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Morphology and molecular ordering in films of polypyrrole *p*-toluene sulfonate

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The molecular ordering in films of the conducting polymer, polypyrrole *p*-toluene sulfonate, has been investigated by using electron microscopy and optical dichroism. Various morphological forms have been observed, which we propose can only develop if the polypyrrole chains can continue to grow while still attached to the work electrode. Furthermore, we suggest a model that explains the development of these new features, and which may also explain the formation of fibrillar structures in other conducting polymer systems. Crown copyright © 1996 Published by Elsevier Science Ltd.

(Keywords: polypyrrole; electron microscopy; electrochemical polymerization)

INTRODUCTION

Since the discovery of the conducting properties of polypyrrole in 1979[1], numerous studies have been performed on this polymer and a whole range of related polymeric materials that display electrical conductivity. Although the effects of many physical and chemical parameters have been investigated, a characteristic that does not vary greatly throughout all these studies, is the morphology that results from the electrochemical polymerization process. Such films have either compact nodular surface structures or open fibrillar morphologies (*Figure 1*).

The electrochemical polymerization of polypyrrole results in free-standing films, which exhibit a surface morphology that is usually described as either nodular[2] or dendritic[3] (*Figure 1a*). Although the precise appearance depends upon the conditions under which the specimens were prepared, the general pattern of growth (on solid planar electrodes using conventional electrochemical techniques) is of a continuous dense film immediately adjacent to the electrode, which subsequently degenerates into the commonly reported nodular surface morphology. Polyaniline is another material that has been extensively studied. In contrast to polypyrrole, the electrochemical polymerization of aniline gives films which are either fibrillar (*Figure 1b*) or granular[4–7], depending upon the conditions employed.

In this present paper we describe the various morphological forms seen in polypyrrole *p*-toluene sulfonate films that have been prepared via a one-step electrochemical oxidation process. Some of these features can be seen in the micrographs from other researchers, although, due to the particular emphasis of their studies, the presence and significance of these 'new' features have been largely overlooked. One of these forms has a considerably increased surface area which could be highly significant when considering potential uses for these materials, and, furthermore, may also shed light on the development of fibrillar morphologies in other systems such as polyaniline.

EXPERIMENTAL

Films of polypyrrole with *p*-toluene sulfonate as the counter ion were prepared via a one-step electrochemical oxidation process from aqueous solution, as described elsewhere[8,9]. The work electrode was either a piece of indium tin oxide (ITO) glass, or gold sputter-coated glass; the counter electrode was a carbon rod, with the reference electrode being a saturated calomel electrode (SCE). For all of the samples considered here, the anodic potential was maintained at a constant 1.2 V (vs. SCE) during the growth of the films, and growth was generally terminated after a total charge of 12 C has passed through the electrochemical cell. Following polymerization all of the specimens were thoroughly washed with distilled water and then acetone. The specimens to be sectioned for optical dichroism and transmission electron microscopy (TEM) measurements, were prepared as follows. Strips of polypyrrole *p*-toluene sulfonate film were placed in gelatin capsules which were then filled with LR white embedding medium (supplied by The London Resin Company)[10,11]. After curing, the samples were cut from the resin blocks in preparation for ultramicrotomy. Sections, 80 nm thick, were cut for TEM, while optical observations were performed on 300 nm thick specimens. Scanning electron microscopy was performed using a Philips SEM 515 microscope after sputter-coating the polymer with gold.

RESULTS

'Elongated' growths

Figure 1a shows the growth surface of a polypyrrole

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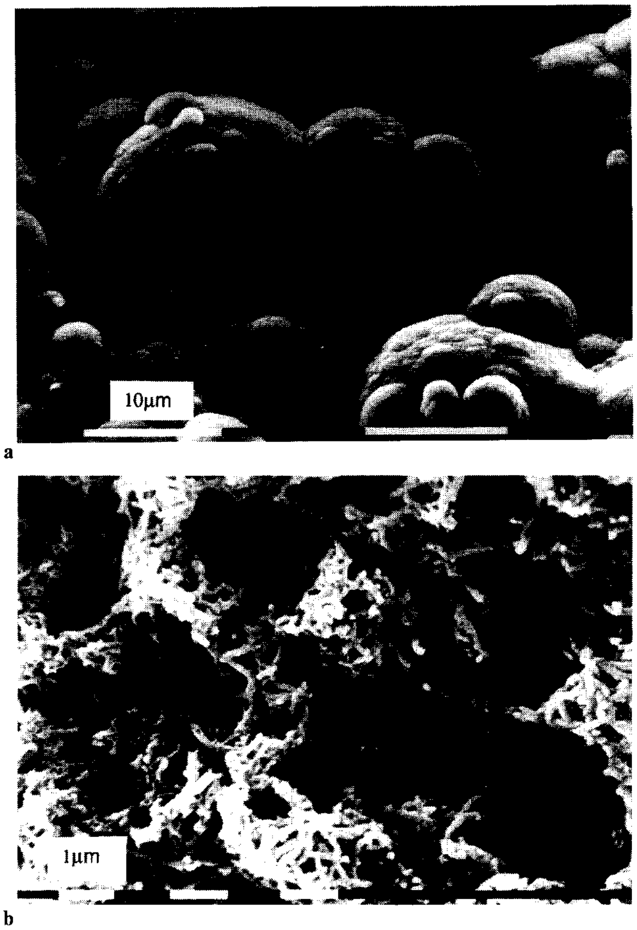

Figure 1 Scanning electron micrographs showing (a) nodular surface morphology of a film of polypyrrole *p*-toluene sulfonate, and (b) fibrillar surface morphology of a film of polyaniline

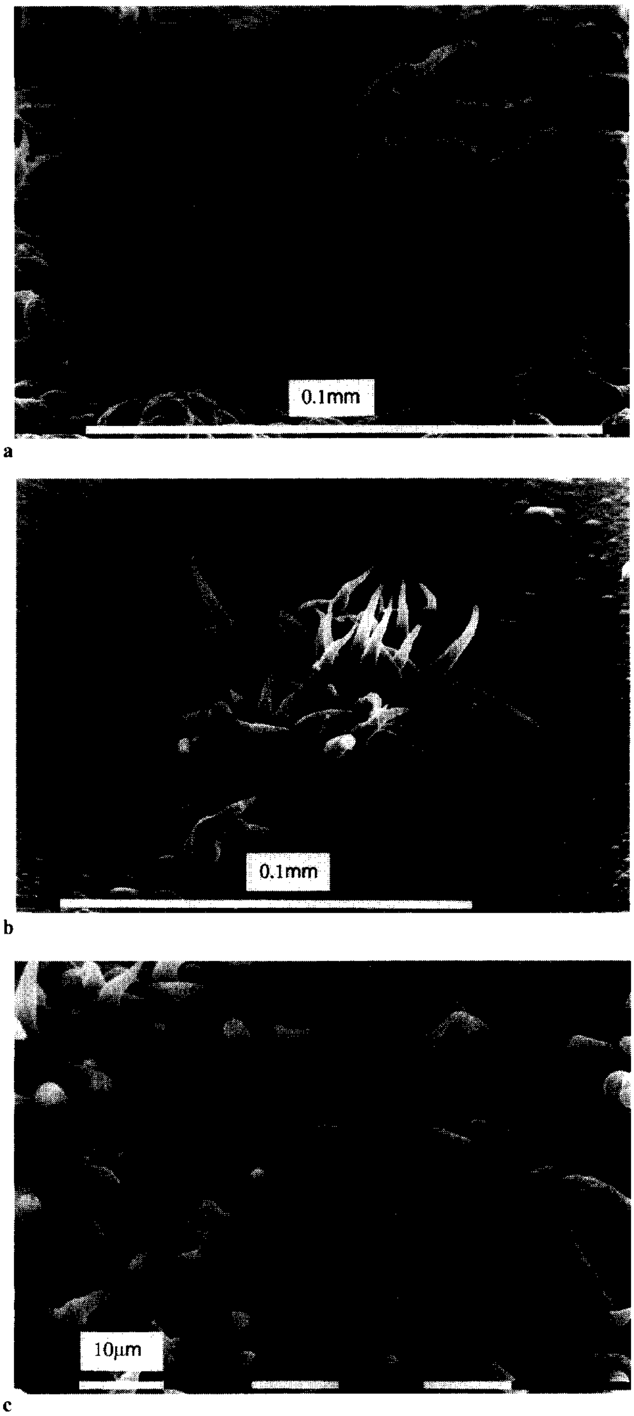

Figure 2 Scanning electron micrographs of (a) individual elongated tentacle-like growths, (b) clusters of similar growths developing from the surface of the polypyrrole *p*-toluene sulfonate film, and (c) a film almost entirely covered with these growths

p-toluene sulfonate film, in which the typical 'cauliflower-like' nodular structure can be seen[2,8,12]. However, in addition to this usually reported surface morphology another morphological form is often found, as shown in *Figure 2*. After 12 C of charge have passed through the cell, these elongated tentacle-like growths are ca. 60 μm in length on a basal film which is only ca. 10 μm in thickness; they may occur either singularly (*Figure 2a*), in clusters (*Figure 2b*), or *en masse* over the film surface (*Figure 2c*). The polypyrrole film around these growths appears completely normal, displaying the usual nodular-type morphology and, even when the surface is almost entirely covered with these features, nodules can still be detected in the gaps. These elongated growths can also be seen in the micrographs of Iyoda *et al.*[13] (although these authors make no mention of the presence of these features), and those of Maddison and Unsworth[8], who refer to occasional 'barb-like' features on some samples grown under specific conditions. These 'barb-like' features[8] would seem from our studies to be immature versions of the growths shown in *Figure 2*. For convenience, these features have become known as 'icing', due to their shape in the early stages of development. These structures exhibit two types of surface morphology. Although in *Figures 2b* and *2c* the surface appears smooth, a closer inspection reveals that the surfaces have a very fine granular structure on the scale of 0.1 μm. In contrast, *Figure 2a* shows the other case, where the 'icing' is totally covered with the nodular growths that are normally associated with the base film. Clearly these features differ significantly from the basal film, although what causes the usual mode of growth to change so dramatically is not totally understood. The existence of a diffusion gradient caused by a depletion of polymerizable species at the work electrode could, for example, lead to interfacial instability, much as in the theory of cellation in binary alloys[14]. Nevertheless, this does not explain the varying degrees of surface coverage, an often non-uniform distribution of such growths across the sample surface, and the marked variation from sample to sample grown under, as far as we can tell, identical conditions. Additionally, Scharifker *et al.*, through careful electrochemical experimentation, have dismissed diffusion as a factor affecting the growth of polypyrrole films[15].

In order to clarify the following discussion, the word 'orientation' is used here to describe the molecular trajectory relative to the work electrode, while 'arrangement' describes the arrangement of the molecules within the film or 'icing' relative to the local surface. It may be inferred, from the observation that the surface morphology of the 'icing' and the basal film is primarily the same, that the molecular arrangements in both are the same. The optical dichroism of a 300 nm section from a polypyrrole *p*-toluene sulfonate film is shown in *Figure 3*. When the basal film is aligned parallel to the polarizer (direction arrowed: *Figure 3a*) the basal film appears dark, while the 'icing' growth (labelled as I), which is growing approximately at right angles to the film and hence aligned at right angles to the polarizer, appears light. Rotating the sample through 90° (*Figure 3b*) reverses the contrast within the specimen, i.e. lighter regions become darker, and vice versa. Additionally, close examination shows that the dichroism associated with the 'icing' growth extends into the basal film; well defined boundaries exist between the two regions, which appear to originate from a point. A dark internal boundary, which is invariant to the sample orientation, runs along the length of the 'icing' dividing the growth into two halves. These micrographs show clearly that the molecules in the film and the 'icing' have different molecular orientations, which are approximately perpendicular to each other. In view of previous electron diffraction[11], X-ray[16,17], and neutron scattering[18,19] studies, it can therefore be concluded that in all cases the polypyrrole molecules and *p*-toluene sulfonate counter ions lie approximately parallel to the growth surface.

Although highly informative, optical dichroism in polypyrrole is limited by poor light transmission, and poor angular sensitivity, i.e. the film still appears significantly dark when not aligned exactly along the direction of the polarizer. This affects the certainty with which small variations in the molecular arrangement in different parts of the sample can be determined. Better spatial resolution of the molecular arrangements may in principle be achieved by using electron diffraction. Minto and Vaughan[11] (in contrast to comments made by Geiss *et al.*[20]) have shown that polypyrrole *p*-toluene sulfonate samples are moderately beam stable, and do not suffer from significant mass transport or degradation of diffraction patterns for reasonable periods. This technique therefore constitutes a viable means of probing the local molecular order in this material. *Figure 4* shows a bright field TEM image of a section from an embedded polypyrrole *p*-toluene sulfonate film which includes a longitudinal section (I) through an 'icing' growth. From this it is clear that these features develop as an integral part of the basal film (F) and are not an artifact. The inserted electron diffraction patterns taken from the areas indicated show strikingly that the molecular organization is partially ordered on a local scale. This result is in agreement with previous electron diffraction studies[11,20], but certainly would not be expected from published X-ray or neutron scattering data[16–19,21], where the latter generally report these materials to be disordered solids. Nevertheless , this contradiction (and the high optical birefringence seen in sections of polypyrrole *p*-toluene sulfonate[22,23]), can be explained by the manner in which these techniques probe the structure. Electron diffraction probes correlations of the order of intermolecular spacings over the restricted area of the electron beam, whereas X-rays average similar correlations, over the entire area of the beam, which is typically ca. 1 mm in diameter. Since, as will become apparent in the following section, the molecular orientation at different places within the film varies, and due to the manner in which X-ray and neutron scattering data are collected from stacks of polypyrrole films[16–19], the overall effect is to reduce the observed order within the films.

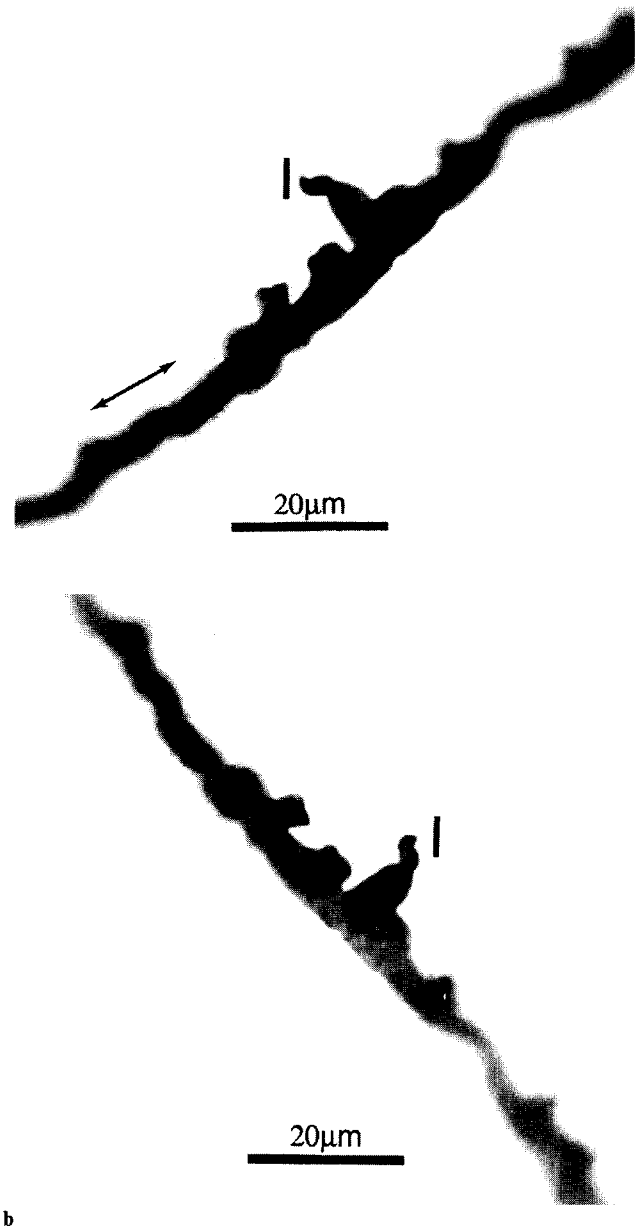

Figure 3 Optical micrographs showing dichroism in a 300 nm section from a polypyrrole *p*-toluene sulfonate film displaying an 'icing' growth (labelled I), with the basal film aligned (a) parallel to the polarizer, and (b) perpendicular to the polarizer

An electron diffraction pattern taken from an area

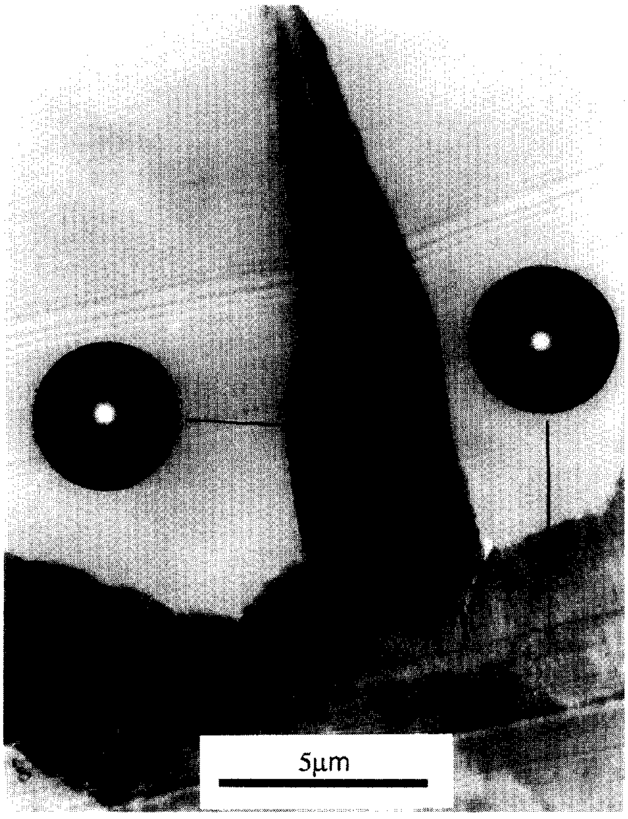

Figure 4 Bright field transmission electron micrograph from an 80 nm thick section of a polypyrrole *p*-toluene sulfonate film showing a longitudinal section through a piece of 'icing': the basal film is labelled as F and the 'icing' growth labelled as I. The insets show the electron diffraction patterns from the indicated areas

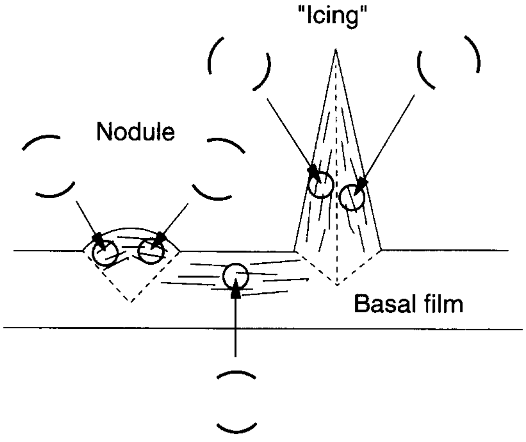

Figure 5 Schematic diagram showing the molecular arrangements in the different regions of a polypyrrole *p*-toluene sulfonate film, where the lines represent the molecular trajectory as determined by electron diffraction

within the basal film (*Figure 4*) clearly indicates that the molecules are arranged approximately parallel to the electrode surface, and hence, also approximately parallel to the film surface. Similarly, the molecules in the 'icing' growth are arranged approximately parallel to the sides of the feature. As such, the dark line running along the length of the 'icing' growths in *Figure 3a* may correspond to a discontinuity lying along the axis. Considering that the molecules within these two parts of the films are growing in approximately perpendicular directions, the local molecular ordering, as measured by the arcing in the diffraction patterns, is remarkably similar. Thus, it would appear that the same mode of growth in these two areas has caused the same local molecular arrangements, and produced the same surface morphology.

Figure 5 shows a schematic diagram summarizing the molecular orientations in each of the distinct regions of a polypyrrole film, i.e. the basal film, nodules[11] and 'icing' as determined by electron diffraction, and inferred from optical dichroism and birefringence observations[22]. Internal discontinuities within films of polypyrrole *p*-toluene sulfonate have previously been observed[11,22] by using both TEM and optical microscopy. Recently, Wallace and coworkers[23] have produced similar micrographs and, furthermore, have shown that during tensile tests polypyrrole *p*-toluene sulfonate tends to fail along the internal boundaries associated with nodules within the film. (These results in no way contradict our own data on rapid fracture in polypyrrole films[24].) A well defined morphology such as this, implies a growth mechanism that is far more complex than that normally attributed to polypyrrole, namely the growth of chains in solution, followed by precipitation of the chains on to the work electrode[15,25–28]. First, there is no apparent reason why the molecules of the basal film should reorientate to grow away from the work electrode to form 'icing' growths. Secondly, simply from their aspect ratio, the rate of development along the length of the 'icing' is clearly much greater than the lateral growth rate.

In summary, the above discussion concerns a form of growth of polypyrrole which has not been described in detail before. These features, we believe, are not merely curiosities but may provide an insight into the fundamental growth mechanisms which lead to the morphological variations seen in electrochemically polymerized conducting polymer systems, and may also have potential practical applications. Clearly, films covered with large amounts of 'icing' possess an extremely high surface area. The actual surface area of a nodular polypyrrole film, compared to a smooth work electrode of identical lateral dimensions, is approximately 50 times greater[29]. Approximating the 'icing' as cones, a simple calculation implies a further increase in surface area by a factor of 15 times, for a surface which is entirely covered with 'icing' growths (with the dimensions in *Figure 2a*), when compared to the normal nodular film. Hence, the actual increase in surface area for a film covered with 'icing', as compared to a smooth work electrode, is of the order of 750 times. Consequently, such films could be of great importance when considering some potential uses of conducting polymers. For example, let us consider the application of conducting polymer films as sensors[30]. This relies on the diffusion of chemical species into and out of the film to produce large changes in electrical conductivity. The response time of such devices is ultimately controlled by diffusion processes and, as such, an increased surface area could be one simple way of improving this parameter.

Interfacial discs

A related morphological phenomenon has recently been discussed by us, namely the radial growth of

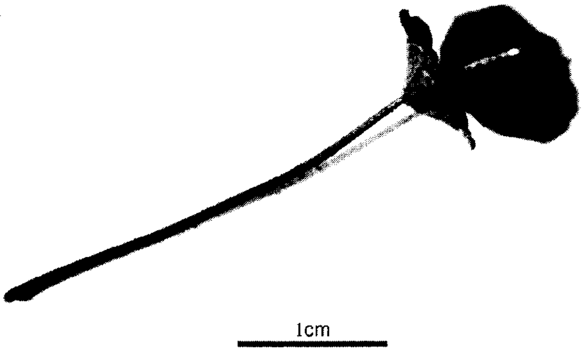

Figure 6 Stereo optical micrograph showing the growth of polypyrrole on a wire electrode. Film growth has occurred on the wire and also along the air/solution interface, thus resulting in a disc-shaped feature

polypyrrole *p*-toluene sulfonate along an air/liquid interface from a Pt/Pd wire work electrode (*Figure 6*)[22]. Optical measurements showed that the polypyrrole molecules within this feature are oriented orthogonally to the wire work electrode (i.e. the molecules are arranged in the plane of the disc), whereas those on the work electrode are arranged parallel to its surface. As in the 'icing' features discussed above, this morphological form is also therefore characterized by molecular reorientation relative to the film on the work electrode, and possesses an aspect ratio which indicates relatively rapid growth in the plane containing the molecules.

For these disc-shaped structures, it was proposed that growth occurs in two different manners. First, rapid growth occurs along the air/liquid interface by the addition of polymer growing from the edge of the disc, and then, secondly, thickening occurs by the deposition of polymer from solution uniformly across the disc. This leads to a tapered cross-section and effectively a chronology of polypyrrole growth from the edge of the disc to the centre, i.e. the thinnest and newest material at the edge, and the thickest and oldest material at the centre.

Bulbous growths

Figure 7 shows two other related features which grew on gold-coated glass electrodes. One is large and bulbous and completely closed (*Figure 7a*), while the other, although similar in shape, is open at one end (*Figure 7b*). These features stand nearly 300 μm high, on top of a film which is only 10 μm thick, i.e. these features would appear to have developed at a rate which is 30 times that of the underlying film. The outside wall of the closed growth is ribbed, with the normal nodular structure superimposed. Conversely, the open growths, although ribbed, exhibit a nodular appearance which becomes less marked on proceeding from the base towards the open end; here the surface only has very small nodules, and is suggestive of polypyrrole in the early stages of film development. The inner wall is smooth and featureless, except for the ribbing.

Careful observation during the electrochemical synthesis of these samples shows that small gas bubbles form on the work electrode surface, presumably as a result of the increased current density that results from using gold-coated electrodes in place of ITO glass. We propose that the growth of polypyrrole around these bubbles subsequently results in the features described above. In the case of *Figure 7a*, the entire bubble has been engulfed by the conducting polymer film, whereas in *Figure 7b* polymerization was terminated before this point was reached. The variation in surface morphology between the top and bottom of the growths is analogous to the variation between the centre and edge of the disc-shaped growths[22], namely the top of the growth has only just formed, while the bottom part, i.e. next to the work electrode, has been growing for the longest period of time. Hence, these features are entirely analogous to the disc-shaped growths discussed by us previously[22]; in both cases, growth has occurred progressively along the gas/liquid interface. Due to the very thin walls of these bulbous growths, it has not been possible to investigate the molecular arrangements within these features by TEM or optical microscopy. Nevertheless, the similarity in both the appearance and mode of development (compared to the disc-shaped growths) would seem to imply that the molecules are arranged similarly in both arrangements, and as such, we propose that the polypyrrole molecules have reorientated from being parallel to the work electrode surface (in the basal film) to parallel to the gas/liquid interface.

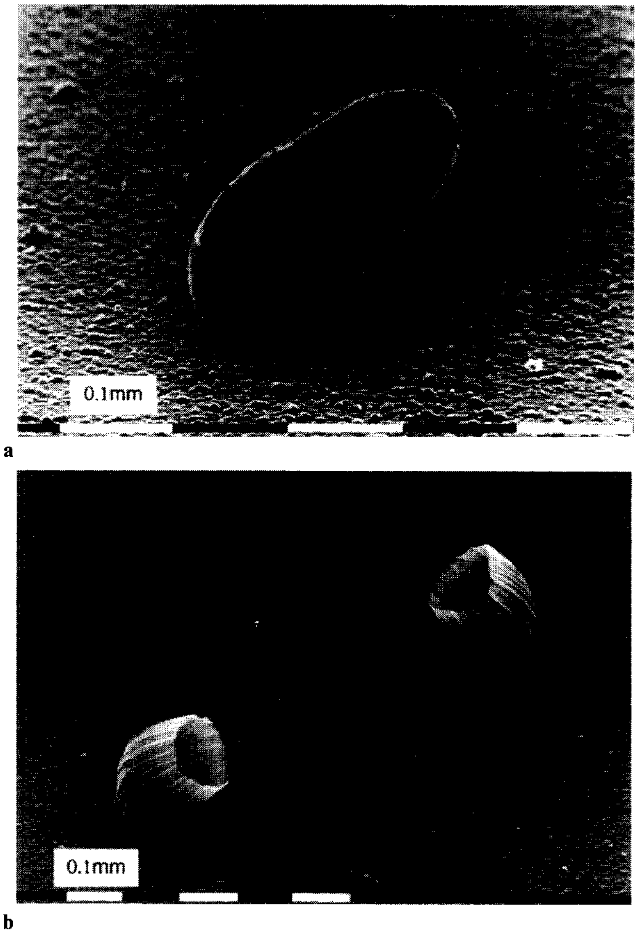

Figure 7 Scanning electron micrographs of (a) a large bulbous ribbed feature, and (b) two large open-ended ribbed features developing on the surface of a polypyrrole *p*-toluene sulfonate film

The observation of growth around gas bubbles may help to explain the appearance of polypyrrole films grown by others in ITO electrodes, when high current densities have been employed. Such conditions result in films which are covered in many spherical growths, each displaying the normal nodular surface appearance (for example, see Figure 5 in ref. 2). However, there is one significant difference between the features described above and those reported by others. In our work, these large objects have been produced with a small potentiostatically applied voltage (1.2 V), with the increased current density being caused by a change in the work electrode material, whereas, for samples grown galvostatically on ITO electrodes, increasing the current also increases the applied voltage. This may explain why in this case we have a few large objects, as compared to many much smaller objects, which have presumably formed around many smaller bubbles.

Summary of results

In the above sections, a wide range of morphological forms have been described. Despite their apparently disparate nature, we propose that they nevertheless develop by related modes of growth. For all of the features described in this paper, growth in the plane containing the polypyrrole molecules occurs much more rapidly than growth perpendicular to this plane. It should be noted that the plane containing the polypyrrole molecules varies from place to place throughout the film (as electron diffraction has shown) and, more precisely, it is rapid growth along the chain trajectory that is the recurrent theme.

A propensity for polypyrrole to grow along interfaces is a feature which we have repeatedly observed under different growth conditions[31]. This has also been reported recently by Shapiro and coworkers[32,33], who have described the growth of polypyrrole across various non-conducting materials in a thin film cell. Growth did not occur across all of the materials, e.g. glass inhibited the growth. These authors have proposed that the absorption of monomers on to the substrate surface acts as a route for the nucleation of oligomers depositing from solution. A similar route for nucleation has been proposed by other workers[34], but has been opposed by other studies[35–37]. This explanation, along with other issues regarding the growth of polypyrrole films, remains contentious and is discussed further below.

DISCUSSION

In the cases of both 'icing' and the bulbous growths, the molecules within the features have reorientated relative to the underlying basal film and, subsequently, the rate of growth in the plane containing the molecules has been higher than the rate of thickening. Additionally, it has frequently been observed that, at the start of electrochemical polymerization, small islands of polypyrrole form on the work electrode and then rapidly spread to cover the entire surface. The growth of polypyrrole films can therefore be considered to be a two-stage process. First, the deposition of the primary polypyrrole layers/nuclei occurs, either via polymerization of absorbed species on the work electrode[33,34], or by the deposition of oligomers (polymerized in solution) on to the work electrode[35–37]. The second stage concerns how these sites then develop; possibilities include the random deposition of chains forming in solution, preferential deposition of chains at growth centres, or the continued growth of already deposited chains on the electrode. Many workers support the idea of nucleation and growth (see ref. 38, and references therein), i.e. growth from preferred sites. Nevertheless, the term 'growth' is often used in an unclear manner, with authors not stating clearly whether they mean the growth of a polypyrrole chain on the work electrode, or growth of the nucleated site by the addition of oligomers precipitating from solution, thus increasing its size but not the molecular weight of the chains.

Consider the growth of the large open bulbous features or the interfacial disc[22]; here there is no electrode on which the films could grow, only the previously deposited polypyrrole film. Nevertheless, the rate of growth in the plane of the film is very much greater than the rate of thickening. If growth were to occur only by the deposition of oligomers from solution, then this observation would imply that deposition at the edge of the feature is highly favoured over precipitation on to the existing polypyrrole surface. In contrast, if monomers were absorbed on to the air/liquid interface, then growth in the plane could proceed as suggested by others[25,33,34], via the polymerization of these monomers at the edge of the feature. The monomers could either join on to the already deposited chains in the film, or react together and produce effectively another nucleation site. Clearly, monomers would not be able to react ahead of the advancing film, since there would be no electrical path back to the electrode. Thus, the film would enlarge in the plane of the molecules by the successive addition of monomers/oligomers at the edge of the feature, and thickening would subsequently take place through the precipitation of oligomers from solution on to the film.

In the case of 'icing' the situation is fundamentally different. These features are growing entirely surrounded by electrolytic solution, there is no interface and, thus, there can be no absorbed monomers to influence their development. Nevertheless, the rate of growth in the plane of the molecules is still much higher than the rate of thickening, although less so than where there is the influence of an interface. Although this seems to imply that absorption of monomers on to the substrate (e.g. the gas/liquid interface or the surface of a bare work electrode) may well be a factor in film growth, the very fact that 'icing' exists in the absence of an interface clearly suggests that other processes must also be operative. Thus, for these features to develop faster in the plane of the molecules, preferential growth must be occurring along the chain axis, either by preferential deposition of oligomers at the tip of the 'icing' or by the reaction of monomers/oligomers with the chain ends of the polypyrrole molecules that have already deposited. The former case seems unlikely, since the feature is composed entirely of polypyrrole molecules and *p*-toluene sulfonate counter ions, and is surrounded by an isotropic electrolytic solution. As such, the possible sites for a chain to deposit should be equally favoured and therefore random precipitation would not result in features of the observed shape. If, however, the growth of chains were to continue after deposition, then this behaviour, combined with the additional precipitation of chains from solution can lead to the observed shape. We have previously proposed such a method of growth to

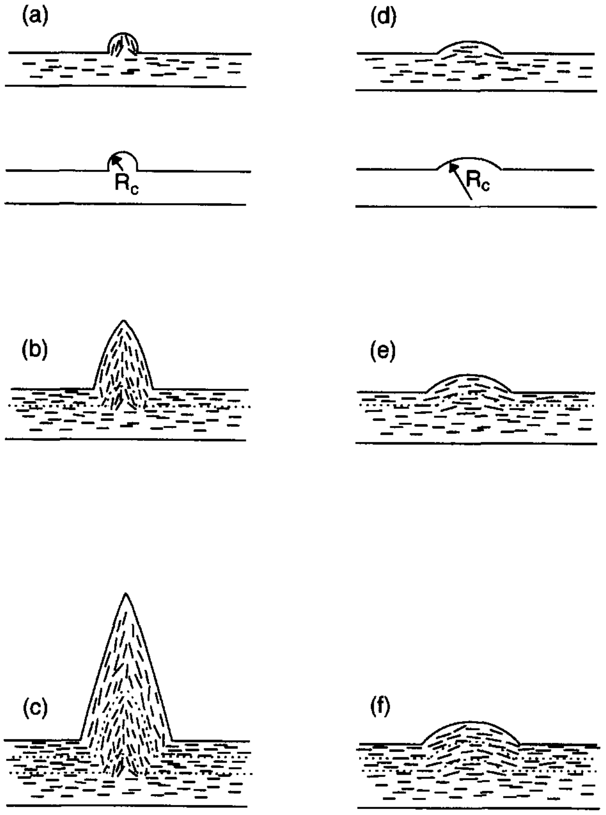

Figure 8 Schematic diagram showing the development of (a)–(c), an 'icing' growth from a protuberance of small R_c, and (d)–(f), a nodule from a protuberance of large R_c; the lines represent the molecular trajectory in different areas of the film

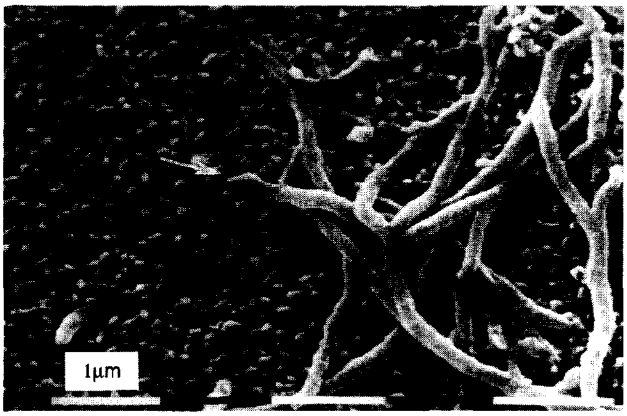

Figure 9 Scanning electron micrograph of a polyaniline film in the early stages of growth, apparently showing an 'icing' growth (arrowed)

account for the formation of a polypyrrole film along an air/liquid interface[22]. Additionally, Mitchell and coworkers [39] have suggested that interactions between the polypyrrole chain, counter ions and the electrolyte can lead to the chain remaining partially solvated after becoming 'tethered' to the work electrode. In this model, the counter ions surround the free chain, thereby shielding it from the electrolyte; it is thus the interaction of the counter ions with the electrolyte that allows the chain to remain free. At the free chain-end, pyrrole monomers/oligomers in solution can react with the tethered molecule, thus extending the chain length. When it exceeds some critical length, part of the solvated portion then deposits on to the electrode[15,39]. This model is fundamentally the same as that proposed by us previously[22], but additionally it provides a basis for explaining variations in the observed morphology of samples grown under identical electrochemical conditions, but with different solvents[9].

The relevance of such molecular processes to morphological evolution can be illustrated by considering a small protuberance on an otherwise planar growth front (*Figure 8a*). If the radius of curvature (R_c) is small, then some of the chains will be orientated away from the work electrode. As already observed, rapid growth occurs along the chain direction, and thus these chains will develop as shown schematically in *Figures 8b* and *8c* and the small protuberance will grow quickly away from the electrode. Simultaneously, other molecules will deposit from solution on to the surfaces of this growth, so causing the feature to thicken. This thickening will occur at a uniform rate across the entire sample. If the radius of curvature of the instability is large (*Figure 8d*), then the trajectory of chains within the instability will remain predominantly close to the plane of the basal film and the structure itself will not therefore develop away rapidly from the work electrode (*Figures 8e* and *8f*).

Under the appropriate conditions, electrochemically prepared polyaniline grows by initially forming a continuous featureless layer across the electrode surface[5], which subsequently degenerates into the typically reported fibrillar morphology[4–7] (*Figure 1b*). This has clear parallels with the mechanism discussed above. As the radius of curvature of an instability on the film surface becomes smaller, the aspect ratio of the resulting feature will increase, and longer and thinner tapered growths will develop. Compare, for example, the aspect ratio and lateral dimensions of the three related morphological forms described in this present paper. When the radius of curvature becomes sufficiently small, the result will not be tapered growths but, instead fibres will be produced. Thus, the fibrous morphology of polyaniline may have the same origin as the 'icing' on polypyrrole. This assertion is reinforced when the polymerization conditions for aniline are changed so as to produce a dense continuous film. *Figure 9* shows the surface of a polyaniline film which has been grown for a short period of time. At this early stage in the development of the film, fibres have only just begun to form; however, as well as the fibres a long tapered growth can also be discerned (arrowed). Thus, fibres are not the only form of surface morphology found on polyaniline, as 'icing' growths can also develop under appropriate conditions.

CONCLUSIONS

Two 'new' morphological forms of polypyrrole *p*-toluene sulfonate have been reported. In the case of growth around gas bubbles, a mode of growth has previously been proposed by us that can be extended to account for these features. The other mode of growth leads to a new morphological form of polypyrrole *p*-toluene sulfonate. Electron diffraction and optical dichroism has been used to show that the molecular orientation in these 'icing' growths is approximately perpendicular to that in the basal film. By considering the development of these features, a model for the growth of polypyrrole has been proposed. This model requires that polypyrrole chains can continue to grow while being still attached to the work electrode surface. Furthermore, a scheme that describes the development of the observed morphological features of polypyrrole films has been suggested. A means of unifying this model with the fibrillar morphology of polyaniline is also proposed.

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