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Template Synthesis of Electronically Conductive Polymer Nanostructures

CHARLES R. MARTIN

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

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Nanochemistry is an emerging subdiscipline of the chemical and materials sciences that deals with the development of methods for synthesizing nanoscopic bits of a desired material and with scientific investigations of the nanomaterial obtained.[1,2] Nanomaterials have numerous possible commercial and technological applications including use in electronic, optical, and mechanical devices,[1−5] drug delivery,[6] and bioencapsulation.[7] In addition, this field poses an important fundamental philosophical question: How do the properties (e.g., electronic, optical, magnetic, etc.) of a nanoscopic bit of a material differ from the analogous properties for a macroscopic sample of the same material?

There are now numerous chemical methods for preparing nanomaterials.[1,2] My research group has been exploring a method we call "template synthesis" (see, e.g., refs 7−22). This method entails synthesizing the desired material within the pores of a nanoporous membrane. The membranes employed have cylindrical pores of uniform diameter (Figure 1). In essence, we view each of these pores as a beaker in which a piece of the desired material is synthesized. Because of the cylindrical shape of these pores, a nanocylinder of the desired material is obtained in each pore. Depending on the material and the chemistry of the pore wall, this nanocylinder may be solid (a fibril, Figure 2A) or hollow (a tubule, Figure 2B).

The template method has a number of interesting and useful features. First, it is a very general approach; we have used this method to prepare tubules and fibrils composed of electronically conductive polymers,[7−13,19] metals,[14−21] semiconductors,[22] and other materials. Furthermore, nanostructures with extraordinarily small diameters can be prepared. For example, Wu and Bein have recently used this method to prepare conductive polymer nanofibrils with diameters of 3 nm (30 Å).[23] It would be difficult to make nanowires with diameters this small using lithographic methods. In addition, because the pores in the membranes used have monodisperse diameters, analogous monodisperse nanostructures are obtained. Finally, the tubular or fibrillar nanostructures synthesized within the pores can be freed from the template membrane and collected. Alternatively, an ensemble of nanostructures that protrude from a surface like the bristles of a brush can be obtained (Figure 2B).

We began our template-synthesis work in 1985 by electrochemically synthesizing the electronically conductive polymer polypyrrole within the pores of a nanoporous polycarbonate filtration membrane.[8] Since then we[7,9−13,19] and others[23−28] have explored, in some detail, the electrochemical, electronic, and optical properties of template-synthesized conductive polymers. I review my work in this area in this Account. Topics discussed include the membranes used to do template synthesis, the electronic properties of template-synthesized conductive polymer fibrils and tubules, and the morphology of the template-synthesized conductive polymers.

Membranes Used

"Track-Etch" Membranes. A number of companies (e.g., Nuclepore and Poretics) sell micro- and nanoporous polymeric filtration membranes that have been prepared via the "track-etch" method.[29] As indi-

Charles R. Martin obtained his B.S. in chemistry from Centre College of Kentucky in 1975. He did graduate work in the Department of Chemistry at the University of Arizona, with Henry Freiser, and postdoctoral work at the University of Texas, with Allen J. Bard. Martin began his academic career in 1981 in the Department of Chemistry at Texas A&M University. In 1990 he moved to the Department of Chemistry at Colorado State University. Professor Martin's research interests are in nanomaterials, electrochemistry, electronic conductive polymers, and polymer films for membrane-based chemical separations.

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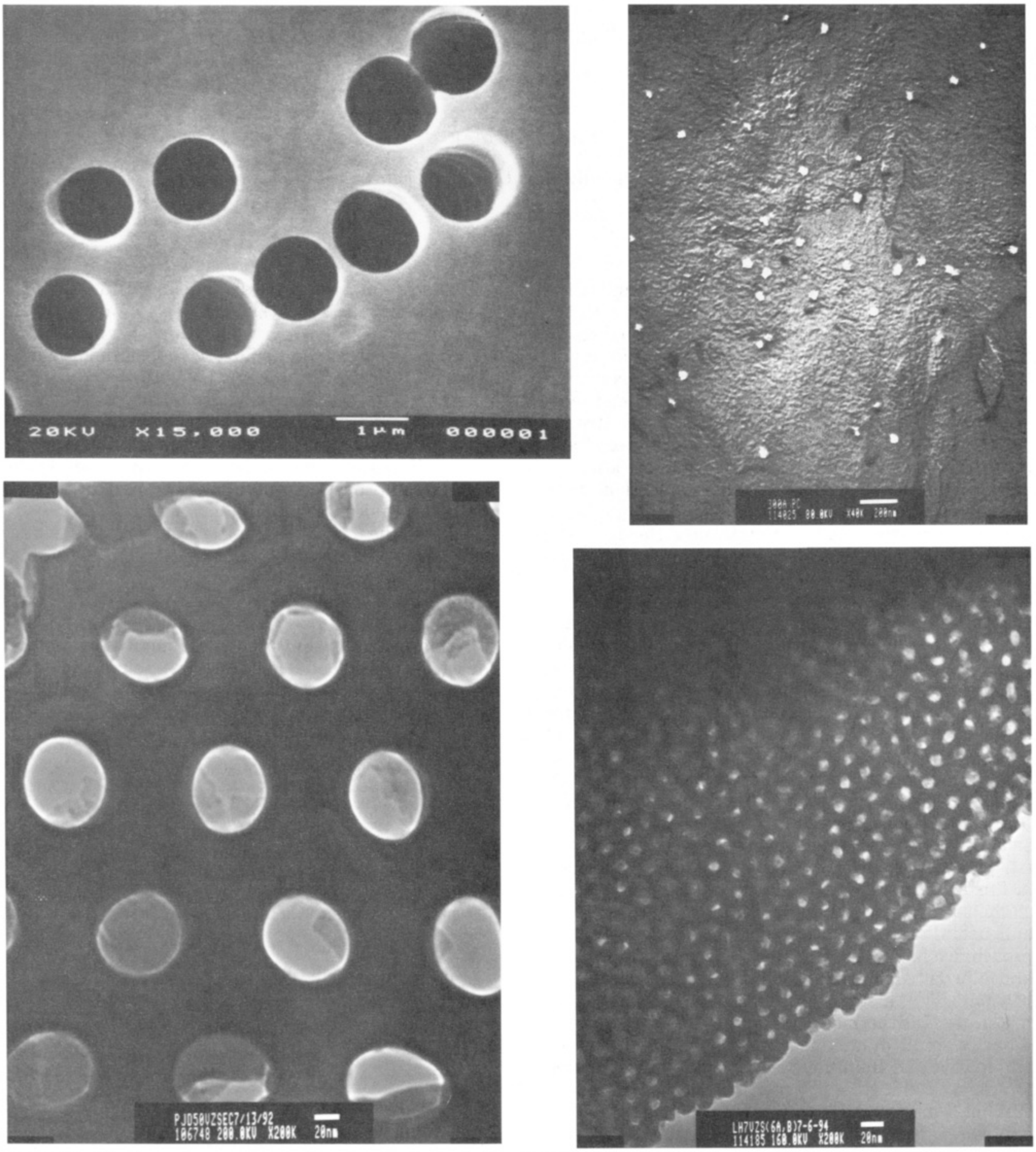

Figure 1. Electron micrographs of polycarbonate (A, top left, and B, top right) and alumina (C, bottom left, and D, bottom right) template membranes. For each type of membrane, an image of a larger pore membrane is presented (A and C) so that the characteristics of the pores can be clearly seen. An image of a membrane with extremely small pores is also presented (B and D). (A) Scanning electron micrograph of the surface of a polycarbonate membrane with 1-μm-diameter pores. (B) Transmission electron micrograph (TEM) of a graphite replica of the surface of a polycarbonate membrane with ca. 30-nm-diameter pores. The pores appear "ragged". This is an artifact of the graphite replica. (C, D) TEMs of microtomed section of alumina membranes with diameter pores of ca. 70 nm (C) and ca. 10 nm (D).

cated in Figure 1A,B, these membranes contain cylindrical pores of uniform diameter. The pores are randomly distributed across the membrane surface. Membranes with a wide range of pore diameters (down to 10 nm) and pore densities approaching 10^9 pores/cm^2 are available commercially. The most commonly used material to prepare membranes of this type is polycarbonate; however, a number of other materials are amenable to the track-etch process.[29]

Porous Alumina Membranes. Membranes of this type are prepared electrochemically from aluminum metal.[30] As indicated in Figure 1C, the pores in these membranes are arranged in a regular hexagonal lattice. Pore densities as high as 10^{11} pores/cm^2 can

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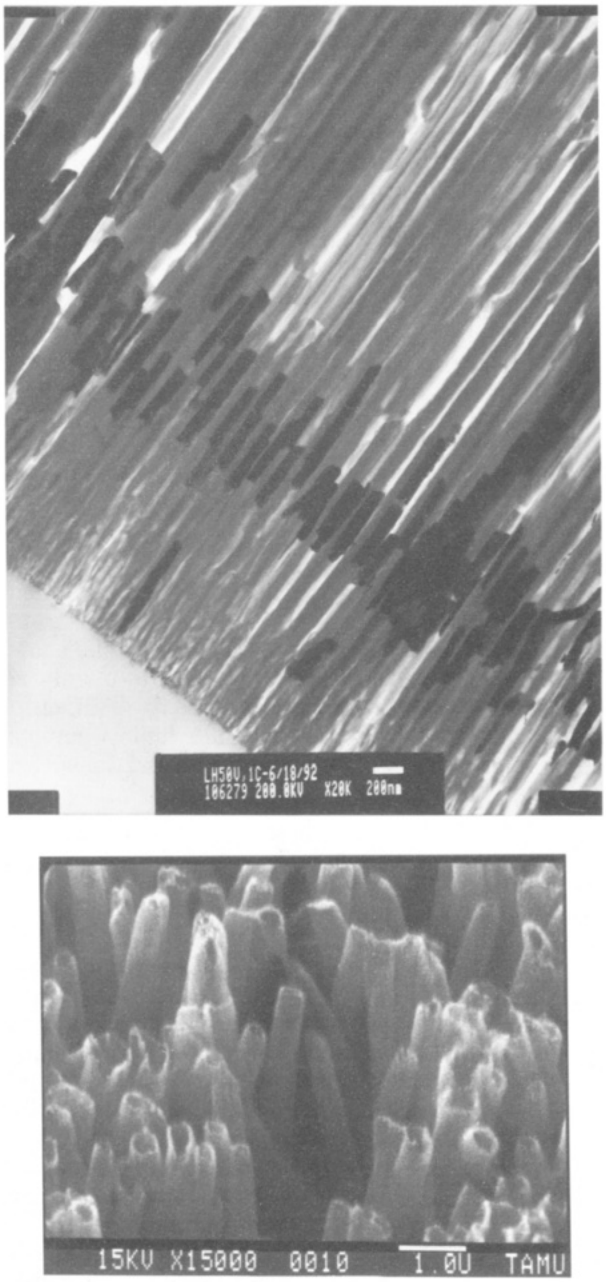


Figure 2. (A, top) Transmission electron micrograph of a microtomed section of an alumina template membrane showing ca. 70-nm-diameter Au nanofibrils within the pores. (B, bottom) Scanning electron micrograph of an array of template-synthesized poly(*N*-methylpyrrole) tubules. The tubules protrude from an electrode surface.

be achieved.[31] While such membranes are sold commercially, only a limited number of pore diameters are available. We have, however, prepared membranes of this type with a broad range of pore diameters.[16–18] We have made membranes with pores as small as 5 nm, and we believe that even smaller pores can be prepared.

An interesting feature of the porous aluminas is the ease with which the chemistry of the pore wall can be altered via reaction with a hydrolytically unstable silane.[15,19,20,32] For example, we have shown that gold tubules can be electrochemically synthesized in these membranes if a cyano group is first attached to the pore walls.[20] This was accomplished via the chemistry shown in eq 1, where $-OH$ represents a hydroxyl group on the pore wall. Because an enormous number of silanes of this type are commercially available, this chemistry provides a general route for putting nearly any desired functional group on the pore walls in these membranes.

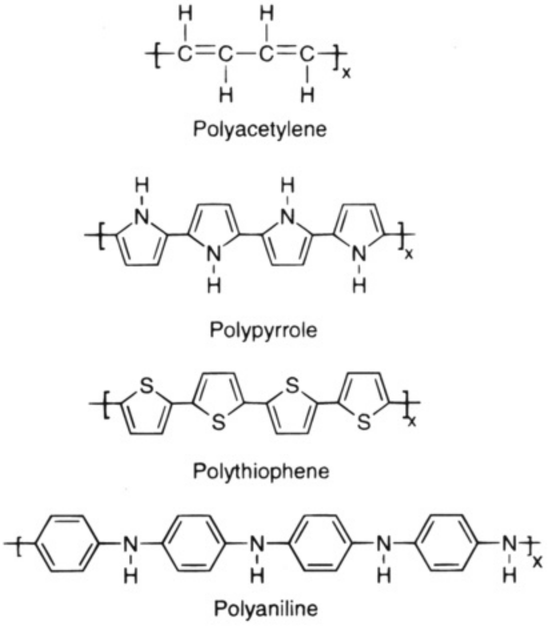
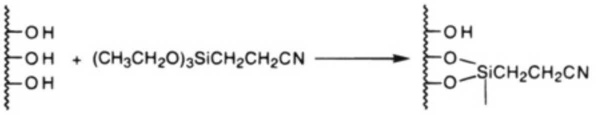


Figure 3. Some electronically conductive polymers.



(1)

Other Nanoporous Materials. Tonucci et al. have recently described a nanochannel array glass membrane.[33] Membranes of this type containing pores with diameters as small as 33 nm and densities as high as 3×10^{10} pores/cm^2 were prepared. Beck et al. have prepared a new, large-pore-diameter xeolite.[34] Douglas et al. have shown that the nanoscopic pores in a protein derived from a bacterium can be used to transfer an image of these pores to an underlying substrate.[35] Finally, Ozin discusses a wide variety of other nanoporous solids that could be used as template materials.[1]

Template Synthesis of Conductive Polymers

Brief Introduction to Conductive Polymers. In the 1970s chemists began to prepare new types of organic polymers that are good electronic conductors;[36] some examples are shown in Figure 3. Note that these

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materials are conjugated along the polymer chain. This is a necessary, but not sufficient, cause for conduction in these polymers. In order to be conductive, charge carriers must be created by oxidizing or reducing the polymer.[36,37] These processes have been given the misnomer "doping" in the literature.

The mechanisms by which these materials conduct electricity have been discussed in some detail (see, e.g., refs 38 and 39). The most important consideration from a chemical viewpoint (and from the viewpoint of this Account) is that *enhanced electronic conductivities are obtained if polymers with enhanced molecular and supermolecular order can be prepared.*[39-42] Polymers with enhanced molecular order contain fewer conjugation-interrupting defects, such as sp^3-hybridized carbons or twists and kinks in the polymer chain. In polymers with enhanced supermolecular order, the polymer chains are ordered via stretching and/or crystallization of the polymer.

Using these approaches, conductivities in excess of 100 000 S cm^{-1} have been achieved for highly-ordered polyacetylene;[43] this is approaching the conductivity of copper. Unfortunately, the "doped" forms of polyacetylene are so reactive that it appears unlikely that this material will be useful for any of the proposed applications[44] of conductive polymers. Conductivities for the more chemically stable materials (e.g., polypyrrole and polyaniline) are many orders of magnitude lower. Hence, developing strategies for improving the conductivities of these polymers is an important research objective. As we will see, template synthesis provides a route for achieving this objective.

Template Methods. Most of our work has focused on polypyrrole, poly(3-methylthiophene), and polyaniline (Figure 3). These polymers can be synthesized via oxidative polymerization of the corresponding monomer. This may be accomplished either electrochemically[8,12,37] or by using a chemical oxidizing agent.[40,45,46] We have adapted both of these approaches so that they can be used in template synthesis of conductive polymers within the pores of our nanoporous template membranes. The easiest way to carry out electrochemical template synthesis is to coat a metal film onto one surface of the membrane and then use this film to electrochemically synthesize the desired polymer within the pores of the membrane.[12] Chemical template synthesis can be accomplished by simply immersing the membrane into a solution of the desired monomer and its oxidizing agent.[7,11,45]

In developing these template synthetic methods, we made an interesting discovery. When these polymers are synthesized (either chemically or electrochemically) within the pores of the polycarbonate membranes, the polymer preferentially nucleates and grows on the pore walls.[9,19,47] As a result, polymeric tubules are obtained at short polymerization times (Figure 2B). These tubular structures have been quite useful in our fundamental investigations of electronic conductivity in the template-synthesized materials (vide infra). In addition, tubular structures of this type have a number of proposed technological applications.[48] For example, we have shown that capped versions of our tubules can be used for enzyme immobilization.[7]

The reason the polymer preferentially nucleates and grows on the pore walls is straightforward.[19] While the monomers are soluble, the polycationic forms of these polymers are completely insoluble. Hence, there is a solvophobic component to the interaction between the polymer and the pore wall. There is also an electrostatic component because the polymers are cationic and there are anionic sites on the pore wall.[19]

Finally, by control of the polymerization time, conductive polymer tubules with thin walls (short polymerization times) or thick walls (long polymerization times) can be obtained. This point is illustrated nicely by the transmission electron micrographs shown in Figure 4.[45] For polypyrrole, the tubules ultimately "close up" to form solid fibrils. Hence, by controlling the polymerization time we can make hollow polypyrrole tubules or solid fibrils. In contrast, the polyaniline tubules will not close up, even at long polymerization times.[45]

Enhanced Conductivity. The easiest way to measure the conductivities of our template-synthesized fibrils is to leave them in the pores of the template membrane and measure the resistance across the membrane.[9,10] Provided the number and diameter of the fibrils is known, the measured trans-membrane resistance can be used to calculate the conductivity of a single fibril. Conductivity data obtained in this way for polypyrrole fibrils are shown in Figure 5.[10] While the large-diameter fibrils have conductivities comparable to those of bulk samples of polypyrrole (e.g., electrochemically-synthesized films), the conductivity of the smallest-diameter fibrils is over an order of magnitude higher. Analogous enhancements in conductivity have been observed for template-synthesized polyaniline[11,45] and poly(3-methylthiophene).[9]

This trans-membrane conductivity method is a two-point measurement. Contact resistance is always a worry with such measurements; indeed, we must apply substantial pressure across the membrane (7×10^3 psi) in order to obtain reproducible resistance data.[10] We have recently developed a method for forming thin films from our template-synthesized nanostructures.[11,45] This has allowed us to make four-point conductivity measurements on these nanomaterials (without applying pressure during the measurement). The thin films are prepared by dissolving the template membrane, collecting the conductive polymer nanofibrils or nanotubules by filtration to form a film across the surface of the filter, and then compacting this film in an IR pellet press.[11,45]

Figure 6 shows scanning electron micrographs of cross sections of thin films prepared in this way from polyaniline and polypyrrole nanotubules. Note that because of the high pressure used in the compaction

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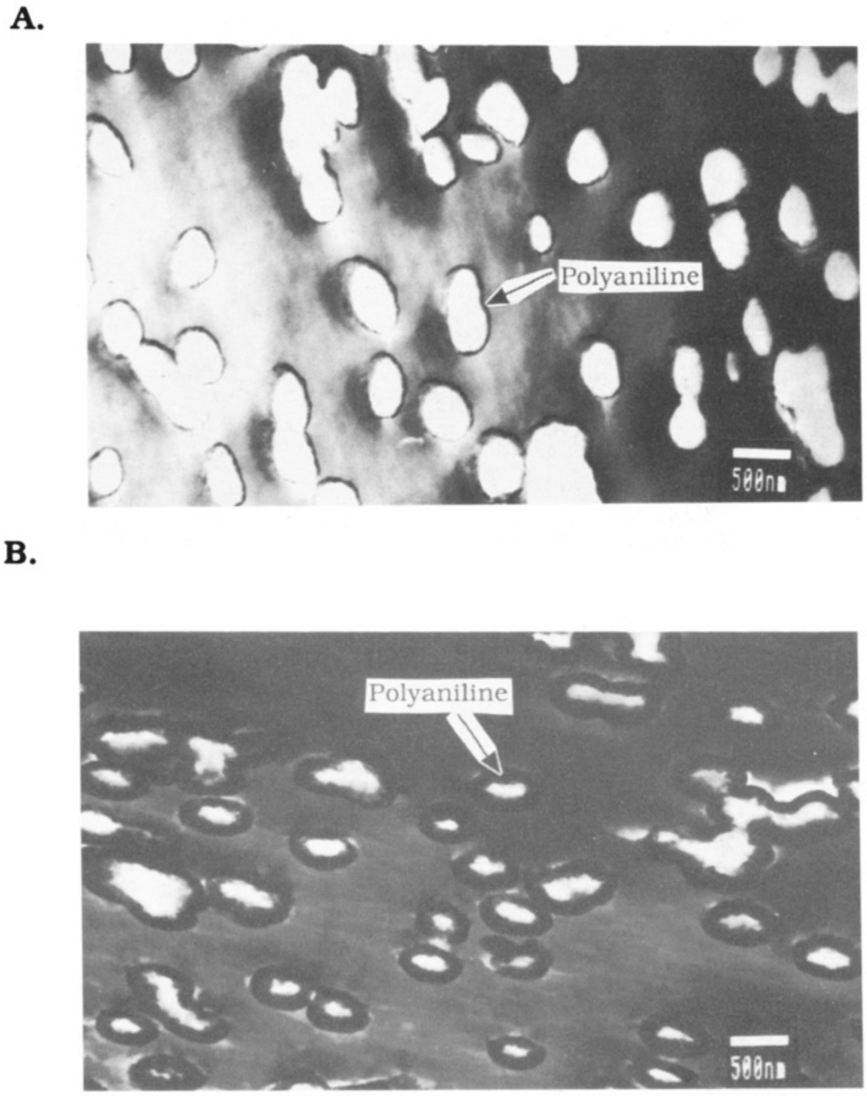

Figure 4. Transmission electron micrographs of thin sections of a polycarbonate membrane during the template synthesis of polyaniline. Polymerization time was 30 min (A) and 6 h (B). Note thickness of polyaniline layer on pore walls in A vs B.

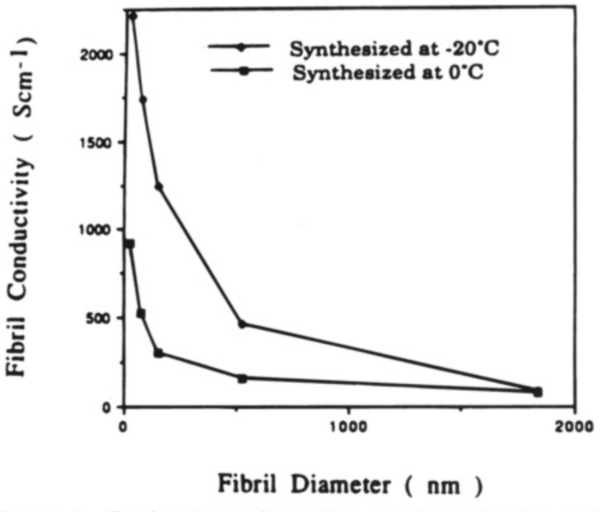

Figure 5. Conductivity of template-synthesized polypyrrole tubules vs diameter of the tubules. Data for two different synthesis temperatures are shown.

Table 1. Conductivity as a Function of Tubule Diameter for Polyaniline Films Made from Template-Synthesized Tubules

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

step (6×10^4 psi) the tubular structure can no longer be seen in the cross section of the polyaniline film (Figure 6A). In contrast, the tubular structure is still clearly evident in the film prepared from the polypyrrole nanotubules (Figure 6B). That the polypyrrole nanotubules can survive the high pressures used during the film-compaction step is quite remarkable and indicates that these tubules are either very strong or very resilient.

Table 1 shows four-point conductivity data for films prepared from polyaniline tubes of various diameters.[11,45] In complete agreement with the two-point data (Figure 5), conductivity increases as the diameter of the tubules used to prepare the film decreases. The conductivity for the film prepared from the narrowest tubes is over 5 times higher than a film prepared, under the same conditions, from bulk polyaniline.[11,45] While conductivities of films prepared from polypyrrole tubules show the same trend (increasing conductivity with decreasing tubule diameter), the conductivities obtained are lower than those obtained by the

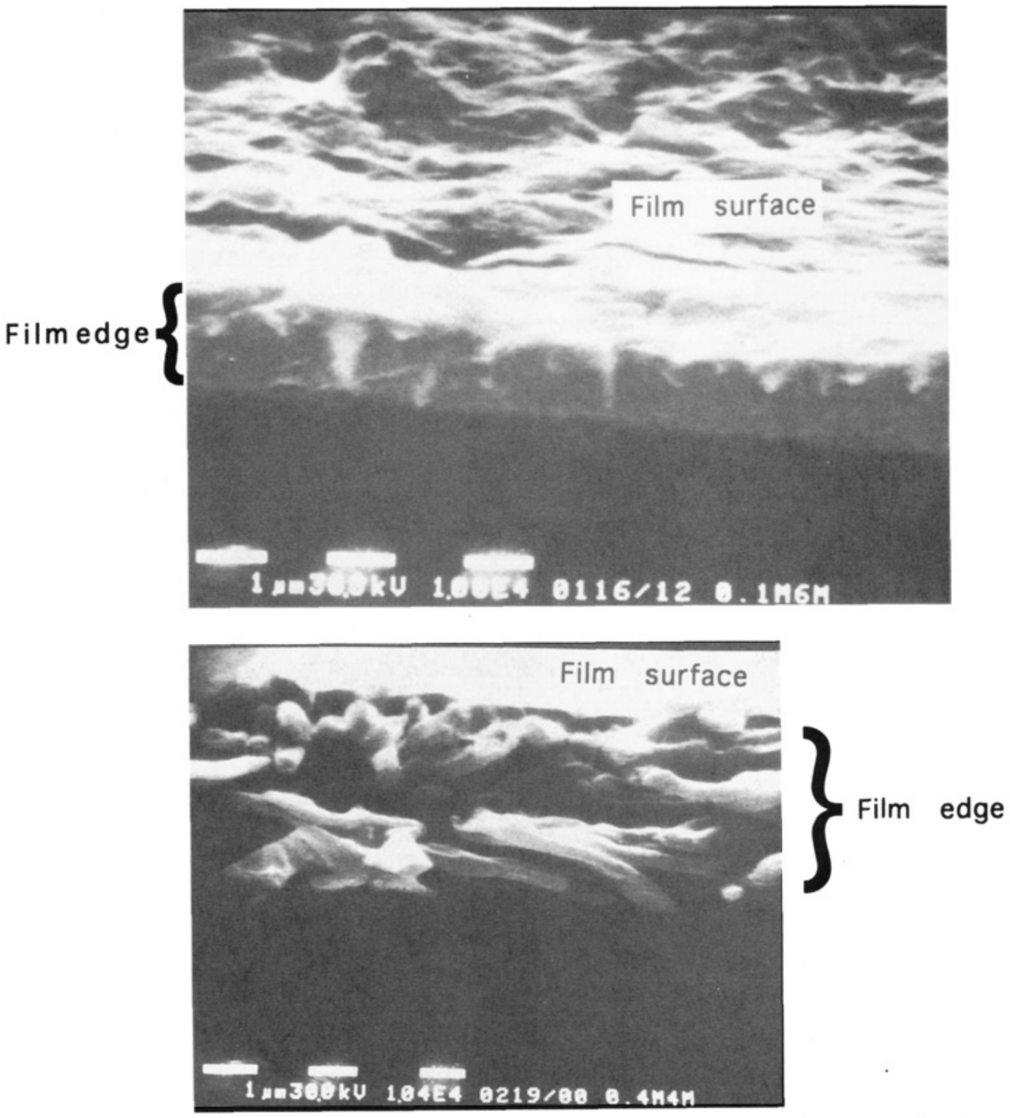

Figure 6. Scanning electron micrographs of cross sections of films made from template-synthesized conductive polymer tubules: (A, top) polyaniline tubules; (B, bottom) polypyrrole tubules.

two-point method because, as Figure 6B clearly shows, these films are not space filling.

Enhanced Molecular and Supermolecular Order. It seemed likely that the enhancements in conductivity we observed might be caused by alignment of the polymer chains. We have used a classical technique called polarized infrared absorption spectroscopy (PIRAS) to explore this possibility.[10,13,46] The template membrane containing the conductive polymer nanofibrils (or tubules) is mounted in the sample chamber of a Fourier-transform infrared spectrometer. The membrane is then probed with orthogonally-polarized beams of IR radiation. One beam is polarized perpendicular to the axes of the fibrils, and the other has a component that is parallel to the fibril axes.

In general, if the integrated absorption intensities of the perpendicular and parallel polarizations are the same, the polymer chains show no preferred orientation. In contrast, if nonequal absorption is observed, the polymer chains show some degree of alignment. The extent of this alignment can be assessed by calculating a parameter called the dichroic ratio, which is the ratio of the integrated absorption intensities of the parallel and perpendicular polarizations.[10,13,46] In our case, the smaller the dichroic ratio, the greater the extent of polymer chain alignment.

Recall from Figure 4 that by controlling the polymerization time we can prepare tubules with very thin walls (Figure 4A) or tubules with thick walls (Figure 4B). Hence, if PIRAS data are obtained as a function of polymerization time, we can explore the extent of polymer chain alignment in the layer of conductive polymer that is deposited directly onto the polycarbonate (short polymerization times) and in subsequently-deposited layers (long polymerization times). Figure 7 shows the results of such an experiment. We find that the layer of polypyrrole that is deposited directly on the pore wall is ordered (low dichroic ratio) but that the extent of order decreases in subsequently-deposited layers (dichroic ratio approaches unity). Analogous results were obtained with polyaniline tubules.[45]

These data show that a template-synthesized conductive polymer fibril or tubule has a layer of ordered polymer chains at its outer surface and that the extent of this chain order decreases toward the center of the nanostructure. This "anatomy" is shown schematically in Figure 8. The narrowest template-synthesized tubules and fibrils have the highest conductivities

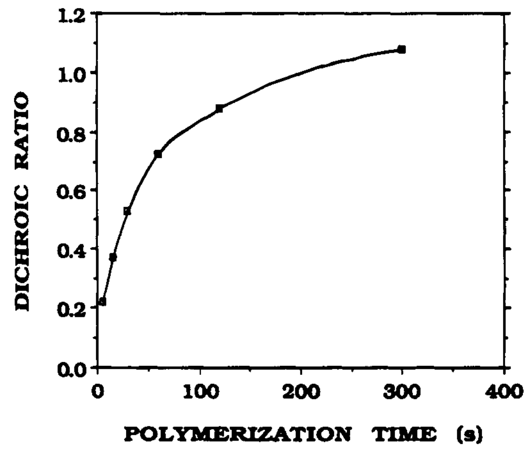

Figure 7. Dichroic ratio for polypyrrole tubules (synthesized in a polycarbonate membrane with 400-nm-diameter pores) as a function of polymerization time. Since polymerization time controls tubule wall thickness (see Figure 4), the x-axis is also a wall thickness axis. The band at 1560 cm^{-1} (see Figure 9A) was used to obtain the data.

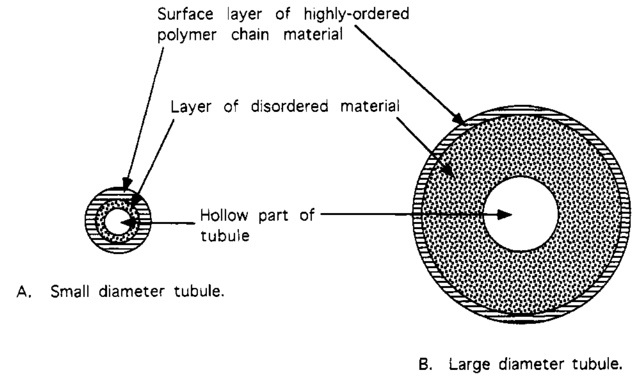

Figure 8. Anatomy of template-synthesized tubules.

because they contain proportionately more of the ordered (and less on the disordered) material (Figure 8).

I will provide an explanation for the genesis of this interesting anatomy in the following section of this report. I would like first, however, to ask the question, What effect might this enhancement in supermolecular order have on the extent of delocalization along the polymer chains (i.e., on the molecular-level order)? We have recently developed an infrared spectroscopic method for obtaining a qualitative measure of the extent of delocalization in polypyrrole.[40] This method is based on theoretical calculations done by Tian and Zerbi.[49,50]

Tian and Zerbi conducted a theoretical analysis on the vibrational spectra of polypyrrole.[49,50] This theory successfully predicts the number and position of the main IR bands and also predicts how the intensities and position of these bands change with the extent of delocalization along the polymer chains (i.e., with the conjugation length). The bands at 1560 and 1480 cm^{-1} (Figure 9A) are especially affected by changes in the conjugation length. These changes can be most easily visualized by taking the ratio of the integrated absorption intensity of the 1560-cm^{-1} band to the integrated absorption intensity of the 1480-cm^{-1} band; we call this ratio I_{1560}/I_{1480}.[40]

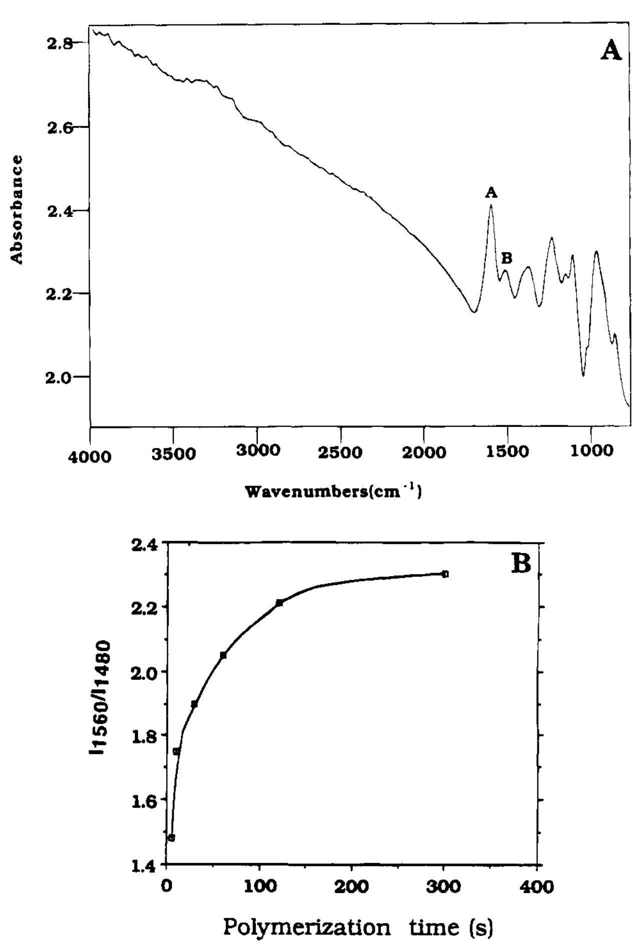

Figure 9. (A) IR spectrum of polypyrrole showing the 1560-cm^{-1} (designated A) and 1480-cm^{-1} (designated B) bands. (B) Plot of I_{1560}/I_{1480} vs polymerization time. Since polymerization time controls tubule wall thickness (see Figure 4), the x-axis is also a wall thickness axis. Membrane as in Figure 7.

According to Tian and Zerbi's analysis, I_{1560}/I_{1480} is inversely proportional to the extent of delocalization.[49,50] In order to test this prediction we chemically synthesized a family of polypyrroles that ranged from being relatively defect free to having high concentrations of defect sites along the polymer chains, and we used various chemical and instrumental methods of analysis to identify and quantify the various defect sites.[40] As might be expected, polymers with high concentrations of defect sites showed low conductivities, and defect-free polymers showed the highest conductivities.[40] More importantly, we found that Zerbi's prediction concerning the effect of extent of delocalization on I_{1560}/I_{1480} was correct: polymers with high concentrations of defect sites (short conjugation lengths) showed high values of I_{1560}/I_{1480} whereas polymers with low concentrations of defect sites (long conjugation lengths) showed low values of I_{1560}/I_{1480}.[40]

Figure 9B shows the application of this method to template-synthesized polypyrrole tubules. As per Figure 7, FTIR data were obtained at various times during the polymerization of polypyrrole tubules within a template membrane that contained 400-nm-diameter pores. Note that I_{1560}/I_{1480} increases with polymerization time (i.e., with wall thickness). This clearly shows that the layer of polypyrrole that is deposited directly on the pore wall has extended conjugation relative to subsequently-deposited layers. Hence, these data mirror the PIRAS data shown in Figure 7.

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These analyses of conductivity and extent of supermolecular and molecular order have led us to an important generalization: alignment of polymer chains (improvement in supermolecular order) typically produces an increase in conjugation length (improvement in molecular-level order). This observation makes sense because, in order to align, the polymer chains must be linear (i.e., straight), and linear chains will have fewer kinks and bends that interrupt conjugation. Finally, by improving molecular and supermolecular order in this way, we obtain materials with enhanced electronic conductivities.

Why Do the Polymer Chains Align in the Template-Synthesized Polymers? PIRAS experiments on the as-received polycarbonate filtration membranes show that the polycarbonate is stretch-oriented.[46] Because of this stretch orientation, the polycarbonate chains are preferentially aligned perpendicular to axes of the pores. Are the conductive polymer chains in our tubules and fibrils likewise oriented perpendicular to their axes? To answer this question we conducted PIRAS experiments on reference conductive polymer samples[46] of known chain orientation. These analyses showed that, for both polypyrrole and polyaniline, the polymer chains on the outer surface are, indeed, aligned perpendicular to the axis of the tubule or fibril.

Hence, it appears that the first layer of conductive polymer chains that deposits on the pore walls lies in registry with the oriented polycarbonate chains on the wall. This idea of inducing order in a polymer film by synthesizing it on an ordered polymeric substrate has been demonstrated with other systems.[51] The disordered central core results because the order-inducing influence of the pore wall is ultimately lost in subsequently-deposited layers. An analogous effect occurs when polypyrrole is electrochemically deposited on electrode surfaces;[52] i.e., the first layer of polymer chains lies parallel to the electrode surface, but this preferential orientation is lost in subsequently-deposited layers.

Mechanism of Conductivity in Template-Synthesized Nanotubules. We have learned from the various analyses reviewed above that a small-diameter template-synthesized nanotubule has a high proportion of ordered (and highly-conductive) polymer chains on its outer surface and a low proportion of disordered (lower-conductivity) material in its center (Figure 8A). In contrast, a large-diameter tubule contains a relatively smaller proportion of ordered material and has a larger proportion of disordered central core (Figure 8B). How might these changes in relative amounts of ordered vs disordered material affect the mechanism of conduction in these nanomaterials? We have been exploring this question in a collaboration with Professor H. D. Hochheimer in the Physics Department here at Colorado State University and Dr. Pei-Herng Hor of the Texas Center for Superconductivity.[53]

We have investigated the temperature dependence of conductivity of thin films prepared from small- and large-diameter polypyrrole and polyaniline tubules.[53] We have discovered that, for both polymers, the films prepared from the small-diameter tubules show two-dimensional (2-D) Mott variable range hopping (MVRH),[54,55] over a temperature range from ca. 10 to 160 K. In contrast, for both polymers, the films prepared from the large-diameter tubules showed 3-D MVRH over the same temperature range.[53] Hence, template synthesis provides a route for reproducibly and predictably changing the dimensionality of conduction in a conductive polymer thin film.

We believe this change in the dimensionality of conduction to be perfectly reasonable, given the unique anatomy of the template-synthesized tubules (Figure 8).[53] In the small-diameter tubules, the charge carriers prefer to hop in the ordered surface layer because there is a relatively large proportion of this material and because this layer has higher electronic conductivity than the smaller proportion of the underlying disordered material (Figure 8A). However, because this surface layer is so thin, conduction is constrained to two dimensions.[53] Epstein et al. observed an analogous effect in films prepared from polyacetylene fibrils.[56] In contrast, in the large-diameter tubules the charge carriers prefer to hop in the disordered central region, in spite of its lower conductivity, because there is just so much more of this material, relative to the ordered surface layer (Figure 8B). Furthermore, because the disordered layer is thick, conduction is not constrained to 2-D but is, instead, 3-D.

Conclusions

We have learned that template synthesis provides a route for controlling the extent of molecular and supermolecular order in electronically conductive polymers. This allows us to predictably vary not only the magnitude of the conductivity but also the conduction mechanism within the material. Hence, these template-synthesized nanostructures are proving to be useful materials for exploring the fundamentals of the conduction process in conductive polymers. Such investigations are under way in my laboratory and in the laboratories of my various collaborators.[53] In addition, while I have not been able to discuss it here, these template-synthesized nanostructures have a number of possible technological and commercial applications in areas such as bioencapsulation[7] and biosensors. We are currently exploring these possible applications.

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