Electronically Conductive Polymer Fibers with Mesoscopic Diameters Show Enhanced Electronic Conductivities

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Polyheterocyclics have been the subject of intense recent research interest.[1] This interest seems from the fact that the oxidized forms of these polymers are electronically conductive. We have recently discovered that polyheterocyclics synthesized within the mesoscopic[2] pores of a host membrane show dramatically enhanced electronic conductivities. Preliminary results of these investigations are reported in this correspondence.

Polypyrrole (PP) and poly(3-methylthiophene) (PMT) were synthesized within the pores of Nuclepore membranes (10 μm thick; available from Nuclepore Corp., Pleasanton, CA); these membranes contain linear, cylindrical pores (Figure 1A). Synthesis was accomplished by allowing the membrane to separate a solution of the monomer from a solution of a chemical oxidizing agent. (For PP—0.6 M aqueous pyrrole and 2 M aqueous $FeCl_3$. For PMT—0.6 M 3-methylthiophene (CH_3CN) and 1.0 M $Fe(ClO_4)_3$ (CH_3CN)). The monomer and oxidizing agent diffuse toward each other through the pores in the membrane and react to yield PP or PMT.

This heterogeneous chemical synthesis proved to be more complicated (and interesting) than we had initially anticipated. The nascent conductive polymer nucleates along all of the surfaces of the host membrane. For example, Figure 1B shows an electron micrograph of a membrane after a brief (1 min) polymerization period. The irregular surface structure indicates that a layer of PP has deposited over the face of the membrane[3] (compare Figure 1 (part A and B)). Electron micrographs of the opposite side of the membrane are identical.

Figure 1 also indicates that the pores in the membrane have been partially filled with PP. (The pores in the virgin membrane, Figure 1A, were 1.0 μm in diameter; after polymerization the pores were ca. 0.5 μm in diameter, Figure 1B.) Eventually, the pores become completely filled,[4] and conducting polymer fibers are obtained.

Thus, the first interesting feature of this heterogeneous chemical synthesis is that *ultrathin-film (<200 nm), electronically conductive composite polymer membranes* are obtained. Both porous (Figure 1B) and nonporous conductive composite polymer membranes can be synthesized. We are currently investigating the generality of this ultrathin-film composite membrane-formation process.

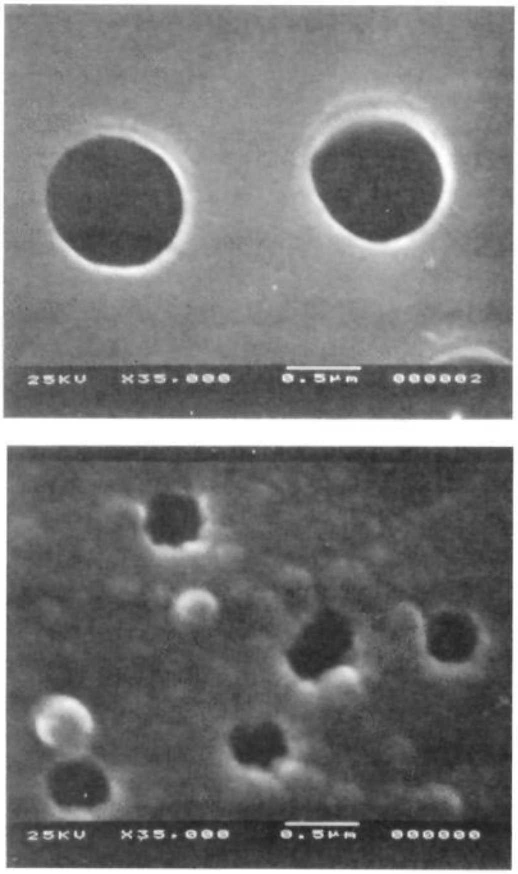

Figure 1. Electron micrographs of surfaces of 1.0 μm pore diameter Nuclepore membrane: (A) virgin membrane and (B) after 1 min polypyrrole polymerization period (see text).

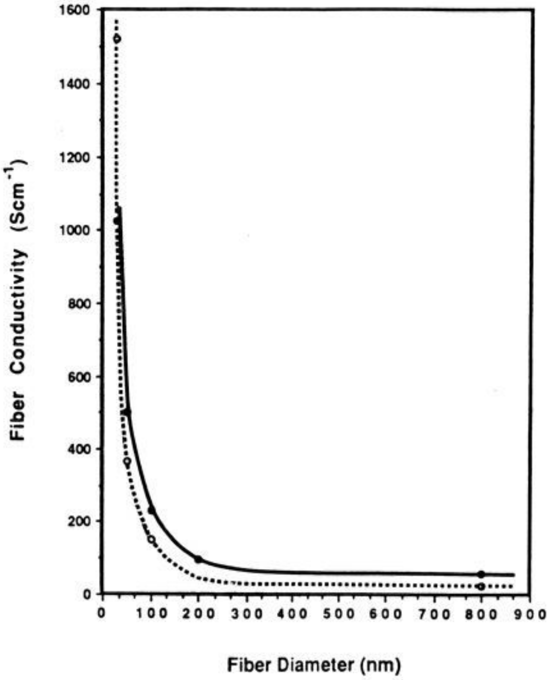

Figure 2. Plot of conductivity of polyheterocyclic fiber vs diameter of the fiber: (--○--○--) poly(3-methylthiophene) and (—●—●—) polypyrrole.

The most interesting and important feature of this heterogeneous synthesis is, however, the enhanced electronic conductivities exhibited by the polymer fibers. Fiber conductivities were obtained by measuring the resistances across the composite membranes; only membranes with completely filled pores were investigated. The membrane was placed on a bed of fine (0.8 μm) Pt particles, which served as one electrode for the resistance measurement. The second electrode was a 0.25-mm diameter Pt wire, sealed into a 0.4-cm diameter glass tube. A pressure of 18 psi was applied to the upper (Pt wire) electrode to insure uniform contact with the composite membrane. A Fluke Model 8050A digital multimeter was used to measure the resistance across the membrane. We

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[1] (a) Feldberg, S. W. *J. Am. Chem. Soc.* **1984**, *106*, 4671. (b) Street, G. B. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vol. 1. (c) Waltman, R. J.; Bargon, J. *Can. J. Chem.* **1986**, *64*, 76.

[2] (a) Nimtz, G.; Marquardt, P.; Stauffer, D.; Wilfried, W. *Science* **1988**, *242*, 1671. (b) Imry, Y. In *Directions in Condensed Matter Physics*; Grinstein, G., Mazenko, G., Eds.; World Scientific: Philadelphia, PA, 1986; and references therein.

[3] The chemical identity of the surface layer was confirmed by UV–vis reflectance spectroscopy, conductivity data, and cyclic voltammetry.

[4] The time required to completely fill the pores varied with pore diameter. For polypyrrole, the time required varied from 8 min for the 800-nm diameter pores to 120 min for the 30-nm diameter pores.

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have shown that this method yields negligible contact resistance and highly accurate conductivity values.[5]

The measured composite membrane resistance (R_m) is given by

$$R_m = R_{s1} + R_{pf} + R_{s2} \tag{1}$$

where the R_s's are the resistances of the thin polyheterocyclic surface layers, and R_{pf} is the parallel sum of the resistances of the polyheterocyclic fibers that run through the membrane. It is easy to show that R_{s1} and R_{s2} are much smaller than R_{pf}.[6] Furthermore, since the number of fibers in the membrane is known,[7] the conductivity of a single fiber can be calculated from R_m.

Figure 2 shows the effect of fiber diameter on conductivity along the fiber axis. The widest fibers investigated have conductivities roughly equivalent to those of conventional, electrochemically synthesized PP and PMT (10–100 ohm^{-1} cm^{-1}).[1b,c] Conductivity increases gradually with decreasing fiber diameter for fibers with diameters of hundreds of nm (Figure 2). Conductivity increases dramatically when the fiber diameter approaches mesoscopic values (i.e., tens of nm[2]). The conductivities of the 30-nm diameter fibers are over an order of magnitude higher than the conductivities of the conventional polymers.[1b,c]

Alignment of the polymer chains (by stretching) has been shown to enhance conductivities in conductive polymers.[8] We propose that synthesis in the confined space of the mesoscopic pore causes the polymer chains to align along the pore axis. This alignment causes the conductivity along the axis to be higher than in conventional (nonaligned) films. We are currently conducting electron diffraction experiments on the mesoscopic fibers to see if experimental evidence for alignment can be obtained.

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(5) Conductivity values for homogeneous PP films were obtained by using this method and the more conventional four-point method; identical values were obtained. The four-point method cannot be used on these ultranarrow fibers.

(6) The surface layers are less than 200 nm thick and cover 100% of the surface area; the fibers are 10 μm long and occupy 1% (or less) of the surface area. Furthermore, for several membranes, we measured the resistance, scraped off the surface layers, and then remeasured the resistance; R_m values with and without the surface layers were identical.

(7) Determined electron microscopically, see: Cheng, I. F.; Whiteley, L. D.; Martin, C. R. *Anal. Chem.* **1989**, *61*, 762. Another question arises—does conductive polymer grow through the bulk of the host membrane? To answer this question, we attempted the heterogeneous synthesis on membranes, identical to Nuclepore, but without pores. Conductive polymer did not form in these, chemically identical, nonporous membrane.

(8) (a) Ogasawara, M.; Funahashi, K.; Iwata, K. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 159. (b) Ozaki, M.; Ikeda, Y.; Arakawa, T. *J. Polym. Sci.* **1983**, *21*, 159.

Conductive Polymer Bronzes. Intercalated Polyaniline in V_2O_5 Xerogels

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It is well-known that organic molecules such as aniline, pyrrole, and thiophene yield, upon chemical or electrochemical oxidation, technologically promising, robust, electrically conductive polymers.[1,2] Progress in elucidating the real structure of these materials is hampered by their invariably amorphous nature.[3] Furthermore, owing to their limited processability, even oriented specimens for important anisotropic studies are rare or lacking. In this communication we report the successful in situ intercalation/polymerization of aniline in layered $V_2O_5\cdot nH_2O$ xerogels[4,5]

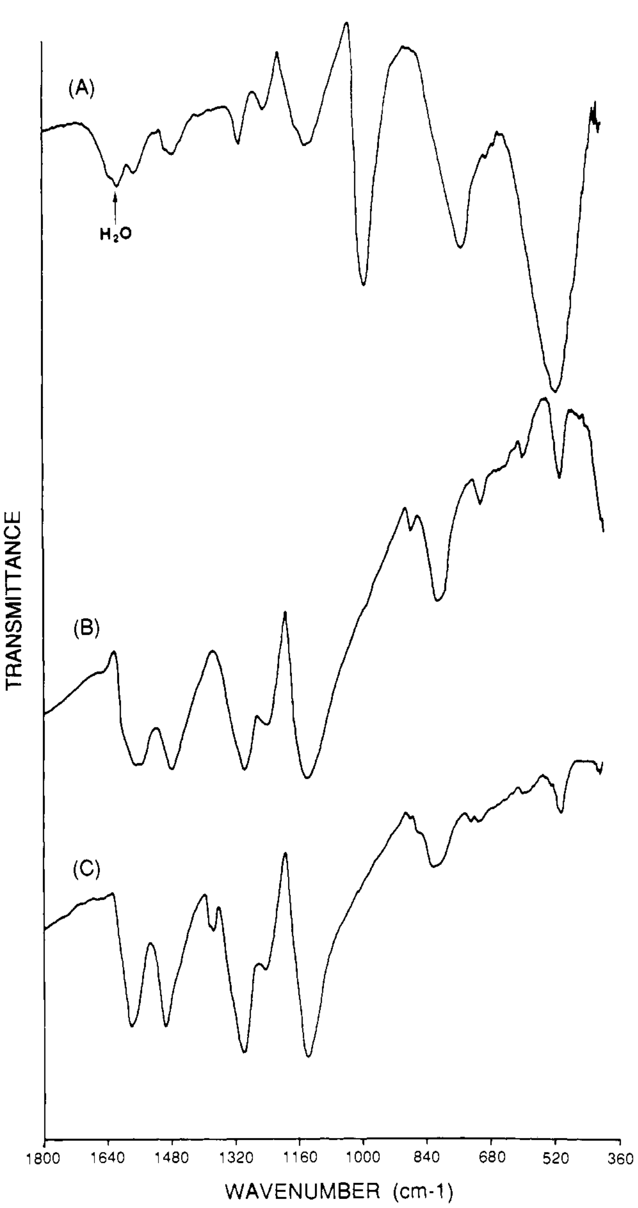

Figure 1. FT-IR spectra of (A) $(C_6H_4NH)_{0.44}V_2O_5\cdot 0.5H_2O$ (I) (The bands occurring below 1000 cm^{-1} are due to the V_2O_5 framework.); (B) authentic sample of polyaniline hydrochloride as prepared chemically by a literature procedure;[15c] and (C) material isolated by dissolving the V_2O_5 framework in 2% aqueous NaOH and then acidified with HCl. Similar spectra were obtained upon dissolution of I with aqueous HCl. Samples were run as KBr pellets.

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(1) (a) Electrical and Magnetic Properties of Low Dimensional Solids; Gillespie, R. J., Day, P., eds.; Proceedings of a Royal Society Discussion Meeting, The Royal Society: London, 1986. (b) See, for example: Proceedings of the Conference on Electronic Processes in Conducting Polymers; Vadstena, Sweden, August 1986 [*Synth. Met.* **1987**, *21*]. (c) Marks, T. J. *Science* **1985**, *227*, 881–889.

(2) (a) For a recent review of the field, see: Proceedings of the International Conference on Science and Technology of Synthetic Metals (*ICSM'88*); Aldissi, M. Ed.; *Synth. Met.* **1989**, *27–29*, references therein. (b) Handbook of Conductive Polymers; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vol 1 and 2.

(3) Delabouglise D.; Garreau, R.; Lemaire, M.; Roncali, J. *New J. Chem.* **1988**, *12*, 155–161.