Template-Synthesized Polyaniline Microtubules

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Microtubules composed of polyaniline (PANi) were obtained by synthesizing PANi within the pores of microporous template membranes. These template-synthesized polyaniline tubules showed enhancements in electronic conductivities over conventional forms of analogous polymers. The origin for this enhancement in conductivity was studied using a host of techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), and polarized infrared absorption spectroscopy (PIRAS). We have used TEM to monitor the growth of PANi within the pores of the membrane. For short polymerization times, a thin skin of polymer lines the pore walls. With increase in polymerization time, the polymer grows in thickness. PIRAS data show that the polymer deposited directly on the pore wall is highly ordered relative to subsequently deposited polymer. This ordering of the polymer chains is responsible for the enhancement in conductivity. PIRAS was also used to show that the polymer chains are preferentially aligned perpendicular to the tubule axis.

Introduction

We have been exploring a new approach for preparing nanomaterials.[1-13] This approach, called "template synthesis", entails synthesis of a material within the pores of a nanoporous membrane. The membranes employed have cylindrical pores of uniform diameter. Because the desired material is synthesized within these pores, a nanoscopic cylinder of the material is obtained; the diameter of this cylinder is determined by the diameter of the pores in the "template" membrane. We have used this approach to synthesize nanocylinders of electronically conductive polymers,[1-7] metals,[8-13] semiconductors,[14] and carbon.[15] We have also shown that tubular nanostructures (i.e., hollow nanocylinders) of these various materials can be obtained via this approach. Finally,we have shown that the aspect ratios of the nanocylinders prepared via this method can be controlled at will. Hence, this template approach is proving to be a versatile method for synthesizing nanomaterials.

Table 1. Specifications of the Polycarbonate Template Membranes Used in These Studies

pore diam (nm)	pore density[a] (pores/cm^2)	thickness[b] (μm)
100	3×10^8	7
200	3×10^8	11
400	1×10^8	11

[a] From Poretics Corp. product literature. [b] Measured using a digital micrometer.

Our previous work on electronically conductive polymer nanocylinders and tubules showed that these template-synthesized nanostructures can have electronic conductivities of over an order of magnitude when compared to bulk samples (e.g., powders, or thin films) of the same polymer.[1,4-6] Such enhancements in conductivity were observed in template-synthesized nanocylinders composed of polypyrrole,[1,4] poly(3-methylthiophene),[1,4] and polyacetylene.[6] We have recently used the template method to prepare nanotubules of the electronically conductive polymer polyaniline.[5] In analogy with our previous investigation, we have found that the dc conductivities of these polyaniline nanostructures are higher than bulk samples of this polymer.[5] We have found that this enhancement in conductivity results from an enhancement in the extent of order in the template-synthesized polyaniline. We present the results of these investigations in this paper.

Experimental Section

Materials. The starting material, aniline (Aldrich 99%) was twice-distilled prior to use. Purified water, obtained by passing house-distilled water through a Milli-Q (Millipore) water purification system, was used to make all the solutions. Sodium vanadate, HCl, and *p*-toluenesulfonic acid were used as received. Poretics microporous polycarbonate membrane filters (Poretics Corp.) were used as the template membranes. These membrane filters are available in a variety of pore diameters and pore densities. The specifications for the membranes that were used for these studies are shown in Table 1.

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* Corresponding author.

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(1) Cai, Z.; Martin,C. R. *J. Am. Chem. Soc.* **1989,** *111,* 4138.
(2) Martin, C. R.; Van Dyke, L. S.; Cai, Z.; Liang, W. *J. Am .Chem. Soc.* **1990,** *112,* 8976.
(3) Martin, C. R. *Adv. Mater.* **1991,** *3,* 457.
(4) Cai , Z.; Lei , J.; Liang , W.; Menon , V.; Martin , C. R.; *Chem. Mater.* **1991,** *3,* 960.
(5) Martin, C. R.; Parthasarathy, R.; Menon, V. *Synth. Met.* **1993,** *55,* 1165.
(6) Liang, W.; Martin, C. R. *J. Am. Chem. Soc.* **1990,** *112,* 9667.
(7) Penner, R. M.; Martin, C. R. *J. Electrochem. Soc.* **1986,** *133,* 2206.
(8) Brumlik, C. J.; Martin, C. R. *J. Am. Chem. Soc.* **1991,** *113,* 3175.
(9) Penner, R. M.; Martin, C. R. *Anal. Chem.* **1987,** *59,* 2627.
(10) Tierney, M. J.; Martin, C. R. *J. Phys. Chem.* **1989,** *93,* 2878.
(11) Foss, C. A.; Tierney, M.; Martin, C. R. *J. Phys. Chem.* **1992,** *96,* 9001.
(12) Foss, C. A.; Hornyak, G. L.; Stockert, J. A.; Martin, C. R. *Adv. Mater.* **1993,** *5,* 135.
(13) Foss, C. A.; Hornyak, G. L.; Stockert, J. A.; Martin, C. R. *J. Phys. Chem.* **1992,** *96,* 7497.
(14) Klein, J. D.; Herrick, R. D. II.; Palmer, D.; Sailor, M. J.; Brumlik, C. J.; Martin, C. R. *Chem. Mater.* **1993,** *5,* 902.
(15) Parthasarathy, R.; Phani, K. L. N.; Martin, C. R., unpublished result, Colorado State University, Sept, 1993.

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Polymer Synthesis. Gregory et al.[16] have developed a method for coating textiles with conductive polymers. We have used a similar procedure for chemically synthesizing polyaniline (PANi) within the pores of the polycarbonate template membranes. In this method, the template membrane is immersed in a precooled (5 °C) solution that was 0.325 M in aniline and 1 M in HCl. An equal volume of precooled (5 °C) oxidant solution containing sodium vanadate[17] (0.125 M) and *p*-toluenesulfonic acid[18] (0.5 M) in 1 M in HCl[19,20] was then added. The mixture was left for polymerization for 2 h at ca. 5 °C. During this period, polyaniline was produced from the monomer and deposited within the pores of the membrane.

We have found that the polyaniline obtained preferentially deposits on the pore walls and on both faces of the template membrane. Because the polymer deposits on the pore walls, polyaniline nanotubules that run through the entire thickness of the membrane are obtained. Analogous results were obtained when polypyrrole[4] and poly (3-methyl thiophene)[4] were synthesized in such membranes. The surface layers that coat both faces of the membranes were removed by polishing with 1 μm alumina powder. The membrane was then ultrasonicated in 1 M HCl to remove the alumina powder. In some experiments, it was desirable to isolate the polymer tubules. This was done by dissolving the template (polycarbonate) membrane in dichloromethane and collecting the resulting polymer tubules by filtration on an alumina filter.[6,8] These polymer tubules were then repeatedly rinsed with copious quantities of dichloromethane to remove traces of the polycarbonate template membrane.

As a control, bulk polyaniline was synthesized under identical conditions but without the use of a template membrane. This yielded a precipitate of polyaniline which was collected by filtration. The precipitate was rinsed in HCl and then dried. Finally, sodium vanadate[17] was used for all the syntheses rather than the more commonly used ammonium persulphate.[19,20] This is because we have found that PANi grows nonuniformly within the pores of the template membrane (i.e., some pores become filled with PANi and others apparently do not) when persulfate is used as the oxidant.

Electron Microscopy. Scanning electron microscopic (SEM) images of the polyaniline nanotubules were obtained by dissolving the host membrane and collecting the tubules as described above. A Phillips 505 electron microscope was used. The PANi tubules were sputtered with a thin film of gold prior to imaging. Transmission electron microscopy (TEM) studies were carried out using a JEOL 2000 TEM. TEM was used to monitor the growth of PANi within the pores of the membrane. The TEM samples were prepared as follows: The polyaniline/polycarbonate composite was immersed in a 1% (w/v) aqueous OsO_4 solution for 2 h. The OsO_4 selectively stains the PANi. The stained membrane was then embedded in an epoxy resin. Thin facial slices of the membrane were obtained by microtoming the embedded sample. These microtomed sections were obtained for a variety of polymerization times and pore diameters.

Polarized Infrared Absorption Spectroscopy (PIRAS). We have shown that PIRAS can be used to study the extent of polymer chain orientation in template-synthesized electronically conductive polymers.[4,6] We have conducted analogous experiments on template-synthesized polyaniline. As before, the data were obtained using a Mattson Galaxy Fourier transform infrared spectrometer. The polarizations used for PIRAS analysis are shown in Figure 1.[4] An Al wire grid polarizer was used to control polarization. The polarization $I_\perp$ is orthogonal to the axes of the PANi tubules. The integrated absorbance by the PANi tubules of this polarization is labeled $A_\perp$. The polarization vector for the beam labeled I_{30} makes an angle of 30° with respect to the tubule axes and its integrated absorbance is A_{30}. A_{30} has a component in the parallel direction and is therefore related to $A_\parallel$, where $A_\parallel$ is the integrated absorbance intensity for a beam polarized parallel to the tubule axis.

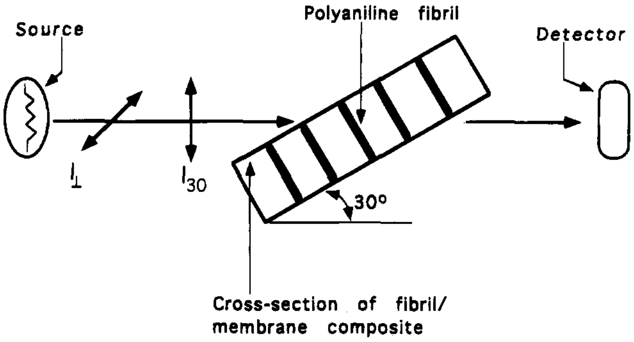

Figure 1. Experimental setup for the PIRAS experiments.

The dichroic ratio, defined as $R = A_\parallel/A_\perp$, quantitatively describes the polymer chain orientation within a sample.[21,22] In general, $R = 1$ implies no preferred orientation of the polymer chains. A value of R that deviates from unity shows that there is some preferred polymer chain orientation. A_{30} is related to $A_\parallel$ and $A_\perp$ via[21,22]

$$A_{30} = A_\parallel \cos^2(30°) + A_\perp \sin^2(30°) \qquad (1)$$

Dividing both sides of eq 1 by $A_\perp$ and rearranging yield

$$\mathrm{R} = A_\parallel/A_\perp = {}^1/_3(4A_{30}/A_\perp - 1) \qquad (2)$$

Spectra of the PANi tubules were obtained by subtracting spectra of the polycarbonate (PC) background from the PANi/PC composite membrane. First, prior to the synthesis of the PANi tubules within the membrane, the template membrane was mounted in the FTIR sample holder and background spectra were obtained for the two different polarizations shown in Figure 1. These spectra showed strong IR bands for polycarbonate.[4] Polyaniline tubules were then synthesized in the pores of the template membrane as described above. The membrane was retained in the sample holder during tubule synthesis. This was done to ensure that spectra were obtained, after polymerization, on the same portion of the membrane as was used to obtain the spectra before polymerization. After template synthesis, the surface layers were removed by polishing with alumina powder. The membrane was cleaned using 1 M HCl and then placed back in the spectrophotometer. Spectra were once again recorded for the two different polarizations (Figure 1). Subtraction of the corresponding background spectra yielded PANi spectra for the two polarizations. The bands at 1600 and 1500 cm^{-1} [23,24] were used for these PIRAS analyses. Table 2 shows typical raw absorption data used for such analyses. These data were included so that the reader could get a feel for the relative magnitude of the absorption before and after incorporation of PANi.

The evolution of the PANi spectrum was studied as a function of polymerization time. The polymerization time was varied from 30 min to 2 h. All of the PIRAS spectra were obtained for polymer grown in the same membrane filter (400 nm pore diameter membrane).

Preparation of Thin Films from the Template-Synthesized PANi Tubules. Thin films were prepared as

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(16) Gregory, R. V.; Kimbrell, W. C.; Kuhn, H. H. *Synth. Met.* **1989**, *28*, C823.

(17) Armes, S. P.; Aldissi, M.; Hawley, M.; Beery, J. G.; Gottesfeld, S. *Langmuir* **1991**, *7*, 1447.

(18) Kulkarni ,V. G.; Mathew ,W. R.; Wessling, B.; Merkle, H.; Blaettner, S. *Synth. Met* .**1991**, *41*, 1009.

(19) Macdiarmid, A. G.; Chiang, J. C.; Halpern, M.; Huang, W. S.; Mu, S. L.; Somasiri, N. L. D.; Wu, W.; Yaniger, S. I. *Mol. Cryst. Liq. Cryst.* **1985**, *121*, 173.

(20) Chiang, J. C.; Macdiarmid , A. G. *Synth. Met.* **1986**, *13*, 193.

(21) Monnerie, L. In: Ward, I. M., Ed. *Developments in Oriented Polymers;* Elsevier: London, 1987; Vol. 2.

(22) Zbinden, R. *Infrared Spectroscopy of High Polymers*; Academic Press: New York, 1964; p 186.

(23) Cromack, K. R.; Jozefowicz, M. E.; Ginder, J. M.; Epstein, A. J.; McCall, R. P.; Du, G.; Kim, K.; Li, C.; Wang, Z. H.; Druy, M. A.; Glatkowski, P. J.; Scherr, E. M.; Macdiarmid, A. G. *Macromolecules* **1991**, *24*, 4157.

(24) Monkman, A. P.; Adams, P. *Synth. Met.* **1991**, *40*, 87.

Table 2. Integrated Absorption Intensities for the Polycarbonate/Polyaniline Composite Membranes at the Indicated Polymerization Times[a]

polymerization time (min)	$A_{\parallel}$ 1500	$A_{\parallel}$ 1600	$A_{\perp}$ 1500	$A_{\perp}$ 1600
0	1.274	0.759	1.231	0.708
30	1.705	1.236	1.564	1.052
60	2.148	1.698	1.999	1.512
120	2.454	1.965	2.364	1.933
240	2.548	2.109	2.542	2.083

[a] Polymerization time = 0 is for the polycarbonate membrane before incorporation of polyaniline. $A_{\perp}$ is the perpendicular polarization, and $A_{\parallel}$ is the parallel polarization.

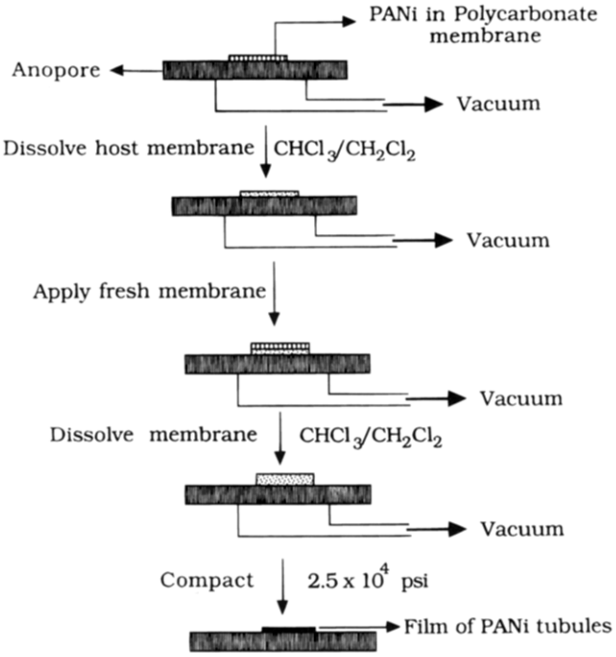

Figure 2. Schematic of the procedure used to prepare thin films from the PANi tubules.

follows: PANi was synthesized in the polycarbonate membrane as described above. The surface layers of PANi were removed from the PC membrane. The PANi/PC samples were vacuum-dried for 2 days prior to dissolution of the host membrane. It has been shown that this vacuum drying period is necessary to stabilize the conductivity of PANi.[20] The PANi tubules were then isolated from the PC membrane. The procedure [5] that we have used to do this is shown in Figure 2. The PANi/PC composite was cut into rectangular strips of ca. 4 mm in width and 2.5 cm in length. An Anopore microporous alumina filtration membrane was placed in a vacuum filtration flask and the PANi/PC membrane strip was placed on the Anopore filter. Chloroform and dichloromethane were used to dissolve away the polycarbonate membrane. The PANi tubules were left on the Anopore support. Another PANi/PC composite strip was laid down over these PANi tubules and the process was repeated. This process was repeated until a sufficient amount of PANi tubules were collected. Typically six membranes were dissolved to form the PANi films investigated here. The PANi/Anopore was left overnight in dichloromethane to remove traces of polycarbonate. The PANi tubules were then compacted using an IR press at a pressure of 2.5×10^4 psi so that a thin film of PANi was obtained. This film coated the surface of the Anopore filter. Dc conductivity measurements[5] were made on this film of PANi tubules using the four-probe method.

Results and Discusssion

Scanning Electron Microscopy. Scanning electron micrographs (SEM) of the template-synthesized PANi nanostructures obtained after dissolution of the PC template membrane are shown in Figure 3. These images clearly show that nanotubules are obtained when PANi is synthesized within the pores of the template membrane. Nanotubules of this type were also observed previously when polypyrrole and poly (3-methylthiophene) were synthesized in such membranes.[1-4] Tubules of polymer are obtained because the polymer preferentially nucleates and grows on the pore walls. It is also worth noting that these tubules are broken in many places. This may be contrasted to the case of polypyrrole tubules which retained their structural integrity after dissolution of the template poly-

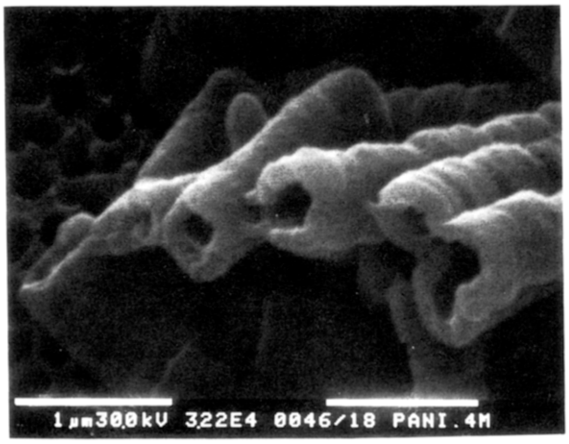

Figure 3. Scanning electron micrograph of polyaniline microtubules.

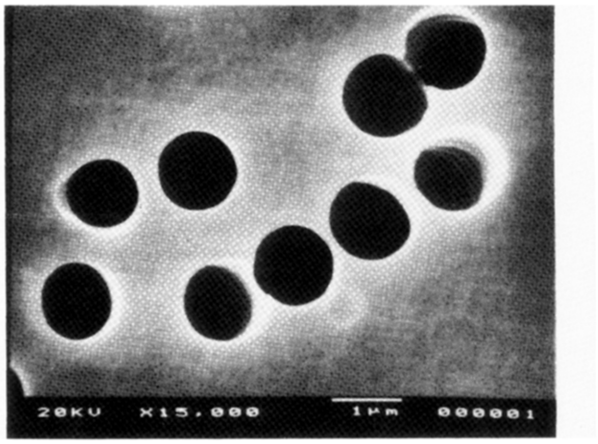

Figure 4. Scanning electron micrograph of polycarbonate template membrane.

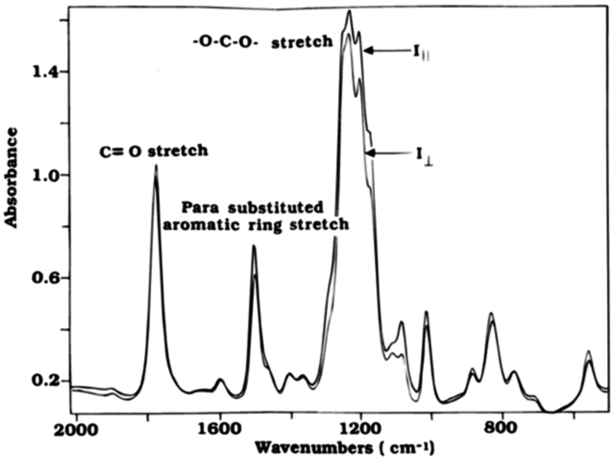

Figure 5. PIRAS data for 400 nm polycarbonate membrane.

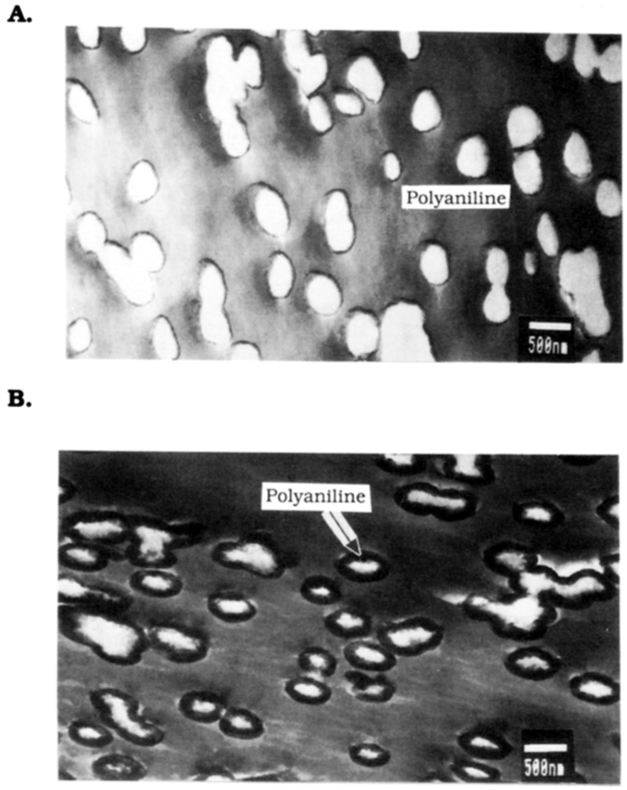

Figure 6. Transmission electron micrographs of microtomed sections of the polycarbonate membrane after synthesis of PANi tubules within the pores of the membrane: (A) polymerization time = 30 min; (B) polymerization time = 6 h. Pore diameter = 400 nm.

carbonate membrane; i.e., the polypyrrole did not break during dissolution and collection.

Finally, there are striations on the sides of these PANi nanotubules. The pore walls of the template membrane possesses similar striations. This can be seen in the scanning electron micrograph shown in Figure 4. A portion of the pore wall is visible in one of the pores in the upper right-hand corner. Striations, analogous to those seen on the tubules, are seen on the pore walls.

We believe that these striations result because the polycarbonate membrane is stretched during processing. Stretching aligns the polycarbonate chains in the stretch direction. Experimental proof of this alignment is provided by the PIRAS data shown in Figure 5. In addition to aligning the polymer chains, stretching also aligns the crystalline domains within the polymer. We believe that the striations result because the aligned crystalline domains etch at a lower rate than the amorphous material between the domains. As a result, the aligned crystalline domains appear as striations. We have obtained some aligned but noncrystalline membranes, and we are exploring this point further.

Transmission Electron Microscopy. Figure 6 shows TEMs for microtomed thin sections of PC/PANi composite membrane after two different polymerization times. From Figure 6A, it can be seen that after short polymerization times, the PANi nucleates along the walls and forms a very thin skin; that is, a tubule with a thin wall is obtained. As the polymerization time increases, polymer grows inward from the pore walls leading to increased tubule wall thicknesses (Figure 6B). Again, this reinforces the notion that the polymer grows from the pore walls into the center of the pore.

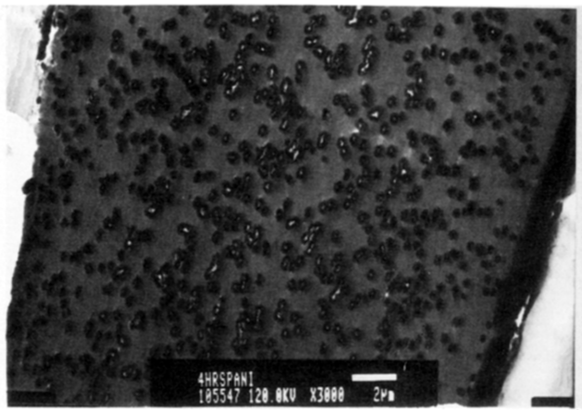

Figure 7. Transmission electron micrograph of a microtomed section of polycarbonate membrane after synthesis of PANi tubules within the pores of the membrane. Polymer synthesized for 4 h in 400 nm pore diameter membrane.

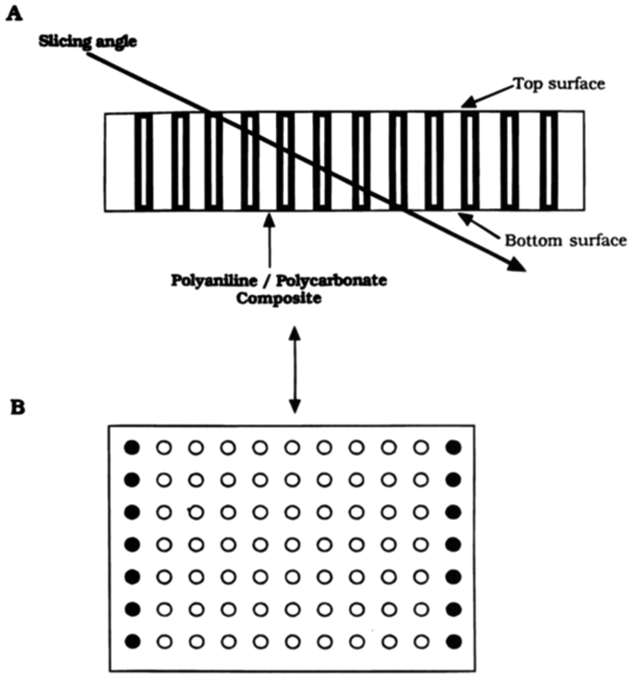

Figure 8. (A) Schematic of microtoming procedure used to obtain the TEM image shown in Figure 6. (B) Simulation of what the TEM image of the slice obtained as per Figure 7A should look like if the PANi tubules are capped at both membrane surfaces.

We have found that it is impossible to completely fill these pores with polyaniline. That is, tubules are obtained even at long polymerization times and even if fresh monomer and oxidant are added. This is because the surface layers eventually grow completely across the membrane surface and block the pore ends. As a result of this, the monomer and the oxidant can no longer enter the pores, and further polymerization within the pores is not possible. Therefore, solid polyaniline fibers cannot be formed by this method. However, microtubules that are blocked on either end are obtained. Such “microcapsules”[25] might prove to be interesting and useful microstructures for chemical or bioencapsulation.

That capped microtubules are ultimately obtained is proven by the TEM image shown in Figure 7. The thin section used to obtain this image was microtomed as shown in Figure 8A. A slice that angles across the

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(25) Parthasarathy, R.; Martin, C. R. *Nature* **1994**, *369*, 298.

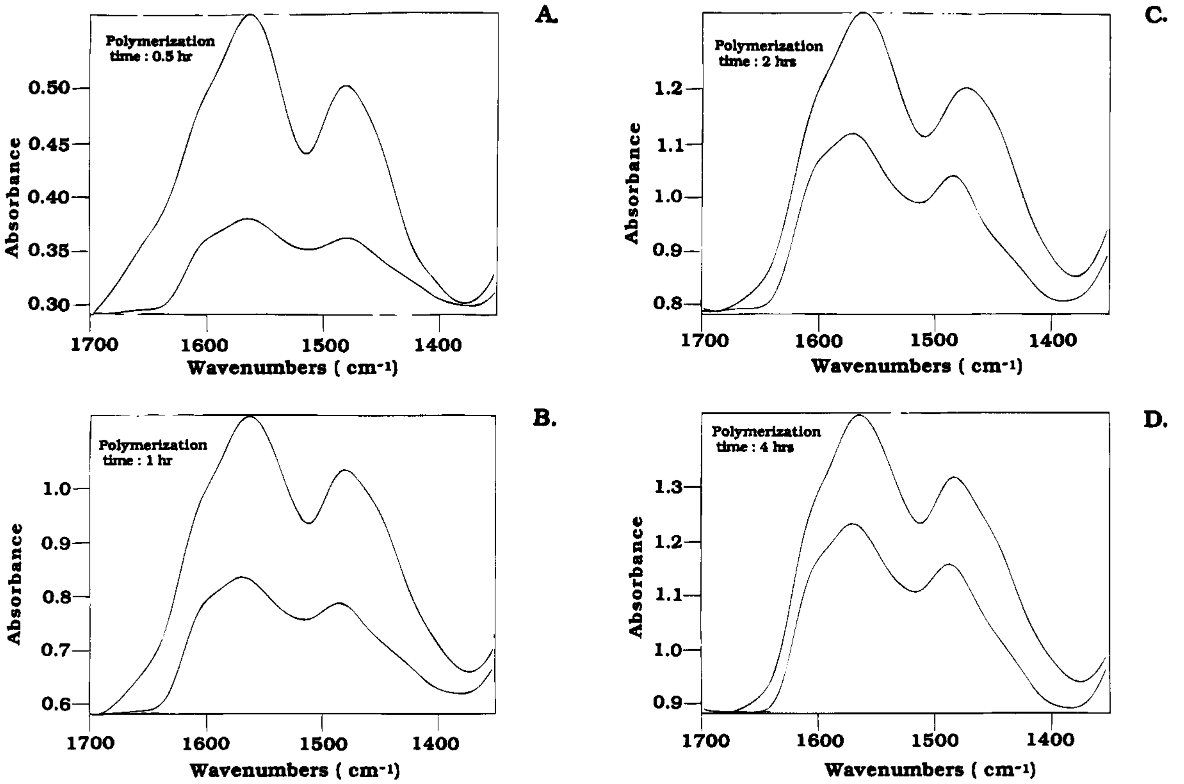

Figure 9. PIRAS data for polyaniline tubules of four different wall thicknesses. Outside diameter of tubules = 400 nm.

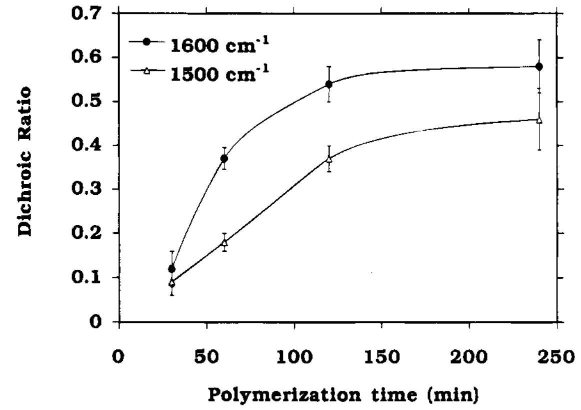

Figure 10. Dichroic ratios (at 1600 and 1500 cm^{-1}) for polyaniline tubules of various wall thicknesses. Outside diameter of tubule = 400 nm. Wall thicknesses controlled by varying polymerization time.

entire width of the membrane was obtained. If the tubules within the membrane are capped, the TEM image of this thin microtomed slice will appear as shown schematically in Figure 8B. The pores on one side of the image will appear to be plugged with PANi because this portion of the sample was obtained from the top surface of the membrane where the PANi tubes are capped. In contrast, the pores in the middle of the image will contain rings of PANi because the caps are only present at the surfaces of the membrane. Finally, the pores will appear plugged at the other side of the image due to the caps present on the bottom surface of the membrane. The TEM image shown in Figure 7 shows exactly these characteristics.

Polarized Infrared Absorption Spectroscopy. We have shown that PIRAS can be used to investigate the extent of polymer chain orientation in template-synthesized fibers and tubules.[4,26] PIRAS data for polyaniline tubules synthesized for various polymerization times are shown in Figure 9. The extent of dichroism for tubules polymerized for a very brief time (thin-walled tubules) is high, indicating that the polymer chains in these thin-walled tubules are highly oriented. However, as polymerization time increases (i.e., the thickness of the tubule wall increases), the extent of dichroism decreases (compare the relative intensities of $I_\perp$ and I_{30} in Figure 9). As would be expected from the absorption spectra in Figure 9, a plot of the dichroic ratio versus polymerization time (Figure 10) shows that pronounced dichroism is observed at short polymerization times but that the extent of dichroism decreases at long times. This implies that for short polymerization times, there is greater order existing in the polymer chains. In other words, the initially formed polymer is highly ordered. As the polymerization time increases (i.e., as the tubule wall thickness increases), the polymer that is subsequently deposited becomes progressively disordered. We have observed a similar effect when polypyrrole films are synthesized at electrode surfaces.[27]

The PIRAS data discussed above clearly show that the polymer chains in these tubules are at least partially aligned. These data do not however show the direction of alignment of the polymer chains. Two possible orientations of the polymer chains relative to the tubule axis are possible (Figure 11). If the angle that the transition moment makes relative to the chain is known, then we can distinguish between these two cases. Investigations on stretch-oriented PANi films have shown that the transition moments for the 1500 and 1600 cm^{-1} bands are directed parallel to the chain axis.[23]

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(26) Menon, V.; Martin, C. R., manuscript in preparation.

(27) Cai, Z.; Martin, C. R. *J. Electroanal. Chem.* **1991**, *300*, 35.

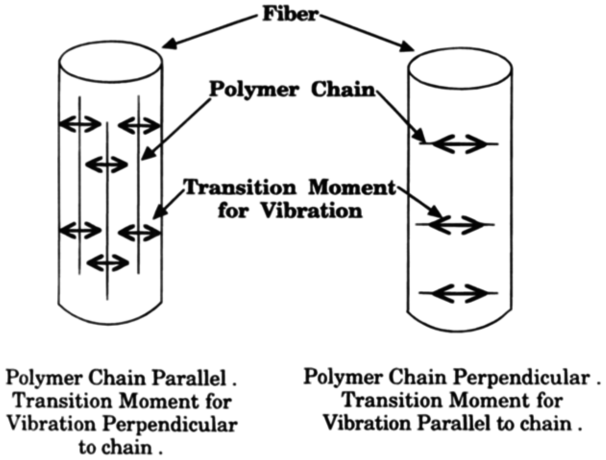

Figure 11. Two possible orientations of the polymer chains and the transition moment relative to the tubule axis. Both orientations would yield enhanced absorbance of $I_\perp$.

Recall that $I_\perp$ and I_{30} are defined relative to the axis of the tubules. As indicated in Figure 9, when dichroism is observed, it is always the perpendicular mode that is preferentially absorbed. Because the transition moment for these vibrations is parallel to the polymer chain, these data unequivocally show that the polymer chains in these tubules are preferentially oriented perpendicular to the tubule axes. As indicated above, we believe that this perpendicular orientation results because the polymer chains along the pore wall are similarly oriented (Figure 5).

Thin Films. As indicated in Figure 2, we have developed a procedure for making thin films from the template-synthesized tubules. An SEM of a cross section of a PANi thin film prepared via this method is shown in Figure 12. This image was obtained by cracking the Anopore support membrane in liquid nitogen. SEM reveals uniform thin skins of PANi on the support membrane (Figure 12). It is interesting to note that the fibrillar structure of polyaniline is completely destroyed upon application of pressure. This can be contrasted to the case of PPy where these films do not lose their tubular structure upon compaction.[5] These thin films allow for four-point conductivity measurements on the template-synthesized materials.

Figure 12. Scanning electron micrograph of a cross section of a polyaniline film prepared from a 0.1 μm outside diameter PANi tubules.

Table 3. Conductivity as a Function of Tubule Diameter for Polyaniline Films Made from Template-Synthesized Tubules[a]

tubule diam (nm)	conductivity (S cm^{-1})
100	50 ± 4
200	14 ± 2
400	9 ± 2

[a] Bulk conductivity of polyaniline: 9 S cm^{-1}.

Dc Conductivity. Previous papers have shown that conductivity of template-synthesized conductive polymer nanostructures increases as the pore diameter decreases. However, these previous conductivity measurements were made using a two-probe method.[4] Since we now have a methodology for making thin films, four-probe measurements can be made on these films. These data are tabulated in Table 3. In complete analogy with previous results,[4] the conductivity increases as the diameter of the tubule decreases. Small-diameter tubules show the highest conductivity because such tubules contain a higher proportion of ordered chain material. Finally, the conductivities of these template-synthesized PANi tubules were compared to the conductivity of bulk polymer synthesized under identical conditions. The conductivity of the bulk polymer was 9 S/cm^{-1} (four-probe method). Hence, the conductivity of thin films prepared from the narrowest of tubules is higher than the conductivity of bulk PANi.

Conclusions

Polyaniline was synthesized in the pores of microporous polycarbonate template membranes. From electron microscopy studies, it was revealed that the polymer nucleates along the walls and grows inward. PIRAS results showed that the polymer chains are oriented in a direction that is perpendicular to the tubule axis. The extent of orientation decreases as the walls of the tubules become thicker. This orientation is transferred from the polycarbonate host membrane due to a templating effect.

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