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On the formation of tubules by polypyrrole doped with perfluorobutyrate

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Abstract

It has been reported that, under certain conditions, electropolymerization of pyrrole in aqueous solution produces bud and flute-like structures. Although these features have been interpreted in terms of an orienting effect of the electrode surface on the resulting films, others have ascribed them to the production of oxygen during the oxidative process. The results of our experiments involving electropolymerization on a met-glass surface, rotating ring-disk measurements and scanning electron microscopy strongly support the second interpretation.

Introduction

Recently, Vork and Janssen [1] reported that electropolymerization of pyrrole in aqueous solution in the presence of tetraethylammonium tosylate on a nickel electrode led to the formation of a polypyrrole film which had 'tube-like bulges'. Electron micrographs were presented that showed both the existence of short open tubules projecting from the surface and longer closed tubules of apparently different lengths. The appearance of these tubules was found to depend upon the current density employed and the time of polymerization. The number of tubes per unit area depended on the current density and their length depended on the time. The surface of polypyrrole films prepared in acetonitrile had the familiar 'cauliflower' appearance usually found for electrochemically prepared films which has been attributed to a process of nucleation followed by three-dimensional growth [2]. Vork and Janssen [1] found that the conductivities of the films prepared in water and acetonitrile were essentially the same. Other workers have also observed the formation of tubules under certain conditions in aqueous solutions [3, 4], as well as helical fibers [5, 6]. While our work was in progress, Unsworth *et al.* [7] reported the results of a cyclovoltammetric study on the process which leads to the formation of tubules during the electropolymerization of pyrrole. In this communication, we report our findings on the electrochemical polymerization of pyrrole in aqueous perfluorobutyrate in which tubular structures are formed; our results are consistent with the conclusions of Unsworth *et al.* and provide new definitive proof of the process which leads to the formation of tubules.

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Experimental

Electrochemical experiments were carried out in a Cypress mini-cell using either indium-doped/tin oxide coated glass (Donnely Corp.), platinum foil or Ni78/B14/Si8 metallic glass foil (Goodfellow) as the working electrode. Potentials were referenced to the saturated calomel electrode. Either Pt foil or mesh was used as the counter electrode. Cyclic voltammetry and controlled potential electrolysis were carried out using a JAS model JJ 1276 waveform generator driving a Southampton potentiostat. Rotating ring-disk experiments were carried out using a Pine Instrument Co. AFRDE4 bipotentiostat, MSRX analytical rotator and AFMT28T Pt ring-disk electrode. The cell was home-made and was constructed to be air-tight and have a working capacity of 20 ml. All solutions were purged with nitrogen for 5 min prior to the experiments, and a nitrogen atmosphere was maintained at all times. The SCE was used as the reference electrode for measurements taken on aqueous solutions while a silver wire pseudoreference was employed for non-aqueous solutions.

An aqueous solution containing the appropriate amount of sodium perfluorobutyrate was prepared by titration of perfluorobutyric acid (PCR, Inc.) with standard sodium hydroxide. Pyrrole (Aldrich) was distilled under vacuum just prior to use. Distilled water was further purified using a Barnstead deionizer. Tetrabutylammonium perfluorobutyrate was prepared by titration of an aqueous perfluorobutyric acid solution

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with tetrabutylammonium hydroxide (Aldrich) to a pH near neutral. $TBAOOC(CF_2)_2CF_3$ was purified by extraction into methylene chloride; the solution was filtered, dried and evaporated to dryness on a rotary evaporator. The product was recrystallized from ethyl acetate and dried under high vacuum for 2 d. All electrochemical measurements were carried out using solutions 0.15 M in perfluorobutyrate and 0.06 M in pyrrole.

Results and discussion

In our study of the polymerization of polypyrrole in the presence of a variety of fluorinated anions as dopants [8], we found that the gross morphologies of the resulting films were not greatly different from one sample to another and showed the characteristic 'cauliflower' surface generally observed for formation of polypyrrole films [8, 9]. There appeared to be a rough correlation of conductivity with smoothness of the surface as noted earlier by Wu [10]. In the case of aqueous sodium perfluorobutyrate-doped polypyrrole, however, some curious flute-like structures were formed. Such species have been observed by Vork and Janssen [1] as a result of galvanostatic electropolymerization of pyrrole on nickel in aqueous tosylate and by Cahalane and Labes [4] by potentiometric electropolymerization of pyrrole in aqueous tosylate at 2.3 V on vitreous carbon or stainless steel covered by a Nuclepore membrane. Vork and Janssen attribute the formation of the hollow tubular structures to orientation of the pyrrole chain in a spiral [1]. The predominantly *syn* conformation of the chain turns the hydrogen atoms bound to nitrogen on the pyrrole ring in towards the center of the spiral forming a hydrophobic region in which the *p*-toluene sulfonate is sandwiched such that the polar sulfonate groups extend out into the hydrophilic region and the phenyl groups occupy the central hydrophobic region. Helical coils for this material have been observed by Yang *et al.* [6] using scanning tunneling microscopy. Cahalane and Labes [4] ascribe the growth of the hollow fibrils and their much higher conductivity to the orienting effect of the Nuclepore, a polycarbonate membrane with cylindrical pores 0.015–14.0 μm in diameter. However, our films were grown on an indium-doped tin oxide-coated glass electrode which was not expected to exhibit a significant orienting effect. In Fig. 1, the scanning electron micrograph 17a shows polypyrrole buds growing from the surface of the film. Scanning electron micrograph 17b shows the morphology of the surface of these buds which resembles the usual globular texture of the films grown without the tubular features. Scanning electron micrograph 18a shows some of the buds in a later period of growth in which the sides of the tubes have become striated, as observed by Cahalane and Labes [4] in their studies of $PPY^{+}\,^{-}Tos$, and the ends of the tubules have opened. The striations look similar to those reported by Yamaura *et al.* [9] for stretched films. It is noteworthy that tubules of this particular morphology have been seen only for polypyrrole grown in aqueous solution; 3-substituted polythiophenes have been observed to form long fibrils when grown in non-aqueous solutions [4, 11, 12], but the structures are entirely different from the tubules reported here and by previous workers [1, 3, 4, 7]. All of these facts are consistent with growth of polypyrrole around gas bubbles resulting from oxidation of water in the electrolyte and subsequent stretching of the films prior to bursting from increased gas pressure; the dramatic increase in the conductivity noted by Cahalane and Labes [4] could be due to stretching of the film before the tubule burst. Since the potential was not controlled in one case [1], was 2.3 V in the other [4] and was 1.2 V in our case, electrolysis of the solvent at these high potentials could account for the formation of oxygen. This possibility has been suggested previously by Maddison and Unsworth [3] on the basis of the observation of spherical hollow structures which result from growth of $PPY^{+}\,^{-}Tos$ at high current densities, and later cyclovoltammetric evidence for this process was reported [7]. The low conductivity of polypyrrole formed by the polymerization of pyrrole in aqueous solution has been ascribed to the presence of carbonyl groups arising from production of oxygen during the process [13, 14].

Three experiments were carried out to test this hypothesis. The first involved studying the electropolymerization of pyrrole in the presence of perfluorobutyrate on a metallic glass foil electrode. Tubules were observed to grow on this completely amorphous surface under the same conditions observed for those which grew on the ITO electrode (Fig. 2); these results clearly indicate that in the case of polypyrrole grown in aqueous perfluorobutyrate the formation of tubules cannot be attributed to any orienting effect of the electrode.

In the second experiment, electropolymerization of pyrrole in aqueous perfluorobutyrate was carried out at the disk of a rotating ring-disk electrode while monitoring the current at the ring which was set at the potential required for the detection of oxygen (−0.45 V). A normal nucleation loop for the electropolymerization of the pyrrole monomer was observed when the current at the disk was recorded and concurrent with this was a growth in the current observed at the ring corresponding to oxygen production (see Fig. 3). The polymeric film produced at the disk showed the hollow tubular structure when it was examined under a microscope.

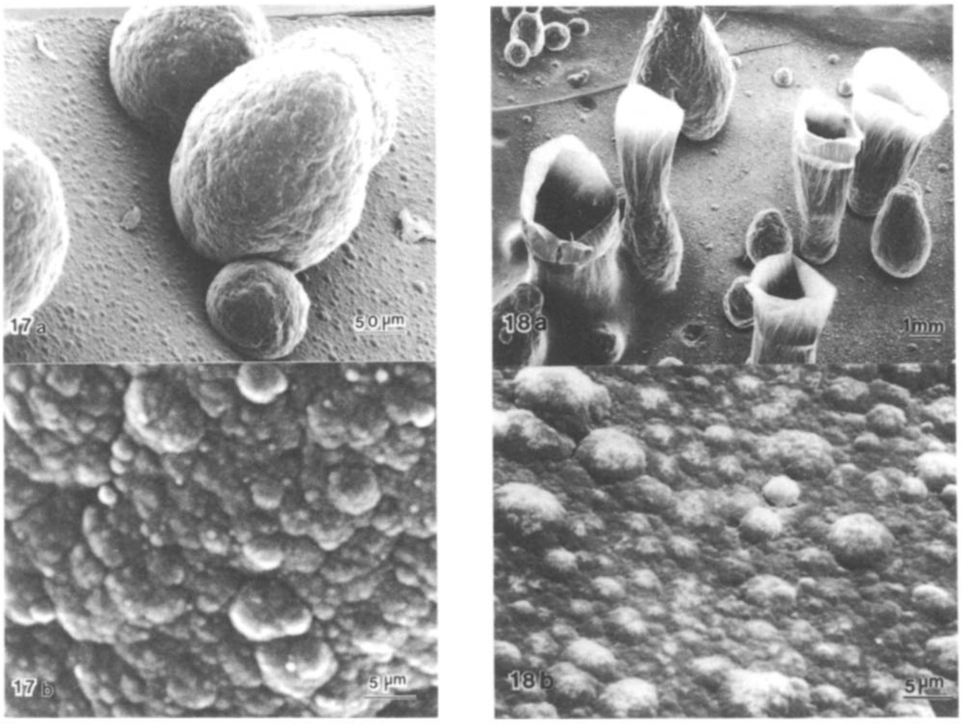

Fig. 1. Scanning electron micrographs of $PPY^{+}\,{}^{-}OOC(CF_2)_2CF_3$. Conditions: 0.06 M pyrrole, 0.15 M $NaOOC(CF_2)_2CF_3$, aqueous solution, CV method, −0.4 to 1.2 V, conductivity = 17 S cm^{-1}. Micrograph 17a: buds on surface of film. Micrograph 17b: surface of buds. Micrograph 18a: tubules occurring along with buds. Micrograph 18b: surface of film parallel to electrode face.

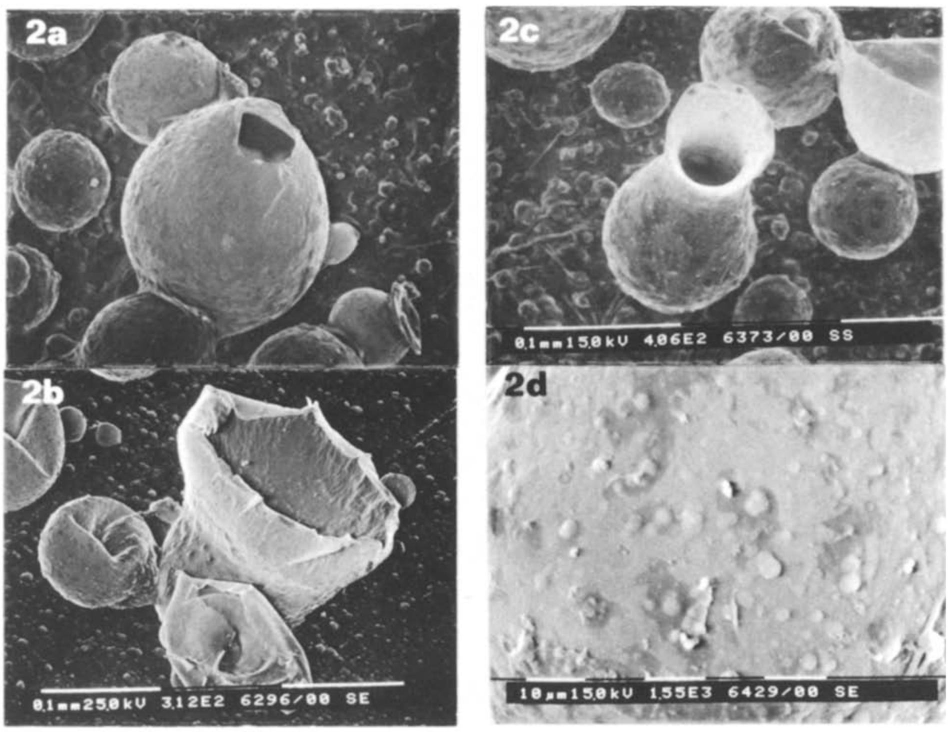

Fig. 2. Scanning electron micrographs of $PPY^{+}\,{}^{-}OOC(CF_2)_2CF_3$. Conditions: 0.06 M pyrrole, 0.15 M $NaOOC(CF_2)_2CF_3$, aqueous solution, CV method, −0.4 to 1.2 V. Micrograph a: buds on the surface of the film. Micrographs b, c: tubules in various stages of development. Micrograph d: surface of tubular structures.

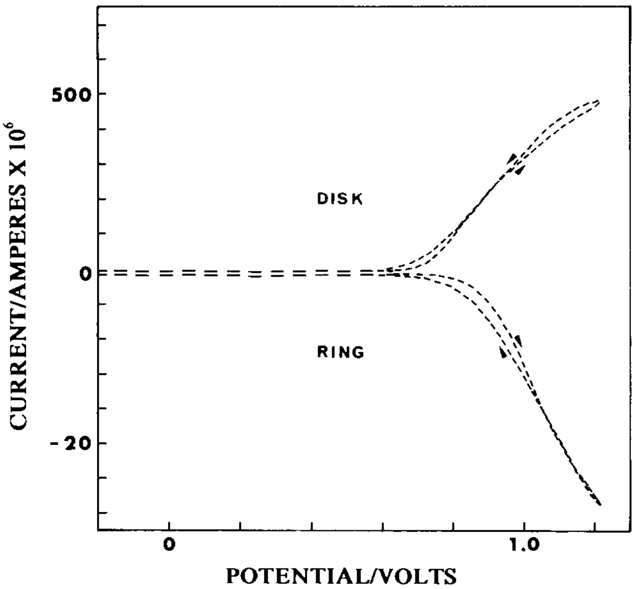

Fig. 3. Top: cyclic voltammogram at disk, 50 mV s^{-1}, 0.15 M aqueous $NaOOC(CF_2)_2CF_3$, 0.06 pyrrole. Bottom: ring at −0.45 V, $\omega = 100$ rpm.

The third experiment involved rotating disk electropolymerization of pyrrole in a non-aqueous solvent (acetonitrile) with tetrabutylammonium perfluorobutyrate as electrolyte. As noted earlier [13], polymerization did not occur readily in the dry solvent, but a thin film could be produced when a small amount of water (1%) was added [15]. The film was powdery and the cyclic voltammogram did not show evidence of the usual nucleation and three-dimensional growth process. No evidence for oxygen production at the ring was observed.

Conclusions

(1) The tubular morphology of the polypyrrole prepared in the presence of perfluorobutyrate suggests that some polymerization occurred around gas bubbles. The presence of burst tubules and striations on them perpendicular to the surface observed by us and the high conductivity of the similar tubules formed by $PPY^{+-}Tos$ [4] are consistent with stretching of the film owing to increasing gas pressure within the buds.

(2) The growth of tubules during the electropolymerization of pyrrole in the presence of perfluorobutyrate on an amorphous surface demonstrates that an orienting surface is not necessary to produce these structures.

(3) The simultaneous production of polypyrrole and oxygen during electropolymerization in aqueous perfluorobutyrate as shown by the rotating ring-disk experiments demonstrates that oxygen gas is produced in the process.

(4) The lack of a response at the ring electrode during electropolymerization in non-aqueous solution with a small amount of water added demonstrates that oxygen gas is not produced under these conditions.

(5) All of these results indicate that the tubules observed in the electropolymerization of pyrrole in the presence of perfluorobutyrate are the result of oxygen production. The results also suggest that similar tubules, observed when a nickel electrode was employed by Vork and Janssen [1] and modified stainless-steel electrodes were employed by Cahalane and Labes [4], probably result from the same process and orientation by the substrate may have little to do with the formation of the type of structures observed in these cases.

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