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Notes

Camphorsulfonic Acid Fully Doped Polyaniline Emeraldine Salt: *In Situ* Observation of Electronic and Conformational Changes Induced by Organic Vapors by an Ultraviolet/Visible/Near-Infrared Spectroscopic Method

Younan Xia[*,†] **and Alan G. MacDiarmid**[*]

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104

Arthur J. Epstein

Department of Physics and Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

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Introduction

Recently, polyaniline (PANI), the oldest organic polymer ever synthesized, received renewed scientific and technological interest due to its richness in its chemistry/physics and its potential/practical applications in electrical devices.[1] Usually, polyaniline was processed from a good film-forming solvent, *N*-methyl-2-pyrrolidone (NMP), in the nonconductive form of emeraldine base (EB) and then doped into the conductive form of emeraldine salt (ES) by protonic acids.[2] Films of PANI-ES prepared in this way usually have a conductivity of 1–5 S/cm, though with increasing crystallinity by thermal stretching conductivities can exceed 100 S/cm.[3] More recently, it was found that, by using "functionalized" protonic acids (for example, camphorsulfonic acid, HCSA) as dopants, the resulting PANI–HCSA complex was soluble, in the conductive form of emeraldine salt, in common nonpolar or moderately polar organic solvents.[4] The conductivities of PANI–HCSA films processed from these solvents, however, vary over a very wide range, from $\approx$0.1 S/cm in chloroform to $\approx$200–400 S/cm in *m*-cresol. In order to understand this large difference in conductivity, further studies were conducted by us and other groups. Based on the results of EPR,[5] lyotropic liquid crystallinity,[6] dielectric constants,[7] viscosity,[8] UV/vis/near-IR, X-ray, and conductivity measurements,[9,10] it has been suggested that polymer chains of PANI–HCSA may have different conformations, and therefore different conjugation lengths, in different solvents. For example, an HCSA fully doped PANI chain has a more expanded coil-like conformation and hence a longer conjugation length in solvents such as *m*-cresol, *p*-cresol, 3-ethylphenol, 2-chlorophenol, and 2-fluorophenol than in solvents such as chloroform, NMP, DMF, and benzyl alcohol.[9,11] Corresponding to either expanded coil-like or coil-like conformations in solutions, films of PANI–HCSA have either high conductivity ($\approx$200 S/cm) or low conductivity ($\approx$0.1 S/cm), respectively.[9,12]

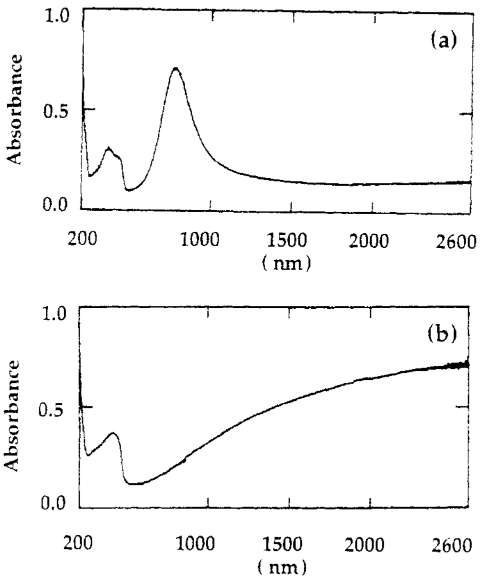

Figure 1. UV/vis/near-IR spectra for HCSA fully doped polayaniline emeraldine salt films spun from chloroform (a) and *m*-cresol (b), respectively. The three distinctive peaks at 360, 440, and 780 nm for the films spun from chloroform are consistent with a coil-like conformation and a localized polaron structure (shorter conjugation length). The absorption peak at 440 nm and the "free carrier tail" in the IR region for the films spun from *m*-cresol are consistent with an expanded coil-like conformation and a delocalized polaron structure (longer conjugation length).

Here we report our *in situ* observation of the electronic and conformational changes induced by organic *vapors* by the UV/vis/near-IR spectroscopic method when films of PANI–HCSA spun from chloroform or NMP were exposed to *m*-cresol *vapor* at room temperature in a specially designed cell.

Experimental Section

The PANI-EB powder used in the present study was synthesized chemically according to our previously reported procedure.[13] Elemental analysis, UV/vis, and FTIR spectroscopic measurements were carried out to assure that the EB powder was in the EB oxidation state.[14,15] Powder samples of PANI–HCSA were made by mixing intimately 0.409 g (1.129 mmol) of EB powder with 0.524 g (2.258 mmol) of d,l-camphorsulfonic acid (Aldrich) in a mortar. Solutions ($\sim$2% w/w) were prepared by adding $\sim$0.05 g of the PANI–HCSA mixture into $\sim$2-mL solvents and sonicated at 25 °C for $\sim$10 h. The resulting solutions were further filtered through a 0.45-μm-micropore filter to remove any undissolved particles.

In situ measurements of UV/vis/near-IR spectra were done in a cell constructed by sandwiching an O-ring between two quartz plates.[16] Thin films with dimensions of $\sim$1 cm^2 and a thickness of $\sim$0.1 μm were spun onto one of the two quartz plates with a spinner (Headway Inc.). After tightening the cell with clamps, 2 drops of *m*-cresol was delivered to the bottom of the cell via a syringe/needle and the UV/vis/near-IR spectra were recorded on a spectrometer (Perkin-Elmer Lamda 9) from 200 to 2600 nm.

Results and Discussion

Figure 1 shows the UV/vis/near-IR spectra of HCSA fully doped polyaniline emeraldine salt films spun from chloroform and *m*-cresol, respectively. As discussed previously,[4–9,12] different polymer conformations are responsible for these two totally different spectra. Figure 1a, with three distinctive peaks at 360, 440, and 780 nm,

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[†] Present address: Department of Chemistry, Harvard University, Cambridge, MA 02138. e-mail: yxia@gmwgroup.harvard.edu.

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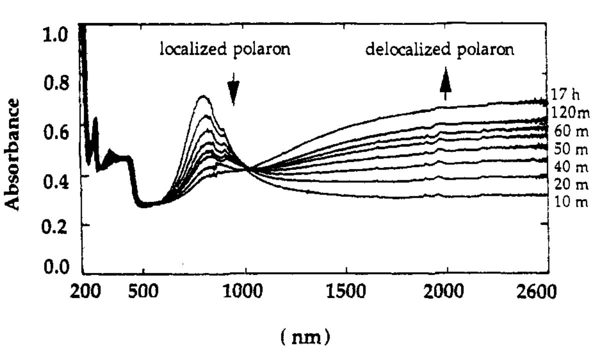

Figure 2. Change in UV/vis/near-IR spectra when PANI–HCSA thin films spun from chloroform were exposed to *m*-cresol *vapor* at room temperature for different times. The sharp peak at 260 nm is due to *m*-cresol. As the exposure time increased, the absorbance corresponding to the localized polarons (at ~780 nm) decreased, while the absorbance corresponding to the delocalized polaron band (the "free carrier tail" centered at ~2600 nm) increased.

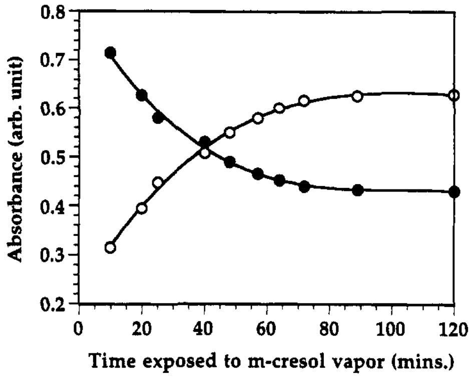

Figure 3. Change in absorbance at 2600 nm (open circle) and of the peaks at 780–820 nm (filled circle; this peak was red-shifted due to the fact that it was partly overlapped with the "free carrier tail"), respectively, when thin films of PANI–HCSA spun from chloroform were exposed to *m*-cresol vapor for different times. The absorbance at 2600 nm is characteristic of a delocalized polaron band, while the absorbance at 780–820 nm is characteristic of localized polarons.

is consistent with a localized polaron structure (shorter conjugation length) and a coil-like conformation for the polymer chain, while Figure 1b, with one peak at 440 nm and a "free carrier tail" commencing at ~1000 nm which increases steadily in intensity to ~2600 nm, the maximum value obtainable by the spectrometer, is consistent with a delocalized polaron band structure (longer conjugation length) and an expanded coil-like conformation for the polymer chain.

Figure 2 shows the change in UV/vis/near-IR spectra when thin films of PANI–HCSA spun from chloroform were exposed to *m*-cresol *vapor* at room temperature. As the exposure time increased, the intensity of the absorption peak (≈780 nm) corresponding to the localized polarons decreased and the free carrier tail corresponding to the delocalized polaron band increased (Figure 3). As *m*-cresol molecules diffusing into the polymer film, they solvated the dopant counterions as well as plasticized the polymer chains, and hence a local conformational change from coil-like to expanded coil-like was triggered.[17] Because this conformational change reduced the twisting defects between the repeating units of the polymer chain, the conjugation length was increased in this process. Another interesting feature in Figure 2 is the isosbestic points at ~600 and ~1000 nm, respectively. The appearance of isosbestic points in the UV/vis/near-IR spectra implies that there are no measurable intermediates in this conformational conversion and that the absorption peaks shown in Figure 2 are dominated by the transitions within an individual polymer chain (i.e., intrachain transitions). After exposure, the *m*-cresol absorbed by the film could be removed either by heating at 80 °C for several minutes or by dipping into acetone for several minutes, yet the UV/vis/near-IR and the surface resistance of the film were unchanged.

In addition to the enormous change observed in the UV/vis/near-IR spectra, other measurements are also consistent with an increase in conjugation length. For example, the surface resistance of the films was reduced from ≈200 KΩ/square to ≈2 KΩ/square after exposure to *m*-cresol vapor and the films became insoluble even in boiling chloroform after exposure. This implies that the crystallinity of the films is increased after exposure to *m*-cresol *vapor*. Similar results were also obtained when thin films of PANI–HCSA were spun from a ~2% solution in NMP (w/w) and subsequently exposed to *m*-cresol *vapor* at room temperature in the same way. It was also found that other solvents such as *p*-cresol, 2-chlorophenol, 2-fluorophenol, and 3-ethylphenyl had the same function as *m*-cresol in this process.

The above observations provide a possible way to fine-tune the properties (electronic, electrical, and optical) of conjugated polymers, in this case, HCSA fully doped polyaniline emeraldine salt. They also provide a possible way to fabricate chemical sensors (artificial nose) based on this system.[18] The decreasing in solubility of the films after exposure to *m*-cresol *vapor* also opens the door for a new method for preparing patterns of conducting polymers on solid substrates, and this should find applications in the area of microelectronics.

Conclusions

In summary, we have demonstrated the feasibility of using a UV/vis/near-IR spectroscopic method to study the changes of conformation and conjugation length for conjugated polymers. Thin films of PANI–HCSA spun from chloroform or NMP have a coil-like conformation and shorter conjugation length, while those films spun from *m*-cresol have an expanded coil-like conformation and longer conjugation length. The coil-like conformation can be irreversibly converted to the expanded coil-like conformation by exposure to *m*-cresol *vapor* at room temperature.

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(11) No light scattering experiments have ever been done on the solutions of PANI-HCSA in *m*-cresol and chloroform. But, based on the results obtained with the indirect methods mentioned here (EPR, viscosity, UV/vis/near-IR, etc.), it is generally accepted that polymer chains of PANI-HCSA have different conformations and conjugation lengths in these two kinds of solvents. In the text, we use the terms of "expanded coil-like" and "coil-like" to distinguish these two different conformations.

(12) The polymer conformations were kept ("locked into place") during the film-making process because the UV/vis/near-IR spectra of the solutions are similar to the spectra of the thin films. This is also consistent with the results of dielectric constant, X-ray, and conductivity measurements on the free-standing films.

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(14) Elemental analysis (Calc: C, 79.56; H, 4.97; N, 15.47. Exptl: C, 79.18; H, 5.26; N, 15.97). The UV/vis spectrum of the dilute solution in NMP showed two peaks at 327.8 and 635.4 nm, respectively. The FTIR spectrum of a KBr pellet showed a vibrational mode at 832 cm^{-1}.

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