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Template Synthesis of Electronically Conductive Polymers

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TEMPLATE SYNTHESIS OF ELECTRONICALLY CONDUCTIVE POLYMERS

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ABSTRACT

We have recently developed a method for synthesizing micro and nanoscopic fibers and tubules of electronically conductive polymers. This method entails synthesis of the polymer within the pores of a microporous host membrane. Conductivities in the narrowest of these "template-synthesized" tubules and fibers can be significantly higher than in conventional forms (e.g. powders or thin films) of the analogous polymer. These previous conductivity data were based on a two-point measurement of the resistance of the host membrane after synthesis of the conductive polymer fibers within this membrane. In this paper we will show results of conductivity measurements on thin films composed of the template-synthesized tubules and fibers. A four-point conductivity measurement was used on these thin films. These four-point measurements corroborate the earlier two-point conductivity data and, again, show that the template-synthesized materials are significantly more conductive.

INTRODUCTION

We have been exploring the idea of using the pores in microporous membranes as templates for the synthesis of micro and nanomaterials. (1-13) The membranes employed have linear, cylindrical pores of equivalent diameter. Electron micrographs of the surfaces of two such membranes are shown in Figure 1. Membranes of this type are sold commercially and are used as filters. Rather than viewing these membranes as filters, we view the pores in such membranes as micro "beakers," and we synthesize materials (e.g. polymers, metals, or semiconductors) within these tiny beaker. Because of the cylindrical pore geometry (see Figure 1), synthesis of a material within the pore yields a micro or nanocylinders of the material. (The distinction between "micro" and "nano" is ambiguous. We define a nanocylinder as cylinder with a diameter of 100 nm (1,000 Å) or less.) Figure 2 shows electron micrographs of various micro and nanocylinders prepared via this approach. Note that both solid and hollow cylindrical structures can be prepared.

We call this approach for obtaining micro and nanomaterials "template synthesis" because the pores in the membrane are used as templates. It is a general synthetic method; we have used this approach to prepare micro and nano polymers (1-8), metals (1, 9-12), and semiconductors (13). In the metals area, we are interested in making micro and nano electrodes and we are interested in the optical properties of nanometals. In the semiconductor area we are attempting to see if the template synthesis method can be used to prepare monodisperse quantum wires (13).

Finally, we are especially interested in electronically conductive polymer nanofibers and nanotubules synthesized via the template method (1-8). Such conductive polymer fibers and tubules are the subject of this paper. We have shown that template-synthesized electronically conductive polymer nanofibers

can have electronic conductivities that are orders of magnitudes higher than conventional forms (e.g. powders or thin films) of the same polymer (5-8). We have observed such enhancements in conductivity from template-synthesized polypyrrole (5,6), poly(3-methyl thiophene) (5), polyacetylene (7), and polyaniline (8). This enhancement in conductivity results from enhancements in molecular and supermolecular order in the template-synthesized material, relative to a more conventional form of the same material (6).

Our previous conductivity data for the template-synthesized conductive polymers were based on two-point measurements of the resistance of the host membrane after synthesis of the electronically conductive polymer fibers within this membrane (5-7). Four-point conductivity measurements are always preferable to two-point measurements. Furthermore, the two-point method used previously required that the pore density and pore size in the host membrane be accurately known. We have recently developed a method for forming thin films of template-synthesized conductive polymer tubules and fibers and we have conducted four-point conductivity measurements on these thin films. These more reliable four-point measurements corroborate the earlier two-point conductivity data. That, is the four-point conductivity measurements also show that the template-synthesized polymers are significantly more conductive.

EXPERIMENTAL

Nuclepore polycarbonate filters were used as the host membranes (Figure 1A, 1-8). These membranes have cylindrical pores with highly-monodisperse diameters. Membranes with pore diameters ranging from 100 nm to 400 nm were used in these investigations. In our previous investigations, tubule and fibril polymerizations were carried out by allowing the membrane to separate an aqueous solution of the monomer from an aqueous solution of a chemical oxidizing agent. We have since developed an easier method for

conducting these template syntheses. In this method, the host membrane is simply immersed into a solution containing both the monomer and the oxidizing agent. This method is based on the work of Kuhn et al. (13). Conductive polymer tubules are obtained within the host membrane.

We will present conductivity data for polyaniline tubules synthesized within these membranes. The monomer solution was 0.325 M in aniline and 1 M in HCl. The oxidant solution was 0.125 M in sodium vanadate, 1 M in HCl, and 0.5 M in p-toluenesulfonate. The template membrane was immersed in the monomer solution and an equal volume of the oxidant solution was added. Polymerization was allowed to proceed for two hours. We have shown that the conductive polymer preferentially nucleates and grows on the pore walls (5-8). As a result of this surface-growth, conductive polymer tubules are obtained. After polymerization, the polyaniline surface layers were removed by polishing the faces of the membrane with alumina powder, and the tubule-impregnated membrane was rinsed with 1 M HCl.

The procedure outlined in Figure 3 was used to prepare thin films from the template-synthesized polyaniline tubules. The tubule-containing polycarbonate membrane was placed onto the surface of a microporous alumina filtration membrane (Anopore (7,9)) and these membranes were placed in a vacuum filtration apparatus. Chloroform was then applied to the surface of the polycarbonate membrane. Because a vacuum is applied to the lower surface of the alumina filtration membrane, the $CHCl_3$ is filtered through the membranes. Polycarbonate is, however, soluble in $CHCl_3$. As a result, the polycarbonate template membrane is dissolved and the polyaniline tubules are deposited onto the surface of the alumina filtration membrane.

This treatment with chloroform was followed by an identical treatment with methylene chloride, which is a better solvent for the polycarbonate

membrane. This subsequent CH_2Cl_2 treatment insures that all of the polycarbonate has been dissolved. After filtering the methylene chloride through the membrane, a second tubule-containing polycarbonate membrane is then applied and the process is repeated (Figure 3). This process can be repeated as many times as desired, so films of any desired thickness can be obtained. The final step is to compact the polyaniline tubules in a pellet press at a pressure of $6x10^4$ psi.

RESULTS AND DISCUSSION

An electron micrograph of a typical thin film composed of template-synthesized polyaniline tubules is shown in Figure 4A. The tubular structure can not be seen in this cross-sectional image. This means that the tubules were crushed under the high pressures used to compact the film. We have obtained analogous thin films from polypyrrole tubules; (Figure 4B); however, for this polymer, the tubule structure is retained in the compacted thin film. This indicates that polypyrrole has better mechanical properties than polyaniline.

Conductivity data obtained from thin films prepared from polyaniline tubules of various diameters are shown in Table 1. There are several interesting points to note from Table 1. First, in agreement with our 2-point conductivity data reported previously (5-7), the conductivities obtained on these thin films, prepared from template-synthesized tubules, increase as the diameter of the tubule used to prepare the thin film decreases. We have shown that this increase in conductivity occurs because the smallest-diameter tubules have highly-ordered polymer chains (6). Second, note that the conductivities obtained for the film prepared from the smallest-diameter tubules is higher than the conductivity of bulk samples of polyaniline. Bulk samples of polyaniline prepared under the same conditions gave conductivities of 9 S cm^{-1}.

CONCLUSIONS

We have shown that template-synthesized polyaniline tubules can be processed into highly-conductive thin films. We have processed template-synthesized polyaniline and polypyrrole tubules into thin films of this type. We have also shown that a more reliable four-point conductivity measurement confirms our early two-point measurements which showed that these nanoscopic template-synthesized fibers and tubules have enhanced electronic conductivities.

Finally, we have previously shown that these enhancements in electronic conductivity results from enhancements in molecular and supermolecular order in the template-synthesized conductive polymers (6). In particular, we have used polarized infrared absorption spectroscopy to show that the polymer chains in the narrowest template synthesized materials are oriented (6). An obvious question arises from this work - what causes this orientation? The answer to this question can be seen in the electron micrograph in Figure 1A. A portion of the pore wall is visible in one of the pores in the upper right-hand corner of this electron micrograph. Striations are present on the pore wall. These striations arise because the membrane is etch-oriented during processing. Hence, the polycarbonate chains along the pore walls in these membranes are oriented.

As noted above, when conductive polymers are synthesized within the pores of these membranes, the polymer preferentially nucleates and grows on the pore walls. Because the polycarbonate chains along the pore wall are oriented, the conductive polymer chains grown on these walls are also oriented. Qualitative evidence for this orientation can be seen as striations on the outer walls in high-magnification images of the template-synthesized materials (Figure 5). Again, quantitative evidence for this orientation was described in our

previous investigation (6). Hence, the term "template synthesis" has two meanings. First, the pores act as templates that determine the shape and size of the conductive polymer particle produced. Second, the chain orientation present in the host membrane acts as a template to produce analogous orientation in the polymer synthesized within the pore.

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TABLE 1

Four-point conductivity data from polyaniline films prepared from template-synthesized tubules of various diameters.

Diameter of Tubules Used to Prepare the Film (nm)	Conductivity ($S\ cm^{-1}$)
100	50
200	17
400	14

Figure 1. Electron micrographs of the surfaces of two types of template membranes. A. Microporous track-etched polycarbonate membrane (obtained from the Nuclepore Corporations). B. Microporous electrochemically-synthesized alumina membrane (prepared in house).

Figure 2. Electron micrographs of various template-synthesized micro and nanostructures. A. Polypyrrole nanofiber. An array of Pt microcylinders. C. Two polypyrrole microtubules. D. An array of Au microtubules.

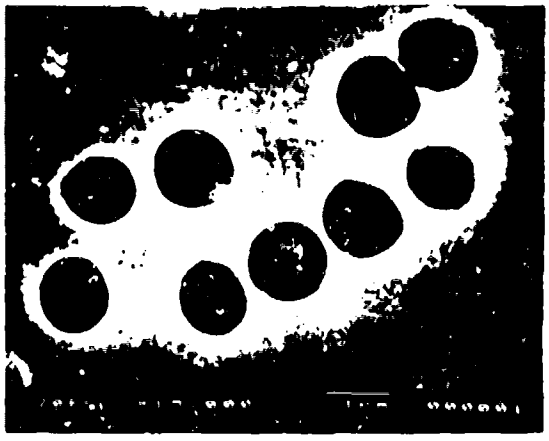
Figure 3. Schematic diagram of procedure used to prepare thin films from template-synthesized fibers and tubules.

Figure 4A. Scanning electron micrograph of a cross-section of a thin film prepared form 100 nm-diameter polyaniline tubules.

Figure 4B. Scanning electron micrograph of a cross-section of a thin film prepared from 50 nm-diameter polypyrrole tubules.

Figure 5. High resolution scanning electron micrograph showing striations on the surfaces of template-synthesized polypyrrole tubules.

A



B

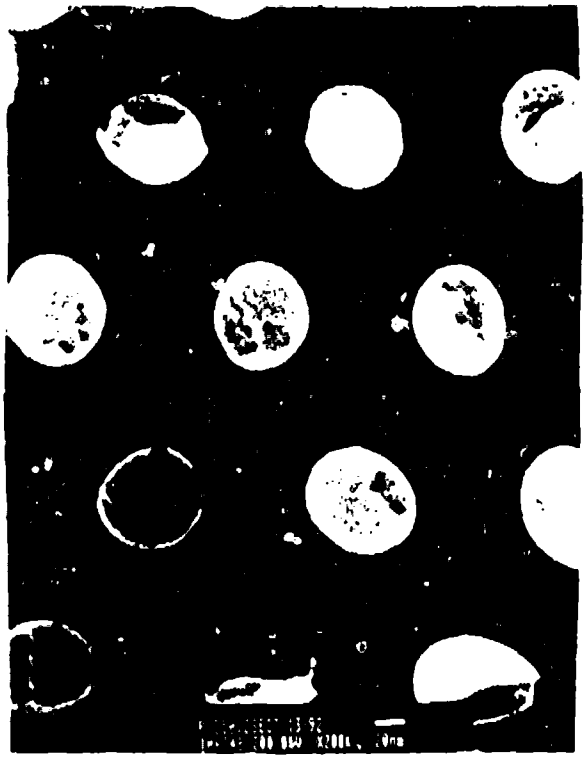
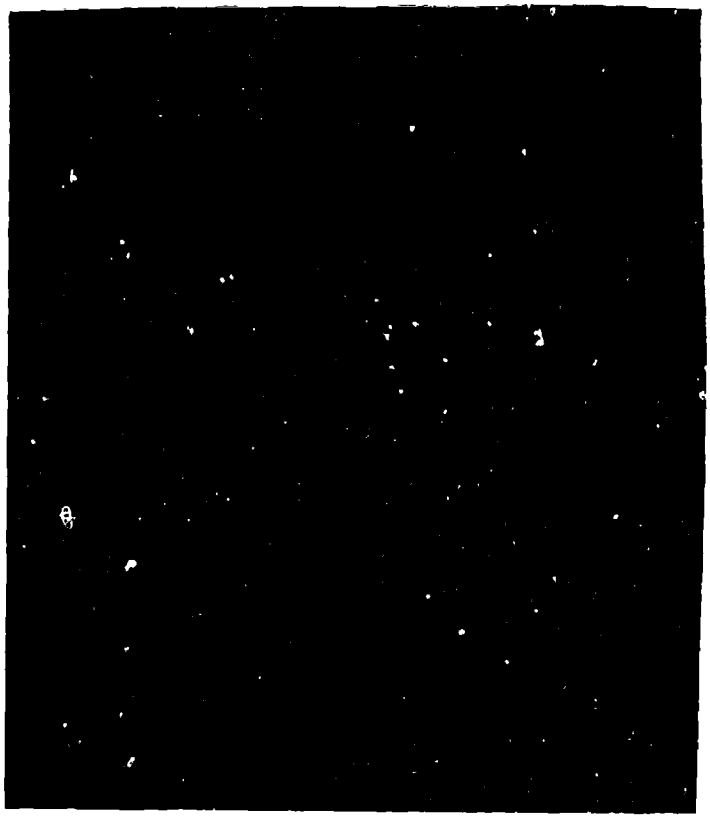


Fig 1


A
0.1 μm


B
0605 10.0U


C


D

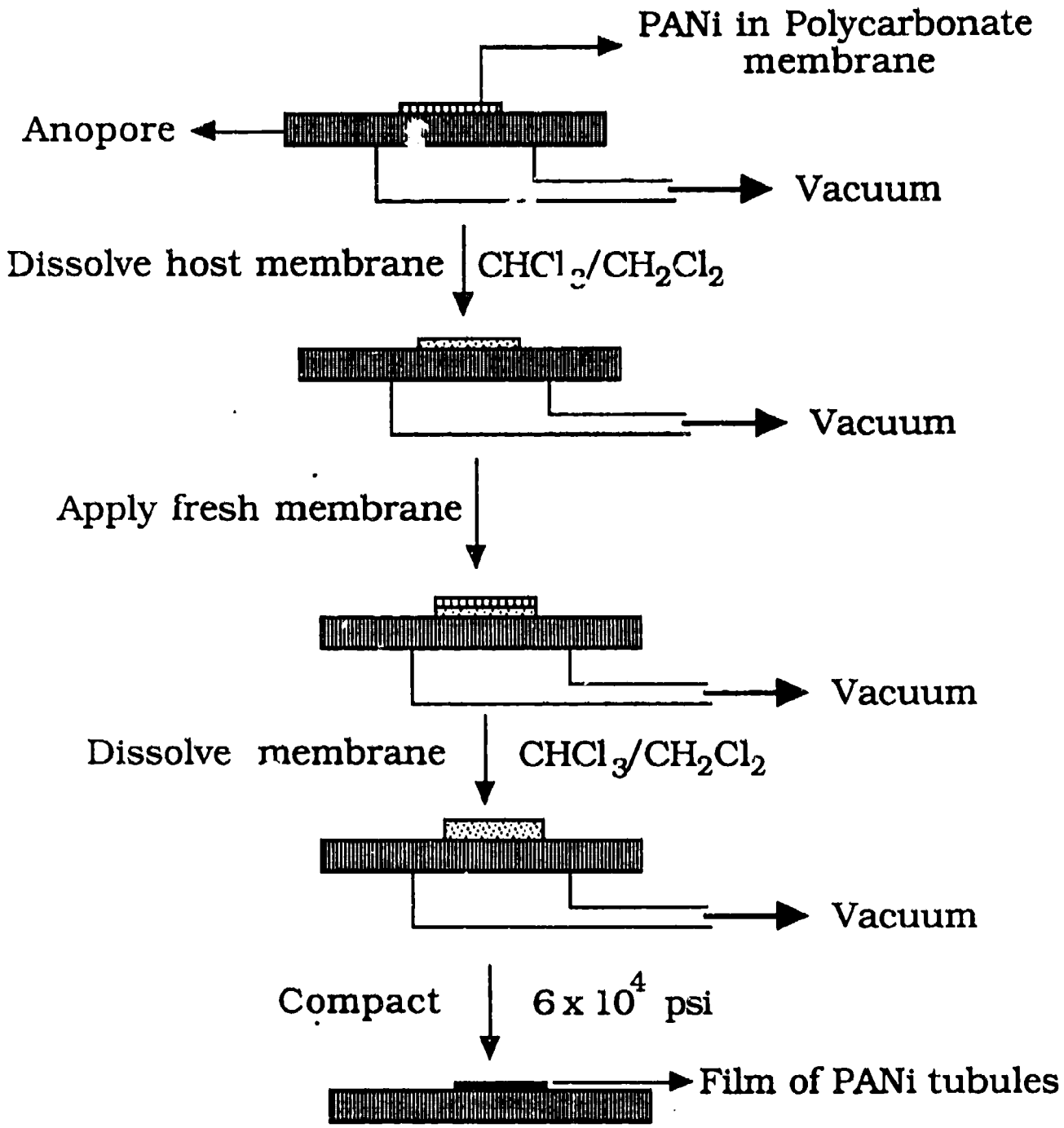
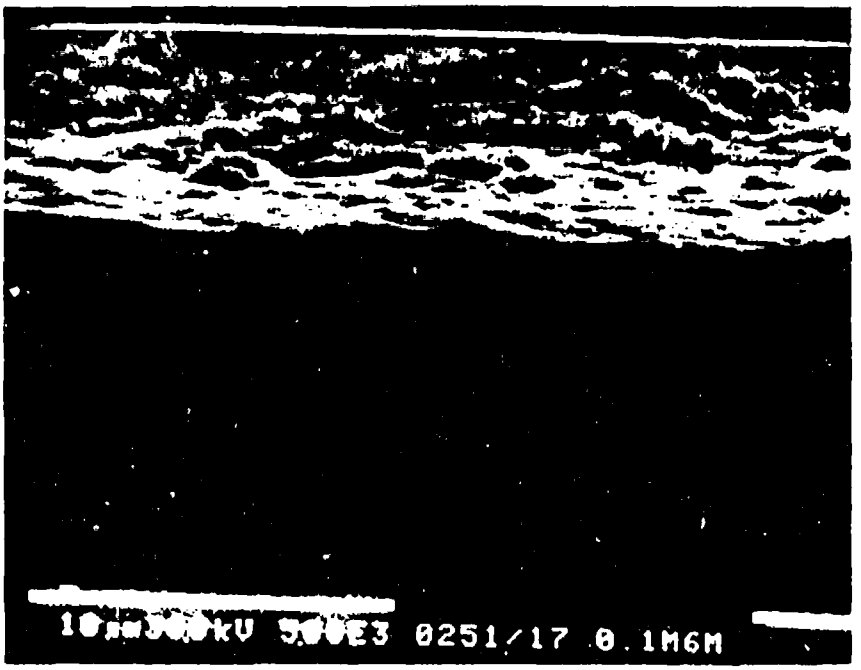

PANi in Polycarbonate membrane
Anopore
Vacuum
Dissolve host membrane
$CHCl_3/CH_2Cl_2$
Vacuum
Apply fresh membrane
Vacuum
Dissolve membrane
$CHCl_3/CH_2Cl_2$
Vacuum
Compact
6×10^4 psi
Film of PANi tubules

Fig 3

A



B

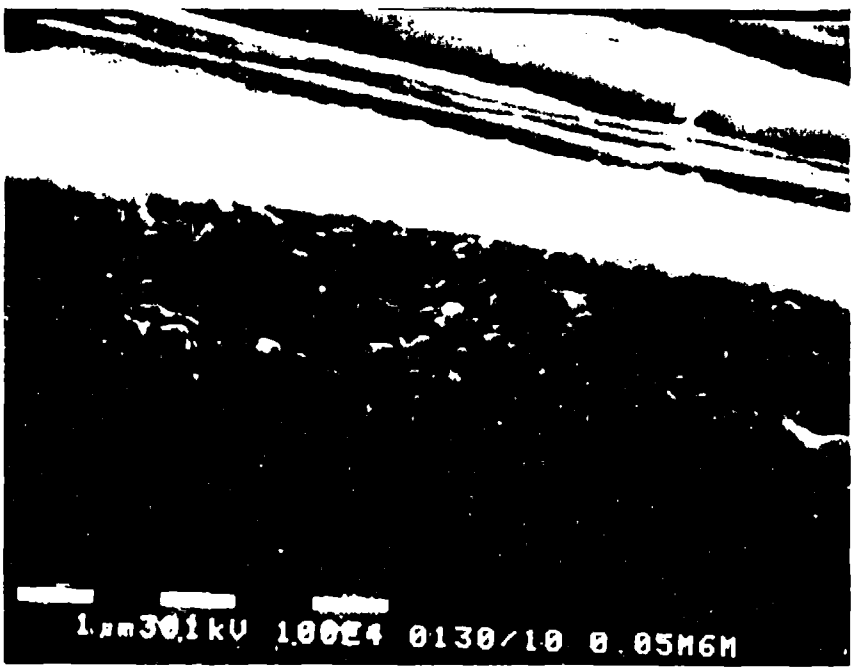


Fig 4


lum300kV 436E4 0015 00 0 4 HOR