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Conducting polymers with controlled fibrillar morphology

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Electrically conducting polymers have been prepared from pyrrole by electrodeposition through two types of isoporous membranes. When pyrrole is polymerized through isoporous polycarbonate membranes, with the polycarbonate subsequently removed with chloroform, a relatively low density of short filaments is produced. Membranes of large pore diameter gave few, rough filaments, but as the pore size decreased the number of filaments increased and their walls were much smoother. A method in which the filaments are contiguous with a supporting sheet is described. When honeycomb structured γ-alumina membrane is employed, a quite different product is possible. A very high density polymer of long, hexagonal filaments appear after the γ-alumina is leached using sodium hydroxide. This material has a very high surface area and structural regularity. It has potential as an electrode material in which switching from conducting to non-conducting states could be efficiently achieved by rapid expulsion of counter-ion.

1. Introduction

Polymers are generally highly insulating materials. Without additives, conventional polymers have conductivities ranging from about 10^{-14} to 10^{-17} Seimens per centimetre ($\mathrm{S\,cm^{-1}}$) compared with metals having conductivities from 10 to $10^6\,\mathrm{S\,cm^{-1}}$. With low conductivity, polymers are used as insulators in diverse electrical applications. However, disadvantages arise from electrostatic charge development, and in electrical and mining applications polymers contain high levels of conducting fillers, such as carbon black and metal powders. These composites can have intermediate to high conductivity.

Since 1970, polymers which are intrinsically conductive have been synthesized [1, 2]. These have a conjugated unsaturated polymeric backbone, and typically contain a low molecular weight species counter-ion or dopant. Several hundred chemically distinctive classes of polymers have been shown to have intermediate to high conductivities [3, 4]. Generally they are synthesized using highly active catalysts or are made by electrodeposition, although a new class has emerged in which dehydrohalogenation by controlled thermal degradation is performed [5].

By far the most common categories of polymers are derived from acetylenic monomers, or from five membered heterocycles. Polyacetylenes and diacetylenes have been produced in many laboratories, notably at BASF [6] where on a weight basis, conductivities higher than those for copper have been reported [7]. However, such polymers are hard to process and usually quite unstable, and so require substantial modification for practical devices.

The other major class are based on cyclic monomers, in particular pyrrole and thiophene. During the past decade, over a thousand papers and patents have appeared, reflecting intense interest which can be attributed to several factors. Polypyrroles can possess high thermal stability, and are far more durable than polyacetylenes. They are relatively simple to synthesize, and can be made with a wide range of conductivities, depending on dopant type and level, and other factors. The major limitations with these polymers are their poor ductility, lack of processability and opacity.

Despite the enormous volume of scientific literature, relatively few papers concentrate upon polypyrroles with tailored morphologies. The surface appearance of electrodeposited films on various substrates has been described for example [8–10], and the microstructure has been examined by X-ray diffraction [11, 12]. Further, orientation of polymers has been cited by several groups as enhancing conductivity [13, 14].

A small number of notable papers exist in which the formation of polypyrroles with distinctive structures are described. Nodular or cauliflower polypyrrole textures are frequently formed on flat but rough electrodes, and this appears to be consistent with a dendritic mechanism [15, 16]. The formation of fractals during electrodeposition of metals and other solids is described in considerable detail in a recent monograph [17]. Fractal aggregates have been described by Kaufman and co-workers [18–20], where, for example, fern-like structures radiate from a central anode rod towards an annular cathode.

Any disorder resolved at one particular magnification persists at higher orders of magnification. Thus branching, surface irregularities etc., lead to very high surface areas and thus make this category of material potentially useful as surface-active substrates in catalysis, switching devices and as components in composites.

Another approach to making high surface area structures is to polymerize pyrrole in association with microporous membranes. For example, in an attempt to combine the useful mechanical properties of polyvinyl chloride (PVC) with the high conductivity of polypyrrole, composite membranes in which a PVC host is impregnated with polypyrrole have been made [21]. However, the PVC in this case was not porous and so long polymerization times were required and the films were essentially thin laminates.

A new type of process, in which polypyrrole was grown in a free-standing membrane, and then removed intact from the electrode, has been recently developed [22]. The membrane comprised of an open pore polytetrafluoroethylene (PTFE) hydrophobic membrane (Gore-tex) which has been rendered ionically conductive by impregnation with perfluorosulphonate ionomer (Nafion). When the membrane was stretched over the platinum disc electrode and a current applied, the polypyrrole was found to grow through the membrane. This is in contrast to previous polymerizations on, for example, PVC coated electrodes, where the polypyrrole interposes between the electrode and PVC [23].

A further advance has been subsequently reported (Fig. 1) [24, 25], where polypyrrole is grown through isoporous (i.e., having rod-like or cylindrical pores of similar diameters) polycarbonate (PC) membranes, the host PC then being subsequently dissolved away to leave a filamentary polypyrrole structure.

In that work, host membranes with pore diameters ranging from 10 nm to 12 μm are claimed to be potentially suitable, although the structures shown refer to the 1 μm pore diameter membrane (trace-etched polycarbonate membranes with pore diameters ranging from 0.015 to 14 μm are readily available under the trade names Isopore and Nuclepore).

The polypyrroles as described by [26, 27] are designed to have high switching rates, as ion transport will be facilitated by their high surface area morphologies.

The advantages of the prior methods are that the polycarbonate membrane can be readily extracted using a range of organic solvents, to which the polypyrrole is resistant, and in principle it should be possible to produce a range of filament diameters. However, to date no direct evidence of varying filament size product has been provided in the literature.

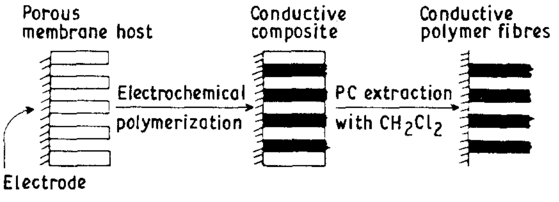

Figure 1 Formation of fibrillar polypyrrole according to Penner and Martin [22].

The available range of isoporous PC membranes are not ideal, because their pore density and film thickness (ranging from 6 to 11 μm) are both low, resulting in relatively short (i.e., 10 μm) and widely spaced filaments.

In this work we describe a modified synthesis of polypyrroles, using PC membranes with diameters ranging from 0.2 to 5 μm. The morphologies for each grade of membrane are described. Secondly, we report for the first time the use of honeycomb structured alumina membranes (i.e., Anotec), and describe resulting polypyrroles with long filaments of high surface area and density.

2. Experimental procedure

2.1. Materials

All chemicals, if not otherwise mentioned, were reagent grade and used without further purification. Polymerization solutions consisted of pyrrole monomer (Sigma Chemical Company), dopant electrolyte (tetraethylammonium-*p*-toluene sulphonate, Alfa/Aldrich Chemical Company) and distilled water. The ratio of pyrrole:dopant concentration was maintained at 3:1, as this has previously been found to be optimum [28], and the initial pyrrole concentration was 0.75 $\text{mol}\,\text{l}^{-1}$.

Polypyrrole polymer composites were prepared by electrochemical polymerization in aqueous solution. A simple, one compartment cell, containing both anode and cathode, was used. The cathode material was a carbon block and the anode materials varied from titanium for use with free-standing membranes to silver paint and gold for coated membranes.

An attempt was made to employ free-standing membranes attached to a titanium electrode, following generally the method of Penner and Martin [22]. Titanium electrodes 5 cm × 2 cm × 0.035 cm were polished with 1200 SiC emery paper and with a 1 μm microid diamond compound on a LECO polishing cloth. A 1 cm × 2 cm rectangle of polycarbonate membrane (Nuclepore), 0.2 μm pore size was then intimately attached to the titanium electrode using various adhesives about the membrane perifery. This titanium/polycarbonate laminate was then used as the anode, placed 2 cm from the carbon plate electrode, and a voltage of 6–7 volts and current of about 10 mA applied.

2.2. Polymerization

Isoporous polycarbonate films 10 μm thick and with pore diameters of 0.2, 1, 3 and 5 μm were obtained from Nuclepore Corporation and Millipore Corporation (Isopore). A rather thick layer (about 20 nm) of gold was deposited on one side of the membrane using a vacuum coating unit. 1 cm × 2 cm rectangles were then prepared, and double-sided adhesive tape applied to about 80% of the gold-coated side. The remainder of the gold area was contacted with a titanium terminal, enabling a good electrical connection to the

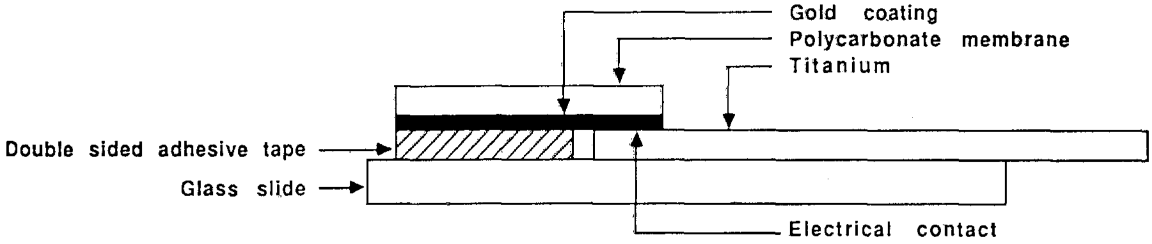

Figure 2 Side view of gold/polycarbonate anode assembly.

power supply. A glass microscope slide was attached to the other side of the double-sided tape, so that the polycarbonate membrane was firmly secured and made rigid. The complete anode assembly, as shown in Fig. 2, was then placed in the aqueous electrodeposition mixture as previously described.

Polymerizations were performed for varying times, depending on specific current densities, until a black continuous layer of polymer could be resolved. Typically a period of about 10 min was satisfactory. The anode was then dismantled and the polycarbonate host membrane (together with gold film) removed by immersion in several washes of chloroform, a total of 0.5 h. Products were examined by optical and electron microscopy.

2.3. Polymerization using anotec – alumina membrane hosts*

Anotec γ-alumina membranes are prepared by an anodizing process [29] and have the morphology shown in Figs 3 and 4 [30]. Hexagonal pores with a nominal diameter of 0.2 μm persist through the membrane, with some constriction at the top and bottom surfaces. The membranes used in these experiments were 50 μm thick.

As the γ-alumina is resistant to organic solvents, the first experiments employed a conductive film prepared by painting colloidal silver suspended in amyl acetate. Subsequent experiments used a conductive gold film, with an anode assembly being similar to that for polycarbonate (Fig. 2) except that single-sided tape was applied to the gold layer. Thus an air gap remained between the Anotec membrane and the glass slide (Fig. 5), which facilitated subsequent manipulation of the product.

Electrodeposition time for this type of electrode was typically 1 h. Unlike the previous experiments, leaching of the membrane host requires more aggressive conditions.

To separate the γ-alumina without destroying the polypyrrole, screening experiments were performed to discover the optimum level of exposure to sodium hydroxide leachant. From the Anotec literature [30] it is evident that γ-alumina dissolves readily in NaOH, but it is also known that conductivities and structure of polypyrrole are affected by exposure to bases.

Thus in separate experiments 300 μm thick, polypyrrole films prepared on titanium electrodes were exposed to 1 M aqueous NaOH for times from 0.5 to 48 h. The back surface of polypyrrole stripped from the electrode is shown prior to exposure (Fig. 6) and after 0.5 h (Fig. 7). It can be seen that some modest microscopic changes have occurred, attributable to changes in counter-ion levels, but that the matrix has essentially survived with little alteration.

From those experiments and the observation that total leaching of the γ-alumina is accomplished in less than 1 h by 1 M NaOH, removal of the polypyrrole product from the alumina host was performed by immersion for 40 min.

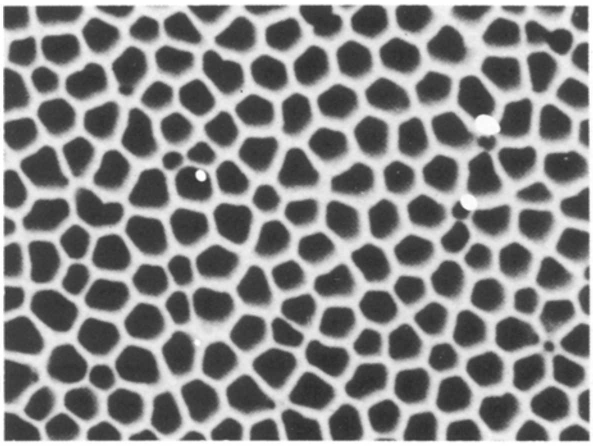

Figure 3 Top surface structure of Anotec membrane [30].

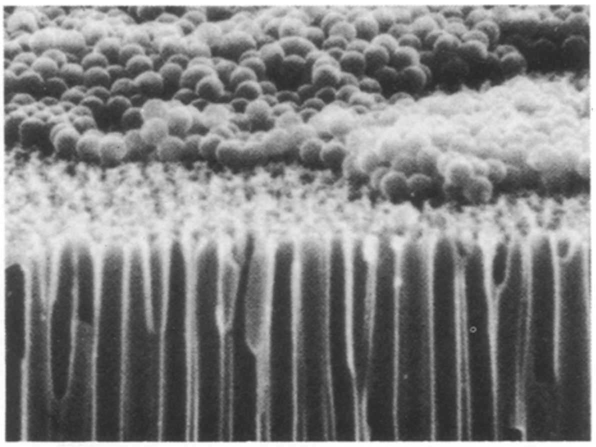

Figure 4 Cross-section of Anotec membrane [30].

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* Recently Martin and co-workers at Texas A and M University [31, 32] have also exploited Anotec membranes using a different method in which a thin skin grows over the gold coated alumina substrate, and in their case non-conductive composites based on divinyl benzene and ethylvinyl benzene are emphasized. Narrow polypyrrole fibres have also been illustrated recently using both Nuclepore and Anapore membranes, with high conductivities ($\approx 7500\ \mathrm{S\,cm^{-1}}$) claimed [33].

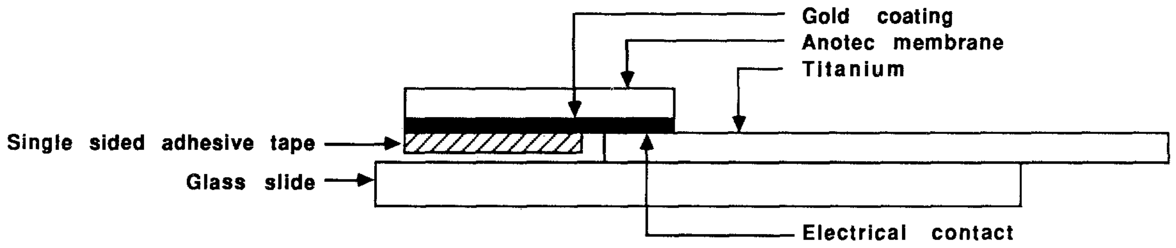

Figure 5 Side view of gold/Anotec host anode.

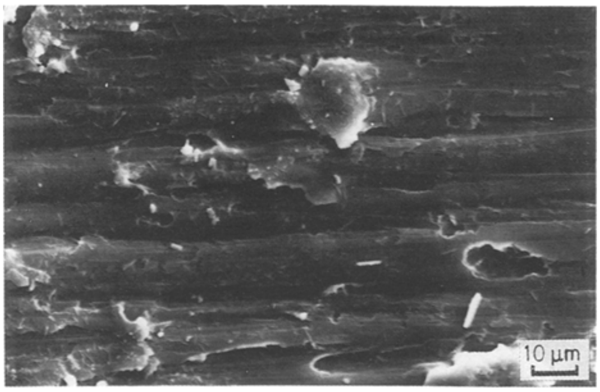

Figure 6 Polypyrrole prior to exposure to NaOH.

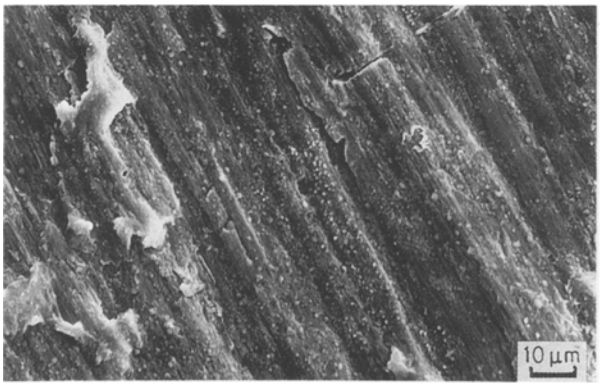

Figure 7 Same sample after 0.5 h exposure to 1 M NaOH.

2.4. Microscopy

Electrodes and filamentary polypyrroles were routinely examined at various stages using a Nikon SMZ stereozoom optical microscope. Morphologies of both uncoated and gold-coated polypyrroles were recorded using a Jeol JXA-840 scanning electron microscope (SEM) using a voltage of 15 kV and filament currents ranging from 10^{-9} to 10^{-10} amps. Where very fine structural detail was to be resolved (with the 0.2 μm pore diameter Anotec membrane), a Cambridge Stereoscan 360 SEM was employed.

3. Results and discussion

3.1. Polypyrroles from polycarbonate membrane hosts

Initial experiments with free-standing polycarbonate films did not lead to desired products. Growth of polypyrrole through the membrane only occurred over a small fraction of the surface, with the majority of the polypyrrole growing between the titanium electrode and the polycarbonate. After removal of the membrane with chloroform, a relatively flat polypyrrole product with few filaments resulted. This is in agreement with Penner and Martin's findings [22] relating to non-adhering membrane/electrode experiments.

With the gold coating, as described in Fig. 2, filaments were abundant. Their formation is summarized in Fig. 8, and can be contrasted with the prior technique given in Fig. 1. In particular, it should be noted that electrodeposition time is not critical in our case, as the 10 μm thick filaments form within the first few minutes, and the outer polypyrrole sheet then proceeds to thicken more or less uniformly with extended polymerization times. It should also be noted that the filaments form a continuum with the outer polypyrrole surface and so are strongly and permanently fixed. This mechanism also applies in the Anotec synthesis described below.

It can be seen that unlike the mechanism shown in Fig. 1, in our case overdeposition should have no effect upon filament length uniformity.

3.1.1. Effect of polycarbonate membrane pore size

Polymerizations according to the scheme in Fig. 8 were conducted using anodes comprising gold-coated isoporous membranes with pore sizes of 0.2, 1, 3 and

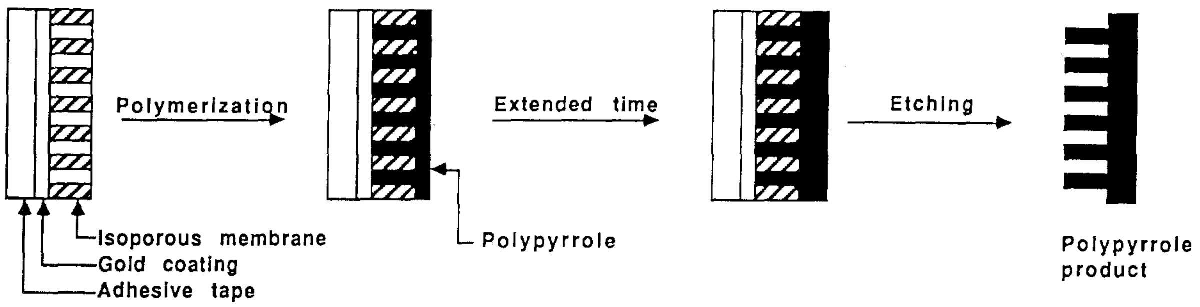

Figure 8 Scheme for synthesizing filamentary polypyrroles.

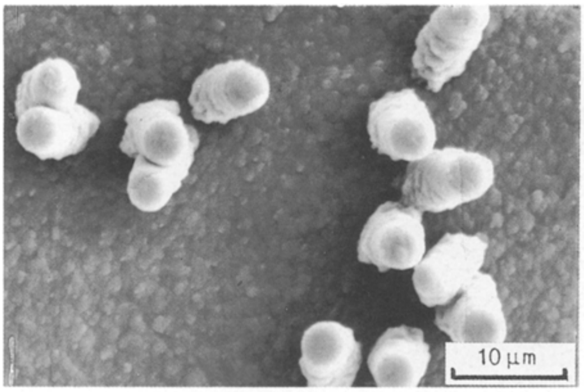

Figure 9 Polypyrrole from 5 μm pore diameter polycarbonate membrane.

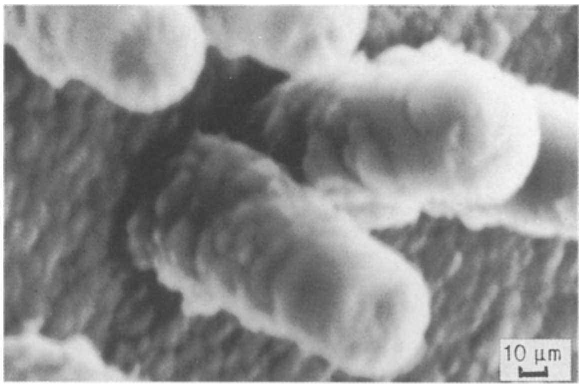

Figure 10 As for Fig. 9, higher magnification.

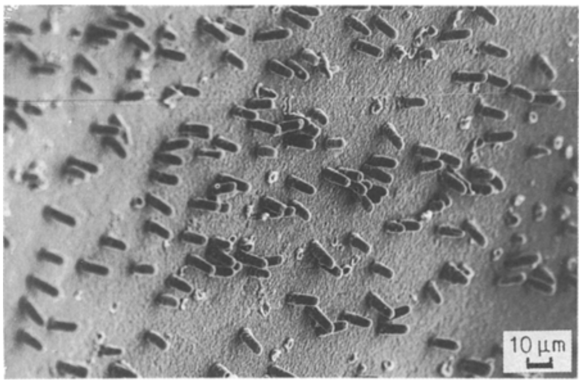

Figure 11 Polypyrrole from 3 μm pore diameter polycarbonate membrane.

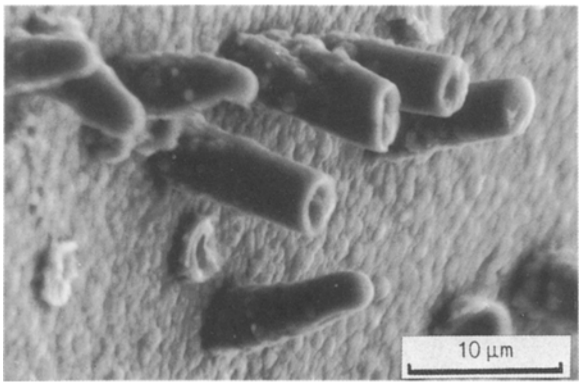

Figure 12 As for Fig. 11, higher magnification.

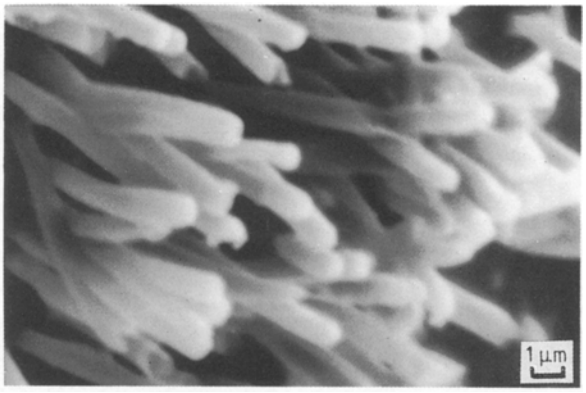

Figure 13 Polypyrrole from 1 μm polycarbonate membrane.

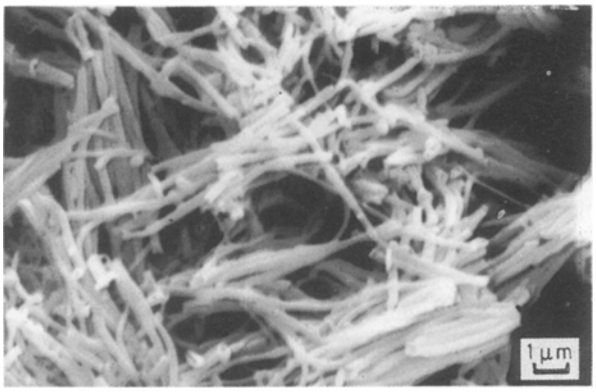

Figure 14 Polypyrrole from 0.2 μm polypyrrole membrane.

5 μm diameter. The structures of the resulting polypyrroles are shown in Figs 9–14 inclusive.

The main trends which emerge are as follows:

(i) Filaments are rather sparsely distributed, particularly where the pore diameter is large. This reflects the low concentration of tracks caused by irradiation of the polycarbonate during membrane manufacture.

(ii) As the pore size decreases, the density of pores and consequently filaments increases.

(iii) The filaments from the 5 μm membrane have very rough surfaces. As the pore diameter decreases, the filaments become much smoother. We assume that the polypyrrole is faithfully replicating the pore morphology, and conclude that 5 μm pores have jagged surfaces due either to more diffuse irradiation or to extended chemical etching.

However, it is evident from these micrographs that polypyrrole surface area will be limited by low filament density and length. Although surface area will increase with decreasing membrane pore diameter, even very small pore sizes will lead to only mediocre products.

3.2. Filamentary polypyrroles from Anotec hosts

Polypyrroles were readily prepared from Anotec membranes painted with silver, but very poor uniformity was found. At lower magnification (Fig. 15) regions in which the filaments were reasonably uniform and perpendicular to the substrate can be resolved, but other regions were characterized by

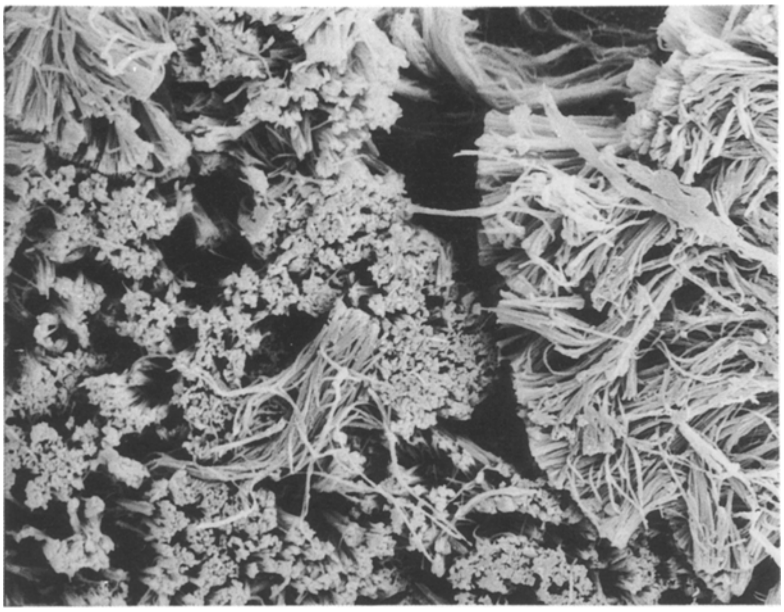

Figure 15 Polypyrrole grown from silver-painted Anotec membrane.

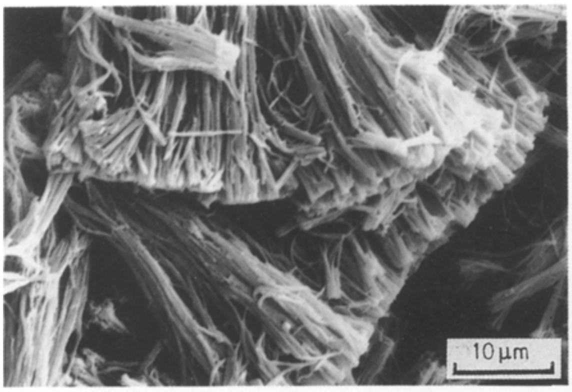

Figure 16 Same sample as Fig. 15 at higher magnification.

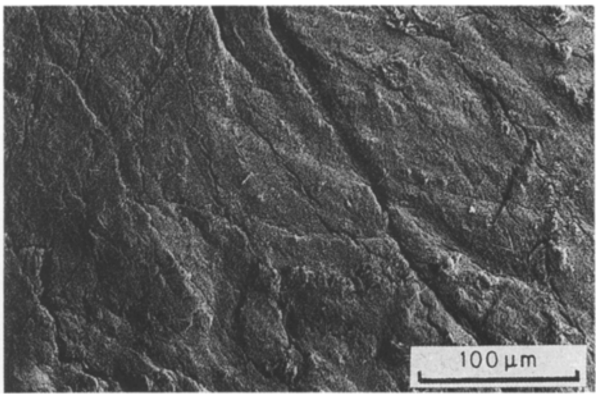

Figure 17 Carpet-like structure of completely leached polypyrrole grown from Anotec.

clumps or sheaves of fibrils (Fig. 16). This non-uniform growth is at regions of varying current density, attributable to variations in silver film thickness and to the granularity of individual silver particles.

In contrast to the above products, excellent filamentary polypyrroles resulted from polymerization through gold-coated Anotec membranes. At low magnifications in the optical microscope and in the SEM the product appears as a smooth carpet, with the high filament density and constant length resulting in a uniform layer (Fig. 17). This contrasts with the structure found after partial dissolution of the γ-alumina by incomplete exposure to NaOH, where clusters of filaments have separated to form a network of cracks or crevices (Fig. 18).

The Anotec membrane used had a pore size of 0.2 μm, similar to that of one of the polycarbonate membranes (Fig. 14). Here, although the resulting filaments are of similar thickness, they are so densely packed together that they provide co-operative support, and so remain erect. This contrasts with the polycarbonate-derived polypyrrole samples where many of the well separated filaments collapse.

Although a suggestion of hexagonal fine structure was found for the Anotec-host polypyrrole filaments under the conditions used the Jeol SEM, high resolution micrographs were not readily obtained. Thus a gold-coated sample was examined in a higher performance Stereoscan 360 SEM, from which fine structure of both sides and ends of the filaments are readily identified (Figs 19, 20). The angular cross-section of the filaments contrasts with the essentially circular filaments derived from the polycarbonate hosts. The

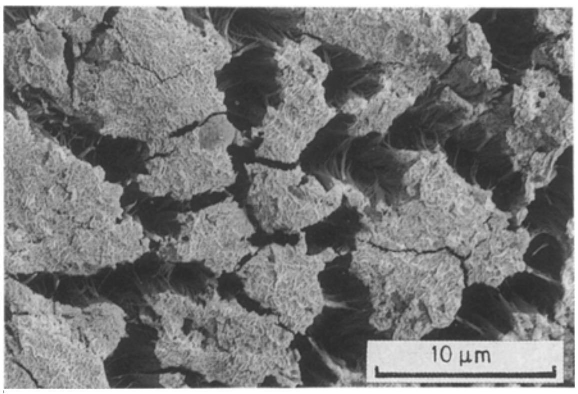

Figure 18 Polypyrrole after incomplete leaching of γ-alumina.

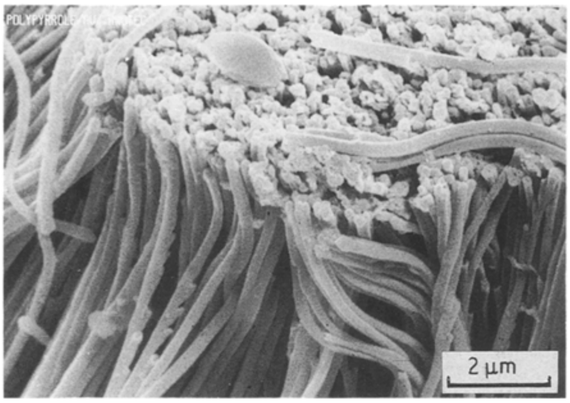

Figure 19 Side view of Anotec host polypyrrole filaments.

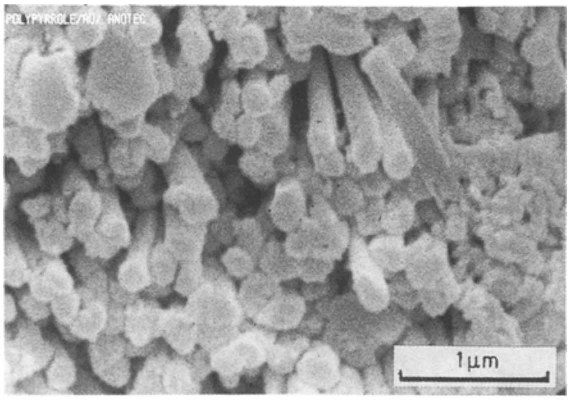

Figure 20 Ends of polypyrrole indicating non-uniform Anotec pore diameters.

range of diameters revealed in Fig. 20 suggests that the hexagonal pores are not entirely uniform, consistent with some variation in cross-section as previously shown in Fig. 3.

4. Conclusions

We conclude from this investigation that polypyrroles can be made with highly regular filamentary structures using a variety of isoporous host membranes. However, where high surface area is desired coupled with high uniformity, the use of γ-alumina membranes of the Anotec type has great potential. Uniformly long, densely packed hexagonal filaments are readily formed, to give polypyrroles which may prove useful in switching and other devices.

Acknowledgements

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