

Structural studies of polypyrroles with fibrillar morphology

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Fibrillar polypyrroles have been prepared by electrodeposition through honeycomb γ -alumina membranes. The morphology has been extensively studied using field-emission scanning electron microscopy. The rate of fibre growth in several solvents has been measured by direct length measurement. The occupation of the host membrane pores by polypyrrole has been examined by ultramicrotome techniques. In extended polymerizations, both solid rods and tubes are found.

1. Introduction

Conducting polymers have been formed in various ways to give different textures. For example, films can be made ranging from thin coatings (≈ 100 nm) [1] through to free-standing films. Indeed, for some time, a 66 μm thick doped polypyrrole film has been commercially available [2]. In these cases morphologies have been studied by electron microscopy and texture by X-ray diffraction. Film morphology can be affected by current density, solvent and monomer type and concentration. We have shown, for example, that extended, rapid polymerization on roughened electrodes yields films with high surface area [3]. Other examples of configurations include rather porous/fibrous films [4], colloids [5] and fractals [6].

There have, however, also been several studies in which highly ordered, fibrillar structures have been described. Martin *et al.* have made fibres with low bulk density by polymerizing pyrrole through isoporous polycarbonate membranes [7] and have also prepared denser fibres, claimed to have enhanced electrical conductivity [8]. Martin has recently described polypyrrole tubes by Fe^{3+} oxidation of pyrrole within a polycarbonate template membrane.

We have previously described improvements which can be gained from polymerizing through "Anotec" γ -alumina hosts rather than "Nuclepore" polycarbonate isoporous membranes [9] which include much greater fibre regularity and density. Here we now consider several aspects of fibre growth in greater detail, and reveal the morphology of products with greater clarity than previously shown.

2. Experimental procedure

2.1. Materials

Pyrrole (Sigma Chemical Company) was distilled prior to use. Tetraethyl ammonium paratoluenesulphonate (Alfa/Aldrich Chemical Company) used as dopant electrolyte, was stored in a vacuum desiccator before use. Propylene carbonate (Sigma Chemical Company)

and acetonitrile were used as-received. Anotec γ -alumina membrane (pore density $\approx 60\%$) with a nominal pore diameter of 0.2 μm and thickness of 65 μm was used as a template for pyrrole polymerization.

2.2. Polypyrrole synthesis using γ -alumina template

A single-compartment cell with a carbon plate as counter electrode and gold-coated membrane as working electrode (anode) was used for electropolymerization of pyrrole through membrane micropores. The anode assembly was the same as previously shown [3]. However, a brief description is useful now.

A rather thick layer of gold was deposited on one side of membrane using a vacuum-coating unit. Single-sided tape was applied to about 80% of the gold-coated side. A titanium rod was used to make an efficient electrical connection between anode and power supply. This assembly was attached to a glass slide with epoxy glue. Silver paint was used as a conductive adhesive between the membrane and the titanium rod. A side view of the anode assembly is shown in Fig. 1.

Electrochemical polymerization was carried out under galvanostatic conditions at room temperature. This was achieved by using a current-limiting device; current was set typically at 4 mA and measured during polymerization.

The polymerization solution contained pyrrole (0.3 M) and dopant (0.1 M). Distilled water, propylene carbonate and acetonitrile each used as solvents. For non-aqueous polymerizations, a small amount of distilled water (1%–2% vol/vol) was added as co-solvent [10]. The polypyrrole-coated membrane was washed with a copious amount of solvent to remove residual dopant and monomer. The host membrane then separated from polymer by immersing the composite in 1 M sodium hydroxide. The resulting fibrillar polypyrrole was rinsed with distilled water and dried under ambient conditions. Formation of fibrillar polypyrrole is shown in Fig. 2. The fibres have been grown

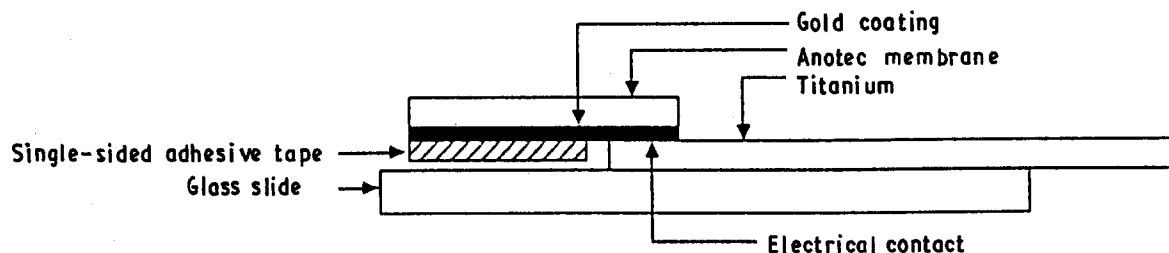


Figure 1 Side view of anode assembly [3].

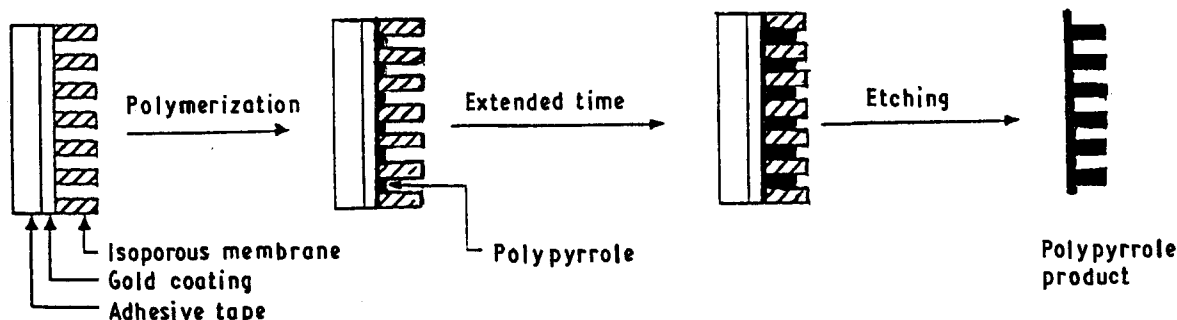


Figure 2 Schematic diagram of fibrillar polypyrrole preparation.

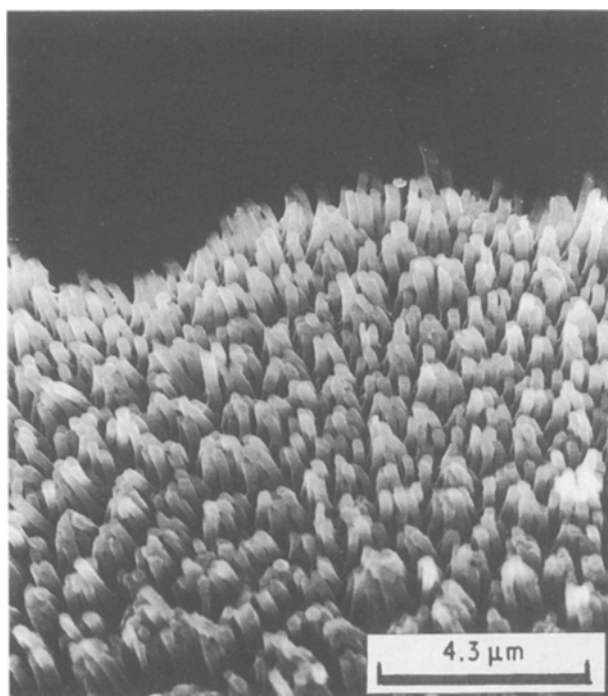


Figure 3 Polypyrrole grown at a current density of 1 mA cm^{-2} .

from the gold-coated side towards the solution side of the membrane. By controlling the polymerization time at constant current density, it is possible to terminate polymerization before covering the solution side of the membrane by polypyrrole film. From micrographs it is obvious that the base of fibres is attached to a thin film of polypyrrole which has been formed at the beginning of electropolymerization, providing a good support for keeping fibres upright.

It has already been suggested that morphology and conductivity of polypyrrole films prepared by conventional electrochemical polymerization depend on both

current density and film thickness [11, 12]. To study the effect of current density on morphology, current densities of 1 and 2 mA cm^{-2} were employed in aqueous polymerizations, but no significant difference in morphology was found (Figs 3 and 4). Current density only affects fibre growth rate by changing charge density during polymerization. To maintain high rates of fibre growth, subsequent experiments were performed using a current density of 2 mA cm^{-2} .

The role of leaching time of the polypyrrole/ γ -alumina composite was also studied as follows. Strong alkalis, commonly used to dissolve γ -alumina, may have a deleterious effect on conductivity, electrochemistry [13] and morphology [9] of conducting polymers. The optimum leaching time corresponds to that when all of the host membrane is removed without adverse effect upon polypyrrole morphology. It was found that at shorter leaching times (i.e. less than 1 h) the fibres are separated from each other, whilst for longer periods they were attached to each other and

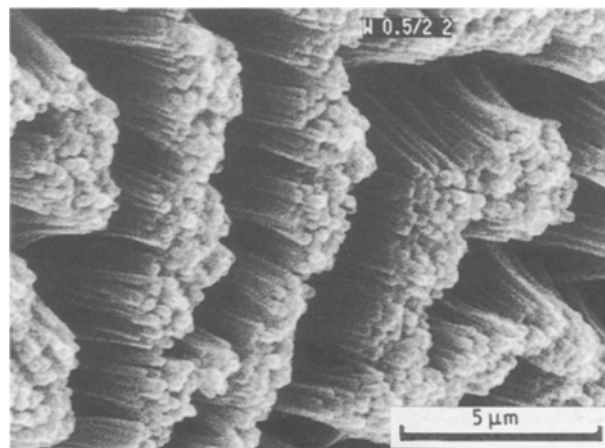


Figure 4 Polypyrrole grown at a current density of 2 mA cm^{-2} .

had less regular cross-sectional shapes (Figs 5 and 6). From these observations, leaching times of from 30–40 min were used.

2.3. Microscopy

Morphologies of gold-coated samples were studied by using a Cambridge Stereoscan S360 scanning electron microscope with an accelerating voltage of 25 kV and a Hitachi S900 field-emission scanning electron microscope at 2 and 10 kV. Sectioning of composite samples was done using a RMC MT-7 ultramicrotome equipped with a power-driven cutting edge. Samples were coated either with gold or platinum.

3. Results and discussion

3.1. Effect of polymerization media

All polypyrroles, regardless of which solvent is employed, have dense fibrillar morphologies. Carpet-like structures are observed in Figs 7–9 (corresponding to polymers prepared in water, propylene carbonate and acetonitrile, respectively). Cross-sections of fibres have similar diameters and geometries. Whilst it often occurs that these fibres, even when separated into clumps, have a rather uniform length and are upright, in some cases the fibres vary in length and start to bend. This variation in length might be attributed to non-uniformity of the gold coating, whilst poor alignment might be due to post-polymerization operations,

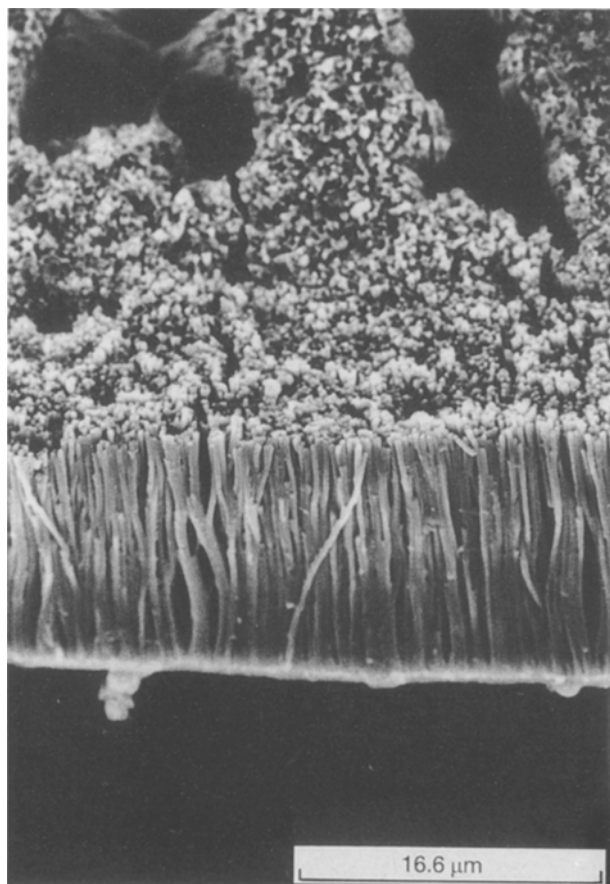


Figure 5 Polypyrrole grown at a current density of 2 mA cm^{-2} for 2 h. Leaching time of γ -alumina, 30 min.

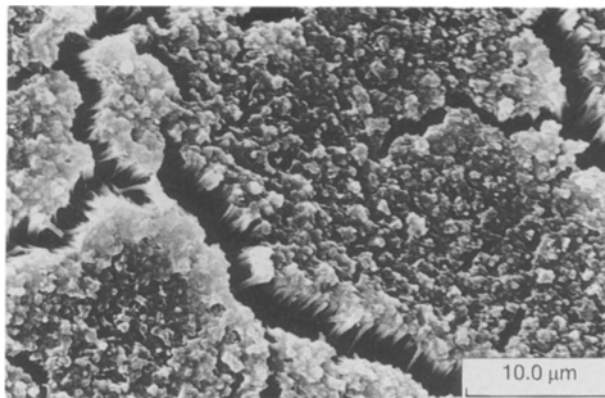


Figure 6 As for Fig. 5. Leaching time 4 h.

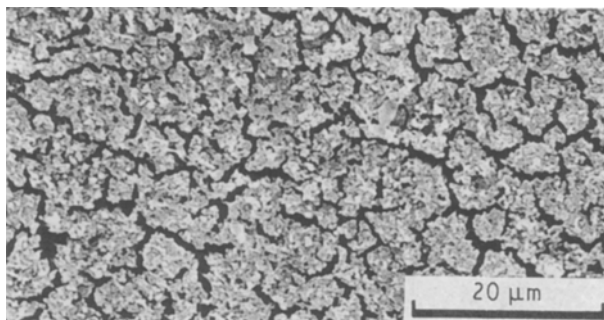


Figure 7 Polypyrrole fibres grown in an aqueous medium.

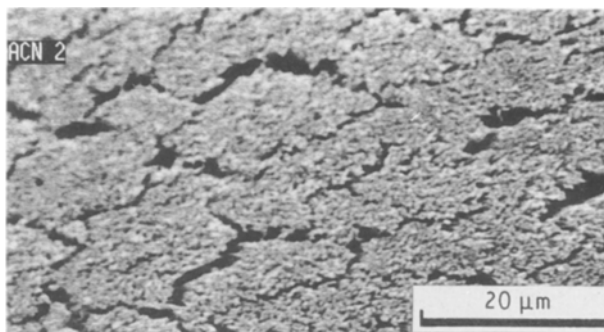


Figure 8 Polypyrrole fibres grown in a non-aqueous medium (acetonitrile).

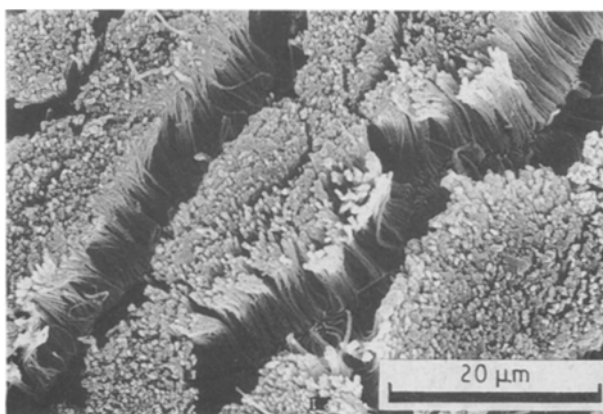


Figure 9 Polypyrrole fibres grown in a non-aqueous medium (propylene carbonate).

including washing or leaching (Fig. 10). Non-uniformity can be observed in composite sections, (i.e. where the γ -alumina remains) as shown in Figs 11–15. The fibres vary in appearance from one sample to the next, but essentially replicate the pore structure of the host. This is particularly evident as we proceeded from the top to the bottom of a single host membrane, as described in further detail below. From the micrographs provided in Figs 7–9 and additional higher magnification studies, we conclude that solvent has little effect upon fibre morphology. Minor differences can be attributed to other factors including washing and/or leaching operations and non-uniformity of membrane structure.

3.2. Growth mode of fibres

The mode of polymer growth within membrane pores was studied by examination of the morphology of sections prepared from composites. High-resolution

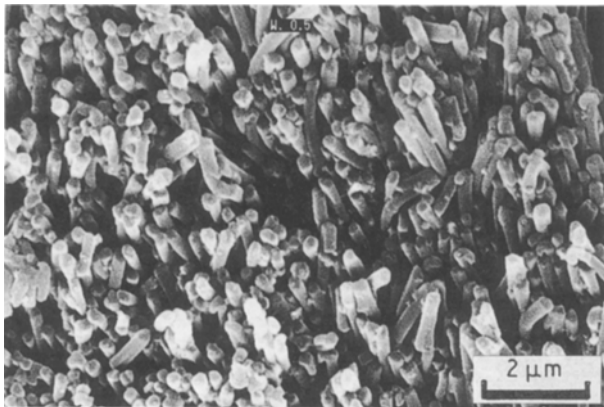


Figure 10 Polypyrrole fibres having different lengths.

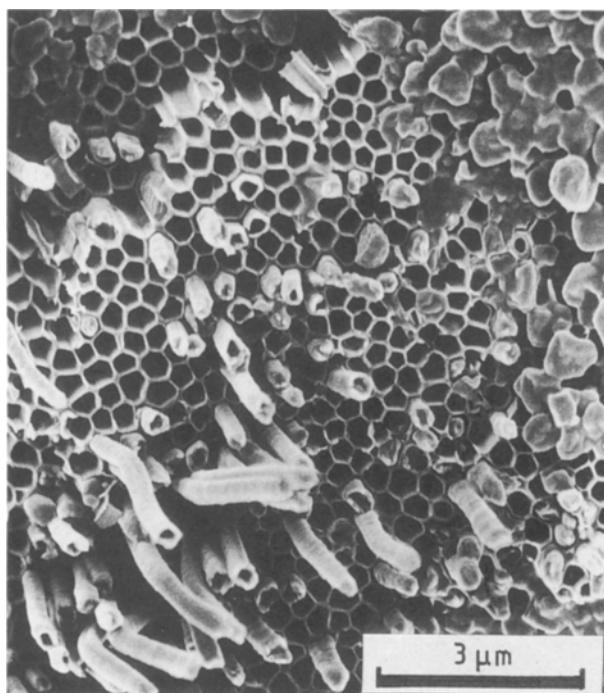


Figure 11 Polypyrrole tubes emerged from honeycomb pores.

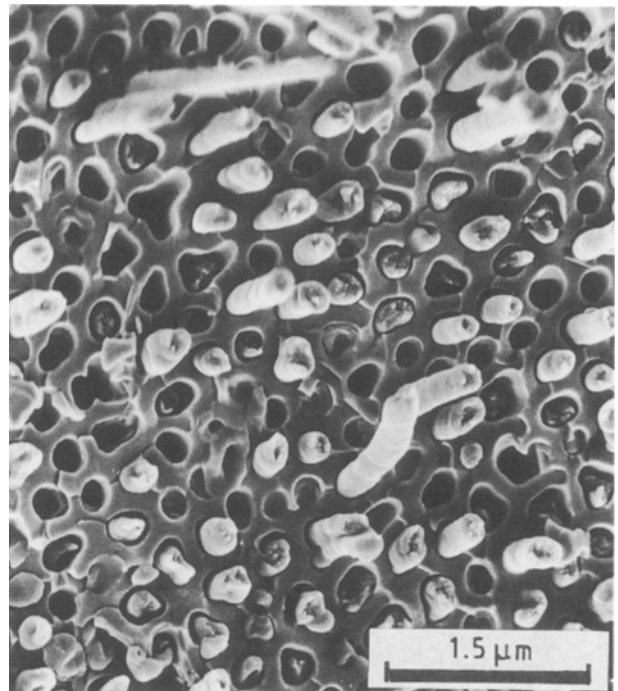


Figure 12 One region of the membrane with lower pore density and non-hexagonal pores.

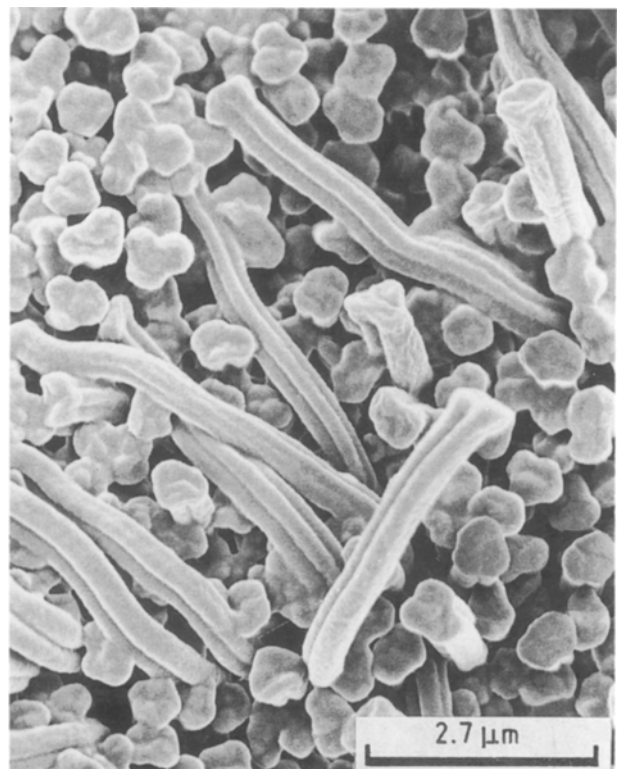


Figure 13 Upper section of ppy/Anotec composite.

electron microscopy at low accelerating voltage (2 kV) was employed in these studies. Figs 11–13 show different parts of the top surface of the γ -alumina/polypyrrole composite. Whilst the membrane is generally viewed as being of an unstricted honeycomb structure (as seen in Fig. 11) it is evident that many parts of the surface depart from having closely spaced hexagonal pores. Thus numerous circular and trilobate

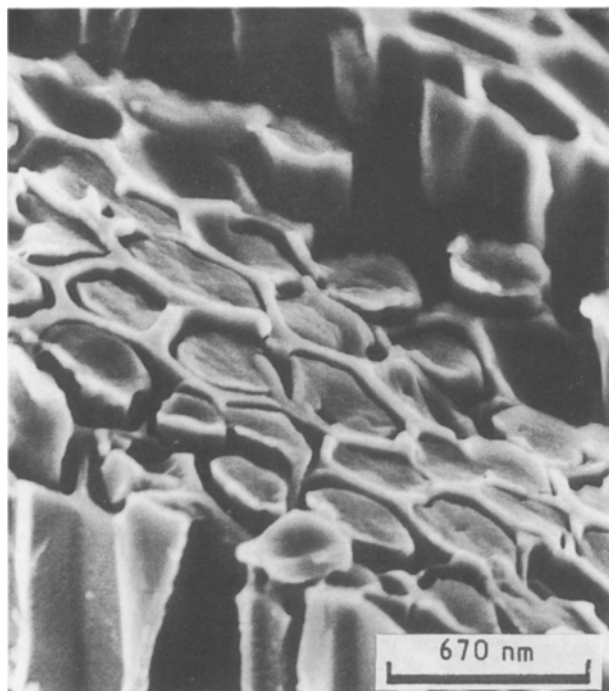


Figure 14 Second section of ppy/Anotec composite.

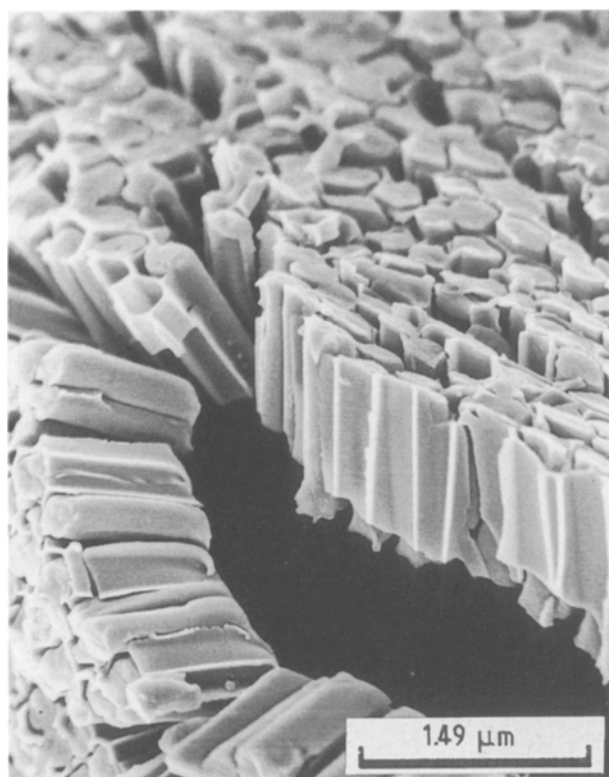


Figure 15 As for Fig. 14 at lower magnification.

holes are evident in the surface shown in Fig. 12 where less polymerization has occurred. Here the separation of each pore by the γ -alumina is much greater (i.e. pore density is lower than for the hexagonal regions). The extruded material seen for a region of high growth (Fig. 13) is predominantly trilobate as well, although some distorted hexagons also exist.

In fact, virtually all of the polypyrrole fibres encountered by us (including those in kinetic studies

below, and after leaching) are cylindrical, contrary to the initial impressions previously reported by us [9]. Some contraction of the polypyrrole during polymerization has occurred due to density differences between monomer and polymer and this inevitably leads to departures in shape between the host-membrane pore and the fibre.

The existence of a range of fibre cross-sectional shapes made investigation of the interior morphology of the host membrane necessary and so sections about 1 μm thick were prepared. Figs 14 and 15 are typical of many slices in the central region (i.e. away from top to bottom) and here the γ -alumina is mainly hexagonal. Again, volume shrinkage of the polypyrrole is evident. This occurs despite the likelihood of strong inherent adhesion between γ -alumina and polymers generally, as found for coated rigid fibres by McGarry and Moalli [14]. Some rupturing of the γ -alumina is unavoidable during sectioning.

Finally, an example of the bottom part of the membrane is shown in Fig. 16 and a structure similar to that seen in Fig. 12 is evident.

The presence of tubes (Fig. 11) with horizontal surface striations could either be simply attributed to the internal appearance of the pore walls or growth of nascent polymer in a layer-by-layer manner. There are some tubes which suggest that polypyrrole at first deposits on the surface of pore walls. They may then grow radially to fill each pore and ultimately form solid fibres. This surface adsorption phenomenon might be attributed to some kind of binding between the nascent polymer and pore walls. Gregory *et al.* [15] and Cai and Martin [16] have observed a similar phenomenon for adsorption of polypyrrole on the surface of fabrics and polycarbonate membranes, re-

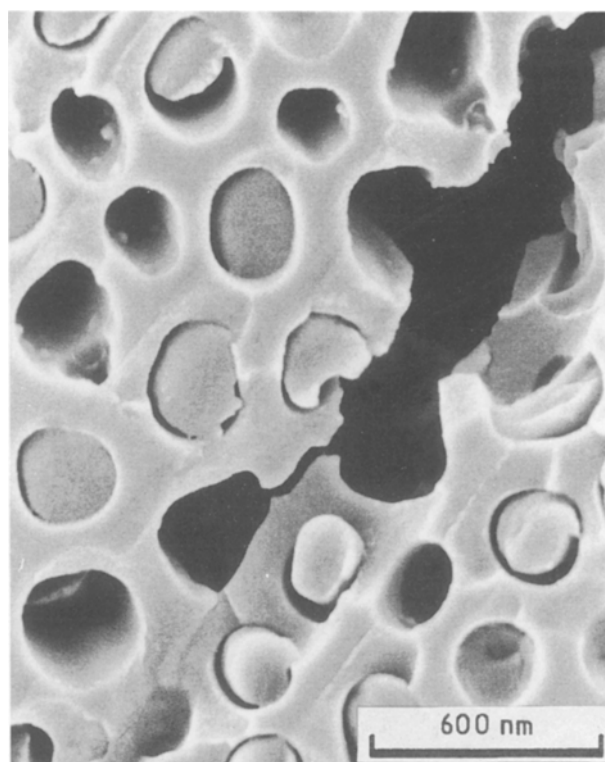


Figure 16 Third section of ppy/Anotec composite.

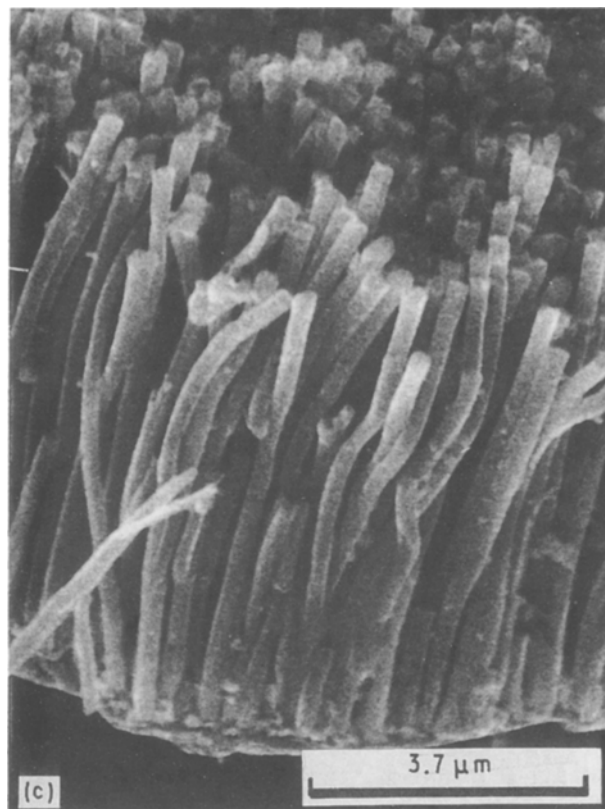
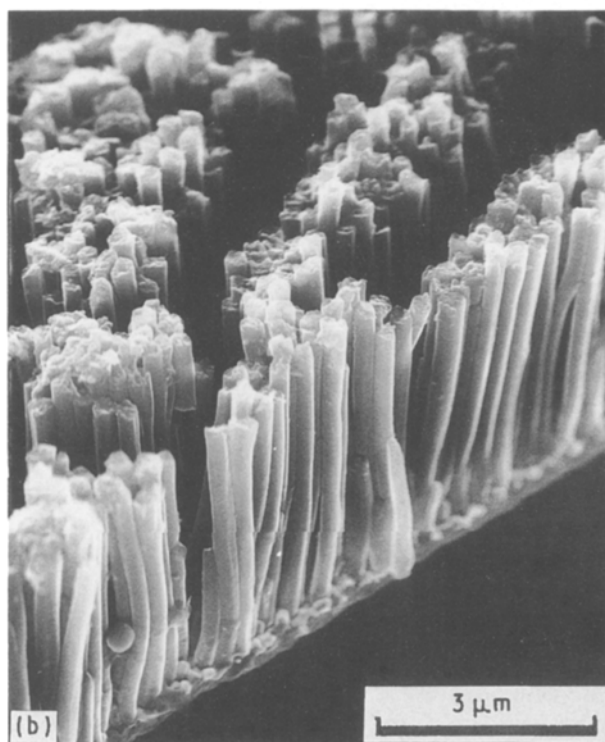
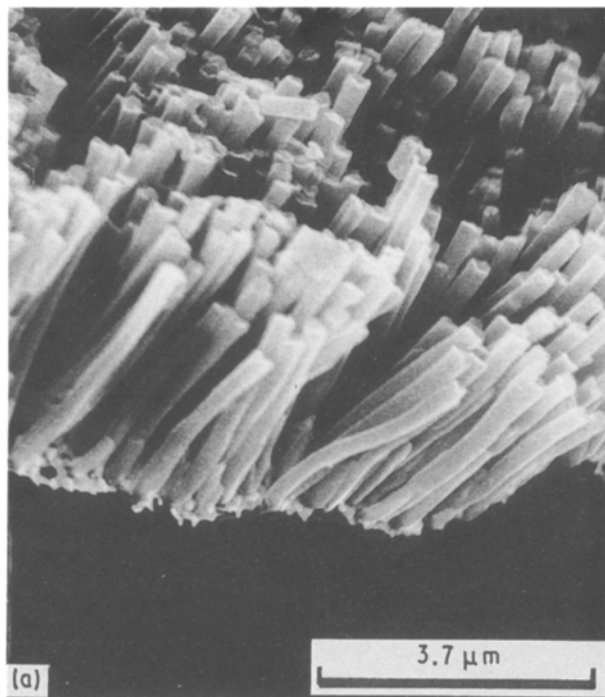


Figure 17 Polypyrrole fibre grown (for propylene carbonate systems) at different times: (a) 5 min, (b) 20 min, (c) 40 min.

spectively. It has been claimed that a “molecular anchor” is responsible for this tube formation [17, 18] although in our case the explanation is less clear, as no deliberate additive of this type is included.

3.3. Growth rate of polypyrrole fibres

The rate of fibre growth within the Anotec template was determined for different solvents. Polymerization times ranging from 5–100 min were used and fibre length was measured directly from the corresponding micrographs. Typical extracted fibres for polymerization times of 5, 20 and 40 min using propylene carbonate solvent are shown in Fig. 17a–c.

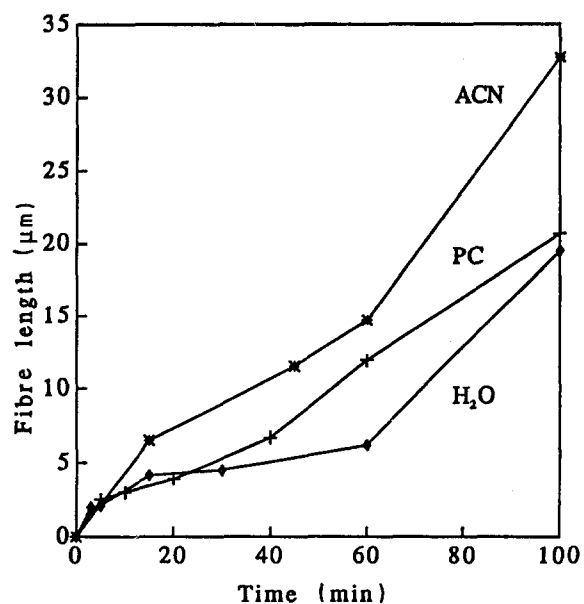


Figure 18 Fibre length versus time for different solvents. $[M] = 0.3 \text{ mol l}^{-1}$, $[M]/[D] = 3$, current density = 2 mA cm^{-2} .

The plot of fibre length versus polymerization time is shown as Fig. 18, from which it appears that growth for all solvents shows a similar trend. The growth rates are in the range $0.15\text{--}0.3 \text{ μm min}^{-1}$ with the acetonitrile appearing to give the fastest growth. These are not to be compared with the production of free-standing films, in which a different order of polymerization rates might be expected. In general times, however, linear growth rates are perhaps two or three

times greater in the latter case than for isoporous membranes.

4. Conclusions

Our studies have shown that in the case of polymerization through sacrificed host membrane, solvent has no significant effect on fibrillar morphology. Micrographs of composite sections have revealed that variations in fibre cross-sectional shape (trilobate, circular and hexagonal) are mainly due to heterogeneities in the host-membrane structure. The presence of hollow fibres in some regions suggests that polypyrrole deposits on the surface of pore walls during the initial stages of polymerization.

Owing to density differences between monomer and polymer, there is contraction during polypyrrole fibre formation, leading to alteration in fibre shape.

Fibre growth kinetics are of similar form for the three solvents studied, with acetonitrile giving the fastest rate.

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