A novel technique for the examination of internal morphologies in thin film specimens: embedding and etching of polypyrrole

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A novel permanganic–etching technique is described which enables internal structural information to be obtained from specimens where, for geometrical reasons, more conventional approaches are inappropriate. Here, composite samples comprising of polypyrrole p-toluene sulphonate films embedded in acrylic- or epoxy-resin matrices are considered together with a number of different permanganic reagents. Etching rates are calculated for each of the polymers, and a range of differential etching effects are considered. In addition to single-stage procedures, in which only one of the components is removed by the etching reagent, a multistage procedure is also described. In this, the etching conditions are first chosen to develop morphological relief in the polypyrrole itself. The composite sample is then exposed to a different reagent which only attacks the embedding material. Finally, reaction by-products are removed from the specimen surface by yet another etchant, designed specifically for this purpose. The system described illustrates the potential of embedding and etching as a technique for handling thin-film, fibre and particulate samples, together with the difficulties that may be encountered.

1. Introduction

Many different techniques now exist to facilitate the study of polymer microstructures by electron microscopy. In transmission electron microscopy (TEM) these may broadly be divided into three categories, direct examination, ultramicrotomy and staining and, finally, etching followed by replication. Whilst the first of these approaches concerns samples which are intrinsically thin (e.g. individual lamellar crystals), both staining [1–3] and etching [4–7] have been applied extensively to bulk materials. Indeed, the technique of permanganic etching was first developed specifically as a means of avoiding the potentially unrepresentative structural information that may be obtained from the examination of thin films (cf. the lamellar habits of poly(vinylidene fluoride) crystallized in bulk [8] and in thin films [9]), fracture surfaces (e.g. biased lamellar profiles in polyethylene [10, 11]) and external free-growth surfaces (atypical morphologies may result from diffusional processes or surface degradation [12]). Similar problems arise in scanning electron microscopy (SEM). If sufficient data can be obtained from existing external surfaces, direct examination is straightforward. However, where internal morphological information is required, techniques must be devised, as for TEM, to expose a representative (i.e. undeformed and non-specific) internal surface which can then be treated to develop meaningful structural relief.

The concept of etching as a means of obtaining structural information, in conjunction with other preparative procedures is therefore equally applicable to both SEM and TEM and a variety of etching techniques exist [4–7, 13], so that the treatment and manipulation of many bulk polymers is now relatively easy. However, obtaining internal morphological information from samples such as films, fibres and particulates, which for simple geometrical reasons are not readily manipulable, can be far more difficult. Films and fibres are generally flexible and cross-sections cannot therefore be readily microtomed; they must be supported before any microtomy can commence. Powders present similar handling problems. Without extensive compaction they do not possess the necessary integrity to be manipulated with ease, yet such a procedure may result in changes in particle shape, size or morphology. However, for all three specimen geometries the necessary support can be achieved by using one of two methodologies; samples can be sandwiched and fixed between pieces of another material or, alternatively, they may be embedded in some suitable matrix material.

This paper reports on the use of permanent embedding, combined with permanganic etching, as a means of handling samples where, for geometrical reasons, a more direct approach is precluded. The procedure described provides support for specimens

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during microtomy and throughout subsequent treatments, and, in the case of SEM and optical microscopy, whilst the specimens are being examined.

Traditionally, permanganic etching [14, 15] has been employed to study representative internal morphologies in a whole range of semi-crystalline polymers [16–20]. The technique works by selectively removing particular morphological elements [13, 21]; in general, amorphous regions are etched away more rapidly than the crystalline parts, resulting in the development of a relief at the specimen surface which is directly related to the underlying microstructure (i.e. the local reaction kinetics depend upon the molecular organization). In multi-component systems many reactions may occur and, by suitably tailoring the etching reagents, many different effects may be generated. For example, in a blend system, one of the components may be removed leaving the other largely intact. Clearly, this general approach can be extended to specimens which have been embedded in a supporting matrix, so producing a composite two–component sample. However, many factors must be considered when designing such an experimental procedure. The interaction of the specimen and the embedding material must be taken into account when choosing both the embedding agent and the etchants that will be used to develop the relief in the composite system. If during the etching process the embedded material were to etch appreciably faster than the surrounding matrix, then later examination of the embedded specimen would be difficult, since its surface would lie below that of the surrounding matrix. Another factor that must be considered is the effect of by–products generated during reaction with either the embedding medium or the specimen itself; how will such species modify the etching process?

Although the methodology described above has general utility for the study of particulates, fibres, and films, this paper, for illustration, concentrates on application of this methodology to the study of thick–film specimens. The sample material chosen was the conducting polymer polypyrrole p–toluene sulphonate and this was used in conjunction with two different types of embedding medium, namely, epoxy and acrylic resins. Four different etchants are described, each of which has a different effect on the embedding agent and the polypyrrole film. Notional etching rates are calculated for the different polymers in the different permanganic etchants.

Examples are given whereby the etching characteristics of samples are matched to those of the embedding medium, so producing a controllable, differential, etching rate between the two components. In addition, a multi-stage etching technique is described in which a sequence of reagents are employed to reveal internal structural features within an embedded film.

2. Experimental procedure
2.1. Specimen materials
The films of polypyrrole p–toluene sulphonate considered here were prepared in a one-step,

electrochemical, oxidation process, reported in detail elsewhere [22–24]. The appropriate quantities of pyrrole monomer and sodium p-toluene sulphonate were dissolved in a suitable solvent (in the examples considered here, this was either distilled water or methanol), and this solution was placed in a three-compartment electrochemical cell. The polymerization was performed at 1.2 V versus a saturated calomel electrode, and was terminated once a charge of 12 C had passed through the cell. This procedure results in free-standing films $\sim 10\mu m$ thick which can easily be removed from the indium tin oxide glass work electrode.

2.2. Resins
Two chemically different classes of embedding media were employed to support the polypyrrole films described above. Lowicryl is a low viscosity acrylic compound supplied by Taab, that can be cured either thermally or by using ultraviolet (u.v.) radiation. Araldite resin MY 753 is an epoxy resin, and this was used in conjunction with hardener type HY 956, both supplied by B and K Resins Ltd. These systems were cured as follows: the Lowicryl monomer, cross-linker and initiator were mixed according to the manufacturer's instructions before being left to cure for 48 h at 60 °C. Lowicryl cured using u.v. radiation (17 h at room temperature) suffered from a serious problem: it contracted substantially during curing. When embedding samples in Araldite, a mixture of four-parts resin to one-part hardener, by weight, was employed, and this was cured at 35 °C for 24 h. To ensure that the resin and hardener were completely mixed, both components were warmed slightly before being thoroughly stirred together in warm glassware.

The above resins were moulded into pellets by casting them within gelatin capsules; any samples for embedding were placed in the resin at this stage. Once cured using the appropriate technique, the gelatin was dissolved away in warm water, leaving any embedded samples clearly visible within the resin pellet. To investigate the effect of the various permanganic etchants (described below) on the cured resins, the pellets of hardened resin were then cut into cylinders of roughly equal length using a hacksaw, before commencement of the etching procedure.

2.3. Permanganic etching
The term permanganic etchant [14] has been used to describe any one of a series of solutions containing potassium permanganate, distilled water, concentrated orthophosphoric acid and concentrated sulphuric acid [25–27]. Etchants are generally prepared using the following procedure. Appropriate volumes of the required acids and distilled water are first mixed together, and then, whilst this solution is being stirred, the necessary amount of potassium permanganate is added. The mixture is stirred until the potassium permanganate has completely dissolved. For all the etchants used in this study a 0.5% weight by volume solution of potassium

permanganate in the appropriate acid mixture was used. Table I gives details of the acid mixtures used in each reagent, and the method by which these etchants were subsequently neutralized.

The effects of the three different permanganic etchants on the resin systems described above were investigated as follows. Samples for etching were placed in glass containers each half filled (~ 15 cm^3) with the appropriate reagent, and the containers were placed on a flask shaker. When the samples had been etched for the required time, the containers were removed from the flask shaker and the samples recovered as follows. Etchant A was neutralized by pouring the sample and etchant slowly into a 2:7 mixture by volume of concentrated sulphuric acid and distilled water to which 1 cm^3 of 100 vols. hydrogen peroxide per 25 cm^3 of etchant had been added (method I). Etchants B and C were both neutralized by pouring the etchant and sample into a solution containing 1 cm^3 of the hydrogen peroxide in 150 cm^3 water (method II). In all cases, samples were then thoroughly rinsed with distilled water and left to dry before being examined. Samples were weighed before and after etching, and the etching period adjusted to investigate the nature of the process.

Films of polypyrrole were etched with a 0.5% weight by volume solution of potassium permanganate in orthophosphoric acid. The acid was made up from crystals (supplied by Merck); a 90% solution by weight in distilled water was found to give the best results (etchant D). This reagent was used both to etch the surfaces of polypyrrole films and to reveal internal detail in microtomed cross-sections. It was neutralized using method II described above.

During the course of this study it was found to be necessary to use an additional etchant (E) in conjunction with reagent A. Etchant E is unusual in that it is not based upon potassium permanganate. Rather, it consists of a 2% weight by volume solution of potassium dichromate, in a 10:4:1 parts by volume mixture of concentrated sulphuric acid, concentrated orthophosphoric acid and distilled water. This reagent was neutralized by simply pouring the sample and solution directly into distilled water. Samples were then rinsed several times with distilled water before being left to dry.

3. Results

3.1. Etching of resins
Fig. 1 illustrates the etching characteristics of the different resins. From this it can be seen that the etching rate of Araldite is higher than that for the Lowicryl samples; this is true for all the etchants considered here. Furthermore, the curing procedure used for the Lowicryl resin does not appear to affect systematically the etching rate that is observed. Therefore, in view of the shrinkage problems encountered with u.v. curing, this approach was not pursued further.

Also, from the data shown, it is clear that as the embedding medium is etched away from the surface of the resin block, the reaction by-products can have

TABLE I The appropriate ratios of the acids making up the various reagents used to etch the embedding media

Etchant	Conc.sulphuric:Conc. Ortho-phosphoric: Water	Neutralization method
A	2:1:0[a]	I
B	5:2:2	II
C	0:4:1	II

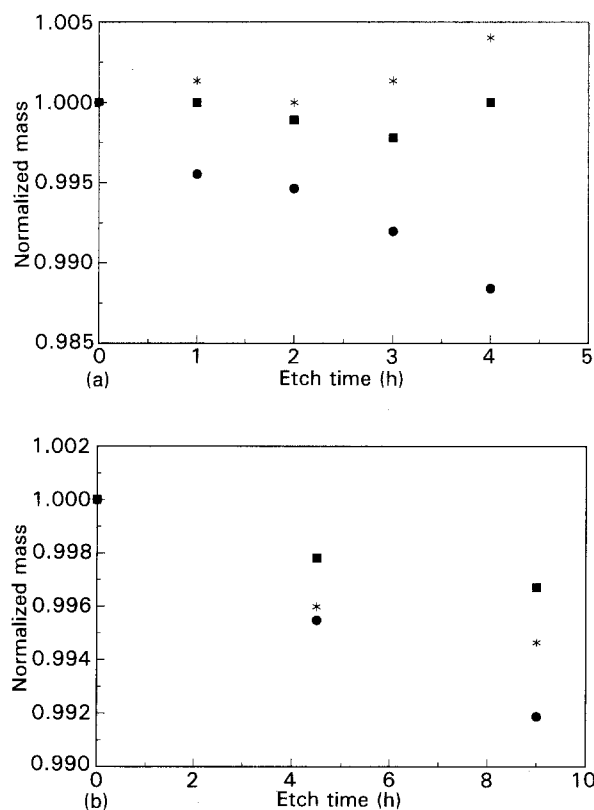[a] The orthophosphoric acid had been dried to a boiling point of 265 °C.

Figure 1 The normalized mass of various resins: (●) thermally cured Araldite, (■) thermally cured Lowicryl, and (∗) Lowicryl cured using u.v. radiation plotted against exposure time to etchant C, with a repeat time of (a) 1 h and (b) $4\frac{1}{2}$ h.

a significant effect, serving to poison or inhibit the remaining etchant; for example, etching for 4 h is not quantitatively equivalent to etching for 1 h and then repeatedly re-etching with fresh etchant to give a total exposure time of 4 h. For Araldite samples, the normalized weight loss after 4.5 h is the same as the weight loss after only 1 h. Thus, at some time during the first hour of exposure to etchant C, the etching process has, effectively, been stopped.

3.2. Calculation of etching rates
From data such as those shown in Fig. 1, nominal etching rates were calculated for each system (embedding medium plus etchant). Assuming that the sample can be considered to be a solid cylinder and that during the etching procedure equal amounts of embedding medium are removed from the ends and sides

TABLE II The etching rate of Araldite when exposed to the various etchants; within experimental error reagents A and B etch linearly with time, whereas C does not

Etchant number	Etching period (min)	Notional etching rate ($\mu m\,min^{-1}$)
A	15	2.68 ± 0.47
	60	3.52 ± 0.43
B	15	0.18 ± 0.03
	60	0.13 ± 0.03
C	60	0.08 ± 0.02
	270	0.03 ± 0.01

TABLE III The etching rate of Lowicryl when exposed to the various etchants; reagents A and B etch linearly with time within experimental error, whereas C is non-linear

Etchant number	Etching period (min)	Notional etching rate ($\mu m\,min^{-1}$)
A	15	0.43 ± 0.16
	60	0.27 ± 0.09
B	15	0.07 ± 0.07
	60	0.14 ± 0.07
C	60	0.031 ± 0.001
	270	0.001 ± 0.002

of the cylinder, then it is simple to relate the weight lost during etching to the amount of material etched from the surface.

Consider a solid cylinder of material density, ρ, which has height, H, radius, R, and mass, M, prior to etching. If, on etching, a layer of material of thickness ε is removed from all surfaces, then the final mass, m, will be given by:

$$m = \pi(R - \varepsilon)^2(H - 2\varepsilon)\rho \qquad (1)$$

Using the starting mass and dimensions to eliminate the density, and ignoring terms in ε^3, since $R \gg \varepsilon$ and $H \gg \varepsilon$ then:

$$\varepsilon^2(H + 4R)-\varepsilon(2RH + 2R^2) + R^2H\left(\frac{M-m}{M}\right) = 0 \quad (2)$$

Solving for the positive root of ε in Equation 2 will give the number of micrometres removed from the surfaces of the cylinder in the period of etching, from which a nominal etching rate can be calculated. Tables II and III show the etching rate for Araldite and Lowicryl in the three different etchants considered here. The uncertainities shown in the tables are derived from repeated measurements.

3.3. Etching of polypyrrole p-toluene sulphonate

Etching rates were also calculated for polypyrrole, but in this case direct thickness measurements were employed. However, the growth-surface morphology of films of polypyrrole p-toluene sulphonate is nodular or cauliflower-like in nature [28, 29], and consequently any attempts to derive etching rates in this way must take into account the appreciable surface roughness (the films are $\sim 10\,\mu m$ in thickness

and the roughness that is present occurs on a micrometre scale). To measure the reduction in thickness of an etched sample, and hence the etching rate, it is necessary to know the original thickness accurately. Moreover, to be able to measure the thickness as a function of etching time it is necessary to either etch and measure the thickness at a known position and then re-etch the same sample, or, as performed here, to etch (for different periods of time) a set of samples all of which were initially of the same thickness. This was achieved as follows.

From a film of polypyrrole p-toluene sulphonate, a small square $\sim 5 \times 5\,mm$ was removed and this was then cut into four smaller squares, as shown in Fig. 2. Each of the smaller squares is of equal thickness at their common corner, i.e. the centroid of the original square. One square was kept for reference purposes, whilst the other three were held flat in gold folding grids and exposed to etchant D. The grids and samples were suspended in etchant D for periods of 10, 20 and 40 min, after which the etchant was neutralized. The thickness of the samples was then determined by SEM.

The small-square specimens, both etched and un-etched, were mounted vertically on SEM stubs, so that their original point of common thickness could be viewed. Samples were manoeuvred in the scanning electron microscope until they were viewed exactly edge on, photographed and reasonably accurate thickness measurements were obtained from these micrographs. Repeated measurements were taken at the common corner so that 95% confidence limits could be determined. Fig. 3 shows the thickness of a sample as a function of etching time. It can be seen that the rate of thinning of the film is somewhat non-linear with time. Hence, as polymer is removed by the action of the etchant, the reaction by-products so formed act to inhibit further etching, much as in the case of some of the resin/etchant systems described above.

Fig. 4 shows the growth-surface appearance of poly-pyrrole before and after extended exposure to etchant D. It is clear from Fig. 4b that this reagent has selectively removed internodular material and in many
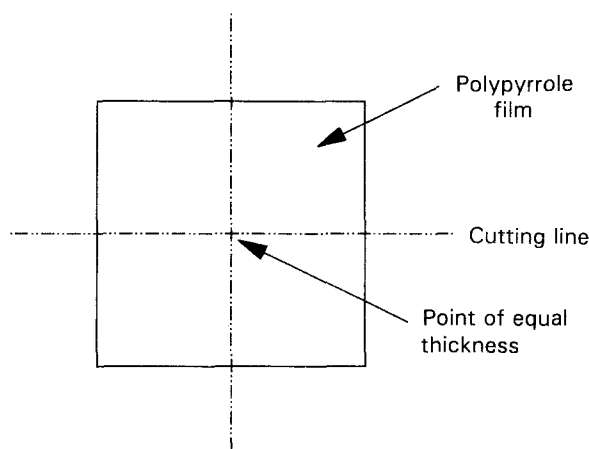
Figure 2 Diagram showing how a piece of polypyrrole film was cut to produce samples with a point of common thickness.
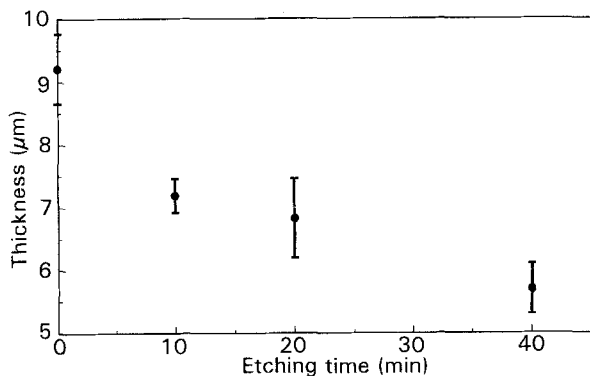
Figure 3 The thickness of a polypyrrole p-toluene sulphonate film plotted against the time of exposure to etchant D. The error bars indicate 95% confidence limits. Although the etching process is somewhat non-linear with time, the etching rates for this sytem are typically of the order of 0.1 μm min⁻¹.
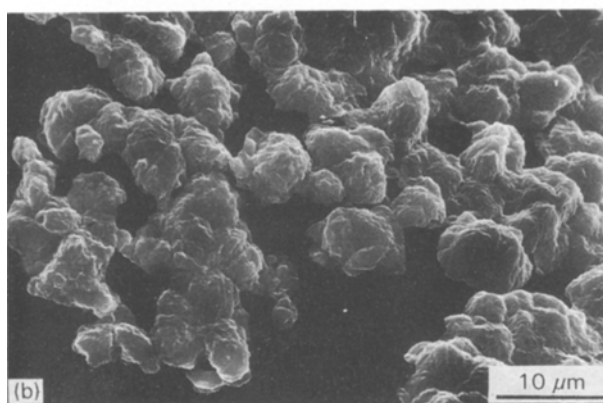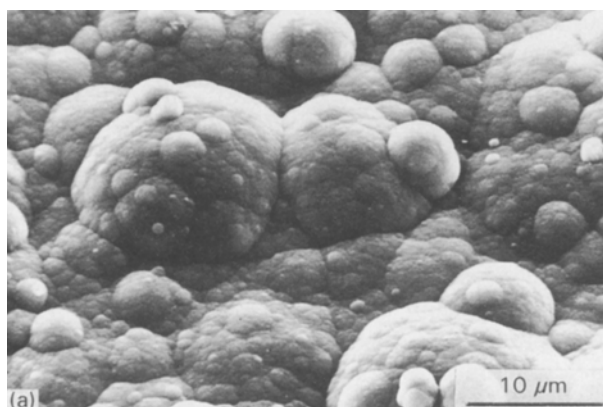

Figure 4 Scanning electron micrograph showing: (a) the growth-surface morphology of polypyrrole p-toluene sulphonate, and (b) the remains of such film after etching for an extended period with etchant D.

places has penetrated through the originally continuous film which exhibits a lace-like appearance after etching. The effects of etchants A, B and C on polypyrrole p-toluene sulphonate films were also investigated. Etchant C was found to attack the films vigorously, in an apparently indiscriminate manner; etchant B only etches the films lightly in the time-scale required to remove a significant amount of embedding agent; and etchant A does not appear to etch the films at all. These interactions are particularly important

and lead directly to the various etching procedures described below.

3.4. Differential etching
3.4.1. Single-stage procedures
Having considered the effect of each of the etchants on the three polymers individually, it is now appropriate to consider composite systems, i.e. samples of polypyrrole films embedded within a resin matrix.

This approach was first used to study films of polypyrrole p-toluene sulphonate prepared from a methanolic rather than the more normal aqueous solution. Under these polymerization conditions, the growth surface of the polypyrrole appears highly wrinkled [24] (see Fig. 5a), the usual nodular surface structure being superimposed upon these gross features. Although it would seem most reasonable that wrinkling is associated with extreme internal voiding, this is not unambiguous from the external appearance of the films alone. Cross-sections produced by fracturing do show internal delamination, but, since films grown from a methanolic solution are brittle, the observed structure may reflect the manner in which the specimens were prepared. To address this point, films were soaked overnight in Lowicryl which is ideally suited for infiltration of any accessible voids
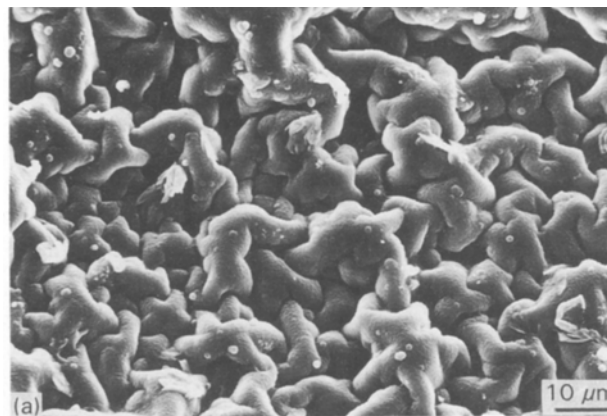

Figure 5 Micrograph showing: (a) the highly wrinkled, growth-surface morphology of a polypyrrole p-toluene sulphonate film grown from a methanolic solution, and (b) a similar film that has been infiltrated with resin and has had planar sections removed from the growth surface. Etchant A has then been used to develop relief, so improving contrast between the two components.

within the film because of its low viscosity. The resin containing the polypyrrole was then cured thermally, and planar sections were removed from the surface of the film. However, direct examination of such samples in the scanning electron microscope resulted in low-contrast images in which it was difficult to differentiate between the sample and embedding resin matrix. Nevertheless, etchant A will not attack the polypyrrole film, and knowing the rate of removal of Lowicryl in this etchant (Table III), it is simple to calculate the exposure time required to remove a few micrometres of resin, and thus improve the contrast between the two components. Fig. 5b shows the surface of a microtomed sample after only 3 min exposure to etchant A; the embedding medium has been etched away leaving the film intact, and a large void can be seen where the top of a wrinkle has been removed. This unambiguously shows that the wrinkles are indeed hollow.

Another example of the use of the etchant A can be seen in Fig. 6. This micrograph shows a sample of polypyrrole film that has been embedded in Araldite, microtomed and then etched. By specifically removing ~ 20μm of the Araldite (7–8 min cf. Table II), the film is left standing proud of the surrounding material (the film is not affected by this etchant), and yet, it is sufficiently supported that it does not lean over so obscuring any of the surface detail. The same nodular growth-surface morphology (labelled A) can be seen in Fig. 4a and the features on the surface can be related to features in the cross-section that is, undulations in the thickness of the film in cross-section can be seen to correlate with nodules being sliced through on the growth surface. Examination of the cross-section through the piece of polypyrrole reveals a number of lines. These features are caused by the microtoming procedure, and they demonstrate that the surface of the polypyrrole film has not been modified during the removal of the embedding medium. This is entirely in line with expectations based upon the effect of etchant A, as described in preceding sections.

However, chemical removal of the Araldite embedding material is not always straightforward.

Commonly, when etchant A is neutralized (according to method I) a thick white film is deposited over all surfaces of the Araldite and the embedded film, totally obscuring the sample. This coating adheres strongly to the surface and cannot be removed by simple rinsing with solvents or by ultrasonic cleaning. The coating is thought to be associated with reaction by-products that are present within the etch and which precipitate out of solution when the etchant is neutralized. However, this undesirable process can be minimized by removing the sample from etchant A, and immediately rinsing it in a stream of acetone, prior to neutralization of the remaining etchant. This procedure would seem to have the effect of keeping the molecular fragments of Araldite in solution in the acetone, and thus displacing them from the sample surface before the remaining etchant is finally neutralized. Although this procedure reduces the amount of precipitate that forms, it does not entirely eliminate the problem. What is required is an etchant that will not attack the embedded film, will not remove any more Araldite, but will remove only the precipitate from the surface. For this purpose etchant E was devised. This etchant removes the precipitate from the supporting Araldite block, and from all the surfaces of the embedded film, which now, after the use of reagent A, stands proud of the surface of the Araldite. After exposure to etchant E, simply rinsing the sample in acetone for 15 min in an ultrasonic bath leaves all sample surfaces clean and ready for examination.

In both the above examples it is the embedding material that has been removed by the etching reagent; in neither case has the polypyrrole been affected by the chosen procedure. Conversely, by suitably modifying the etching reagent the relative etching rates of the two components in the "composite" can be reversed (i.e. the polypyrrole can be etched whilst the matrix is left largely unaffected). Fig. 7 shows a microtomed cross-section of embedded polypyrrole p-toluene sulphonate film that has been exposed to etchant D. The regions labelled A in Fig. 7 are areas of the embedding agent, whereas region B is the embedded polypyrrole film itself. Many of the structures seen within the film correlate with features
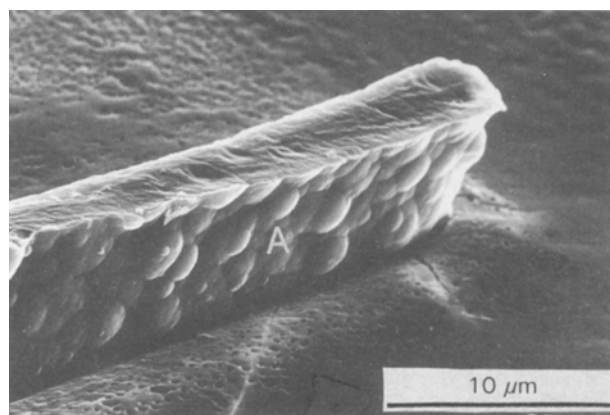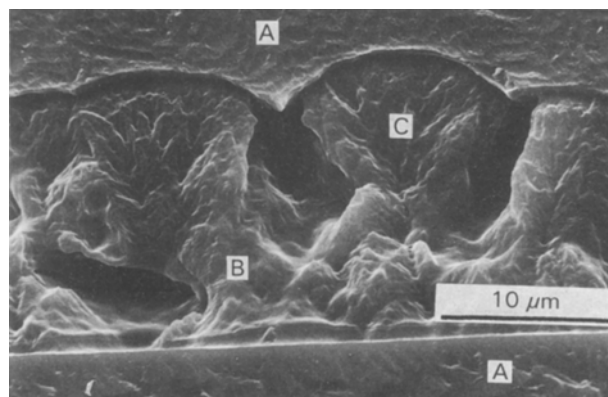

Figure 6 Micrograph showing differential etching between the polypyrrole film and the surrounding Araldite matrix, which has been removed with etchant A. Note the microtome damage, which remains on the cross-section of the polypyrrole film.

Figure 7 Micrograph showing a cross-section of a polypyrrole p-toluene sulphonate film after exposure to etchant D.

on the growth surface; for example, the feature labelled C appears to correspond to a nodule viewed in cross-section. However, the way in which internal detail relates to features present on the surfaces of the films can only be inferred from micrographs such as this. Ideally, what is required is the ability to view an etched cross-section and to see the other surfaces of the film at the same time.

3.4.2. Multi-stage procedures

The above objective can be achieved by combining etchants D, A and E in a sequential etching procedure. The microtomed cross-section is first etched using etchant D to develop detail within the polypyrrole cross-section. The differential etching rate between the two components means that after this step in the procedure the polypyrrole film is lying approximately 1 μm below the surface of the embedding medium. This difference in height relates solely to the polypyrrole removed, since the surrounding Araldite is highly resistant to etchant D. Next, the surrounding Araldite matrix is removed using the method described above, to reveal the surfaces of the once embedded film; as discussed above, this etching step does not involve further modification of the polypyrrole film. Hence, the difference in level between the two components introduced in the last step is
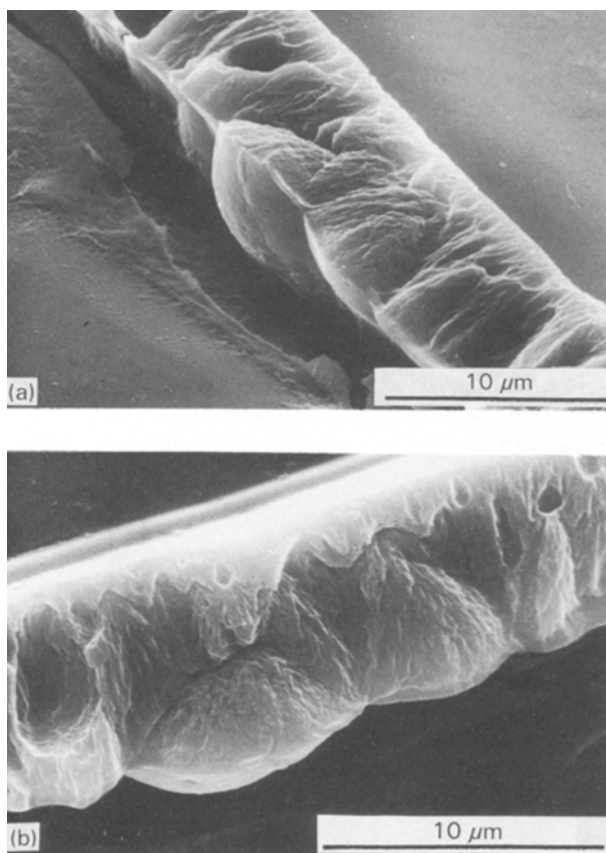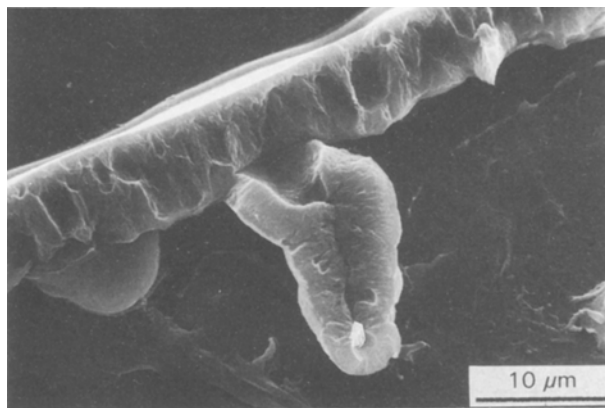

Figure 9 Multi-stage etched sample showing a large conical structure that has grown away from the film surface.

cancelled during this stage. Again, ~ 20 μm is removed from the surface so that the necessary support is retained for the film as well as leaving sufficient of the work-electrode facing and growth surface to be examined in relation to the etched cross-section. Etchant E is then finally used to eliminate the precipitate caused by etchant A, leaving the surfaces clean and ready for examination by SEM.

The great advantage of this technique of sequential etching is demonstrated in Fig. 8a and b. These micrographs show the same area of the film, but viewed from different angles. Fig. 8b is a plan view of the cross-section (a similar view would be seen in an etched, embedded, cross-section from which the surrounding embedding medium had not been removed), and shows a radiating pattern in what appears to be the cross-section of two nodules. By tilting the scanning-electron-microscope stage this is confirmed (see Fig. 8a), and the nodules on the surface of the film are obvious. Fig. 8a shows more clearly than Fig. 8b that the etchant has attacked the film selectively at the points where the nodules seem to end, that is, the area outside the nodule where the radiating pattern does not exist.

Polypyrrole *p*-toluene sulphonate films also exhibit another surface morphological form [30]. These features consist of extended conical-shaped growths ~ 50 μm in length (on a film which is only 10 μm in thickness). Applying the same multi-stage procedure (described above) to these features reveals that they grow as an integral part of the film (Fig. 9). These growths exhibit an internal boundary within the basal film as well as a central groove along their length (revealed by the action of the etchant). The morphology and growth of these and other structural forms is discussed elsewhere [30].

Figure 8 Multi-stage etched sample: (a) The specimen has been tilted, so enabling detail in the cross-section of the film to be related to features that are visible on the growth surface, and (b) a plan view of the same area of the cross-section, showing how the etched cross-section would appear if only etchant D had been used.

4. Conclusion

The results described above clearly demonstrate that embedding coupled with differential etching is a most useful technique for the study of samples by electron microscopy, where for reasons of sample geometry a more direct approach is impractical. Although attention has been focused here upon the study of

thick-film samples it is clear that this methodology has general utility and a similar approach has been used to study water trees, membranes and fibres [31–33]. This study of polypyrrole also highlights many of the difficulties that can be encountered. In etching such a two-phase system many factors have to be considered. These include etchant selectivity, differential etching rates, the effect of reaction by-products on the etching process itself, contamination of the sample surface. Nevertheless, it is clear that, by carefully tailoring the chemistry of the etchants to the embedding material and the specimen, much useful information can be obtained.

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