*Chem. Mater.* **1995,** *7,* 443–445

# Camphorsulfonic Acid Fully Doped Polyaniline Emeraldine Salt: Conformations in Different Solvents Studied by an Ultraviolet/Visible/Near-Infrared Spectroscopic Method

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*Received September 15, 1994*
*Revised Manuscript Received January 18, 1995*

Recently, much attention has been directed to polyaniline (PANI) due largely to its excellent stability and its potential/practical applications in electrical devices.[1] PANI used to be 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] Free-standing films of PANI-ES prepared in this way usually have a conductivity of 1–5 S/cm, though with increasing crystallinity and coherence length by thermal stretching and physical cross-linking (gel-made films) conductivities can exceed 200 S/cm.[3–5] More recently, it was found that PANI-ES could be made soluble in a number of organic solvents by choosing functionalized protonic acids as dopants (for example, camphorsulfonic acid, HCSA).[6] The conductivity of polyaniline films processed directly from these solutions, however, varies over a very wide range, from 0.1 S/cm in chloroform to 200–400 S/cm in *m*-cresol. The present UV/visible/near-IR spectroscopic study originated from the question why films of PANI-HCSA have a conductivity of ∼0.1 S/cm when cast from chloroform, whereas those films with the same composition have a conductivity of ∼200 S/cm when cast from *m*-cresol. This study demonstrates the importance of polymer chain conformation *in solution* in determining the conductivity of conducting polymers *in solid*, as well as the feasibility of using UV/visible/near-IR spectroscopic method to study the conformation of conjugated polymers.

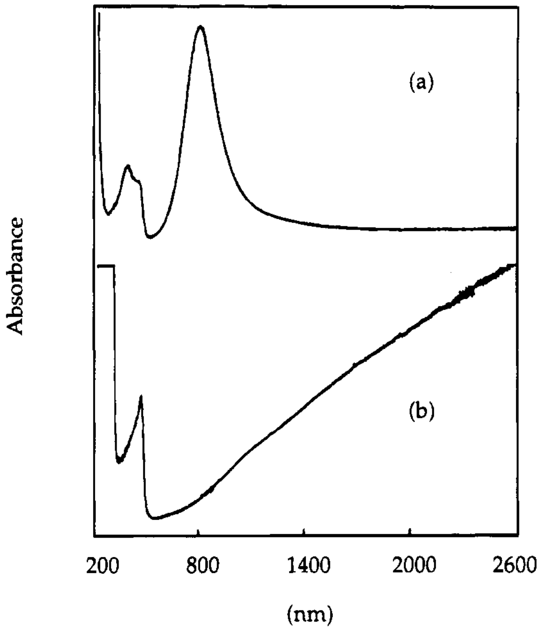

**Figure 1.** UV/visible/near-IR spectra of solutions of PANI-HCSA in (a) chloroform, NMP, DMF, and benzyl phenol and (b) *m*-cresol, *p*-cresol, 2-chlorophenol, 2-fluorophenol, and 3-ethylphenol, respectively.

Eleven solvents were chosen for the present study.[7–9] Only two different UV/visible/near-IR spectra were found for these solutions. The first type of spectrum (Figure 1a), which was obtained for solutions made from chloroform, NMP, DMF, and benzyl alcohol, has three distinctive absorption peaks at 360 nm (3.42 eV), 440 nm (2.80 eV), and 780 nm (1.58 eV), respectively. These polymer solutions (∼2% w/w) were green, and they were not viscous. Free-standing films of PANI-HCSA cast from these solutions were very brittle with conductivities in the range 0.01–0.1 S/cm (Figure 2). The films are strongly disordered as indicated by X-ray diffraction patterns (Figure 3a). The second type of spectrum (Figure 1b), which was obtained from solutions made from *m*-cresol, *p*-cresol, 2-chlorophenol, 2-fluorophenol, and 3-ethylphenol, has an absorption peak at ∼440 nm (2.80 eV), and a steadily increasing "free-carrier tail" starting from ∼1000 nm to the IR region. Note that

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(1) MacDiarmid, A. G.; Epstein, A. J. *Faraday Discuss. Chem. Soc.* **1989**, *88*, 317.

(2) Angelopoulous, M.; Asturias, G. E.; Ermer, S. P.; Ray, A.; Scherr, E. M.; MacDiarmid, A. G.; Akhtar, M.; Kiss, Z.; Epstein, A. J. *Mol. Cryst. Liq. Cryst.* **1988**, *151*, 160.

(3) Joo, J.; Oblakowski, Z.; Du. A.; Pouget, J. P.; Oh, E. J.; Wiesinger, J. M.; Min, Y.; MacDiarmid, A. G.; Epstein, A. J. *Phys. Rev.* **1994**, *B49*, 2977.

(4) Oh, E. J.; Min, Y.; Wiesinger, J. M.; Monohar, S. H.; Scherr, E. M.; Prest, P. J.; MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1993**, *55*, 977.

(5) Cromack, K. R.; Jozofuwizt, M. E.; Ginder, J. M.; MacCall, R. P.; Du, A.; Levy, J. M.; Kim, K.; Li, C.; Wang, Z. A.; Epstein, A. J.; Druyl, M. A.; Glatkowski, P. J.; Scherr, E. M.; MacDiarmid, A. G. *Macromolecules* **1991**, *28*, 4157.

(6) Cao, Y.; Smith, P.; Heeger, A. J. *Synth. Met.* **1992**, *48*, 91.

(7) The solvents used in the present study include: chloroform, NMP, benzyl alcohol, DMF, *m*-cresol, *p*-cresol, 2-fluorophenol, 2-chlorophenol, 3-ethylphenol, 3-isopropylphenol, and 2-methoxy-4-methylphenol. Polyaniline emeraldine base (EB) powder was synthesized chemically according to our previously reported procedure.[8] Elemental analysis, UV/visible, and FTIR spectroscopic measurements were carried out to assure that the powder was in the oxidation state of emeraldine base. HCSA fully doped polyaniline emeraldine salt (PANI-HCSA) powder was made by mixing intimately 0.409 g (1.129 mmol) of EB powder with 0.524 g (2.258 mmol) of (±)-10-camphorsulfonic acid (98%, Aldrich) in a mortar. All the solvents were purchased from Aldrich or Fluka and were used as received. The polymer solutions (∼2%, w/w) were prepared by adding ∼0.05 g of the above PANI-HCSA powder stepwise into ∼2 mL of solvents within ∼10 min. After sonication in a water bath at ∼25 °C for about 10 h, the polymer solutions were filtered through a 0.45-μm-micropore filter to remove undissolved particles. Two drops of a polymer solution was put between a pair of quartz plates (diameter ∼5 cm), and the UV/visible/near-IR spectrum was recorded on a spectrometer (Perkin-Elmer Lambda 9) from 200 to 2600 nm. Spectrum obtained from the thin film (spin-coated on quatz plate, ∼0.1 μm in thickness) is essentially the same as that obtained from solution.[9] Free-standing films (1–10 μm) were cast on glass slides by evaporating at room temperature in a hood. Conductivity was measured with the standard four-probe method. X-ray diffraction measurements were conducted on a Rigaku Diffractometer (Geigerflex).

(8) MacDiarmid, A. G.; Chiang, J. C.; Richter, A. F.; Somasiri, M. L. D.; Epstein, A. J. In *Conducting Polymers*, Alcacer, L., Ed.; Reidel: Dordrecht, The Netherlands, 1987; pp 105–120.

(9) Xia, Y.; MacDiarmid, A. G.; Epstein, A. J. *Macromolecules* **1994**, *27*, 7212.

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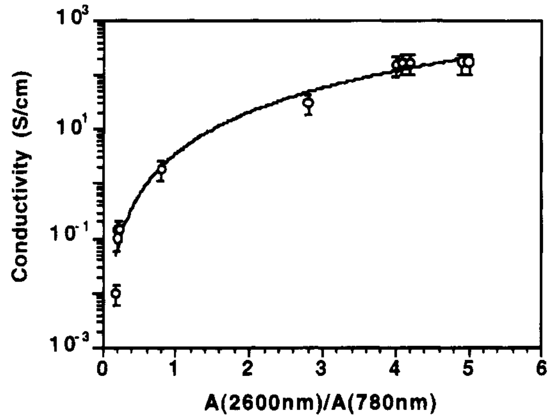

**Figure 2.** Dependence of conductivity on the ratio of the absorbance of delocalized polarons to the absorbance of localized polarons. (Points from bottom to top represent NMP, chloroform, benzyl alcohol, 2-methoxy-4-methylphenol, 3-isopropylphenol, *m*-cresol, *p*-cresol, 3-ethylphenol, 2-fluorophenol, and 2-chlorophenol). As discussed in the text, the absorption at ~2600 nm (free-carrier tail) is characteristic of a delocalized polaron band, and the absorption at ~780 nm is characteristic of a localized polaron band.

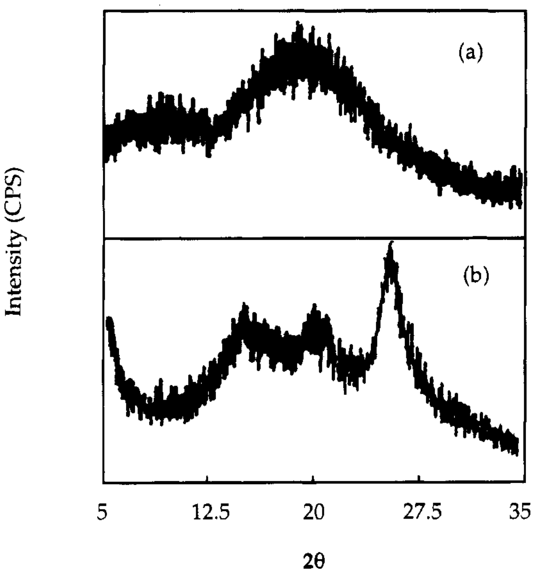

**Figure 3.** X-ray diffraction patterns of free-standing films of PANI-HCSA cast from (a) chloroform, NMP, DMF, and benzyl phenol; and (b) *m*-cresol, *p*-cresol, 2-chlorophenol, 2-fluorophenol, and 3-ethylphenol, respectively.

the "free-carrier tail" in the IR region is characteristic of metallic conductive materials such as metals or iodine doped polyacetylene.[10] These polymer solutions (~2% w/w) were deep green, and they were very viscous. They usually gelled within 2–3 days after preparation. Free-standing films of PANI-HCSA cast from these solutions are quite flexible with conductivities in the range of ~150 S/cm (Figure 2). These films are partly crystalline (Figure 3b) with three distinctive diffraction peaks ($2\theta$) at ~15.9°, ~19.4°, and ~25.1°, respectively.

The band structure of fully protonated emeraldine salt has been studied previously by semiempirical MO calculation[11] and more recently by ab initio calculation.[12] A half-filled "polaron band" that is formed by the interaction between separate polarons (there are two polarons per tetrameric repeating unit) was proposed to explain the observed optical and electrical properties for the fully protonated polyaniline emeraldine salt. On the basis of the results of UV/visible/near-IR spectra (Figure 1), fully protonated emeraldine salt has totally different electronic structures in different solvents. This difference in electronic structure can only be attributed to its difference in geometric structure (or conformation) for the polymer chain.[13] In solvents such as chloroform, NMP, DMF, and benzyl alcohol, the polymer chains of PANI-HCSA have a coillike conformation. The polarons of each tetrameric unit are isolated from each other due to the twist defects between aromatic rings. Therefore, the polaron band has little dispersion in energy (Figure 4a). The three absorption peaks in the UV/VIS/NIR spectrum (Figure 1a) can be assigned as the transitions from π band to π* band, polaron band to π* band, and π band to polaron band, respectively. In solvents such as *m*-cresol, *p*-cresol, 2-chlorophenol, 2-fluorophenol, and 3-ethylphenol, the polymer chain of PANI-HCSA has an expanded coillike conformation. In this more expanded conformation, the twist defects between aromatic rings are removed. The interaction between the adjacent isolated polarons, therefore, becomes stronger, and the polaron band becomes more dispersed in energy (more delocalized, see Figure 4b). As a result, the absorption peak at ~780 nm for the coillike conformation, which is associated with the isolated polaron band, is to be replaced by the intraband transitions within the half-filled polaron band (shown as the "free-carrier tail" in the near-IR region; see Figure 1b). At the same time, the transition between π band and π* band (~360 nm) becomes very weak and finally disappears possibly because the energy gap between π band and the polaron band has been eliminated (Figure 4b).

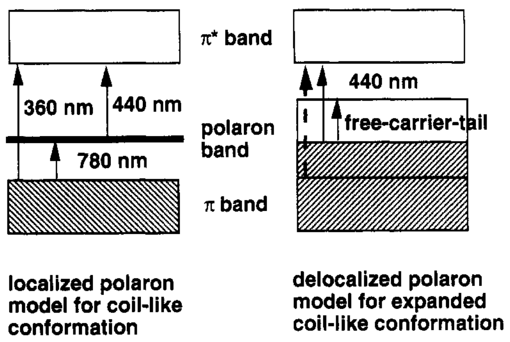

**Figure 4.** Band structures of HCSA fully protonated polyaniline emeraldine salt with (a) a coillike conformation and (b) an expanded coillike conformation, respectively.

The above assumption about the conformational change from solvents to solvents was consistent with viscosity[14] and solution EPR measurements,[15] as well as the observation of lyotropic crystallinity for concentrated solutions of PANI-HCSA in *m*-cresol.[16]

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(10) Monkman, A. P.; Adamas, P. *Synth. Met.*, **1991**, *41–43*, 627.

(11) Stafström, S.; Bredas, J. L.; Epstein, A. J.; Woo, S. H.; Tanner, D. B.; Wang, W. S.; MacDiarmid, A. G. *Phys. Rev. Lett.* **1987**, *59*, 1464.

(12) Baird, N. C.; Wang, H. *Chem. Phys. Lett.* **1993**, *202*, 50.

(13) We do not know the exact conformations of the polymer chains since no light-scattering experiments have been performed on these polymer solutions. In the text, we use the terms of "expanded coillike" and "coillike" to distinguish these two different conformations. The polymer conformations in solutions were kept ("locked into place") during the film-casting process because the UV/vis/near-IR spectra of the solutions are similar to the spectra of thin films made by spin coating.[9]

(14) Avlyanov, J.; Min, Y.; MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.*, in press.

(15) Cao, Y.; Heeger, A. J. *Synth. Met.* **1992**, *52*, 193.

The bulk conductivity of any conducting polymer film can be approximately expressed as a function of intrachain and interchain transitions:

$$\sigma(\text{bulk}) = \mathbf{F}\ (\sigma(\text{intrachain}), \sigma(\text{interchain}))$$

and each term in the above expression is related to the carrier mobility $\mu$ by

$$\sigma = n\mu e$$

here $n$ is the concentration of charge carrier, $e$ is the charge of an electron. When the polymer chains become more expanded coillike, the polaron band becomes more delocalized, the carrier mobility and hence the intrachain conductivity increase. On the other hand, rods crystallize more easily than coils, and the higher crystallinity caused by more expanded coillike conformation results in a higher interchain conductivity since the interchain distance is the shortest in the solid forms. The present model accounts for films of PANI-HCSA have a conductivity of ~150 S/cm when cast from the second type of solvents such as *m*-cresol, while they only have a conductivity of ~0.1 S/cm when cast from the first type of solvents such as chloroform. Because the absorption at ~2600 nm is characteristic of expanded coillike conformation and the absorption at ~780 nm is characteristic of coillike conformation, the ratio between the absorbances at these two wavelengths can be used to estimate the relative ratio of these two conformations. As shown in Figure 2, there exists a monotomically increasing relationship between the conductivity and the ratio of the "free-carrier tail" to the localized polaron in the films of PANI-HCSA. This relationship provides a simple criteria for choosing appropriate solvents to process PANI-HCSA into highly conductive form.

Polyaniline emeraldine salt is a polyelectrolyte, in which the polymer backbone is positively charged with negative counterions sitting in the vicinity of polymer chains. When counterions is removed away from the polymer chain, the static repulsive interaction of the positive charges on the polymer backbone tends to extend the polymer chain from a coillike conformation to an expanded coillike conformation. We think that solvents such as *m*-cresol probably work in this way. We note that these solvents are all phenols. The network of hydrogen bonds formed by phenol groups seems to provide an effective proton-exchange medium by which the counterions can be removed from the polymer chain. The acidity of the phenol group is also found to be important in facilitating and directing this proton-exchanging process between the dopant acids and the imine nitrogens on the polymer chains. When the benzene ring is substituted by electron-pushing groups (for axample, methoxy), the acidity of the phenol group decreases. The polymer chain in this kind of solvents tends to be in a coillike conformation. This is demonstrated by 2-methoxy-4-methylphenol. The UV/visible/near-IR spectrum of HCSA fully doped emeraldine salt solution in this solvent shows a characteristic of isolated polarons, and films cast from this solvent only have a conductivity of ~1.8 S/cm (Figure 2).

In summary, the conformations of PANI-HCSA in different solvents have been analyzed by a UV/visible/near-IR spectroscopic method, together with viscosity measurements on the solutions and X-ray diffraction, conductivity and measurement of microwave frequency dielectric constants on the resulting films. All these results are consistent with the fact that PANI-HCSA has a more expanded coillike conformation in *m*-cresol, *p*-cresol, 2-chlorophenol, 2-fluorophenol, and 3-ethylphenol than in chloroform, NMP, DMF, and benzyl alcohol. With this UV/visible/near-IR spectroscopic method, we can easily choose an appropriate solvent to process PANI-HCSA into a highly conductive form. One of the many advantages of UV/visible/near-IR spectroscopic method is that it can be used to monitor polymer conformational change in situ.[9]

**Acknowledgment.** This work was supported in part by the Office of Naval Research and the National Science Foundation.

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(16) Cao, Y.; Smith, P. *Polymer* **1993**, *34*, 3141.