

Conductometric Sensors Based on the Hypersensitive Response of Plasticized Polyaniline Films to Organic Vapors

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Several reports document the use of electronically conductive polymers as conductometric sensors for water vapor¹ and redox-inactive organic vapors.² Although the changes in conductivity are not large and there is no designed chemosensitivity, it has been pointed out that^{2g,3} the use of an array of such electrodes, each coated with a different polymer, could produce an effective device where the variability in response would produce an identifiable, and perhaps quantifiable, response for specific organic vapors. Underlying such applications are structural and electron transport issues of some fundamental interest, i.e., by what mechanism does vapor absorption change the conductivity?

Recently we have reported on the large increases (10^2 – 10^3) in conductivity observed for one dendritic redox polymer when exposed to water vapor and another dendritic redox polymer when exposed to organic vapors.⁴ Following up on those results, the present study originated in an observation by Kinlen et al. that certain polyaniline (PANI) films (emeraldine form protonated with organic sulfonic acids) dramatically increased their conductivity when washed with methanol or similar solvents to remove excess sulfonic acid.⁵ A related effect known from the beautiful observations of Cao et al. and from Xia et al. is that the properties of PANI films of this type, which have large organic sulfonic acids present, are sensitive to the casting solvent.^{6,7} Cresol

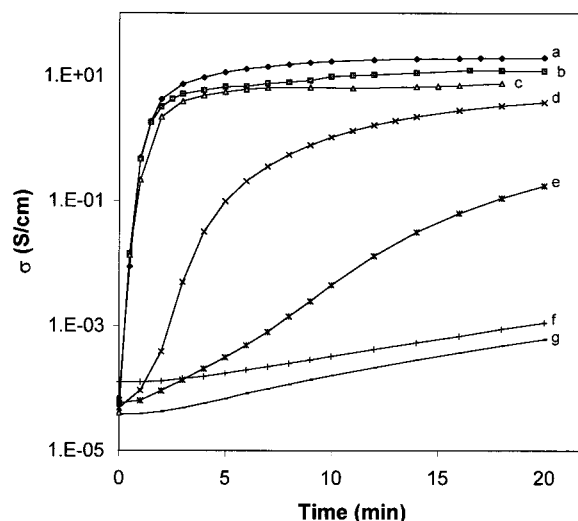


Figure 1. Conductivity of 50 mm PANI films exposed to the vapor above various ethanol/water mixtures (% by volume of ethanol). A, 100%; B, 50%; C, 33%; D, 12.5%; E, 6.6%; F, 1.3%; G, 0%.

as a solvent leads to films with high conductivity; other solvents, such as DMSO, gave low conductivity films. High- and low-conductivity films had different optical absorption spectra and it was possible to correlate the conductivity with the spectra. We discovered that methanol vapor dramatically increased the conductivity of PANI, and herein we describe the phenomenon, how it can be used for sensor technology, and some evidence about its structural origin.

Following the method of Kinlen et al.,⁵ films (1–50 μm) were cast onto glass from a solution in xylene of PANI, excess dinonylnaphthalenesulfonic acid, and the plasticizer 2-butoxyethanol at 80° C at atmospheric pressure in air. Conductivity measurements were made using four copper probes. The films were dried for 30 min at 80°, then 30 min at 65°, and then 30 min at room temperature. Longer drying times did not change the film properties. Initial conductivity values were reproducible within 10% of 5×10^{-5} S/cm. The films were introduced into a closed vessel containing one of several volatile solvents. If methanol or ethanol were present, the conductivity rose within 1 min to stable values near 20 S/cm that did not change when the film was transferred to air. Warming the films in air at 70° C for 3 h also did not reverse the effect. All the conductivity values reported here, regardless of the vapor treatment or no treatment, were ohmic and, even after 1 h, showed no polarization. This suggests electronic conductivity and is inconsistent with ionic conductivity.

The large vapor-induced change in conductivity provides the possibility for the development of a sensitive detection system. To examine this possibility we have measured the change in conductivity due to ethanol vapor in more detail. First, using pure ethanol it was demonstrated that the conductivity rose rapidly with time, but could be stabilized at any intermediate point by removing the ethanol vapor. Second, a series of measurements was made by placing the detector above different ethanol/water mixtures. Since the effect of

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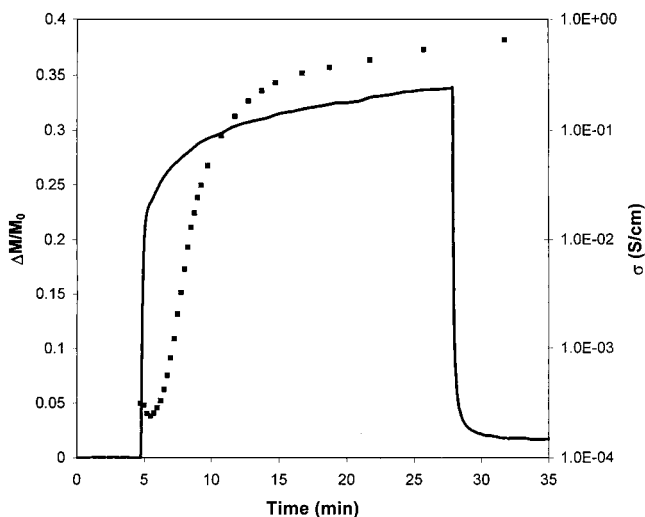


Figure 2. Conductivity (squares) and weight changes from QCM (solid line) for 1 μM PANI films exposed to the vapor above a 20% ethanol/80% water mixture. DM is the mass change, M_0 is the initial mass. Sample placed in the vapor after 5 min.

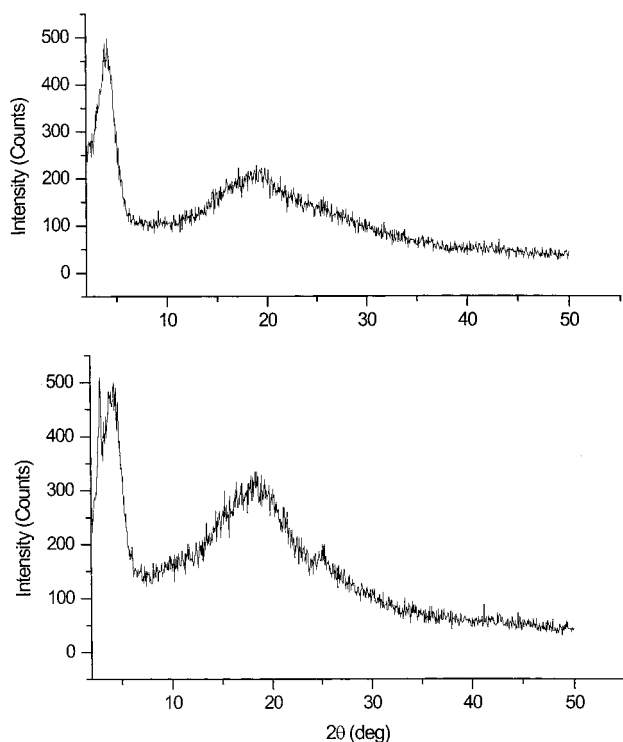


Figure 3. Wide-angle X-ray diffractograms for PANI films before (A) and after (B) exposure to ethanol vapor.

ethanol is much greater than that for water, it was possible to quantitate the ethanol concentration in the solution. It was shown that even 1% ethanol solutions gave measurable changes in conductivity. Extrapolation indicated a threshold level for detection of about 0.05% in solution or 0.01% in the vapor. As a practical test, commercial beer samples,^{2e} a light beer ($\Delta\sigma = 60$ S/cm), and a higher alcohol content ale ($\Delta\sigma = 1260$ S/cm), were distinguished without tasting them until after the measurements. Figure 1 shows data using 50 μm films, where many minutes were required to get relatively constant conductivity for low ethanol concentrations. Using films that were 1 μm thick, useful measurements could be made after about 3 min. Thus,

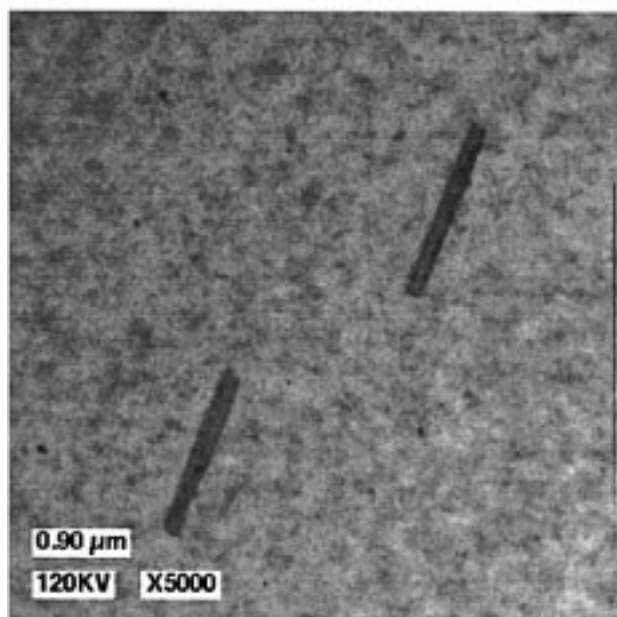
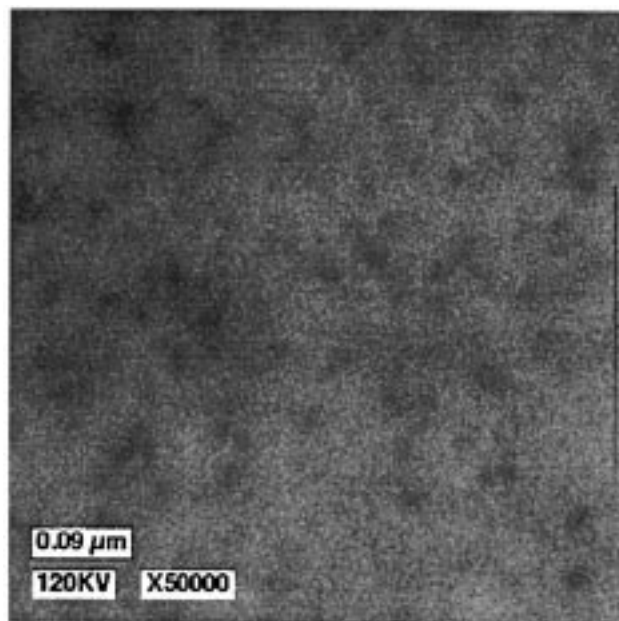


Figure 4. Transmission electron micrographs of PANI films before (top) and after (bottom) exposure to ethanol vapor.

the threshold value and response time are adequate for single-shot sensor applications.

The large dynamic range of the measurements also provided a sensitive differentiation between other organic vapors and water. The conductivity values, which were stable after 10 min for 1 μm films, were as follows: DMF, 5 S/cm; acetone, 0.3 S/cm; ether, 10^{-2} S/cm; water, 10^{-4} S/cm; chloroform, toluene, and hexane, 5×10^{-5} S/cm. The differences in these responses are very large and depend on the polarity of the vapor. In a slightly different approach, we have shown that these PANI films in their highly conducting state (from ethanol treatment) can be made less conductive by exposure to nonpolar organic vapors. Chloroform vapor, for example, reduced the conductivity of a 2 μm film from 20 to 4 S/cm in 2 min. Thus, it would appear that a wide variety of vapors should be identifiable with a simple device.

Initial experiments regarding the mechanism of the large conductivity increases have been undertaken. Changes in the mass of the films resulting from exposure to various pressures of methanol and ethanol vapor were measured using a quartz crystal microbalance.^{3,8-10} These measurements demonstrated rapid and almost reversible uptake of large quantities of alcohol. The amount absorbed and the rate of absorption were, as expected, larger for higher alcohol vapor pressures. NMR analysis of a high conductivity film that had been treated with methanol vapor, "dried" in air, and dissolved (completely) in CDCl_3 showed the presence of methanol, demonstrating that some of the solvent which enters the film from the vapor is strongly bound. Figure 2 shows a comparison of the time course for ethanol uptake and conductivity changes for a 2 μm thick film exposed to the vapor above a 20% solution of ethanol in water. Ethanol entered rapidly and when the sample was placed in air almost all the ethanol left even more rapidly. Of mechanistic interest is a time lag between the mass change and the onset of the conductivity increase.

Wide-angle X-ray diffraction studies (Figure 3) showed changes after treatment with ethanol or methanol vapors. The new diffraction lines at $d = 3.55$ and 29.59 Å indicated vapor-induced crystallization.^{6,11} Transmission electron microscopy (Figure 4) was performed on

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(10) Mass calculated using the Sauerbrey equation. Buttry, D. A.; Ward, M. D. *Chem. Rev.* **1992**, *92*, 1335. The measurements were limited to thin, 1 mm films over the percent ethanol range 1–20% in order to avoid overloading the system.

ultrathin films cast from dilute solution onto gold grids. Before vapor treatment the samples were uniform with particle size less than 10 nm. After an 8 min treatment with ethanol vapor, crystallites formed. We expected that optical absorption spectra might show changes similar to those previously reported^{6,7} in which poorly conducting films showed a strong band at about 780 nm and highly conducting films showed only near-IR absorbance from free carriers without the 780 nm band. It was found, however, that the spectra of poorly⁵ and highly conducting samples were quite similar, with a 780 nm band and free carrier absorption. We hypothesize, therefore, that the large, vapor-induced increase in conductivity results from formation of a more crystalline, more conductive phase.⁵⁻⁷ This phase change accounts for the lag time between solvent uptake and the onset of conductivity increase.

In summary, it has been demonstrated that polar organic vapors cause large increases in the conductivity of these PANI films, that these changes involve crystallization, and that these changes can be used for one-shot vapor differentiation and ethanol quantitation. The low cost of PANI makes this analytical approach of some interest.

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