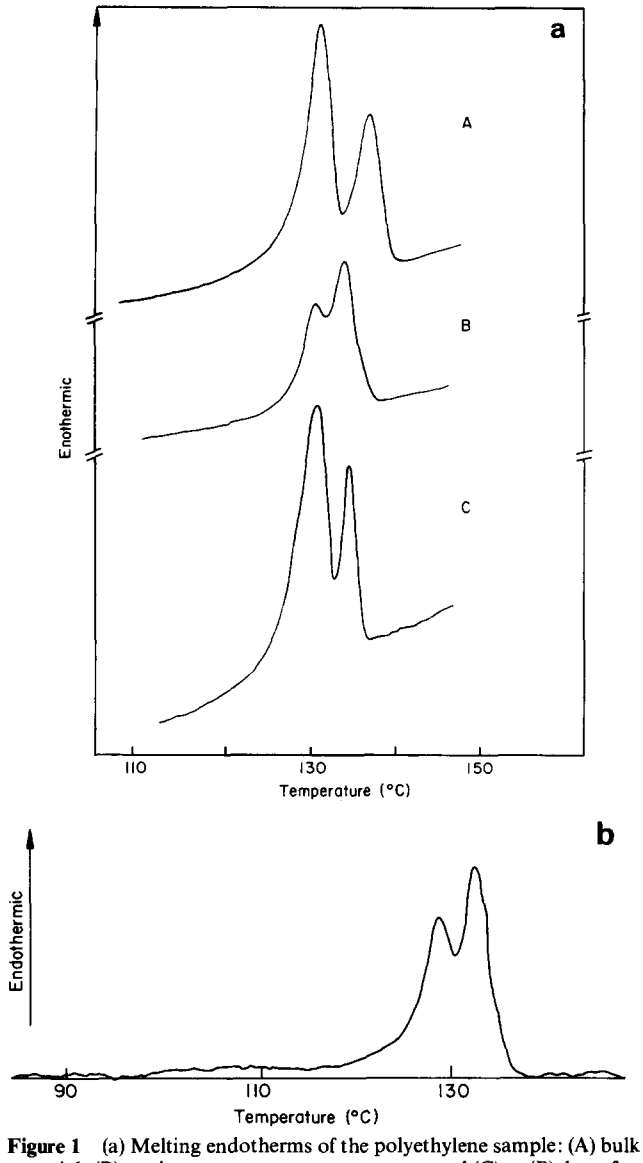

Figure 1 (a) Melting endotherms of the polyethylene sample: (A) bulk material; (B) sections cut at room temperature; and (C) as (B), but after annealing at 131°C. (b) Melting endotherm as in (a) curve B, but with a computer-derived baseline, which shows the extension of the melting region to lower temperatures

The interior morphology of the bulk sample is illustrated in *Figure 2*. In this area there are two principal locations for the lamellae grown at 128°C: wide dominant sheets (marked A), and intervening narrower but separated layers (marked B). Especially between layers B one finds regions (marked C) of the thinner, quenched lamellae. This type of organization has been seen previously in both linear and branched polyethylenes crystallized *in vacuo* and at high pressures[9].

When 5 μm sections were first cut from this bulk sample, their melting endotherms appeared as in *Figure 1a* (curve B), i.e. substantially altered from the bulk material. Not only are both peaks shifted to lower temperatures, but the lower temperature peak is much reduced in magnitude; the peak area ratio has fallen to 0.8 ± 0.2. Such sections were cut at room temperature from a small (< 1 mm) specimen embedded in an epoxy resin formulated for electron microscopy. This procedure gives sections of good quality for optical microscopy and is similar to that used very satisfactorily by us to cut open bulk material before permanganic etching. What is remarkable about the cut sections is the different behaviour between the two peaks, which suggests a selective loss of crystallinity for the quenched population of lamellae. Subsequent tests have shown that much of this is in fact redistributed to lower temperatures, giving a pronounced tail to the melting curve (*Figure 1b*). This Figure is the endotherm of a similar section with the baseline defined by computer subtraction of data for an empty sample pan.

The melting endotherm can, however, be restored to approximately the orignal proportions by annealing sections at 131.0°C for 20 min and then quenching *Figure 1a* (curve C). This treatment melts, then recrystallizes, the original quenched population as well as allowing the isothermally grown spherulites partial recovery in melting point.

These changes can also be detected on the surface of the sections themselves. A direct replica of an unetched section after cutting is shown in *Figure 3*; the direction of cutting is vertical on the page. The section has been deformed into broad bands parallel to the knife edge. Within each band fine lines are visible along the cutting direction. Neither lamellae nor spherulites are apparent. After annealing, a similar section (*Figure 4*) has a much smoother surface, with the broad bands still present but less prominent. On the other hand, the lines parallel to the cutting direction are more marked. They are also finely striated along their length, indicating lamellar recrystallization nucleated along the lines (which one expects to have *c* axis orientation). There is still, however, no indication of the original morphology.

One needs to use sections for adequate measurement of changes during etching because of their high surface to volume ratio. Although the first sections were unsuitable, usable sections suitable for this purpose were obtained by cooling sample and knife with dry ice and liquid nitrogen. Their endotherms are shown in *Figure 5*. Curve A, for

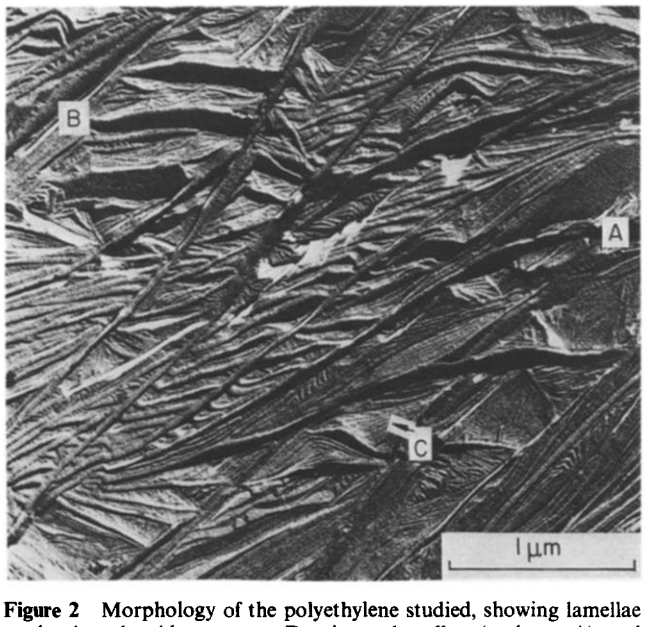

Figure 2 Morphology of the polyethylene studied, showing lamellae predominantly sideways on. Dominant lamellae (such as A) and subsidiary lamellae (e.g. B) are relatively thick and grew at 128°C. The thinner population (e.g. C) formed on quenching and is etched to greater depth. Etched cut surface from bulk

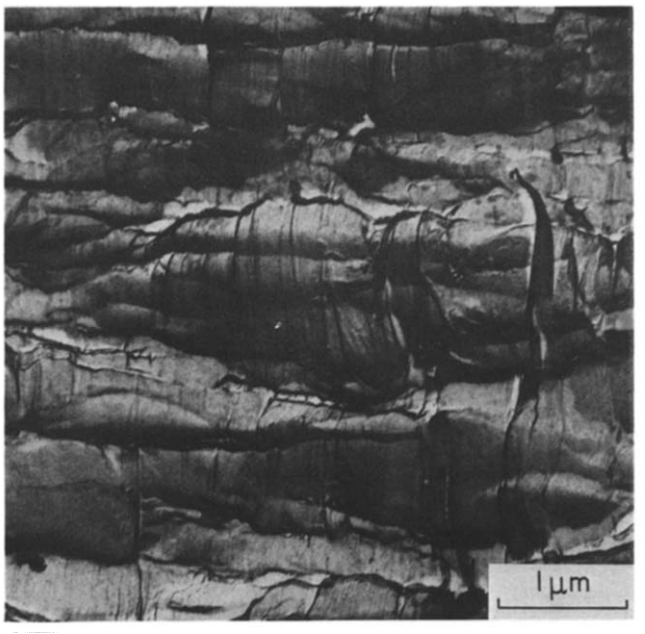

Figure 3 Gross morphology of a 5 μm section after microtoming at room temperature. The cutting direction is vertical on the page

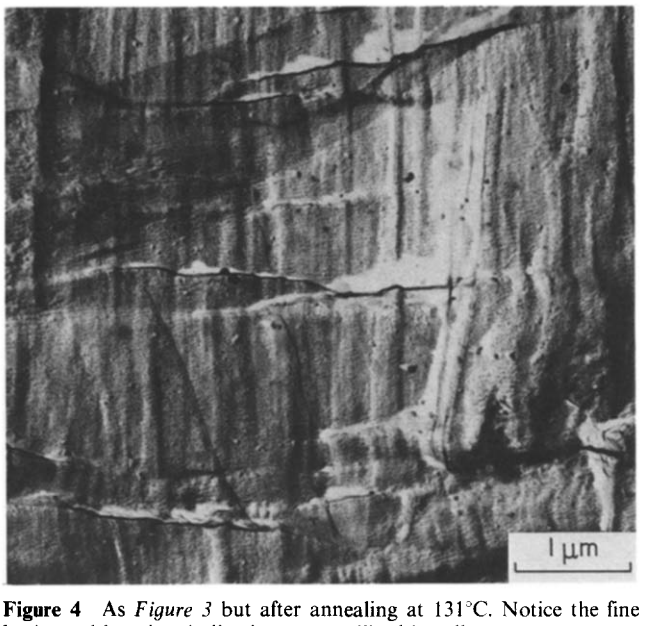

Figure 4 As *Figure 3* but after annealing at 131°C. Notice the fine horizontal layering, indicating recrystallized lamellae

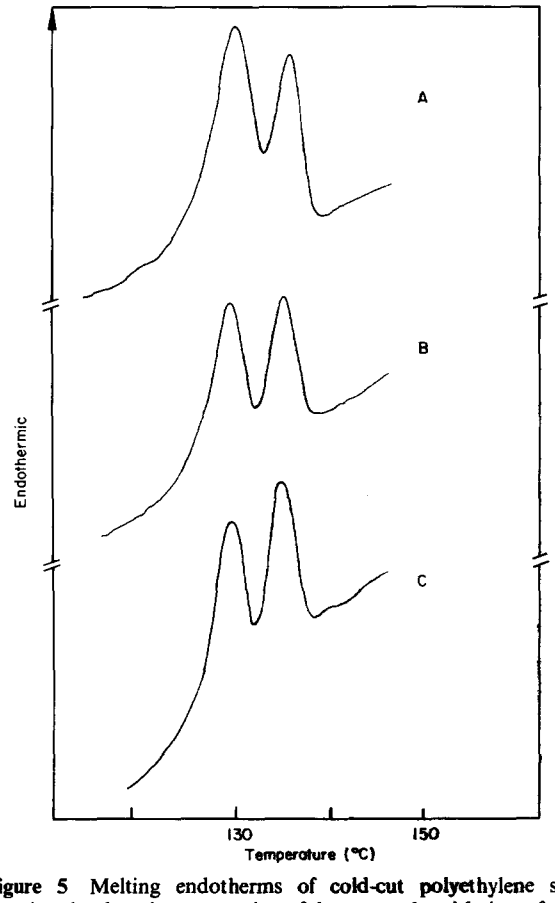

Figure 5 Melting endotherms of cold-cut polyethylene sections showing the changing proportion of the two peaks with time of etching: (A) 0; (B) 60; (C) 100 min

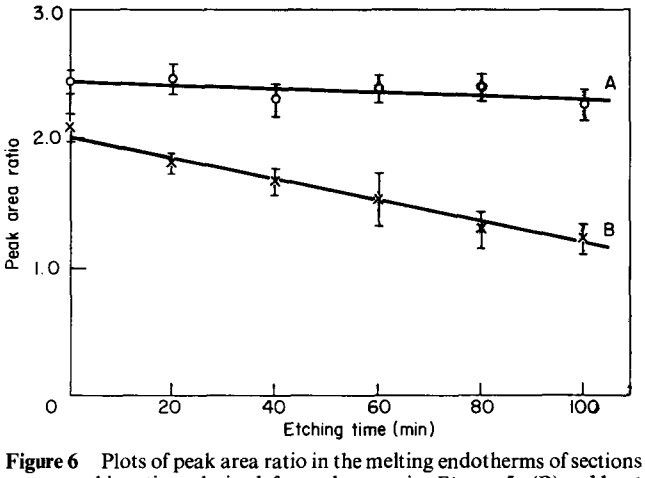

Figure 6 Plots of peak area ratio in the melting endotherms of sections *versus* etching time derived from data as in *Figure 5*. (B) cold-cut sections; (A) the same, but after annealing at 131°C

sections as cut, resembles that for the bulk, *Figure 1* (curve A). The two peaks are at 129.3 ± 0.2°C and 134.6 ± 0.1°C, while the peak area ratio is 2.1 ± 0.1. There is a progressive change in this ratio with etching time because of a corresponding reduction in the relative size of the lower temperature peak (*Figure 5*). The heights of the two peaks are approximately equal after 100 min etching. The peak area ratio decreases linearly with time of etching (*Figure 6* (curve B)), which is evidence for two different constant etching rates for the two populations. There is also a linear decrease in the mass of a section with etching time (*Figure 7*).

The upper line in *Figure 6* is for similar data but on sections that had been preannealed at 131°C for 20 min. These data provide little or no evidence for differential etching rates between populations after the annealing treatment, even though lamellae still have disparate thicknesses. *Figure 8* shows the etched morphology (after 25 min) of an annealed section. It shows the two lamellar thicknesses corresponding to the melting endotherm (*Figure 5*), and although the thinner lamellae can be more eaten down than the thicker (area arrowed), the overall impression is of slight differential etching between layers of different thickness. Lamellar orientation produces a more obvious effect with flat-on layers substantially proud from edge-on ones after etching. By comparison, the appearance of a section cut cold and then etched (*Figure 9*) is much more akin to the bulk material and shows a greater differentiation between the two lamellar populations.

DISCUSSION

Permanganic etching is a most useful technique. It has allowed for the first time the observation and study of

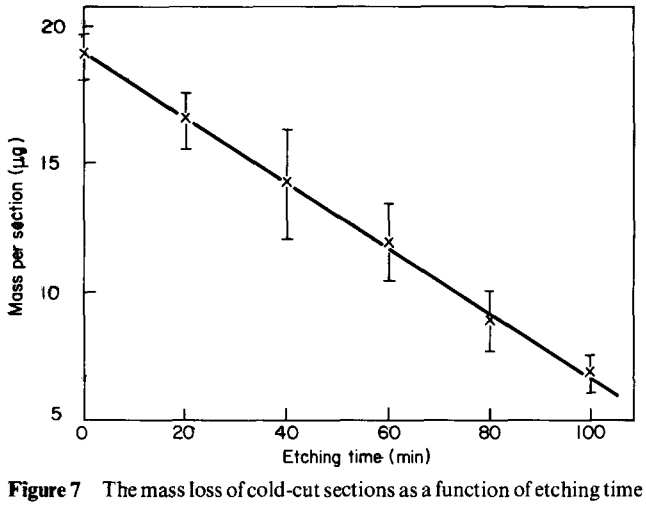

Figure 7 The mass loss of cold-cut sections as a function of etching time

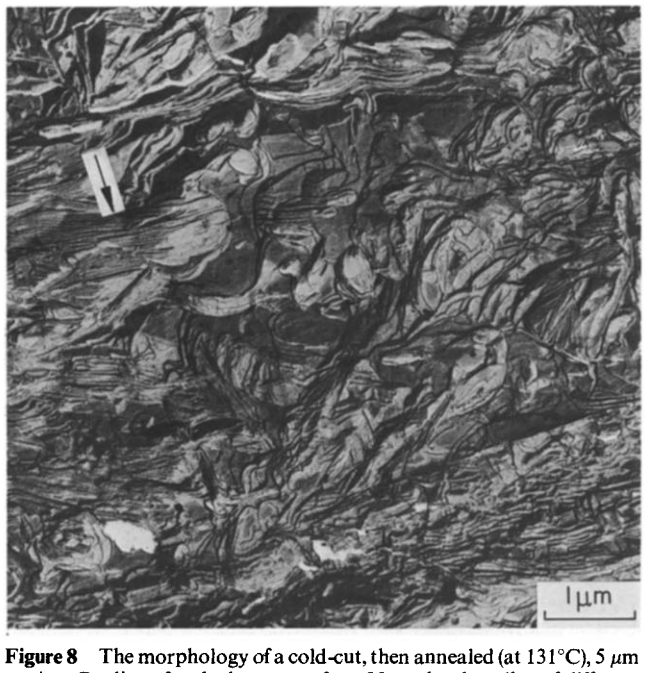

Figure 8 The morphology of a cold-cut, then annealed (at 131°C), 5 μm section. Replica of etched outer surface. Note that lamellae of different thickness in sideways orientation are generally etched to similar depths

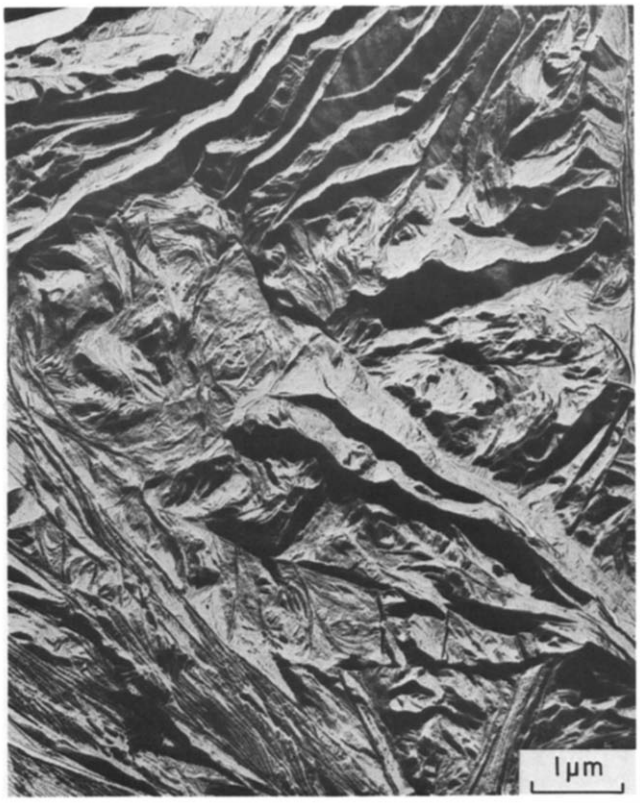

Figure 9 The surface of an etched cold-cut section is similar to that of the bulk polyethylene shown in *Figure 2*

lamellae and their organization in a range of polyolefins and other polymers. Its utility lies in the removal of material selectively from any surface of the polymer to reveal salient detail. It does this not only with great delicacy, but also without rendering the surface friable—which is the case with nitric acid—thereby facilitating study by replication methods. Under good conditions, the detail observable in a surface is limited by the granulation of the shadowing metal, which places it beyond the resolution of conventional scanning microscopes. Lamellae are revealed partly because they are etched away as discrete entities and partly because outlining grooves are produced between continuous lamellae where their edges intersect the etched surface. In addition lamellae etch at a greater rate on their lateral rather than their basal surfaces. The undulating surface topography accompanying the rotating lamellar orientation in etched banded spherulites[2] originates in this way. This basic action is, of course, differential etching, but it is usually also observed that some lamellae have been etched away more than others. For example, it has been observed that when spherulitic growth of polyethylene is interrupted and the sample quenched, lamellae are etched away more the later they are crystallized[6]. At least two reasons suggest themselves for this. One is that the lamellae are progressively thinner so that there will be more surface regions for the etchant to penetrate, the other that shorter and shorter molecules are involved as crystallization proceeds[6,7]. One needs to know which factors bear most responsibility for this second type of differential etching and what additional textural information can be gained by its study. These are the questions that this paper addresses.

The situation revealed by the linear changes of *Figures 6* and *7* is of a steady-state etching process†. One may discuss this situation by reference to a simple model. Consider a section of thickness s and cross-section A containing volume fractions P_1 and P_2 of two populations of lamellae whose thicknesses are respectively l_1 and l_2. We assume that the areas of these two populations revealed on the surfaces A are P_1A and P_2A respectively and that this remains so during etching. We further assume that etching proceeds only on the lateral surfaces of lamellae, with rates v_1 and v_2. Then, at time t, the proportions of the two populations remaining are in the ratio

$$p_1/p_2 = \frac{P_1As - 2v_1l_1L_1t}{P_2As - 2v_2l_2L_2t} \simeq \frac{P_1}{P_2}\left[1 - 2\left(\frac{v_1}{H_1} - \frac{v_2}{H_2}\right)t\right] \quad (1)$$

Here L_1 and L_2 are the lengths of the exposed lateral surfaces in each surface and $H_i = P_iAs/L_il_i$ $(i = 1,2)$ relates to the lengths of lamellae below the original surfaces. The factors of 2 arise because both surfaces of a section are etched.

The fractional loss of volume from the sample is

$$\frac{1}{V_0}\frac{dV}{dt} = \frac{2(v_1l_1L_1 + v_2l_2L_2)}{As} = 2\left(\frac{v_1P_1}{H_1} + \frac{v_2P_2}{H_2}\right) = \frac{1}{M_0}\frac{dM}{dt} \quad (2)$$

where M is the mass of the section if one neglects differences in lamellar density. The graphs of *Figures 5* and *6* are plots of equations (1) and (2) and together yield the quantities v_1/H_1 and v_2/H_2. If we take $H_1 = H_2 \simeq s$, the thickness of the section, then we obtain for the sections cut cold, rates of 3.3 and 1.6 Å s^{-1} for the thinner and thicker populations, respectively. The same analysis for sections that had been annealed at 131°C gave etching rates of 1.8 and 1.6 Å s^{-1} respectively.

It is observed that permanganic etching proceeds by creating grooves between lamellae (*Figure 2*). This suggests that lamellae are removed, segment by molecular segment, following chain scission at the fold surfaces. There are then two possibilities for the relative etching rates of different populations. If the rate of attack at fold surfaces is slow compared with removal of the fold stem remaining, grooves will be shallow and all lamellae will be removed at the same rate (assuming that there are no significant variations of fold surface structure). Conversely, a removal of stems that is much slower than fold scission will lead to layers being removed in times proportional (i.e. rates inversely proportional) to their thicknesses.

† This differs from early recipes for permanganic etching. Although these gave very adequate results on the samples for which they were used, in retrospect they were too severe for more delicate specimens. It has been reported[10] that, for similar conditions, etching is rapidly curtailed and does not proceed steadily as found here. We suspect that the curtailment may be a consequence of accumulation of reaction products at the polymer surface. We have previously shown that this does occur and is linked to the appearance of artefacts that the present formulation avoids[3].

In the absence of data for annealed sections we might well, therefore, have been tempted to assume the latter situation as pertaining to the etched sections. The annealed samples, however, show little or no difference in etching rate between two populations whose melting points, and therefore thicknesses, are close to those of the original sample. We are thus forced to conclude that there is little or no difference in the intrinsic etching rate for these lamellar populations even though their thicknesses differ by two and their molecular masses are in a similar ratio. *A priori*, this is not a surprising conclusion, and is consistent with the shallow grooves observed between lamellae and a mechanism whereby molecular scission at fold surfaces is the rate-controlling step. Nevertheless, the inference has to be reconciled with our abundance of evidence for differential lateral rates of lamellar etching in other circumstances.

The experiments we have made point very clearly to the significant influence of deformation on the extent of etching. When damage is allowed to heal by annealing, differential etching between populations all but disappears. Deformation is unavoidable when microtoming with typical knife geometries. First, a section will undergo macroscopic shear at the knife edge, where it is forced away from the remaining sample. Secondly, it is commonplace to find, as in cutting circular fibres, that the resulting sections become elliptical with a reduced diameter along the cutting direction. Thirdly, the shear imposed by cutting can result in an initially axial molecular direction being rotated by tens of degrees about the shear axis in the direction of cutting and a corresponding change of inclination to the plane of the section. In the present case we have the evidence in *Figure 3* for the formation of a linear block structure perpendicular to the cutting direction. All this is familiar enough. What is notable and, to our knowledge, has not been mentioned previously, is the different response of the two lamellar populations in the sample. It has been recognized that segregation during crystallization will change the constitution of interspherulitic material and render it more prone to yielding and fracture[11], but here we have a more general phenomenon with the deforming population (arrowed *C* in *Figure 2*) intimately distributed throughout the texture.

The thermal analysis data provide information about the nature of the deformations suffered. They show two principal features: lowering of the melting point by *ca.* 2 K with little evident change of peak shape (*Figure 1a*) and a low melting tail (*Figure 1b*). On the first point, the cause of a reduction in melting point is usually either disruption of the lattice and/or a decrease in crystal thickness. In suitable circumstances, which can include microtomy as mentioned above, intralamellar shear can rotate molecules and reduce the distance between fold surfaces at constant interfold length. However, whether this does occur for a particular lamella will depend on its orientation in relation to the shear axis. In polyethylene specifically, the fact that molecules are initially inclined to lamellar normals[7,8] also provides the possibility of increasing the crystal thickness. In short, shear deformation should increase the spread of crystal thicknesses and thereby of melting points. According to *Figure 1*, any such effect is small in practice so that we can conclude that intralamellar shear, at least of the thicker population, is not a principal factor for these samples, even though interlamellar shear is likely to have occurred.

Disruption of the crystal lattice can cause only a reduction in melting point. We are thus still in need of an explanation for the lowering of melting point with little change of peak shape. One possibility, which is the subject of further investigation, is that crystallites are in tension. Nevertheless, in disruption we have, very probably, the reason for the long low melting tail drawn out some 20 K below the lower peak (*Figure 1b*). This tail appears to have derived largely from the lower melting peak, whose relative size has diminished (*Figure 1*). It is also very reasonable to expect disrupted crystals, which will possess more ready sites for reaction with the etchant, to undergo more rapid ablation, in agreement with the observed enhanced etching rate for the thinner population. There is thus a self-consistent interpretation of the data, which is that the observed differential etching between populations is not primarily an intrinsic effect, even when these populations differ in lamellar thickness and molecular mass. Its origin is rather a secondary matter reflecting the greater disruption suffered by this population during sample preparation.

Finally, we consider to what extent these conclusions can be extended to other permanganically etched samples. It is characteristic of this technique that it is capable of discriminating between minute morphological differences. *A priori*, it was not surprising that, for example, polypropylene should etch at a faster rate than polyethylene, nor that lateral surfaces should suffer greater attack than fold surfaces, nor that deformed polymer was especially prone to etching[2]. In all of these cases, there are evident reasons for discrimination. But for lamellae of different thicknesses, the reasons were by no means obvious. Nevertheless, in our studies of melt-crystallized morphologies where we have studied the etched surfaces mostly by cutting and occasionally by fracture, we have usually found that thinner lamellae have been etched to a greater depth than thicker ones. If this were a fundamental feature then an explanation could reasonably be looked for either in the different surface/volume ratios or, at least in polyethylene, in molecular fractionation, which tends to place shorter molecules in thinner lamellae. What we have now shown, in one type of specimen, is that it is secondary deformation that contributes most to differential etching and that neither lamellar thickness nor molecular fractionation is a very significant cause of differential etching in itself. Can this also apply to bulk specimens? It is true that both cut and fracture surfaces will have suffered stress during their preparation, the one by the passage of the knife, the other during crack propagation, but the facts, that etching is normally continued long enough to remove knife marks etc. and that time of etching has never obviously been linked to the discrimination between details in a surface, both undermine the credibility of residual strain being the cause of the differential etching observed. Moreover, it would seem very probable that the finding for annealed sections of little or no differential attack for twofold differences in lamellar thickness and molecular length should be a general one. Such specimens, by being annealed after preparation, will contain the least damaged crystals of all those we have examined. As reasons for differential etching of different populations in bulk samples we would thus seem to be left with two principal possibilities. One is that there is inbuilt strain in samples as a legacy of their crystallization and thermal history (differential contraction?) independent of that created

during sample preparation. The other is that for extreme differences in thickness, notably comparing isothermally crystallized lamellae with a quenched, but still lamellar, matrix, it is reasonable to suppose the quenched population will be inherently more susceptible to chemical attack. This is because of the anticipated changing nature and increasing proportion and dimensions of the disordered or 'amorphous' component of the texture.

The remaining question concerns those cases where differential etching is due to different strains in the sample: why should there have been this differential response to stress? This is not easy to answer and indeed our observations open up wide issues concerning the microstructural changes in deformed polymers, requiring further study. One can, however, note that a simplistic interpretation based just on differences of molecular mass will not suffice. Both the populations here have similar ratios of molecular length:crystal thickness of approximately thirty. We have previously found[12] that this ratio needs to exceed ten to confer ductility on polyethylene samples. Reasons for the greater deformation of thinner crystals needs to be sought, therefore, in a finer scale of texture. Nevertheless, we point out that the differential deformation we observe is unambiguous evidence for the importance of the influence of microstructure on mechanical properties. We have shown that the intimate and systematic spatial variations of texture imposed on a sample during its crystallization history gave a corresponding local variation in properties. Furthermore permanganic etching can respond to and amplify such changes in the way it reveals systematic differences in a sample's history.

CONCLUSIONS

Rates of permanganic etching have been measured for different lamellar populations within the same linear polyethylene sample. Although the thinner (and lower mass) lamellae are eaten away faster it is shown that this is largely a secondary consequence of different responses to the stresses of specimen preparation.

It has been shown clearly that the systematic local variation of microstructure laid down during crystallization produces a correspondingly large variation in mechanical properties throughout linear polyethylene.

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