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On the morphology and growth of electrochemically polymerized polypyrrole

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Samples of polypyrrole *p*-toluene sulfonate have been prepared by electrochemical polymerization from aqueous and methanolic solutions. The morphology and molecular ordering have been studied by scanning and transmission electron microscopy, polarizing optical microscopy and wide-angle X-ray scattering. Specimens prepared from aqueous solution develop as compact films, which exhibit considerable molecular anisotropy; cross-sections are highly birefringent and the local molecular orientation is found to correlate with the nodular surface features. Transmission electron microscopy also reveals evidence of supermolecular ordering within the films, which is consistent with the optical observations. Samples prepared from methanolic solutions appear very different: no evidence of molecular anisotropy or internal subdivision has been observed. These films are massively voided as a result of extensive internal delamination, which occurs after the polypyrrole is deposited onto the work electrode. On the basis of the observed morphologies, modes of growth are proposed, based upon polymerization in solution followed by a degree of further chain development after precipitation.

(Keywords: polypyrrole; electrochemical polymerization; morphology)

INTRODUCTION

Electrochemical polymerization has been used extensively as a means of preparing many conducting polymers (for example, see refs. 1–6). In the case of polypyrrole, free-standing films may be prepared in this way from a solution of pyrrole and some ionic compound in a suitable solvent; commonly, water or acetonitrile are used[1]. In a previous publication[7], we reported on the growth of films of polypyrrole *p*-toluene sulfonate from a novel solvent system, namely mixtures of water and methanol. As the composition of the solvent is changed, its character can be varied from aqueous to organic, and, in this work, a number of significant effects were observed. The incremental addition of methanol to the solvent results in a change in the surface morphology of the film; the growth surface becomes markedly more wrinkled, and the usually reported nodular surface texture[8,9] also changes. These variations are accompanied by a fall in the electrical conductivity of three orders of magnitude, and an almost total loss in the anisotropy of the films as measured by wide-angle X-ray scattering (WAXS).

Additionally, the growth of polypyrrole on linear electrodes (platinum/palladium wire) can result in the development of a supplementary morphological feature. For solvent mixtures containing less than 50% methanol, an extensive disc-shaped structure (see *Figure 1*) develops along the air/liquid surface interface[7]. This feature tapers from the electrode towards its periphery and, typically, has an aspect ratio (radius/maximum thickness) of the order of 70, which indicates that radial development occurs much more rapidly than thickening, i.e. the two mechanisms are different.

Although many of the above phenomena closely mirror the effect of changing the anodic potential in an aqueous system[10], the suppression of interfacial growth at high methanol concentrations suggests that the organic solvent does not only affect the polymerization process as a consequence of variations in the oxidation potential of the monomer, which can result from changes in the solvent composition[11,12]. The polymerization process is affected in a much more fundamental way. However,

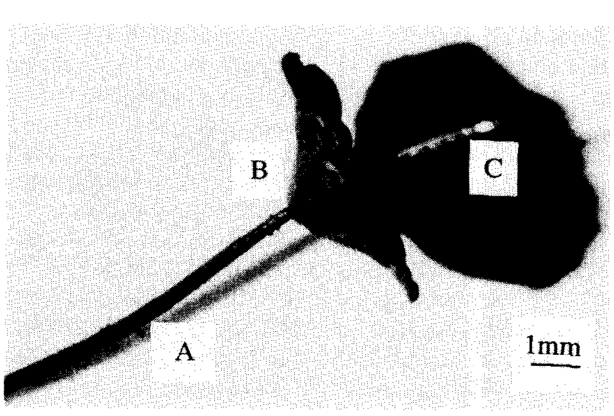

Figure 1 Stereo optical micrograph showing the general growth habit of polypyrrole grown on a wire electrode from an aqueous solution. At A, the polypyrrole-coated wire can be seen; B shows the interfacial disc, which is several millimetres in diameter; at C a portion of uncoated electrode is visible

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electrochemical polymerization from solution is an area that is not fully understood. It is accepted that monomers react in solution to form dimers, trimers and higher oligomers; when the molecular chains can no longer remain solvated, precipitation onto the electrode surface occurs[13–15] following some nucleation step[15–18]. However, what is less clear is whether polymerization then continues on the work electrode[18–20]; most workers simply refer to 'growth following precipitation', without attempting to specify whether the term 'growth' means growth of the film or further growth of the molecules within the film.

In this paper we examine the development of polypyrrole *p*-toluene sulfonate films prepared from methanolic solution as a function of both applied voltage and charge passed through the electrochemical cell; films grown under the same electrochemical conditions from aqueous solution are used for comparison. Finally, the observations are discussed in terms of possible growth processes.

EXPERIMENTAL

Films of polypyrrole, with *p*-toluene sulfonate as counter-ion, were prepared in a one-step electrochemical oxidation process from both aqueous and methanolic solutions. The pyrrole monomer was first purified by distillation under vacuum and, thereafter, stored under nitrogen and refrigerated until use. The required solutions were made up by adding sufficient purified pyrrole and sodium *p*-toluene sulfonate to the appropriate solvent to give 0.1 M solutions of each.

Polymerization was then performed electrochemically in a three-compartment cell, using a Sycopel Potentiostat 801 under computer control. The work electrode was either indium tin oxide (ITO) coated glass (approximately 2 × 4 cm) or a 2 cm length of platinum–palladium wire (20% platinum), the counter-electrode was a carbon rod and the reference electrode a saturated calomel electrode (SCE). In all cases, polymerization was conducted at ambient temperature and no attempts were made to exclude oxygen from the system. For all the samples grown from aqueous solution, the anodic potential was maintained at a constant 1.2 V vs. SCE during the growth of the films; each was allowed to grow until a total charge of 12 C had passed through the electrochemical cell. Alternatively, for the samples grown from methanolic solutions, various applied voltages were used, ranging from 1.2 to 3.0 V vs. SCE; the total charge passed through the cell was varied between 0.1 and 12 C. Following polymerization, all specimens were thoroughly rinsed with distilled water, then acetone and, finally, allowed to dry at room temperature prior to examination.

Specimens were usually stripped from the work electrode for subsequent characterization. However, films that had been grown under conditions where less than 2 C of charge had passed through the electrochemical cell were examined still attached to the ITO glass electrode. Films grown from methanolic solutions were removed by simply washing them off the electrode surface, whereas films prepared from aqueous solutions were detached without difficulty using a razor blade. Specimens were then characterized using polarizing optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and wide-angle X-ray scattering (WAXS).

Samples for optical microscopy and TEM were prepared by first embedding portions of films in a low-viscosity acrylic resin, LR White (cured at 60°C for 24 h). Cross-sections ranging in thickness from 80 nm (for TEM) to 300 nm (for optical microscopy) were cut from the LR White embedded films using an RMC MT-7 ultramicrotome. These sections were prepared under ambient conditions using standard procedures; a ribbon of sections was cut and floated off onto the surface of distilled water and suitable specimens were picked up on copper TEM grids. The internal nature of films grown from methanol was also investigated by the removal of planar sections, cut parallel to the growth surface. For this, pieces of film were soaked for 24 h in Lowicryl, another acrylic resin, to ensure that the embedding agent had sufficient time to diffuse into any cavities within the sample. The resin was then cured according to the manufacturer's instructions. After microtomy, SEM examination of the exposed surface showed very little contrast between the embedding medium and the embedded film and, as a result, direct examination was found to be of little value. Therefore, exposure of the cut surface to a suitable permanganic etchant[21,22] was used to introduce sufficient relief that the polypyrrole and embedding medium could clearly be differentiated from one another (details of this technique are given in ref. 23).

Scanning electron microscopy was performed using a Philips SEM 515. Despite their intrinsically conducting nature, all specimens were coated with gold prior to examination in the SEM. Cross-sections ~80 nm thick, supported by the embedding medium, were examined directly using a Philips EM 301 transmission electron microscope. Transmission optical microscopy of 300 nm thick sections was achieved using a Zeiss Standard GFL polarizing microscope. Sections were examined between crossed polars, and the fast and slow directions within birefringent sections were determined using a quartz sensitive tint plate[24]. For X-ray scattering measurements, samples were prepared by cutting the polypyrrole films into strips, which were then stacked on top of each other with the original orientation kept constant. These multi-layered samples were fixed in place to give a 'block' of material, from which orthogonal scattering patterns ($\chi = 0°$ and $\chi = 90°$) could be obtained. A computer-controlled three-circle diffractometer[25,26] was used, which allowed a fixed angular relation (χ) between the scattering vector (s) and the plane of the sample to be maintained. For $\chi = 0°$, the X-ray beam is incident normal to the plane of the as-grown film, whereas, for $\chi = 90°$, the incident X-ray beam lies within the plane of the sample.

RESULTS

Surface morphology

Variation of anodic potential. Figure 2 shows how the surface morphology of polypyrrole *p*-toluene sulfonate grown from a methanolic solution changes as a function of anodic potential (1.2 V → 3.0 V vs. SCE). In considering these micrographs, it is necessary first to define the basic structural elements (which tend to be superimposed upon one another) that are present. On a macroscopic scale,

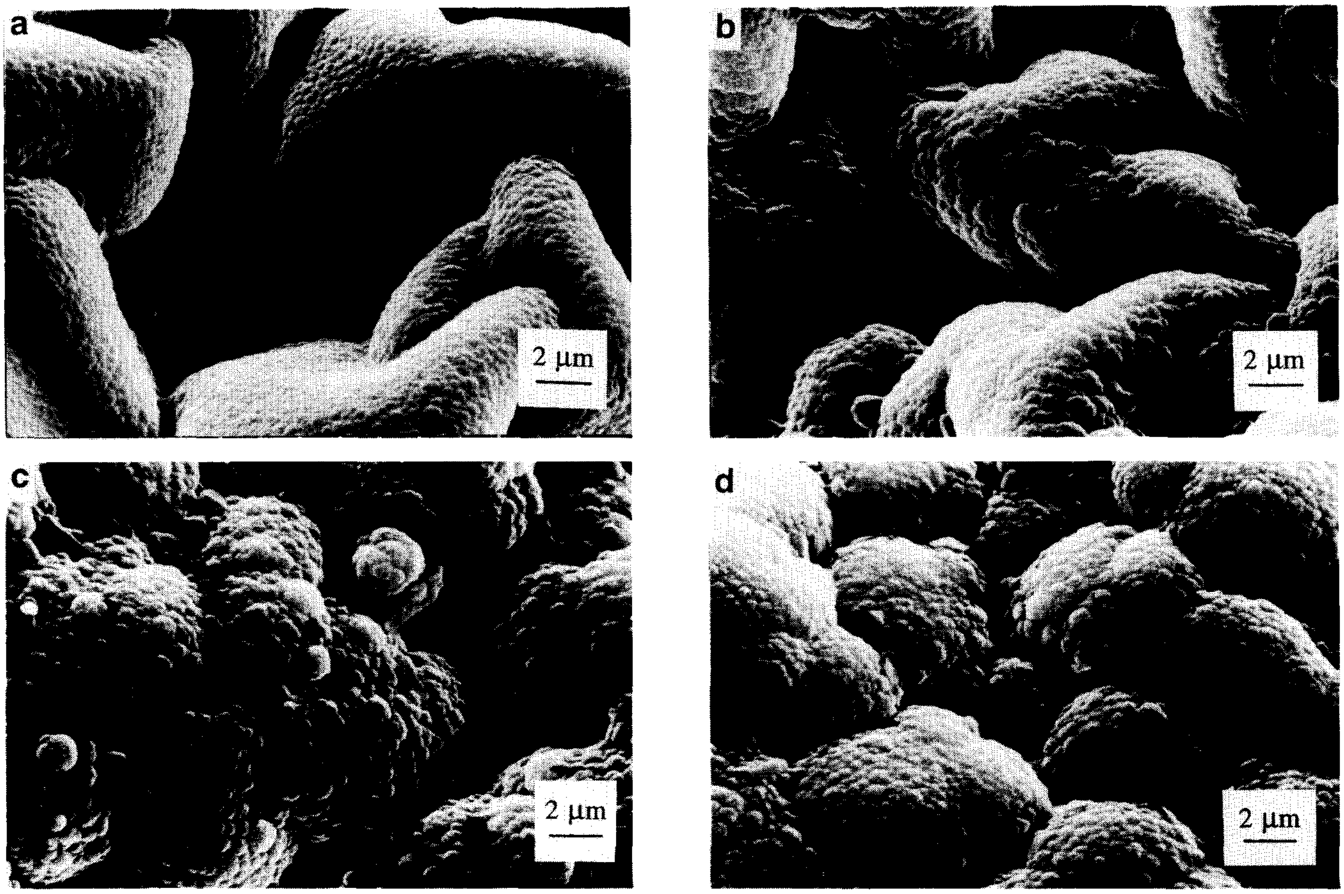

Figure 2 SEM micrographs showing the variation in surface morphology of methanolic films as a function of anodic potential: (a) 1.2 V, (b) 2.0 V, (c) 2.4 V, (d) 3.0 V

all these films exhibit a characteristic wrinkled appearance. These features, which are of the order of tens of micrometres in size, are found to be uniformly distributed over the entire sample surface; similar structures have been reported in polypyrrole[10,27] and polythiophene[4]. At the other dimensional extreme, and superimposed onto the above surface features, a cellular structure on the scale of 0.5 μm is clearly visible. Both these features are most easily seen in *Figure 2a*. Examination of the various micrographs in *Figure 2* clearly demonstrates that, while all the samples shown exhibit both these surface features, a progressive change in surface morphology does occur as the electrochemical potential is varied. For samples grown at 1.2 V (*Figure 2a*), the film is wrinkled and the nodules grow evenly spaced over the whole surface. However, as the applied voltage is increased, so the surface texture becomes increasingly dominated by large nodular structure. These 'macro-nodules' have a diameter of the order of 3–10 μm, the finer-scale cellular structure being superimposed upon their surface. In *Figure 2d* the development of these features is so extensive that the underlying pleated nature of the film is almost completely masked.

Development of surface morphologies. Examining the growth surface of the film as a function of time, or, more accurately, the quantity of charge passed through the electrochemical cell, can prove to be a very useful technique. *Figure 3* shows the growth sequence for polypyrrole grown from methanol, at a constant voltage of 1.2 V vs. SCE.

When the anodic potential is applied to the cell, small dark spots form on the ITO glass electrode; these dark regions rapidly spread until the entire surface of the work electrode is covered. An early stage of film development can be seen in *Figure 3a*, which shows a 0.1 C sample. Although, at this early stage of growth, the film is predominantly flat, it is clear that, even now, wrinkles are beginning to develop in the polymer. As the film slowly thickens, the surface becomes increasingly non-planar; large bulges develop all over the surface (see *Figure 3b*), which increase in size as growth continues. At ~1 C, the pleated film begins to wrinkle on a much larger scale as can be seen in *Figure 4*, where an extreme example is shown. Between 4 and 12 C, the maximum film thickness considered here, further significant morphological changes were not observed.

More detailed examination of the film surface shows it to be smooth up to ~0.5 C, i.e. during the early stages of growth none of the cellular/nodular texture described in the preceding section could be observed. However, after 1 C has passed through the cell, this situation has changed: nodules ~0.1 μm in diameter can be discerned on the sample surface together with the larger-scale features that are principally associated with the wrinkling process that is described below.

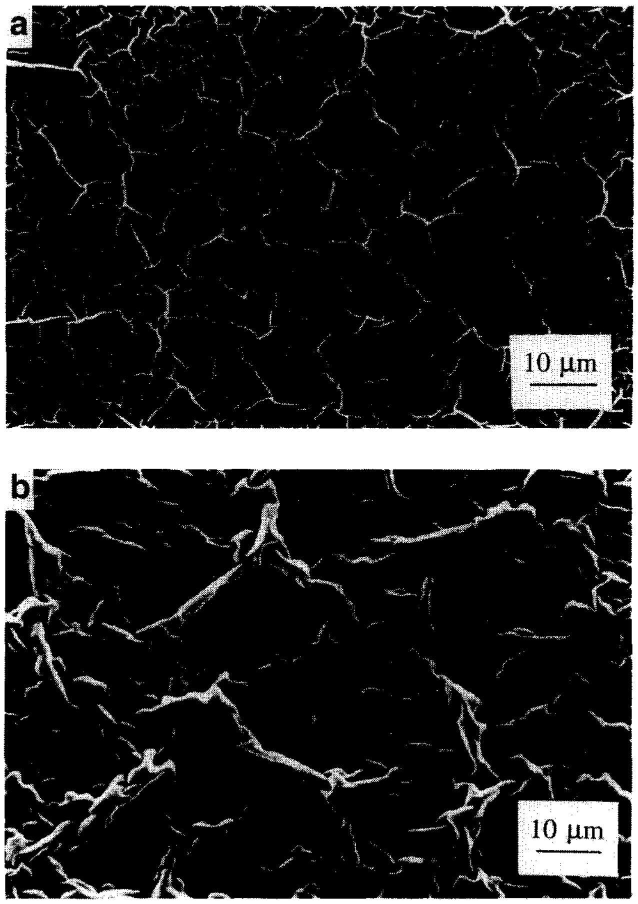

Figure 3 SEM micrographs showing the development of surface morphology of methanolic films prepared at an anodic potential of 1.2 V vs. SCE. In (a) 0.1 C has passed through the electrochemical cell whereas in (b) the total charge was 0.5 C

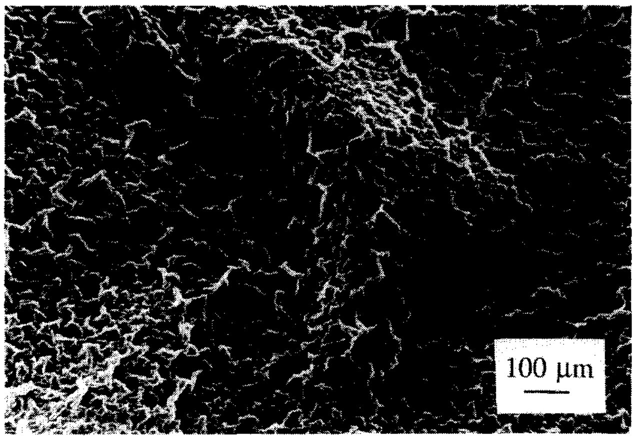

Figure 4 Macroscopic internal delamination in a film of polypyrrole grown from methanol (1.2 V vs. SCE, 1 C)

Internal organization

Delamination and voiding. It is clear from the above discussion that what has been termed 'wrinkling' is a major feature of film growth from methanolic solutions. However, the precise nature of these features, which could be either solid or hollow, cannot be deduced from the external appearance of the films. Previous attempts to study the internal morphology of such samples were confined to the examination of transverse fracture surfaces[7], a procedure that is simple, but potentially prone to bias[28] and the generation of artifacts[29–31]. Whereas polypyrrole films grown from aqueous solutions are continuous in cross-section, similar specimens grown from methanolic solutions appear to show evidence of extensive internal delamination (see *Figure 5a*). However, how such internal features relate to surface features is not clear, and it is possible that the importance of such features may be exaggerated, i.e. the fracture process may unduly bias the transverse surface towards the exposure of internal voids. To address these questions, pieces of film were embedded, sectioned parallel to the plane of the work electrode and etched, as previously described. *Figure 5b* shows the microtomed surface of such a specimen. Where a wrinkle has been cut through during microtomy, it can clearly be seen that the wrinkle is indeed hollow. Thus it can be concluded that the wrinkles seen on the external surface are associated with massive internal delamination that occurs during growth; we do not believe that this corresponds to the porosity that has been reported previously in electrochemically prepared conducting polymers[15,32].

Reference to *Figures 3* and *4* clearly demonstrates that the voids described above develop *after* the polypyrrole precipitates onto the film surface; the polymer does not grow around gas bubbles or pockets of solvent that

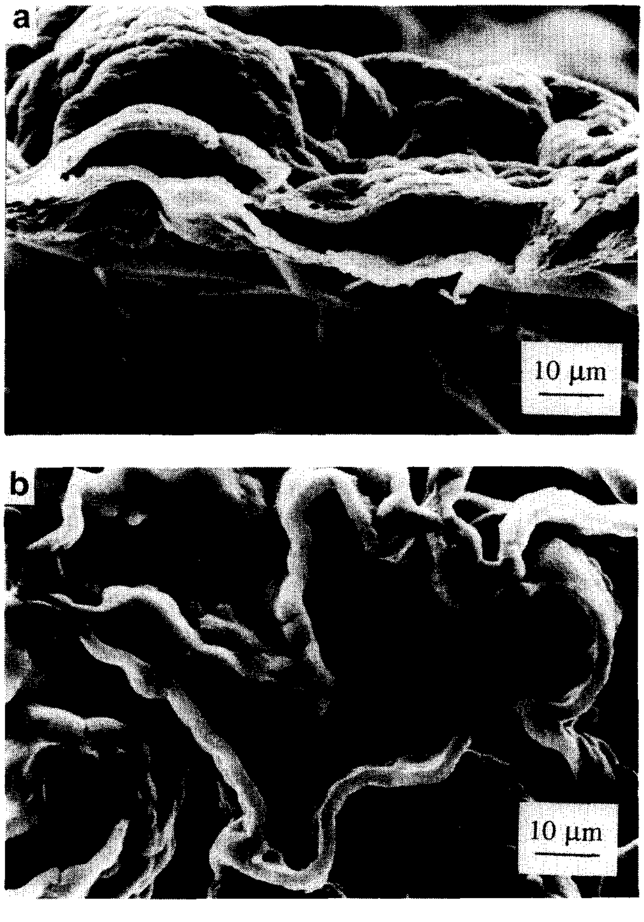

Figure 5 SEM micrographs showing internal delamination within films of polypyrrole grown from methanolic solutions: (a) transverse fracture surface; (b) microtomed and etched surface

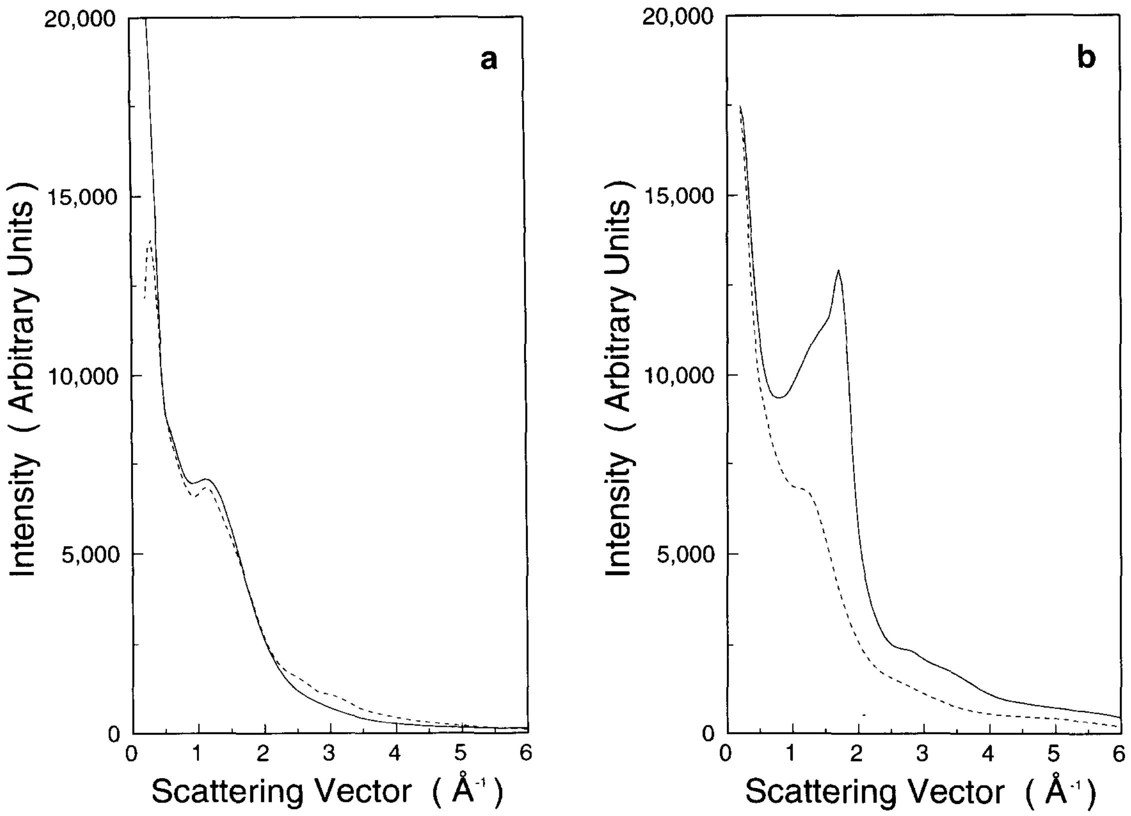

Figure 6 Typical orthogonal X-ray scattering curves from polypyrrole, polymerized (a) from methanolic solution and (b) from aqueous solution. In both cases, the broken curve corresponds to $\chi = 0°$, and the full curve corresponds to $\chi = 90°$

subsequently become incorporated within the film. Rather, we suggest that these features, which correspond to a progressive increase in the surface area of the film with time, result from some molecular reorganization that occurs *within* the film itself. Although little evidence is available to support further speculation, on the basis of the film morphologies, it would appear that internal stresses develop within the film during growth, which are subsequently alleviated by fracture within the plane of the film. Two delamination stages have been observed (compare *Figures 3a* and *4*), showing that these effects cannot be associated with a single process, such as lack of adhesion to the ITO work electrode. The above observations are highly reminiscent of the fracture processes that occur in thin films (compare *Figure 3a* with, for example, figure 35 in the review by Meakin and Skjeltorp[33]). During solvent loss from paint films, for example, shrinkage can result in tensile forces that are ultimately relieved by fracture. Here the converse situation appears to be more appropriate; the overall appearance of the wrinkles is highly suggestive of compressive buckling as a result of an increase in the lateral dimensions of some constituent units within the polymer film. Although much experimental and theoretical attention has been focused on the effects of shrinkage and fracture in a constrained film, we are not aware of any work concerning the consequences of swelling in a thin specimen that is initially attached to a rigid substrate.

Molecular anisotropy. X-ray scattering curves for all the samples grown for 12 C at different applied potentials were collected as described. A representative X-ray scattering curve for a methanolic sample is shown in *Figure 6a*, in which the broken curve corresponds to $\chi = 0°$ and the full curve to $\chi = 90°$. These data, which were obtained from a sample grown at 1.2 V, are typical of those obtained from all the samples grown from methanol; there is a broad peak centred around 1.2 $Å^{-1}$, and comparison of the $\chi = 0°$ and $\chi = 90°$ data reveals little evidence of anisotropy. No discernible trend is evident as the applied voltage is altered. For comparison, *Figure 6b* shows the corresponding X-ray scattering curves for a polypyrrole *p*-toluenesulfonate sample grown at the same applied voltage, but from an aqueous solution. This sample is clearly anisotropic, and similar curves have previously been obtained by Mitchell *et al.*[25,34] and interpreted as showing that the pyrrole rings lie preferentially in the plane of the work electrode, with the counter-ions intercalating between the polymer chains[35]. However, as revealed in *Figure 6a*, films grown from methanolic solutions are, themselves, non-planar. Therefore, in interpreting the above X-ray results, which are obtained from a relatively large scattering volume, two factors must be considered: possible changes in molecular packing within each film; and, in addition, local changes of orientation of the film itself within the X-ray scattering volume. Both factors will appear to randomize the structure and lead to a reduction in the observed anisotropy. Thus, the above cannot, in isolation, be directly interpreted as indicating that films grown from aqueous solution are anisotropic, whereas samples from methanol are entirely isotropic. To determine unambiguously the significance of the WAXS results requires some technique that involves a smaller sampling

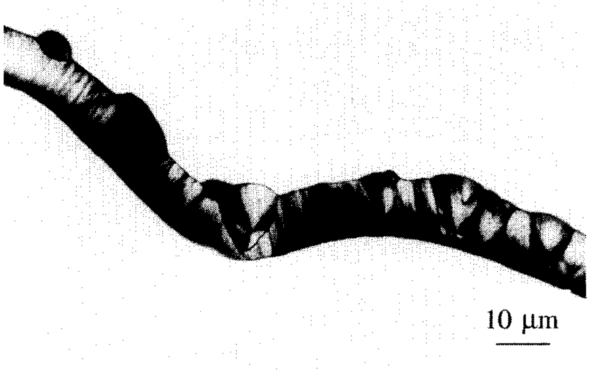

Figure 7 Polarizing optical micrograph showing a transverse section cut from a film of polypyrrole grown from aqueous solution. Although the specimen is viewed between crossed polars, the background appears light as a result of deformation of the embedding medium during ultramicrotomy

volume, enabling spatially resolved information to be obtained.

Optical microscopy. Polarizing transmission optical microscopy provides a powerful means of examining molecular ordering with a resolution ~1 μm. This technique was therefore used to investigate the anisotropy within transverse sections cut perpendicular to the plane of the work electrode. Samples grown from both aqueous and methanolic solutions were examined. Additionally, for samples grown on linear wire electrodes (i.e. samples possessing an interfacial disc), the relative orientation of the polymer chains on the wire and in the disc was also determined.

In view of the X-ray data presented above, optical examination of cross-sections (300 nm in thickness) cut from aqueous films indicates a surprising degree of order. The films are highly birefringent (*Figure 7*), and show maxima and minima in the intensity of the transmitted light as the sample is rotated between crossed polars, and the observed extraction patterns correlate well with surface features. Insertion of a quartz sensitive tint plate (λ-plate) between the polarizer and analyser shows that the sign of the birefringence is independent of the cutting direction; the fast direction always lies in the plane of the film, i.e. the plane in which the molecules lie (from the X-ray data). Thus, the observed birefringence cannot be an artifact of the microtomy procedure. Although attempts to quantify the birefringence proved impossible, because of the limited lateral extent of the polypyrrole within the microtomed sections, simply on the basis of qualitative optical observations such as that shown in *Figure 7*, it would appear that films of polypyrrole *p*-toluenesulfonate prepared from aqueous solution are extremely anisotropic, much more so than would be deduced from the X-ray scattering data described above. The reason for this apparent contradiction concerns the dimensional level being sampled in each experiment. In the WAXS experiment, correlations at the nanometre level are revealed, whereas, optically, anisotropy at the micrometre level is being addressed. In the former case, a slight rotational disordering of the pyrrole rings, for example, would lead to a substantial reduction in the apparent anisotropy of the film, whereas, optically, such a small conformational change would have relatively little effect on the birefringence.

Sections cut from the interfacial disc exhibit similar optical properties to those described above. The material is again highly birefringent (see *Figure 8*), with a fast direction that lies parallel to the air/liquid interface. This simple observation demonstrates that the molecules in the disc again lie within the plane of the feature.

In contrast, examination of sections cut from specimens grown from methanolic solutions appear optically isotropic (non-birefringent) when viewed between crossed polars, and little internal detail is evident. The lack of birefringence supports the assertions made in a previous publication[7], that the films become increasingly disordered (less anisotropic) as the concentration of methanol in the solution increases.

Transmission electron microscopy. Figure 9 contains a TEM micrograph in which a cross-section cut from a film of polypyrrole *p*-toluenesulfonate, grown from aqueous solution, can be seen. In this figure, a large nodule is apparent, together with a smaller nodule that appears to be growing from within the larger structure.

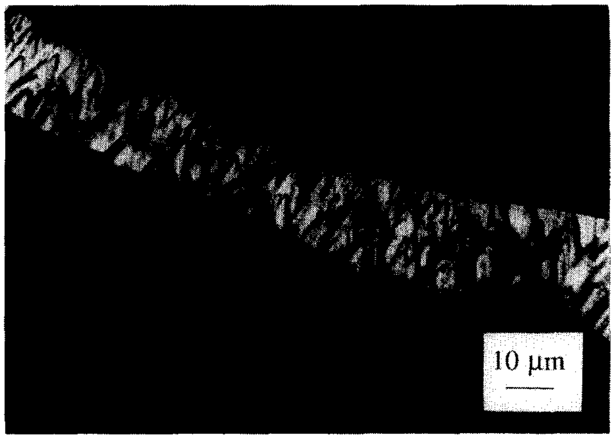

Figure 8 Polarizing optical micrograph showing a transverse section cut from the disc of polypyrrole that develops at the air/liquid interface. The polypyrrole again appears highly birefringent

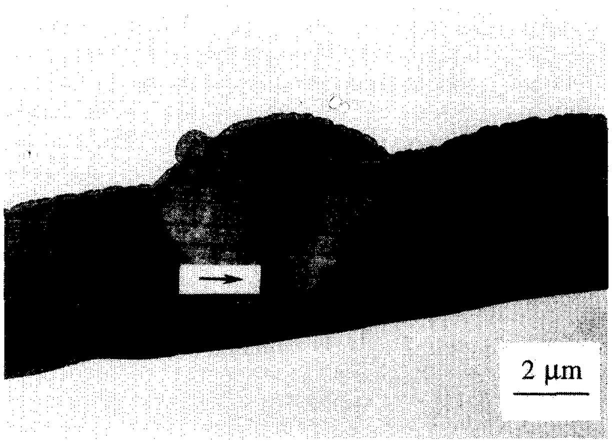

Figure 9 Bright-field transmission electron micrograph showing a transverse section through a film of polypyrrole polymerized from an aqueous solution

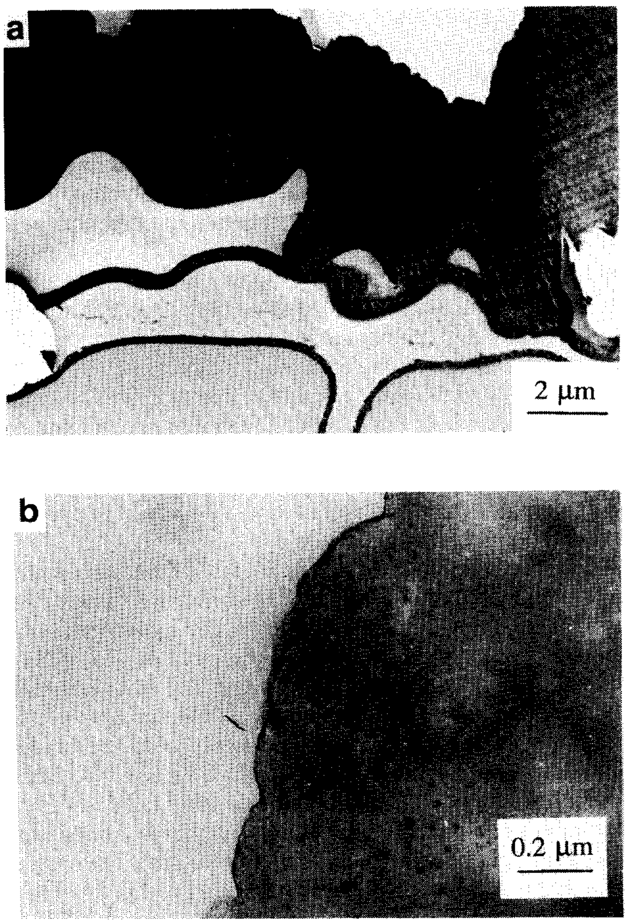

Figure 10 Bright-field transmission electron micrographs showing transverse sections through a film of polypyrrole polymerized from a methanolic solution. In (a) extensive delamination is evident and in (b) a dark layer is visible along the interface between the polypyrrole and the embedding resin

The boundary between the nodule and the surrounding film appears sharp and continuous, whereas the boundary between the two nodules is not so well defined. The parallel lines running across the section show damage caused by the microtomy process. A faint radiating texture can just be discerned within the large nodule, which appears to be emanating from the elongated dark region (arrowed). This micrograph illustrates all the features that are typically seen within a nodular structure when it is examined by TEM (well defined boundaries, radial streaking and a source for the radiating texture). In addition, at both surfaces of the film, the morphology appears to differ from that of the bulk: granular layers are evident. Although there are reports in the literature to suggest that the cross-sections of electrochemically polymerized conducting polymers may not be structurally or compositionally uniform[36–38], in this case, the layers that appear in *Figure 9* are believed to be a geometric effect that is associated with inclination of the polypyrrole film relative to the electron beam. These surface layers disappear when the sample is tilted. Although considerable internal structural variation is clear from *Figure 9*, interpretation depends entirely upon the means by which the contrast is imagined to come about. Since scattering of electrons is related to atomic number, then the radial streaking may correspond to areas of the specimen that contain heavier atoms (so-called *Z*-contrast). Thicker regions will similarly scatter more electrons. Finally, there is the possibility of diffraction contrast resulting from localized Bragg scattering of the electron beam. Nevertheless, whatever the detailed explanation of the contrast seen in the TEM, it is clear that there are considerable spatial variations in chemical composition and/or supermolecular ordering within the polypyrrole polymerized from aqueous solution. This variation is currently undergoing detailed investigation.

Examination of sections cut from films grown from methanolic solution do not reveal the same degree of internal order (see *Figure 10*); for example, no internal boundaries are evident. However, *Figure 10a* does reveal that this film is composed of three distinct layers (~ 150 nm, ~ 370 nm and $\sim 4\,\mu$m in thickness), which contact with one another only at a few localized sites. As can be seen in *Figure 10a*, the two thinner layers appear to be of approximately uniform thickness. Variations in the apparent thickness of the surface layer are thought to be caused by local changes in orientation of the folded regions, and hence this effect is again thought to be geometrical rather than structural in origin. Finally, examination of the growth surface (*Figure 10b*) reveals some evidence of a very thin (high contrast) surface layer (up to 10 nm in thickness) that appears to differ in some way from the bulk.

Thus the internal morphology of samples grown from different solvents is very different and, we suggest, is best explained by a change in the growth process of the films in going from one solvent to the other. As we reported previously[7] for samples grown on linear wire electrodes, the disappearance of the disc-like growth at the air/liquid interface is, similarly, taken to indicate a significant change in the growth process in going from one solvent system to the other.

DISCUSSION

From the results presented above, it is clear that changing the solvent from water to methanol (but keeping other imposed electrochemical parameters constant) has a very significant effect on the morphology of polypyrrole *p*-toluenesulfonate. In the methanolic films, the surface wrinkling and loss of molecular anisotropy closely mirror the effect of changing the anodic potential in aqueous films[10]. However, the invariance of surface wrinkling and the persistently isotropic internal ordering in all methanolic films described here (1.2–3.0 V vs. SCE) both strongly support previous assertions that such phenomena cannot be explained simply in terms of changes in the oxidation potential of the pyrrole monomers as a consequence of changing the solvent. Additionally, the variation in internal morphology and the presence of the interfacial disc in only the aqueous system similarly suggest that the two different film groups have developed in a fundamentally different manner. Although the data presented do not lead clearly and unambiguously to any one conclusion, we feel that some speculation concerning its interpretation is necessary. Consider first the polymerization and growth of polypyrrole films grown from aqueous solution.

Pyrrole monomers first react together in solution to

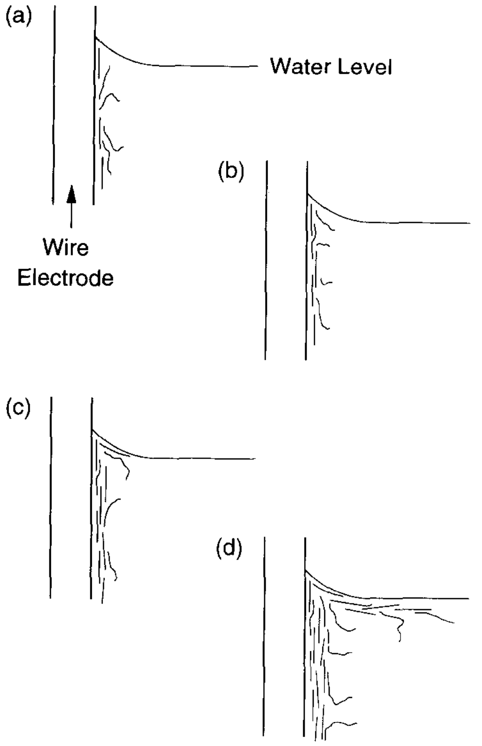

Figure 11 Schematic diagram showing the development of the interfacial disc via collapse of solvated chain ends

build up molecular chains. These oligomeric structures will remain solvated until some critical length is exceeded, at which point precipitation onto the work electrode will occur. If chain polymerization were to continue on the work electrode following precipitation, the polymer chains (plus any associated counter-ions) need not necessarily be immediately confined to the plane of the work electrode; the chains could continue to develop in a loose gel-like layer between the mature polymer film and the growth solution[39]. After partial attachment to the electrode surface, further polymerization may then occur until the growing chain end becomes too long to remain solvated, at which point, precipitation of additional segments will occur. Clearly, the extent to which this occurs will depend on the solvent's ability to solvate the chain ends and prevent them from depositing onto the electrode surface.

Growth along interfaces can easily be explained if polymerization were to continue at the film surface. As the polymer chain end grows by reacting with species still in solution, the chain will become too long to remain solvated at some critical length (L_c), whereupon the chain, or part of the chain, will tend to precipitate from solution. This critical length will depend upon interactions between adjacent segments in the polymer chain and other interactions with molecules and ions in the solution. In the case of aqueous polymerization, the water is likely to be a relatively poor solvent for polypyrrole and L_c is therefore likely to be small. Assuming that interactions between polypyrrole molecules are favoured, compared with interactions with water, it is easy to see why precipitation of growing chains would occur onto a polypyrrole substrate. However, morphological examination of polypyrrole prepared under differing electrochemical conditions suggests that many interfaces constitute acceptable sites for precipitation. In a recent publication, Shapiro and Smith[27] reported on the growth of polypyrrole along insulating surfaces. They observed that, whereas film growth occurs along poly(methyl methacrylate), linear polyethylene, polytetrafluoroethylene, etc., lateral development does not occur along glass; the precise interaction energetics therefore appear to be important. During the study described here we also noted this tendency for growth along insulating interfaces, and suggest that growing, solvated chain ends may provide a mechanism whereby films may develop in this way. Once L_c is reached, a portion of the chain will collapse and form a conducting nucleus on the insulating interface, upon which subsequent thickening growth will occur by precipitation of oligomers from solution. In parallel, lateral development will continue, as further solvated chain ends collapse. This process is shown schematically in *Figure 11*.

As described above, the use of methanol as the electrolyte suppresses the growth of the interfacial disc, possibly as a result of a change in the polymerization process, to a regime where the extent to which polymerization continues after precipitation is reduced. This could occur as a consequence of changes in the interactions between the oligomers, polymer molecules, counter-ions and the solvent. Although we are not aware of any data concerning the relative magnitudes of the interaction parameters between polypyrrole and water, and polypyrrole and methanol, the organic nature of methanol suggests that the interactions will be more favourable in this case. Therefore, in methanol, polymerization in solution is likely to be enhanced, since this solvent should be more compatible with polypyrrole than is water. However, in general, the availability of suitable species to provide and solvate protons during polymerization[40] will be reduced in methanolic solutions. In acetonitrile, it has been shown that the presence of water markedly influences film growth, presumably for this very reason[19]. This factor is likely to be particularly significant where the extent of polymerization reactions is greatest, i.e. near the electrode surface. Hence, for both of these reasons, where polymerization occurs from a solvent system that has appreciable organic character, growth in solution followed by precipitation may be favoured over early precipitation followed by subsequent molecular extension on the electrode surface.

Although the above discussion has been phrased in terms of polymer–solvent interactions, in reality, interactions with solvated ions are also likely to be important. Kassim *et al.*[41] have recently proposed that the variations in the hydrophobic or hydrophilic nature of the counter-ions have an important influence on the mechanism of film growth during aqueous polymerization. These workers have also proposed that, where polymer/dopant/solvent interactions are favoured, the polypyrrole remains partially solvated after attachment to the work electrode.

A reasonable qualitative model can therefore be proposed for film growth from organic and aqueous solutions. However, the mechanism by which the observed delamination occurs is not clear, although volume instability effects have been reported in conducting polymer gels[42], and Qian has proposed that wrinkled surface morphologies of the type reported here can come about as a consequence of changes in the chain conformation associated with chemically induced deprotonation after polymerization[40]. This effect may, therefore, similarly be associated with changes in molecular conformations or composition within some solvated interphase region, or even within the bulk polymer, after deposition on the electrode.

CONCLUSIONS

Observations of both the morphology and internal ordering within films of polypyrrole *p*-toluenesulfonate grown from aqueous and methanolic solutions reveal significant differences, which imply much about the polymerization process in the two solvents.

Films grown from aqueous solution are continuous in cross-section, whereas films grown from methanol delaminate into a number of distinct layers. Two delamination stages have been observed directly, by following the development of the film as progressively more charge is passed through the electrochemical cell.

Optical examination of cross-sections has revealed significant ordering in the films grown from aqueous solution (on the scale of micrometres). Conversely, the optical examination of films grown from methanolic solution reveals no evidence of local anisotropy. These observations are in broad agreement with X-ray scattering data and the conductivity measurements reported previously[7], which also infer a reduction of molecular order for samples prepared from methanol as solvent.

If polymerization only occurs in solution, followed by precipitation onto the work electrode, it is difficult to envisage a method whereby features such as the interfacial disc (which only forms from aqueous solutions) could develop. However, if growth of the polymer chains were to continue on the electrode surface, then these features are much more easily explained. It is therefore proposed that, in aqueous solutions, further polymerization of the polypyrrole molecules occurs after precipitation, whereas, in methanol, polymerization of pyrrole in solution followed by precipitation is the principal means of film growth. This change in the mode of growth comes about as a consequence of changes in the polypyrrole/counterion/solvent interactions near the surface of the growing film.

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