

Permanganic etching of PEEK

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The technique of permanganic etching as already published reveals spherulitic structure and lamellar detail in polyolefines, and has recently been modified for application to isotactic polystyrene. For application to poly(aryl-ether-ether-ketone), or PEEK, neither variant is suitable, but a new modification of the etchant, based on phosphoric acid, allows the morphology of PEEK to be studied under the electron microscope, revealing differences between specimens crystallized at different temperatures.

(Keywords: permanganic etching; poly(aryl-ether-ether-ketone); spherulites; lamellae; melt-crystallized polymers)

INTRODUCTION

The recently developed polymer poly(aryl-ether-ether-ketone), commonly known as PEEK, shows much promise as an engineering material. It is also of theoretical interest as a low-crystallinity material. Its crystallinity as determined by X-ray diffraction is typically of the order of 30%¹, substantially below figures for high crystallinity polymers such as polyethylene. Thus there are both scientific and technological reasons for studying its internal morphology. A natural choice of technique would be one which could show detail in a like manner to the permanganic etchant for polyolefines² which has already provided an abundance of information on lamellar organization which would otherwise be largely inaccessible. For PEEK, however, it is inadvisable to use concentrated sulphuric acid (in which solution its viscosity is usually measured). Instead, this paper describes the development and application of another permanganic etchant based on orthophosphoric acid which has proved suitable for revealing lamellar and spherulitic morphology in PEEK samples.

EXPERIMENTAL

The initial etching work was mainly carried out using an etchant devised for isotactic polystyrene³, consisting of a 1% w/v solution of potassium permanganate in a mixture of 5 parts by volume of concentrated sulphuric acid to 2 parts of orthophosphoric acid (approximately 90%) and 2 parts of water. This was useful but has been superseded by the phosphoric acid based etchants described below.

Two phosphoric acid-based etchants were used in this work. The first was a 2% w/v solution of potassium permanganate in orthophosphoric acid (approximately 90%) as it comes from the bottle; this will be referred to as the etchant without added water. Since this reagent had some disadvantages, it is not the final choice for the etching of PEEK. Therefore its preparation and use will not be described in detail, but in fact they are closely similar to those of the second reagent, which is a 2% w/v solution of potassium permanganate in a mixture of 4

volumes of orthophosphoric acid ex-bottle and 1 volume of water. This will be referred to as the reagent with added water, and is the reagent used in most of this work. Its preparation in detail is as follows. Take 1 g of potassium permanganate which has been ground to a fine powder with a mortar and pestle. Add this to 40 ml of orthophosphoric acid ex-bottle (approximately 90%), which is being vigorously stirred in a conical flask. Stir for 15 min: even after this time some of the permanganate may not have dissolved if there were any large particles left after grinding. Pour off this solution, leaving behind any large particles of undissolved permanganate, add 10 ml of water, and swirl vigorously to mix. This is the required reagent. It slowly decomposes on standing and should be used within about an hour of preparation.

Two batches of PEEK polymer were used to make the samples used for these etching studies. The samples are detailed in *Table 1*.

The several samples from batch A were identical to those used in previous morphological studies and are therefore well characterized in terms of crystallinity and X-ray long period¹. These samples were crystallized isothermally either by rapidly cooling from the melt down to the crystallization temperature (310°C for 1 h and 320°C for 16 h), or by heating from the glassy amorphous state up to the crystallization temperature (200°C, 230°C and 270°C, all for 1 h). Polymer A was reasonably well nucleated so that the resulting spherulitic structures were very small and were often unable to develop past the initial sheaf stage before impinging.

Polymer batch B was a lower molecular weight material. It was also less well nucleated and therefore produced larger spherulites which were easier to distinguish. Samples were prepared from this polymer in the form of discs 6 mm in diameter and about 2.5 mm thick. The discs were melted in a Perkin-Elmer DSC-1B differential scanning calorimeter for 5 min at 420°C and then rapidly cooled to crystallize at 315°C for 1 h.

The disc samples from batch B were cut open and surfaces prepared by cutting with a glass knife on a microtome, while embedded in Tryco-M-Bed frozen with solid carbon dioxide. They were etched with a variety of

reagents, and in the latter part of the quest for a suitable etchant, in order to check the authenticity of the spherulitic detail being revealed, the section immediately prior to the prepared surface was saved for optical microscopy, as in *Figure 1*. Microspherulitic specimens were in the form of thin sheets, and transverse sections of such sheets are very difficult to replicate for transmission electron microscopy. In such cases it is necessary to use a

Table 1 PEEK samples used in this work

Sample	Morphology	Long period (nm) ^a	% Crystallinity ^b
B-315-M	Microspherulitic with areas of larger spherulites		
A-320-M	Uniformly microspherulitic	15.9	37
A-310-M	Uniformly microspherulitic	15.7	30
A-270-G	Very densely nucleated	12.1	27
A-230-G	Very densely nucleated	10.9	24
A-200-G	Very densely nucleated	10.3	19

^a By small-angle X-ray¹

^b By wide-angle X-ray¹

Initial letter = Polymer batch (A or B)

Central number = Crystallization temperature (°C)

Final letter M = Crystallized by cooling from melt

G = Crystallized by heating quenched glass

flat moulded surface, and etch for a time long enough to remove any uncharacteristic surface layers. These samples were etched for 50 min when using the final reagent (with added water).

Samples were etched at room temperature by shaking in sealed bottles containing the reagent. After the appropriate time etching was stopped by adding hydrogen peroxide. The precise procedure for this varies with the particular etchant used, but in the case of the final reagent pouring the mixture into twice the volume of hydrogen peroxide solution (2 volumes strength) has proved satisfactory. The samples were washed several times with distilled water prior to replication. First-stage cellulose acetate replicas were shadowed with gold/palladium alloy and a carbon film evaporated to produce the final replica.

RESULTS AND DISCUSSION

In recent years etching techniques have been developed to reveal the interior morphology of many kinds of polymers⁴, especially crystalline polymers with spherulitic or microspherulitic morphology. Many workers have sought to do this by treatment of surfaces with solvents. The most successful methods involve

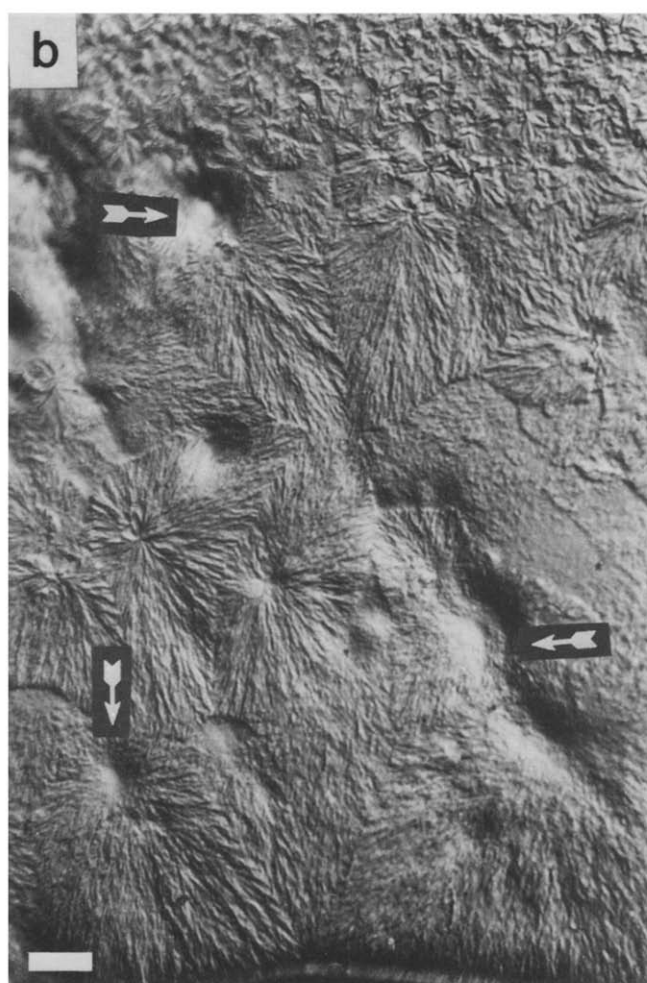


Figure 1 (a) B-315-M, section taken immediately next to stub prepared for etching, seen in circularly polarized light. (b) Same specimen, stub etched with 2% w/v potassium permanganate in orthophosphoric acid ex-bottle, showing accurate presentation of spherulitic detail corresponding to the section in *Figure 1a*, but with irregular pitting of the surface. Scale bars = 10 μm

treatment of a polished surface with a solvent at a temperature well below that at which the crystalline phase of the polymer is soluble⁵, which results in small-scale reorganization of the structure. By this method spherulitic structures are made visible under the reflecting optical microscope, and provided one only requires information at the optical level this presents a faithful picture of the actual morphology. Many workers, however, have used more powerful solvents which actually dissolve the material. This can result in two situations. Firstly, if the dissolved material is not removed rapidly, a thick gel-like layer is formed which, on removal of the solvent, gives rise to spurious spherulite-like structures which, as Kubota has shown⁶, are quite unrepresentative of the actual structure. Secondly, if the material is removed relatively quickly, there remains a surface whose topography is in fact closely related to the spherulitic morphology of the sample. Moreover such a surface is easily replicated for transmission electron microscopy; unfortunately there still remains a thin layer of solvated material which recrystallizes on the surface. So, while the structures observed under the reflecting optical microscope are authentic, the lamellar detail observed under the electron microscope is not, and usually bears no relation to the spherulitic architecture of the sample. A much more productive method has been the use of strong oxidizing agents, among which a solution of potassium permanganate in a mixture of concentrated sulphuric acid and dry orthophosphoric acid² has proved particularly effective in revealing the structure of polyolefines at all levels, from lamellae approximately 10 nm thick to variations over several millimetres in a processed polymer blend⁴.

As was expected, the standard published permanganic reagent, based as it is largely on concentrated sulphuric acid, proved quite unsuitable for PEEK, eating samples away very rapidly and leaving very rough surfaces which showed no trace of the known spherulitic morphology. Attention was therefore turned to the reagent devised for isotactic polystyrene³, which differs from the standard etchant for polyolefines in that it contains a large (approximately 30% by volume) fraction of water. It was found that even this etchant was acting to some extent as a solvent etch, and produced spurious structures, probably lamellae recrystallized from solution, if the etching was abruptly terminated by adding hydrogen peroxide. Nevertheless if the mixture was poured into water and the PEEK specimens allowed to reside for a few minutes in a much diluted etchant prior to adding the hydrogen peroxide, true lamellar detail was developed on the surface, which was fully in harmony with the observed spherulitic structure. Lamellae were seen to be organized into large spherulites in some regions, while in the microspherulitic regions structures such as those shown in *Figure 2a* were observed, including the sheaflike spherulitic precursor at top of picture. However experiments with etchants containing sulphuric acid and much larger quantities of water gave surfaces which were very rough with the spherulitic detail totally obscured, even though individual lamellae were being revealed. In the search for an etchant suitable for a one-stage procedure attention was therefore turned to solutions of potassium permanganate in phosphoric acid alone.

Initial results using a 2% w/v solution of potassium permanganate in orthophosphoric acid ex-bottle (without

added water) were indeed encouraging. *Figure 1a* shows an optical micrograph, taken under circularly polarized light, of a section of macrospherulitic PEEK specimen taken immediately adjacent to the surface prepared for etching. *Figure 1b* shows the surface after etching as seen in Nomarski differential interference contrast. In the region of large spherulites the one-to-one correspondence between individual spherulites in both specimens is seen to be exact, although precise areas of each spherulite will differ slightly owing to the etchant having removed a layer from the surface. The region of massive nucleation with many smaller spherulites is also the same in both specimens. Detailed measurement shows that the edge of the specimen has been eaten away by about 10 μm . In general the edges of specimens are more heavily eroded by etchants than are the broad surfaces, so one might estimate that most of the region shown has been eaten away to a depth of perhaps 2 μm . However besides the authentic spherulitic structures there are also irregular pits in the etched surface (arrowed); although these are quite unlike the artefacts described in connection with etching of polyolefines², they are, nevertheless, certainly another kind of artefact. Moreover the lamellar detail revealed by electron microscopy of replicas of such surfaces was not totally satisfactory. It was genuine, but somewhat blurred as if a very small amount of solvent action had still taken place.

To reduce solvent action, therefore, 20% by volume of water was added to the orthophosphoric acid, making the final etchant with added water as described in the Experimental section. This procedure provides crisp lamellar detail under the electron microscope, and at the same time gives much smoother etched surfaces. They are not always completely flat, but sometimes pitted with very broad, smooth and shallow craters. These in no way mask any genuine structural detail, and are not at all apparent under the electron microscope.

The results for high molecular weight PEEK crystallized at various temperatures are shown in *Figures 2b-f*, at a medium magnification suitable for displaying spherulitic architecture; finer lamellar detail is shown in *Figure 3*. The samples crystallized by cooling from the melt to 320°C and 310°C (*Figures 2b, c*) are very similar to each other, and stacks of lamellae with a periodicity of about 15 nm are clearly seen. These samples are, moreover, quite similar to the microspherulitic regions of the low molecular weight sample crystallized at 315°C shown in *Figure 2a*, although this was etched by the original two-stage procedure. These specimens of melt-crystallized PEEK, then, have a characteristic appearance, in the same way that other polymers such as polyethylene and polypropylene give characteristic and easily recognizable appearances on etching.

The samples crystallized by heating the glass are rather different. They show (*Figures 2d, 2e, 2f*) coarse variation on a scale of 0.5 μm , an order of magnitude smaller than obtains for melt-crystallized PEEK. This is consistent with the anticipated much higher nucleation density for crystallization from the glass. On a smaller scale, lamellae are present whose spacing is ca. 10 nm (*Figures 3d, 3e, 3f*), in accord with small-angle X-ray measurements on these samples. Observation of this fine structure is difficult and it is helpful to enhance contrast by slightly underfocussing to bring a degree of phase contrast to the image.

Lamellae crystallized from the glass are both thinner and smaller than their melt-crystallized counterparts. There does, however, seem to be an increase in thickness for crystallization at 270°C (Figure 3d) over that for the lower temperatures (Figures 3e, ef). There is a further large increase, consistent with the previous small-angle X-ray measurements, for crystallization at 310°C and 320°C

(Figures 3b, 3c). This is coupled, as has been noted above, with an evident spherulitic development for the melt-crystallized samples. It is also noteworthy that, despite the low figures for crystallinity, the samples appear comparably full of lamellae to the highly crystalline polyethylene⁷ and isotactic polypropylene⁸. This suggests that non-crystalline regions are associated with lamellae,

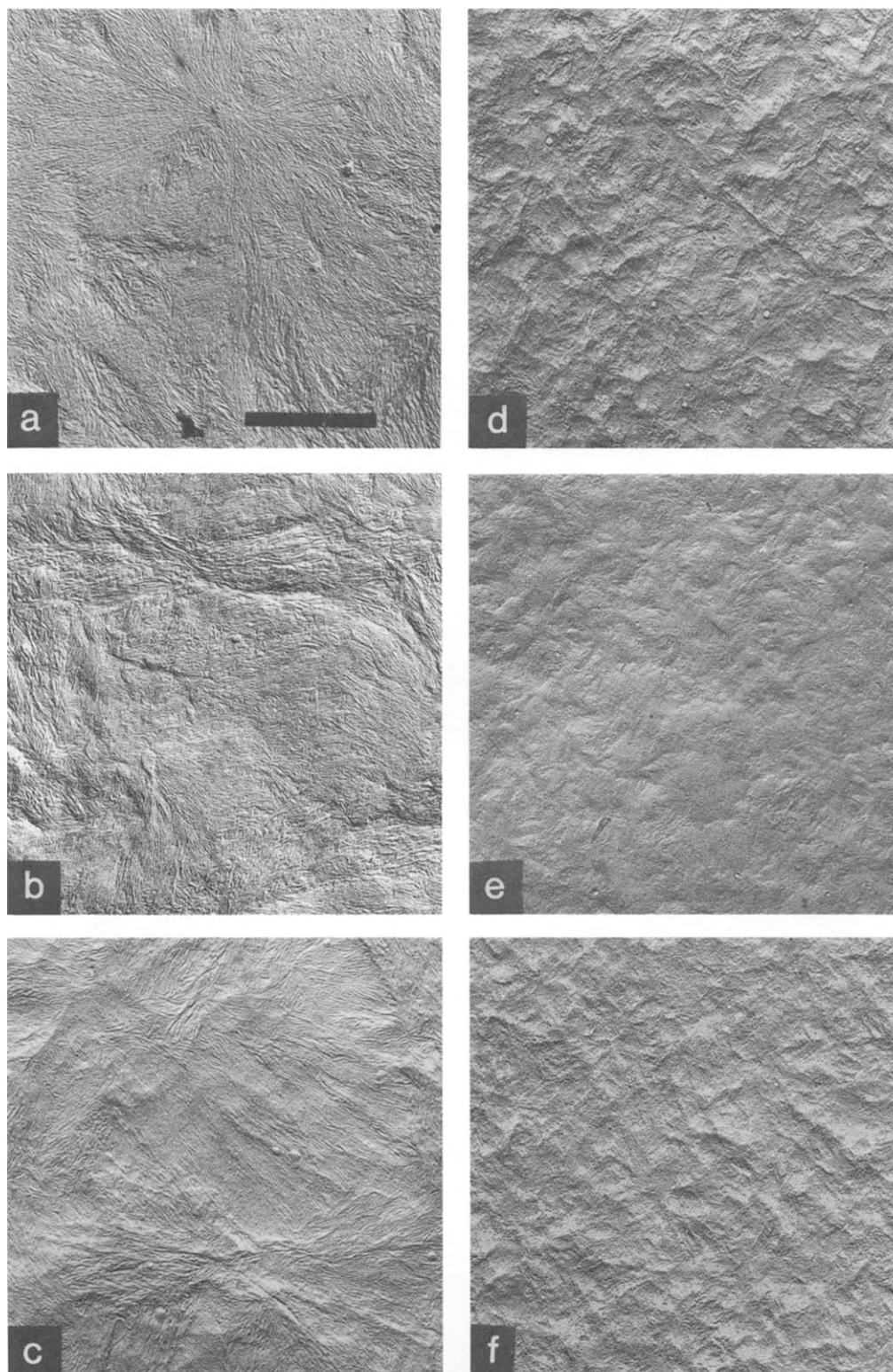


Figure 2 Electron micrographs of replicas of PEEK at medium magnification, showing spherulitic structure. (a) B-315-M, etched with sulphuric acid-phosphoric acid-water mixture with final treatment in diluted aqueous etchant. Other specimens etched with final recipe (with added water). (b) A-320-M and (c) A-310-M, showing microspherulitic structure. (d) A-270-G, (e) A-230-G and (f) A-200-G, showing much more densely nucleated structure, together with less clear lamellar detail, owing to lack of resolution due to grain size of shadowing metal. In these three pictures an increasing amount of underfocus helps to reveal the lamellar structure in high contrast. Scale bar = 1 μm

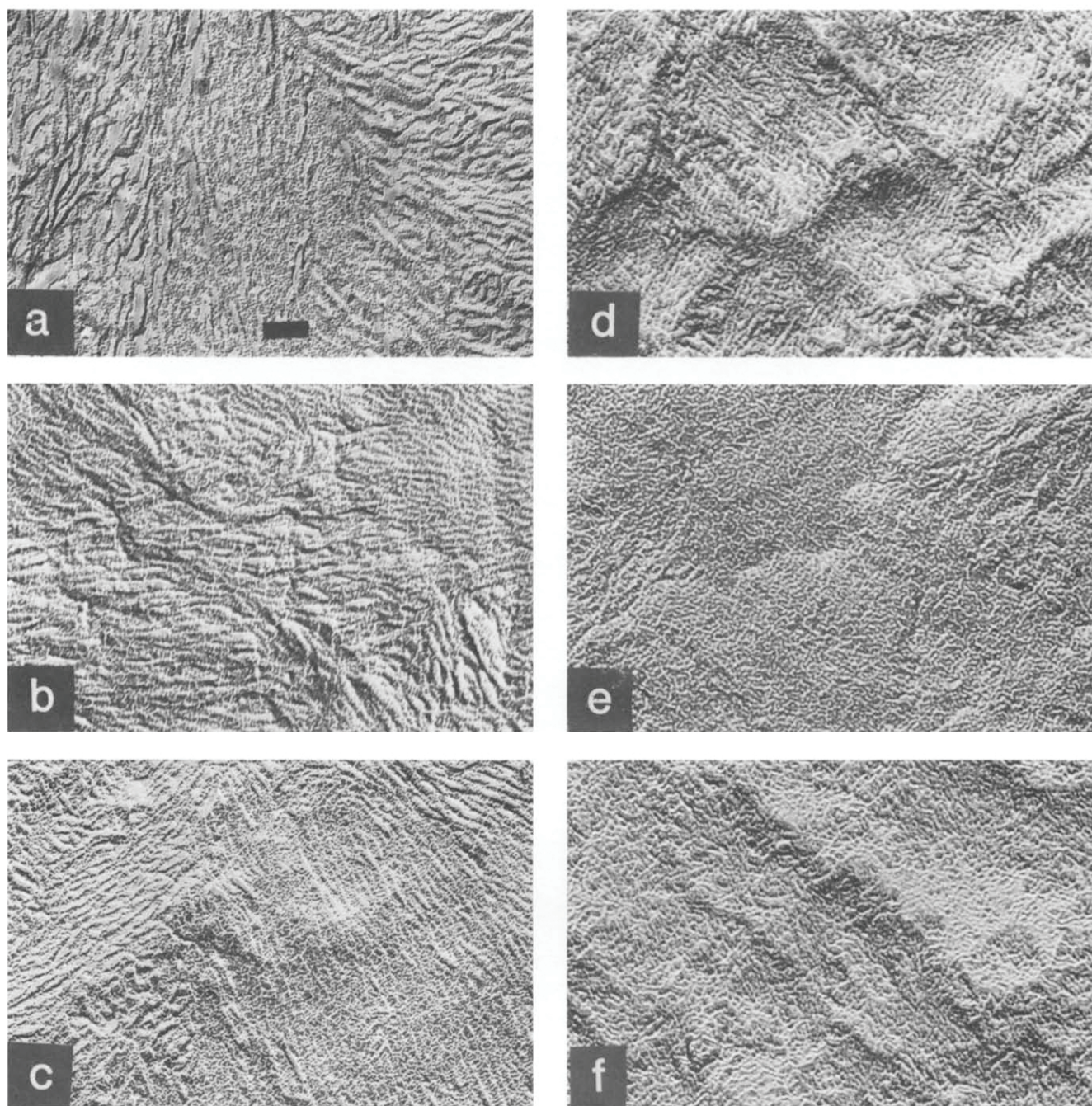


Figure 3 Electron micrographs of replicas of PEEK at high magnification, showing lamellar detail. (a) B-315-M, etched with sulphuric acid-phosphoric acid-water mixture with final treatment diluted aqueous etchant. Other specimens etched with final recipe (with added water): (b) A-320-M, (c) A-310-M, (d) A-270-G, (e) A-230-G and (f) A-200-G. (b)-(f) are details of the corresponding pictures in *Figure 2*, with the same degree of underfocus in (d)-(f). Scale bar = 100 nm

which is also the assumption made in the analysis of the X-ray patterns¹.

In conclusion, then, we now have a usable etchant for PEEK. It evidently reveals spherulitic detail agreeing with that observed optically. It also reveals lamellae adequately, with higher thicknesses and different morphologies for higher crystallization temperatures. This fact and the resemblance of lamellar organization to that observed previously in various polyolefines^{7,8} engender confidence that the lamellar detail revealed is genuine. It is not, however, claimed that it is necessarily the optimum in terms of concentration or etching time. However further progress in the electron microscopy of

etched PEEK is limited by replication techniques rather than by etching itself.

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