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This is the final report for the DURIP grant "DURIP Electrochemistry-Surface Spectroscopy Instrument". The funds obtained via DURIP grant were used to purchase a research-quality Fourier-transforms infrared spectrometer. This FTIR was used to investigate preferential orientation of polymer chains within ultranarrow electronically conductive polymer fibers. This investigations have shown that the polymer chains are preferentially oriented parallel to the fiber axis. This helps explain the enhanced electronic conductivities observed in some of these ultranarrow conductive polymer fibers.

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DURIP Electrochemistry-Surface Spectroscopy Instrument

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Air Force Office of Scientific Research

Project RF 6212

FINAL REPORT

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Introduction. This is the final report for the DURIP research grant "DURIP Electrochemistry-Surface Spectroscopy Instrument". The funds made available from DURIP were used to purchase a research-grade fourier-transform infrared spectrometer (Mattson Cygnus). This report details how this FTIR was used in pursuit of the scientific objectives of the chemical research proposed in the DURIP proposal.

The objective of this research effort is to investigate polymer interfaces. We have, during this first year, focused on "test polymer"/"host polymer" and test polymer/host ceramic interfaces. The test polymers are electronically conductive polymers (e.g. polyacetylene, polypyrrole, polythiophene, and their derivatives). The host materials are microporous membranes. We are attempting to ascertain how interactions at the interface between the test polymer and the host material affect the properties of the bulk polymer, in regions removed from the interface.

Scientific Background. We have recently shown that electronically conductive polymers can be synthesized within the pores of microporous host membranes (1-4). The host membranes used contain linear, cylindrical pores with diameters in the range of 10 nm to 10 μ m; polycarbonate, nylon, and alumina host membranes have been employed. The conductive polymer is synthesized within the pores of the host membrane using either chemical (4) or electrochemical (1-3) methods.

Synthesis of an electronically conductive polymer within the pores of a microporous membrane yields conductive polymer fibers; the diameters of these fibers are determined by the diameters of the pores in the host membrane; the length of these fibers are determined by the thickness of the host membrane.

A scanning electron micrograph of 200 nm-dia. polyacetylene fibers is shown in Figure 1.

This work is of interest and importance because the conductive polymer fibers obtained show important advantages relative to conventional versions of these polymers. Specifically, the conductive polymer fibers support higher rate of ion-transport and show dramatically higher electronic conductivities than conventional versions of these polymers (1-3)(4). Typical data showing the dramatic enhancement in electronic conductivities of polypyrrole and poly(3-methylthiophene) fibers are presented in Figure 2.

The observed increase in electronic conductivity (Figure 2) forms the basis for the work conducted with the DURIP-purchased instrumentation. We would like to ascertain why electronically conductive polymer fibers with extremely narrow (i.e. mesoscopic (4)) diameters show electronic conductivities which are as much as three orders of magnitude higher than the conductivity of the conventional conductive polymers.

Experimental. Our working hypothesis for the enhanced electronic conductivity of the conductive polymer fibers is that there are both molecular and supermolecular difference between the fibrous and conventional versions of the polymer. We have used ^{13}C NMR with magic angle spinning, X-ray photoelectron spectroscopy, and ultraviolet/visible spectroscopy to probe the chemical differences between the fibrous and conventional polymers. These data suggest that the fibrous versions of the polyheterocyclics have fewer α - β polymerization defects, higher doping levels, and longer conjugation lengths than conventional versions of the analogous polymer (5).

The FTIR purchased with the DURIP funds was primarily used to investigate supermolecular differences between the fibrous and conventional versions of

the various electronically conductive polymers. The working hypothesis here was that synthesis within the extremely narrow pores of the host membrane caused the polymer chains to preferentially orient parallel to the fiber axis. As suggested in the Introduction to this report, this orientation is aided, in the case of the heterocyclic polymers, by adsorption of the nascent conductive polymer fiber to the surface of the host membrane within the pore (4,5). We are currently using the FTIR spectrometer to investigate the chemical nature of this absorptive interaction.

FTIR spectroscopy is ideally suited for ascertaining whether preferential orientation is extant in polymeric samples. The experiment is, in principle, quite simple - A dipole, associated with the polymer, which has a specific and known orientation with respect to the polymer chain is first identified. The sample is then placed within the spectrometer and the transmittance by the sample of s-polarized light, at the frequency needed to excite this oriented dipole, is determined; the transmittance by the sample of p-polarized light at this frequency is then measured.

If the polymer chains show no orientation within the sample, then the sample will absorb the p and s polarized beams to the same extent. However, if the polymer chains show some preferred orientation, then the absorbances of the s and p polarized radiation can be quite different. For example, if the dipole of interest is parallel to the polymer chain, and the plane of polarization of the incident radiation is perpendicular to the chain, absorption is impossible; however, if the plane of polarization is then rotated 90°, the dipole will now be parallel to the plane of polarization and absorption will be possible.

We have used the technique outlined above to study orientation in our

conductive polymer fibers. In order for this technique to work, the fibers must all be parallel to each other. This criterion is satisfied by leaving the host membrane in tact and doing a transmittance experiment on the (parallel) conductive polymer fibers within this membrane. This necessitates, of course, that the host membrane is transparent in the spectral region of interest.

The ideal way to do this experiment would be to impinge the IR beam onto the edge of the host membrane and study the difference in absorption between radiation polarized parallel and perpendicular to the plane of the host membrane. However, the host membranes are so thin (ca. 10 μm) that this ideal configuration is not possible. For this reason, we chose to orient the sample membrane at 45° relative to the incident IR beam and study the absorbencies of horizontally and vertically polarized light.

In this configuration, vertically polarized light has a component which is parallel to the conductive polymer fibers, whereas horizontally polarized light does not. Thus, if the dipole chosen is parallel to the polymer chain, and if the chains are parallel to the fiber axis (as anticipated) vertically polarized light will be preferentially absorbed relative to horizontally polarized light.

We have conducted polarized FTIR experiments, as described above, on both polypyrrole and polyacetylene fibers. The polypyrrole fibers were synthesized in Nuclepore polycarbonate membranes. The methods employed are described in (4). The fibers obtained had diameters of ca. 30 nm. The polyacetylene fibers were synthesized in Anopore alumina membranes (6). These membranes has 200 nm-diameter pores. The following synthetic method was used.

The catalyst used for the polyacetylene synthesis has been described

previously (7). Fifty mL of silicone oil (the solvent for the catalyst) were charged into a 200 mL 3-neck round-bottom flask. The flask was equipped with a magnetic stirrer and septa, covering the necks, were used to either blanket the contents in Ar or evacuate the flask. The silicone oil was first degassed using the freeze-pump-thaw technique. AlEt_3 (16 mL) was then added to the flask and dissolved (with stirring) into the silicone oil. The flask was immersed in a constant temperature bath (at 40° C). $\text{Ti}(\text{OBu})_4$ (20 mL) was then slowly added, with stirring; the mixture was blanketed with Ar during this procedure. After adding the $\text{Ti}(\text{OBu})_4$, the resulting solution was heated at 120° C for 1 hr and then cooled to room temperature.

An Anopore membrane was then immersed into the catalyst solution and the reaction vessel was evacuated, heated to 70° C, and backfilled with Ar; this process (which was repeated two times) forced the catalyst solution into the pores of the Anopore membrane. The excess catalyst was then removed and the cell was again evacuated. Acetylene gas was then admitted and the polymerization process was allowed to proceed (at 0° C) for 2 hrs.

After polymerization, the Anopore membrane was washed with degassed toluene, methanol (containing 5 % HCl), and pure methanol. The membrane was then dried in vacuo. The resulting membranes were covered with thin films of polyacetylene. These thin surface layers were removed by rubbing with a tissue. The "cleaned" Anopore/polyacetylene composite membranes were used for the FTIR analysis. In some cases the host membrane was dissolved away (using 0.1 M NaOH) so that electron micrographs of the polyacetylene fibers could be obtained (e.g. Figure 1).

Results and Discussion. The electron micrograph shown in Figure 1 indicates that beautiful fibers are obtained when polyacetylene is synthesized within

the pores of Anopore membrane. Careful examination shows that the fibers are somewhat narrower than the 200 nm diameter of the pores in the host membrane; the electron micrograph shown in Figure 3 indicates that this is because the fibers do not totally fill the pores in the host membrane.

As indicated above, we have conducted FTIR analyses on both polyacetylene fibers (synthesized as described above) and polypyrrole fibers (4). In both cases the fibers were dispersed in the pores of the host membrane during the FTIR analyses. The polypyrrole data are still very preliminary and will not be discussed here.

The dipole chosen for the FTIR analysis on polyacetylene was the C-H stretching mode which appears at 3024 cm^{-1} (). Previous investigation has shown that this dipole lies predominately parallel to the polyacetylene chain (8). Figure 4 shows FTIR absorption spectra for polarizations predominately parallel (A) and perpendicular (B) to the fiber axis. The higher absorbance of the parallel component suggests that the polyacetylene chains are, indeed, preferentially oriented parallel to the fiber axis.

Conclusion. The data presented here must be considered preliminary in nature. We are currently conducting a much more extensive series of investigations.

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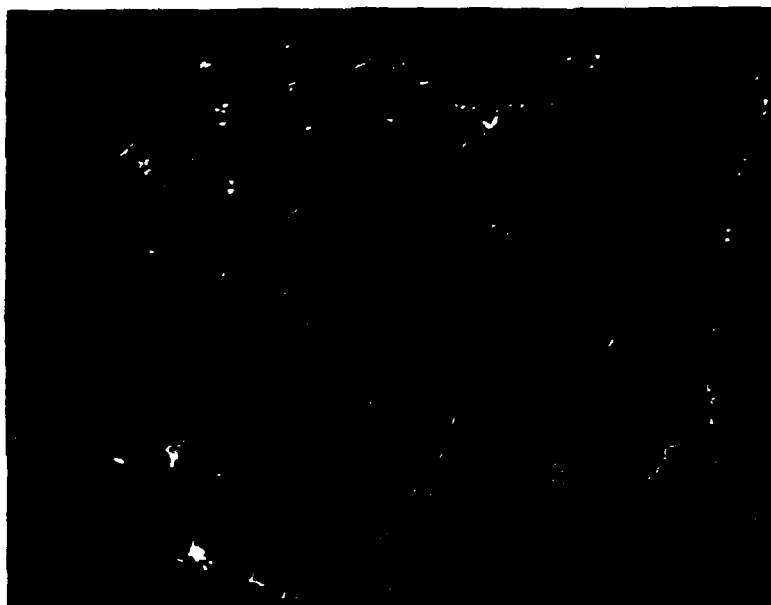


FIGURE 1

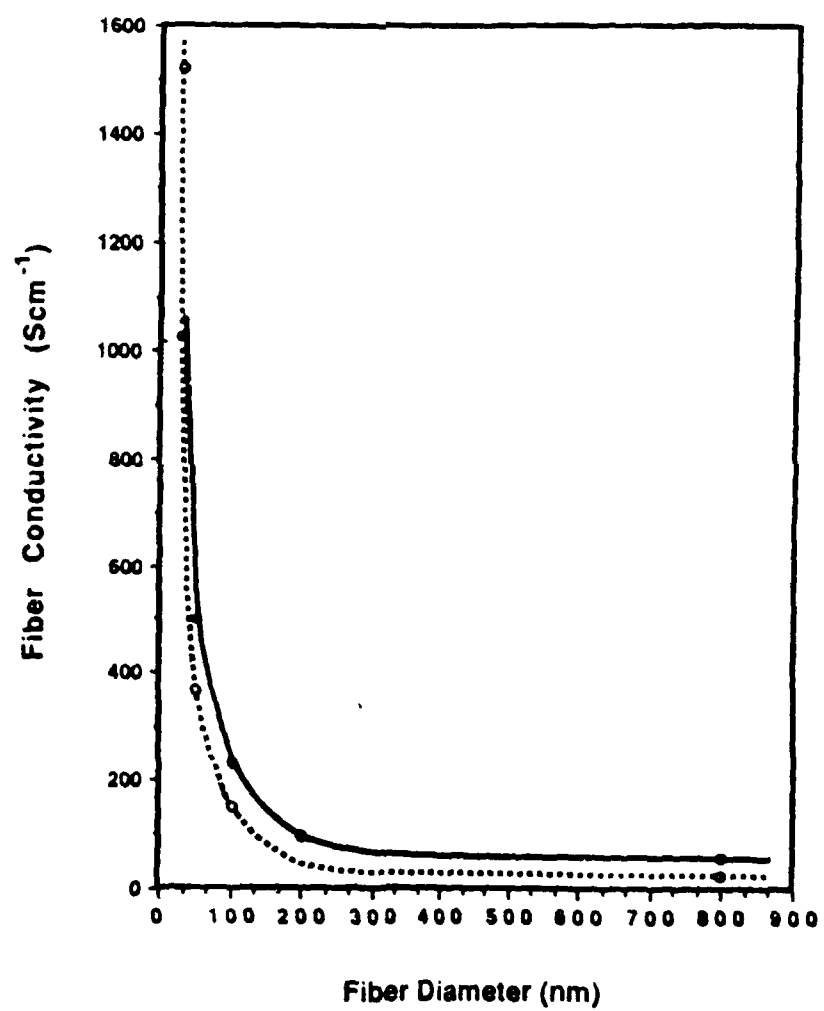


FIGURE 2

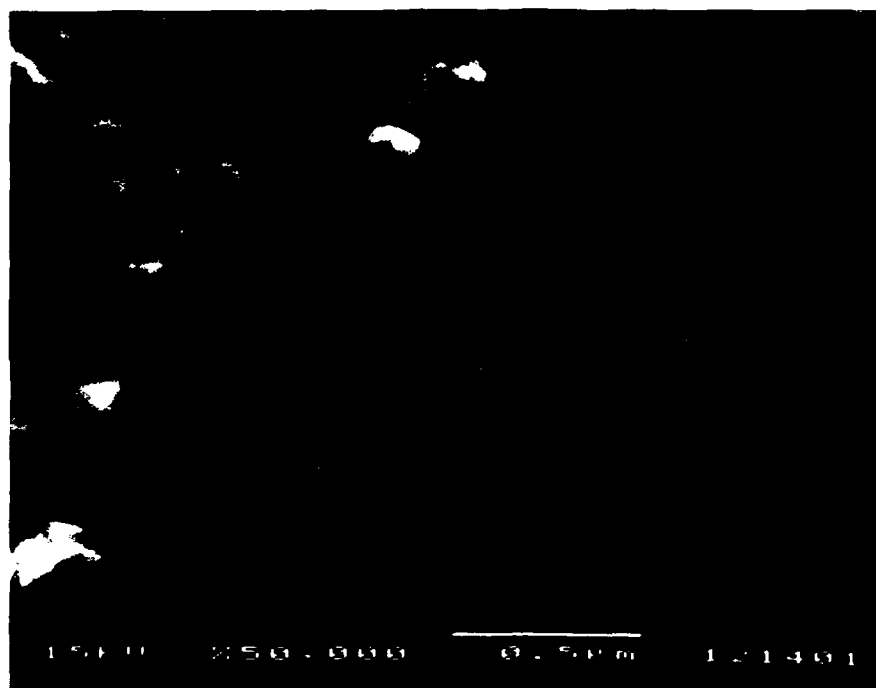


FIGURE 3

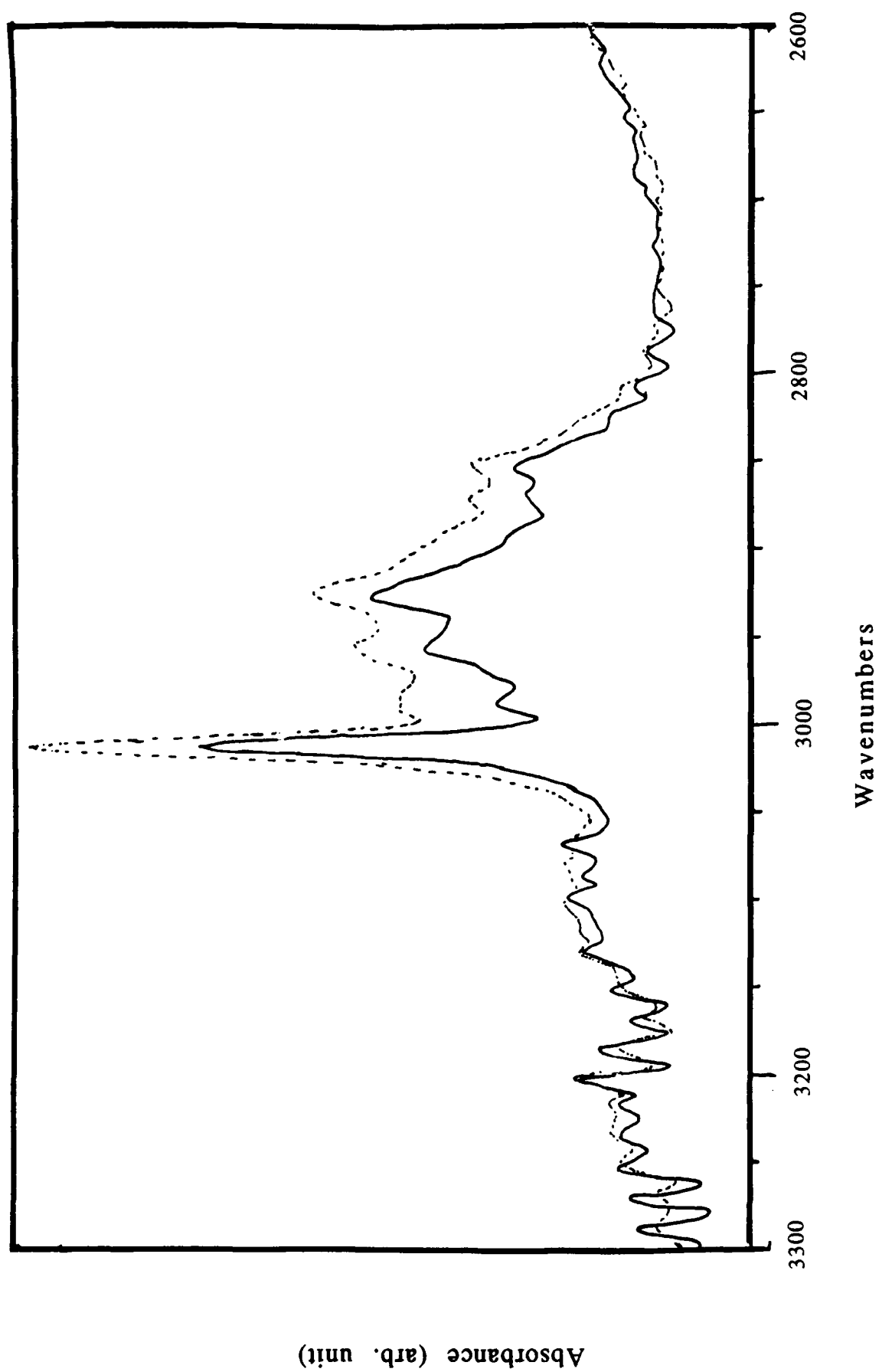


FIGURE 4