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Morphology of polypyrrole films grown in thin-layer cells and on indium–tin oxide conductive glass

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Examination by atomic force microscopy and scanning electron microscopy of the non-conducting substrate poly(methyl methacrylate) and the polypyrrole free-standing film formed at its surface in a thin-layer cell has led to an understanding of how such films may be formed. A mechanism is proposed for the origin of the wrinkle morphology observed in thin-layer cells under certain conditions, and attention is drawn to its similarity to the morphology of polypyrrole films formed on indium–tin oxide glass electrodes. In both cases it is proposed that the porous surface of the substrate on which the film grows acts as a template for nucleation sites.

(Keywords: polypyrrole; thin-layer cell; indium–tin oxide glass)

INTRODUCTION

In a previous publication[1] we described an electrochemical cell which mimics the experimental conditions usually employed in fractal growth of polypyrrole (PPy). It is a thin-layer cell (TLC) consisting of two horizontal parallel walls with a variable gap and with the upper wall attached at right angles to a stainless steel anode and left open at the other end. In a typical experiment, this cell was immersed in a larger vessel containing an aqueous solution of the monomer and electrolyte. Among the various non-conducting materials that were investigated for construction of the upper wall in the initial study, we identified commercial poly(methyl methacrylate) (PMMA) as the most suitable material because it promoted the most rapid lateral growth of PPy film off the metallic anode. The lower wall was a clear glass plate which allowed us to observe film growth either visually or photographically. Development of the PPy film could be followed visually as it first appeared on the anode, proceeding to spread at rates up to nearly 1 mm min^{-1} in the narrow gap between the two horizontal layers of the TLC. Such experiments were conducted at a quasi-constant working electrode potential, resulting in dense, smooth deposits. We observed that when examined by scanning electron microscopy (SEM), these films usually displayed rippled surface markings on the PMMA-facing side, especially on parts of the film which had been growing for some time. These appeared similar to morphologies previously reported for PPy formed on indium–tin oxide (ITO) and on noble metal plated electrodes in aqueous and organic solvents. Such features have been described by others as hillocks or mounds[2], mountain chains[3] or wrinkles[4] and interconnected fibrillar arrays[5], while we referred to them as Y-shapes[1], which is a good description for observations under relatively low resolution by SEM. In this publication we choose to refer to the rippled surface features as wrinkles, a term originally suggested by Sutton and Vaughan[4] which provides a good description of the surface when viewed under high magnification. Examination of the edge of such a film by SEM revealed the surface as a two-dimensional matrix reminiscent of a honeycomb[1]. A recently reported SEM micrograph of PPy doped with large counterions and grown on gold-plated stainless steel in propylene carbonate provides another example of such surface wrinkles and a honeycomb-like edge[5].

This study consists of an investigation into the origin of the two-dimensional morphology of wrinkles. Since our initial report, a new and significant paper appeared[4] which in turn led us to several earlier and equally relevant reports of similar surface morpholgical features previously observed under different experimental conditions, not only for polypyrrole[3–8] but also for poly(3-methylthiophene)[9]. Mitchell and Geri[7] observed wrinkles on the solution-facing side of thin films of PPy doped with *p*-toluenesulfonate (PPyTS) formed in aqueous solutions on ITO conductive glass anodes when using a range of potentials (0.5–1.6 V *versus* a saturated calomel electrode). Their study revealed that the average size of the wrinkles increased with the applied voltage. The wrinkles they observed had an unusual feature similar to the wrinkles observed on PMMA, i.e. a large number of surface deformities resembling blisters covered the wrinkles. From their published SEM micrographs we have estimated that the average size of the blister-like markings is about 5 μm, while the peak to peak distance between the wrinkles is estimated to range between 50 and 100 μm,

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depending on the applied potential employed in the electropolymerization. The conductivities of these films were comparable to those found by us[1]. Their reported SEM micrographs show similar features to those reported more recently by Sutton and Vaughan[4] who studied the growth of PPyTS, also on ITO electrodes, from solutions of methanol and water as well as mixtures of the two solvents. Sutton and Vaughan[4] found wrinkles as surface features on the electrode-facing side, with the wrinkle morphology becoming prominent in mixed methanol–water solutions with a methanol concentration of 40% or higher. The adherence of films to the working electrode was found to be weaker for films prepared in methanol or methanol–water mixtures relative to those synthesized in aqueous solutions. Based on a wide-angle X-ray scattering examination of these films, those grown from solvents with high methanol concentrations were found to be less well ordered, as well as less conductive, leading Sutton and Vaughan to attribute the observed differences in morphology and other properties of their films to the variation in the oxidation potential of pyrrole as a function of solvent composition, in line with Mitchell and Geri's earlier study[7]. These authors[7] had proposed that the wrinkles were caused by accumulation of flat layers of doped PPy at numerous growth centres throughout the entire surface of the electrode, while Sutton and Vaughan[4] tentatively suggested that wrinkles may arise from internal stresses. In a separate study Sutton and Vaughan have demonstrated by etching their films that the wrinkles are hollow[6].

EXPERIMENTAL

Pyrrole (Aldrich) was doubly distilled immediately prior to use. Commercial sodium *p*-toluenesulfonate (Aldrich) was used directly as supplied. Electrochemical polymerization of pyrrole (0.6 M) was carried out at room temperature in aqueous solutions of 0.5 M sodium *p*-toluenesulfonate (NaPTS) buffered at a pH of 5.0 with 0.3 M sodium acetate buffer. No attempt was made to exclude atmospheric oxygen during film deposition. Polymerization was conducted using a home-made potentiostat with the working electrode held approximately at a potential of 0.80 V (*versus* a saturated calomel electrode) in purpose-built single-compartment thin-layer cells. Stainless steel square tubing (Type 304, BHP, Australia) internally lined with glass was used as the working electrode, with both the square electrode geometry and the glass lining serving to reduce unwanted growth of the film towards the inner region containing the reference electrode. Commercial grade PMMA (Shinkolite-A, Mitsubishi Rayon) was used. The protective paper sheet was removed just prior to cell fabrication to reduce scratch damage to the PMMA surface. Unless stated otherwise, no further pretreatment of the PMMA surface apart from washing with distilled water was carried out. A schematic diagram of the thin-layer cell is described elsewhere[1]. In the present experiments a gap width of 760 μm was used. A saturated calomel cell (K401, Radiometer Analytical A/S, Denmark) positioned centrally inside the square tubing and about 9 mm from the edges of the working electrode served as a reference potential source. Epoxy adhesive (Araldite, Ciba–Geigy) was used to bond the glass and the PMMA to the stainless steel during cell fabrication. Electrochemical reaction was usually allowed to proceed for 20 min, after which time the cell was removed from the solution and the glass base of the cell carefully split away from the remainder of the cell to expose the deposited film. Polypyrrole films adhering to the PMMA surface were carefully removed using a scalpel, then purified by Soxhlet extraction in a 1:1 acetonitrile–water mixture for 1 h. Films were placed between microscope slides to reduce curling and dried in a vacuum oven at 60°C for three days.

The indium–tin oxide conductive glass (Donnelly Applied Films, USA) with a nominal resistivity of 15 Ω/sq (14″ × 14″) was degreased in 1,1,1-trichloroethane (AR grade) and dried in an oven overnight prior to use.

Conductivity measurements were carried out with a four-probe device built by the university workshop. Examination of the films was routinely conducted by SEM and occasionally by field emission microscopy (FESEM) and atomic force microscopy (AFM). Scanning electron microscopy was performed with a JEOL JSM-480 instrument, field emission microscopy with a Hitachi S900 unit and atomic force microscopy with a Park Autoprobe LS. X-Ray photoelectron spectroscopy (XPS) was carried out on an XSAM PCI X-ray photoelectron spectrometer (Kratos) in the Surface Analysis Unit, University of New South Wales. A MgKα X-ray source was used.

RESULTS AND DISCUSSION

As discussed in our earlier publication[1], the generally accepted scenario for the electropolymerization of pyrrole is as follows[10]. First, the monomer is oxidized at the working electrode, generating pyrrole radical cations. These may drift away and combine while away from the anode to form dimers and higher oligomers, each coupling resulting in the expulsion of a pair of hydrogen ions. The bipyrrole/higher oligomers are then themselves oxidized to form bipyrrole/oligomeric radical cations which may combine with each other or with a monomeric species. Following this pattern, a concentration of oligomeric species builds up over a period of time. In a conventional three-electrode cell, the oligomers congregate around the working electrode where they are readily oxidized to form an insoluble doped film. Because of the conductive nature of the anode, the initially formed aggregated oligomeric material becomes doped instantly on contacting the anode.

At the time of our initial study it was uncertain whether the rippled surface features were merely replications of the underlying PMMA or were due to residues of adhesive employed to hold in place the protective paper sheet following manufacture. An attempt was made to resolve this issue by SEM examination of the surface of the non-conducting PMMA after sputter coating it with gold. However, this test failed to give an unambiguous settlement of the issue, since the gold-treated surface displayed certain patterns which are more likely to be due to the migration of gold atoms under the electron beam to form microclusters than to duplication of the underlying surface of the PMMA. However, sputter coating the surface with chromium, known to be resistant to migration during SEM analysis, finally settled this issue and allowed us to rule out the existence of any protruding surface features on the virgin PMMA surfaces

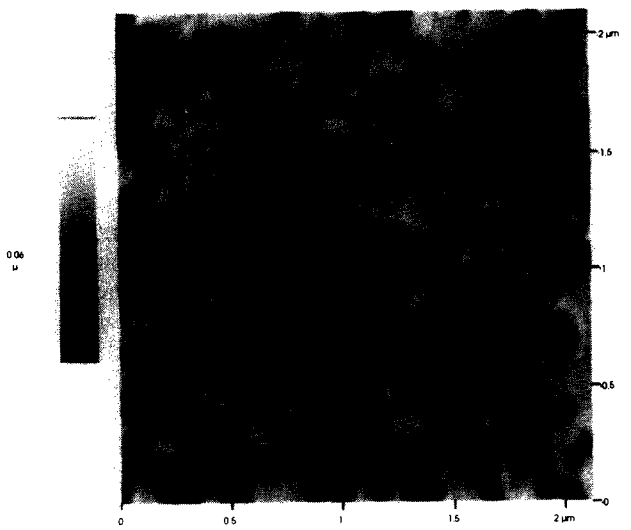

Figure 1 AFM micrograph of the surface of the PMMA used in these experiments

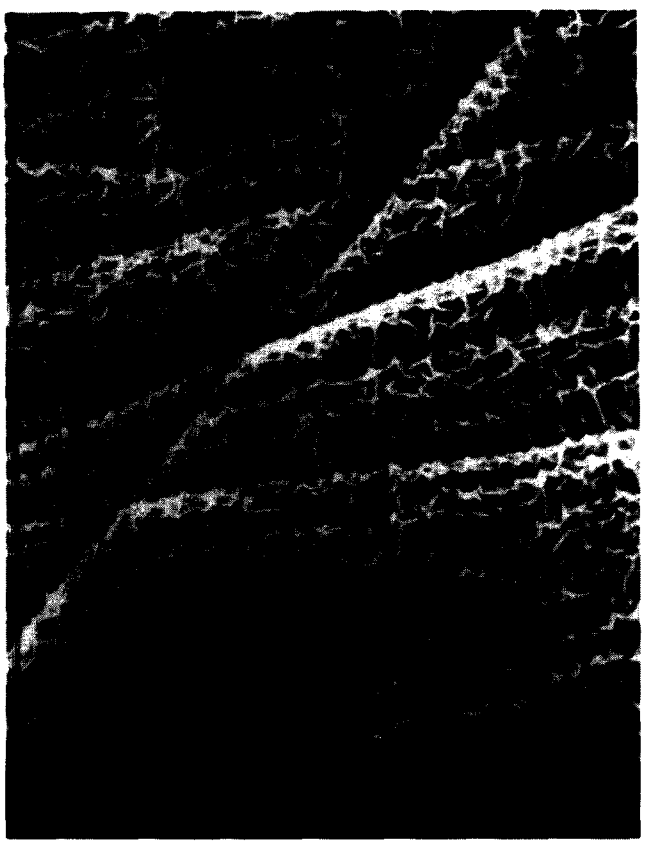

Figure 2 FESEM micrograph of the PMMA-facing surface of polypyrrole

which might have been responsible for the formation of wrinkles.

Since the Cr-coated PMMA surface examined by SEM showed that the underlying substrate displayed no discernible microscale surface features capable of serving as templates, it was decided to examine the PMMA surface under greater magnification by atomic force microscopy (AFM), a technique capable of revealing features of the non-conducting surface at high magnification without the need for any surface treatment which might lead to ambiguous results.

The AFM micrograph shown in *Figure 1* reveals that far from being featureless, the entire surface is marked by numerous small, irregular crevices (50–500 nm) considerably smaller in diameter than the wrinkles (2–4 μm) observed in PPy films produced in a TLC[1] and

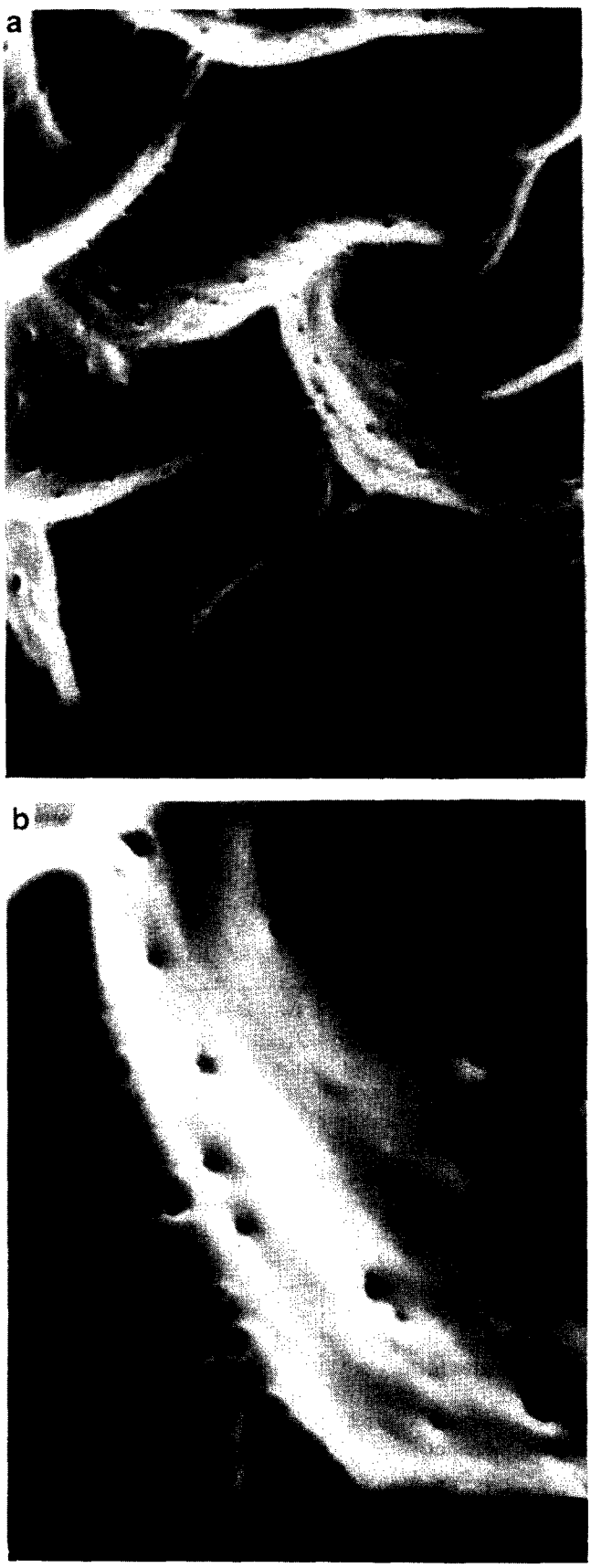

Figure 3 FESEM micrographs of the PMMA-facing surface of polypyrrole: (a) magnification of 15 000; (b) magnification of 50 000

far too small to be observed by SEM. The apparent maximum depth of many of these crevices, estimated from the AFM micrograph, is about 60 nm. An FESEM micrograph of the PMMA-facing side of the PPy film under low magnification is shown in *Figure 2*. Examination under high magnification of the PMMA-facing side of the PPy film under the resolution of FESEM, as shown in *Figures 3a* and *3b*, reveals the more detailed structure of the wrinkle with unexpected holes on and around its surface; some of these are randomly distributed, while others are concentrated on the ridge and its apex. However, the frequency of the holes on the wrinkles observed on our films is smaller than that of blister-like structures found in films produced on ITO, as reported in micrographs of the solution-facing side of PPy in the Mitchell and Geri study[7].

It is instructive to correlate the size of the crevices observed on the PMMA substrate with that of the holes observed on the surface of the wrinkles in the PPy film. The crevices on the PMMA appeared to be variable in size and depth and ranged in size between 50 and 500 nm, while the surface holes on the PPy film were smaller and more uniform in size, about 20–40 nm, and were spaced between 200 and 500 nm apart. The area around some of the holes, viewed under high magnification, bears a resemblance to a cylinder which has been cut off at the base. The size of such holes is consistent with the possibility that polypyrrole nucleates in the crevices on the PMMA surface.

At this stage the following alternative scenario is considered for the formation of PPy films with characteristic wrinkles in a thin-layer cell. In a TLC, as poorly soluble neutral oligomeric species are produced, they may similarly diffuse away or remain near the anode as in a conventional unstirred cell. The chief distinguishing features of the TLC from a conventional electrochemical cell are the restricted diffusion of the oligomeric materials and the inability of fresh supplies of monomer to reach the metallic anode. These features force continued deposition and apparent growth of PPy to proceed entirely on or against the PMMA layer. Interestingly, formation of film is observed preferentially on the upper plate of the cell even when two identical PMMA plates are used. While the aggregation of undoped oligomers on the upper PMMA wall may be due to surface tension effects as discussed by Paik *et al.*[11], it is likely that the lower density of these poorly soluble species relative to the bulk solution may also be an important factor causing them to drift upwards. Finally, adsorption of pyrrole on the growth surface is also thought to play a part in the initial growth of the film, as is evidenced by different rates of growth on different substrates.

Assuming that nucleation sites may be created within the crevices on the PMMA surface, a hypothetical progession of steps in film development is presented in a schematic form, not drawn to scale, in *Figure 4*. Insoluble oligomers drift upwards and settle on the flat PMMA surface as well as in the crevices present in the upper polymer plate, thereby generating potential nucleation sites (*Figure 4a*). According to Fermin and Scharifker[10], soluble species of up to nine monomer units are present in the electropolymerization of pyrrole in aqueous solutions, and hence the insoluble species must be longer than this. In the same study these workers also concluded that further dimerization or growth by combination of oligomers must occur at the electrode surface rather than in solution. Since film growth can only proceed in the vicinity of an electrode which will accept electrons resulting from the oxidation, it is postulated that after covering the metallic anode surface with insoluble oligomers, the PPy film grows out laterally from the working anode, protruding into the narrow gap between the two plates of the TLC as suggested in *Figure 4b*. As the reaction proceeds, both small soluble oligomers and large insoluble oligomers accumulate around the front of the polypyrrole film, which itself becomes an extended anode. It is also proposed that some of the insoluble oligomeric species are deposited in a vertical manner, forming loose bundles that line the walls of the crevices as indicated in *Figures 4b* and *4c*. When contact is made between the PPy anode and the deposited oligomeric film, growth begins on the PMMA surface. As the film continues to expand into the interlayer space, it makes contact with new vertical clusters which can now begin to grow and join the film. Oligomers trapped in the crevices grow into fibrils which are better aligned and are oriented roughly at right angles to the PMMA surface. It is expected that owing to the better chain order in the fibrils, which will make them better conductors, these would grow at a faster rate than the film deposited horizontally on the surface. This postulate offers a reason for the film pushing away from the PMMA surface during its growth, thus forming wrinkles. Variations in crevice depth on the PMMA surface will result in fibrils of different lengths. This will lead to a fluctuation in distance between the growing film and the PMMA, with the

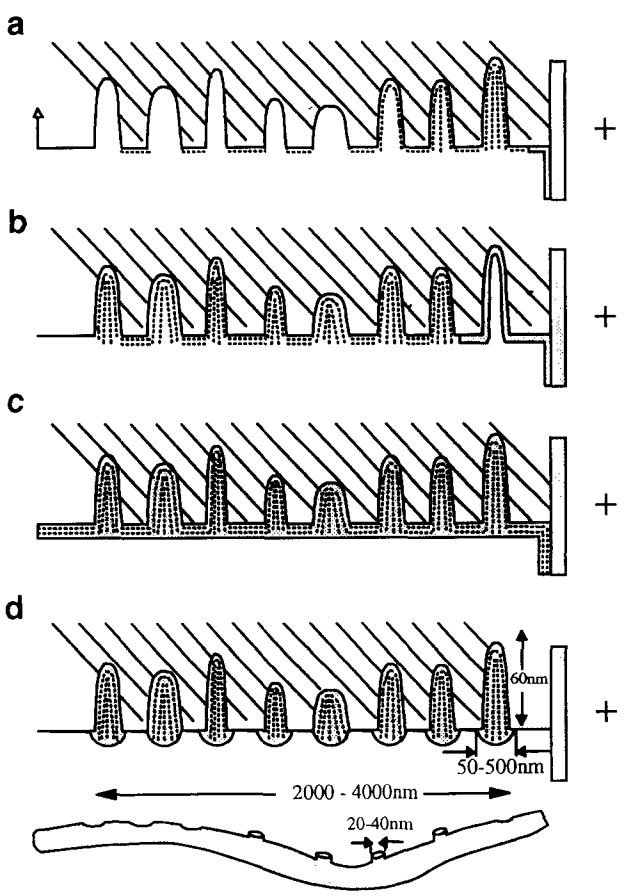

Figure 4 Schematic diagram showing the proposed sequence of deposition of a PPy film on the PMMA surface

Figure 5 SEM micrographs of the ITO-facing side of a PPy film prepared in 0.1 M NaPTS solution: (a) magnification of 500; (b) magnification of 2000

overall result being development of an undulating film anchored by pillar-like fibrils of variable lengths onto the PMMA. This is not illustrated in *Figure 4c*, which only describes a relatively short section of film compared with the size of a wrinkle, with the average distance between holes being 200–500 nm. As shown in *Figure 4d*, after cessation of polymerization when the film is stripped away from the PMMA, the fibrils break away from the film and create the holes in the film evident in *Figures 3a* and *3b*. It would appear that the residual fibrils remain embedded in the upper layer and residual fragments disappear during the film-washing process, since we have been unable to detect such material on the PMMA by SEM. It is signifiicant that most of the holes observed on the surface of wrinkles are quite similar in size and those on the ridges of wrinkles appear as though they were part of snapped-off tubular structures. These observations suggest that the vertical bundles growing from the PMMA crevices resemble tubes rather than rods. This mode of growth would be consistent with fibrils growing from cylindrical nucleation sites, such as those present on a nuclepore-coated Pt anode reported by Penner and Martin[12].

It was of interest to reduce PPy films with the wrinkle morphology in order to learn whether the wrinkle formation was also related to the incorporation of counterions by doping. Earlier we proposed[13] a mechanism for the formation of wrinkles which depended on the incorporation of dopants since the dopant fraction of the film is considerable, typically being about 40% by weight (based on a molar doping level of 25% in the case of PTS^-). Valuable support would have been provided had we been able to dedope PPy films with wrinkles and show by XPS analysis that the reduction in conductivity was simultaneously accompanied by the removal of the tosylate ion as suggested in a recent study[14]. We have examined by XPS one two-year-old film known to possess wrinkles and found its N/S ratio to be 7.1. This film on dedoping gave anomalous XPS results. However, we have been unable to reproduce the wrinkle morphology in fresh films grown in TLCs using new supplies of PMMA, since the new material did not possess the surface characteristics of the original polymer. This was confirmed by AFM micrographs, which revealed smooth, featureless surfaces. We have even attempted to create crevices in the new PMMA plates by annealing them at 105–140°C and by attempting to imprint on these a regular array of holes with ITO glass, but to no avail. Currently, we are exploring various other methods of introducing holes of similar size to those found earlier on the PMMA onto other non-conducting surfaces which can be used in a TLC. In any case, fortuitously the mechanism proposed above is also supported by our preliminary studies of PPy films formed on ITO surfaces, as discussed below.

When considering the origin of the wrinkle morphology formed in the TLC, one notes that a similar, though not necessarily identical, mechanism may operate for a conducting polymer grown in conventional electrochemical cells on ITO electrodes. A published AFM micrograph of ITO[15] itself displays a characteristic morphology reminiscent of the PMMA shown in *Figure 1*, i.e. a jagged surface with deep valleys or crevices distributed over the entire surface[16], the holes being the bare regions on the underlying substrate in between deposited crystalline grains. We have examined PPy films grown on ITO anodes in order to confirm the mechanism we proposed for the wrinkle morphology. In the following discussion we will restrict our report to only those results that are needed to illustrate the proposed mechanism, leaving a full report to be published on its completion as a separate study. Growth of PPy was conducted under similar conditions to those used by Sutton and Vaughan[4], i.e. at a constant potential of 1.2 V *versus* a saturated calomel electrode on ITO electrodes held vertically in a 40:60 methanol–water solvent mixture containing 0.1 M pyrrole and various NaPTS concentrations. Deposited films were characterized by conductivity, SEM and elemental analysis (using XPS). The average thickness of films was around 10 μm – thinner than the films formed in the TLC (about 50 μm). SEM micrographs of the film grown in 0.1 M NapTS solution, taken from the ITO-facing surface, are shown in *Figures 5a* and *5b*. From these figures the distance between wrinkles is estimated to be about 100 μm, while the size of the holes is about 1 μm. In *Figures 6a* and *6b*, showing the features of an ITO-facing film grown in a 0.2 M NaPTS solution, fibrils are found in a small area of the film, resembling those observed by Penner and Martin[12]. These fibrils, which appear to be at a slight angle to the film surface on the hollow side of a wrinkle, appear to be about 3–4 μm long (see the arrows). Fibrils were not found commonly in other regions, but were found in this particular preparation perhaps because of the way that this film was stripped off the electrode. Another section of the same film viewed under the FESEM, displayed in *Figure 7*, revealed numerous needle-like structures scattered around the holes. These are most likely

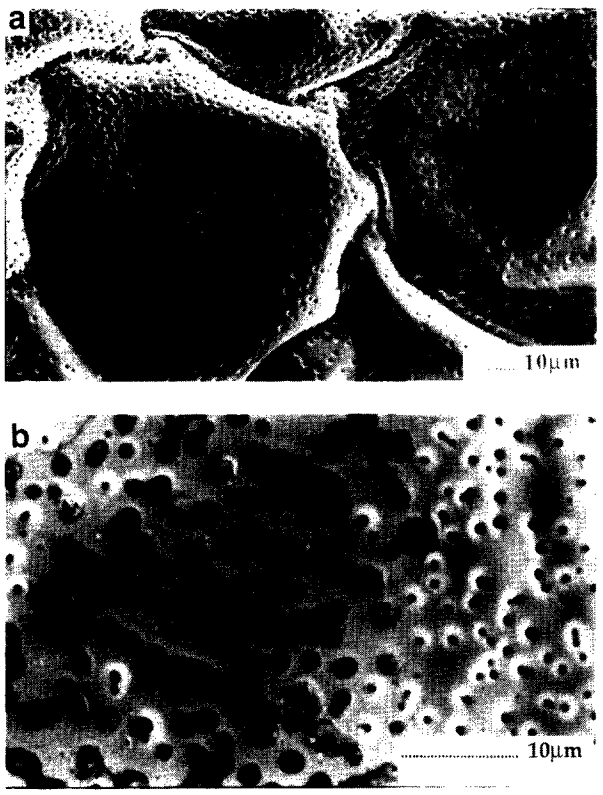

Figure 6 SEM micrographs of the ITO-facing side of a PPy film prepared in 0.2 M NaPTS solution: (a) magnification of 500; (b) magnification of 2000

indium oxide crystals, although this will need to be confirmed.

We have attempted, by photographing areas around the 'holes' at several tilt angles (5, 10 and 40°C), to determine whether the 'holes' are above or below the surface of the film. These attempts led us to conclude that these features are mostly holes rather than surface protrusions. On the other side of the film, the solution-facing side, cauliflower-type features were found of the type usually reported for PPy films. Upon dedoping, the conductivity of the film grown in 0.1 M NaPTS dropped from 1.2 to 3.0×10^{-3} S cm^{-1}. In parallel, the XPS analysis confirmed the expectation of a decrease in the N/S ratio from 1.6 in the oxidized state to 5.3 in the reduced state. In addition, there was no evidence of sodium ions in the reduced film, as might have been expected[14]. An SEM micrograph of a dedoped film prepared from 0.1 M NaPTS solution is provided in *Figure 8*. The same film was examined by conductivity and XPS analysis. Dedoping removes the wrinkles to leave behind a smooth, sometimes cracked surface, while the holes remain.

The following mechanism is therefore proposed for the growth of PPy films on ITO. When a potential is applied to the ITO anode, its surface and intercrystalline crevices begin to become covered by pyrrole oligomers which generate nucleation sites and proceed to grow in the manner suggested schematically in *Figure 9a*. Initially, the growth proceeds approximately at right angles to the anode, generating fibrils (*Figures 8b* and *8c*) of the type evident in *Figure 6*. Once they grow longer than the 'hole' in which they were created, fibrils from neighbouring holes join up, eventually forming a coherent layer parallel to the anode and embedding all the fibrils within the film. When the film growth is stopped and the film is stripped off the ITO anode, the ends of the fibrils still attached to the ITO surface are snapped off, leaving beind holes on the wrinkle surface with only an occasional area of hollow fibrils surviving the treatment, as indicated schematically in *Figure 9d*.

This proposed mechanism for the formation of PPy

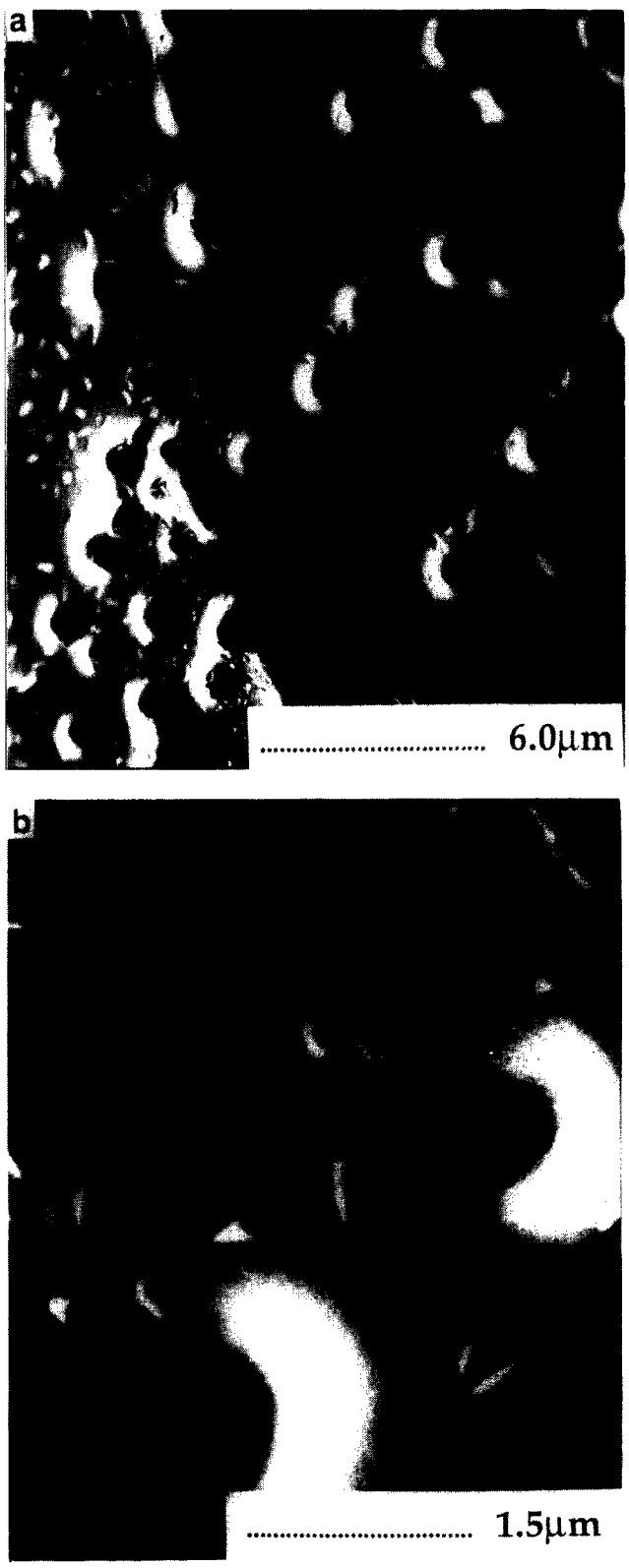

Figure 7 FESEM micrographs of the ITO-facing side of a PPy film prepared in 0.2 M NaPTS solution: (a) magnification of 5000; (b) magnification of 20000

Figure 8 SEM micrograph of the ITO-facing side of a PPy film prepared in 0.1 M NaPTS solution and dedoped (magnification of 500)

on ITO is in agreement with a number of known experimental observations on the growth of PPy films on ITO and shares many features with the mechanism proposed earlier for the formation of film on a non-conductive surface in the TLC. In both cases the prerequisite characteristic of the anodes is a porous surface. For films produced on ITO the features of the structure predicted for this film are consistent with the observed anisotropy reported by other researchers[4,7]. In terms of our mechanism for film formation on porous anodes or surfaces, the origin of the anisotropy is attributed to a certain fraction of the film consisting of fibrils oriented perpendicular to the film while the rest are oriented in a plane parallel to the ITO anode. The ease with which such films are peeled off the anode is also consistent with the postulated fibrillar attachment of the PPy film to the ITO electrode.

In other studies where gold-plated stainless steel[6], titanium[8] and Pt-plated titanium anodes[1,7] resulted in a wrinkle morphology, the origin of holes on the anode surface itself is a subject of speculation. However, these may have been formed after repeated use of the same anode, this practice resulting in pitting of the surface, creating large numbers of minute holes.

In conclusion, it appears that the presence of crevices or holes on the anode surface is a necessary condition for the formation of wrinkles, while the nature of the surface itself is of less importance. In this study we have demonstrated the development of a wrinkle morphology even at a non-conducting surface, PMMA, adjacent to the PPy anode. Additionally, the nature of dopant ions within the film may also be implicated in the formation of wrinkles, as demonstrated in the dedoping control experiment. The factors that determine the distance between wrinkles and their depth are difficult to assess at this stage of understanding, but the factors are responsible for the periodic variations in length of the postulated fibrils. Concerning the porous surface of the PMMA which resulted in wrinkles, the origin of the surface crevices in the material that resulted in a wrinkle morphology appears to be accidental. In the case of ITO, slight fluctuations in the SnO density on the surface are likely to play an additional part. The range of film thicknesses for which wrinkles have been observed both in this and in other studies is 10–80 μm. Thus, the thickness of the film *per se* does not appear to be an important factor in the development of wrinkles.

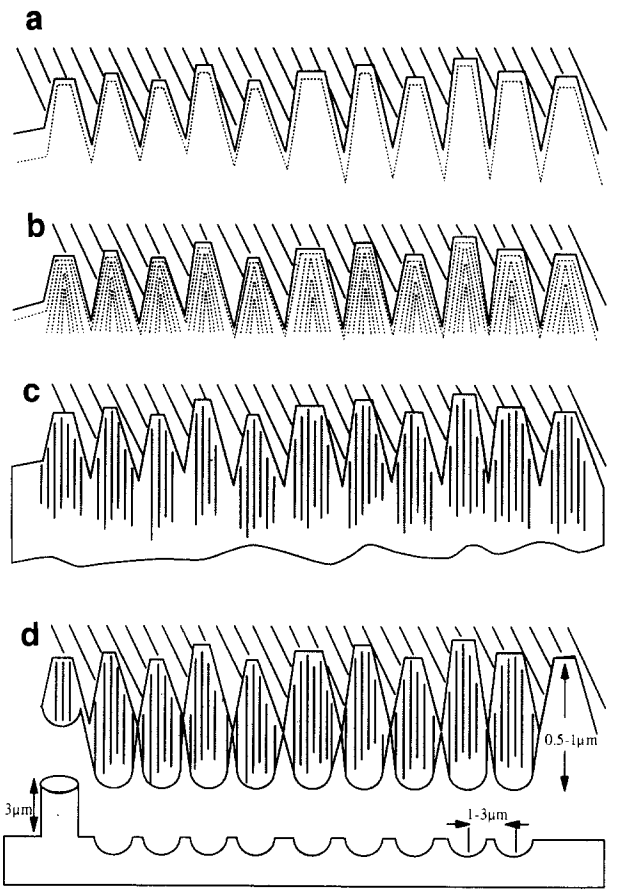

Figure 9 Schematic diagram showing the proposed sequence of deposition of a PPy film on an ITO anode

Consequently, it seems unlikely that stresses developed in the film after it is stripped off the anode for viewing by SEM are responsible for the wrinkle formation, since wrinkles are not generally observed on thin films prepared on Pt anodes.

Assuming a common mechanism for PPy film formation on the two types of anodes, it is not surprising that wrinkles found in films grown on ITO are deeper/taller than those found in films deposited on PMMA in TLCs. Faster growth on the former, due to the conductive nature of the substrate, would be expected to lead to longer fibrils, and these would give rise to larger wrinkles.

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