

## Preparation and Properties of Water-soluble, Poly(styrenesulfonic acid)-doped Polyaniline

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Both persulfate oxidative coupling and anodic oxidation of aniline in dialysed, aqueous poly(styrenesulfonic acid), PSSAH, yields a water-soluble PSSAH-doped polyaniline.

Several research groups<sup>1,2</sup> have reported the synthesis of polyanilines (PANIs) doped with PSSAH which are soluble in organic solvents. They do not report water-solubility, but do use water to wash their products. Commercial NaPSSA<sup>1</sup> or PSSAH<sup>2</sup> was used whereby the former contains up to 40% by weight inorganic sulfates and 10% water depending on the source.<sup>3</sup> We have polymerized aniline in PSSAH that we prepared by acidification of the commercial sodium salt, followed by dialysis to remove low molecular mass impurities. We find that the use of such PSSAH yields a PANI that is generally insoluble in organic solvents and soluble in water. We believe that the use of a sulfate-contaminated PSSAH yields a PANI that has large amounts of sulfate along with the PSSA dopant, and that this product is not water-soluble and is not pure PANI-PSSA.

We prepared this water-soluble material both by persulfate oxidation and by anodic oxidation. During the oxidative polymerization, the mixture passes through several hues, emerging as a viscous, emerald green solution. Evaporation of the water yields an emerald green, granular solid of metallic luster. Neutralization to pH 11 with aqueous NaOH does not cause precipitation of the neutral PANI.

We prepared PSSAH by adding cold, conc. sulfuric acid to a cooled 3 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solution containing PSSA<sup>-</sup>Na<sup>+</sup> (Aldrich, *M<sub>r</sub>* 70 000). Acidification of PSSA<sup>-</sup>Na<sup>+</sup> was confirmed by the appearance of the sulfonic acid protons at  $\delta$  12.41 in the proton NMR spectrum [(CD<sub>3</sub>)<sub>2</sub>SO] of the product. This product was pressed to squeeze out the excess sulfuric acid, dissolved in deionized water, and dialysed<sup>4</sup> for up to one week using no. 6 wet cellulose dialysis tubing (Spectrum Laboratory Products, *M<sub>r</sub>* cut-off 1000) or when the diffusate no longer revealed BaSO<sub>4</sub> precipitate on adding Ba(NO<sub>3</sub>)<sub>2</sub>. We determined the molar acid concentration by titration with standard NaOH solution.

We prepared PSSAH-doped PANI both chemically and electrochemically. For the former, we employed aqueous persulfate oxidation in the standard MacDiarmid procedure<sup>5</sup> substituting PSSAH for HCl. We employed ammonium persulfate as well as potassium persulfate as oxidant. Table 1 shows the solubilities of our product along with those reported

by Li *et al.*<sup>1</sup> All solutions exhibit a Tyndall effect, including those of pure PSSAH. Addition of HCl, H<sub>2</sub>SO<sub>4</sub> or Na<sub>2</sub>SO<sub>4</sub> to aqueous PANI-PSSA causes precipitation of the corresponding PANI salt.

We conducted anodic oxidations at 24.5°C in aqueous solutions that were 0.256 mol dm<sup>-3</sup> in PSSAH and 0.22 mol dm<sup>-3</sup> in aniline using the Diaz cyclic sweep technique.<sup>6</sup> The three-electrode cell employed platinum working and counter electrodes and SCE as reference. During the cyclic sweep, a green cloud moves away from the anode. We obtained an electrode coating only when we performed constant potential electrolysis at 900 mV.

FTIR spectra of the base and salt forms of this product show aliphatic C-H stretching at 2915 and 2850 cm<sup>-1</sup> (PSSAH backbone). Precipitation of PSSA as the barium salt further supports the presence of PSSA in the system.

Fig. 1 shows the cyclic voltammogram (CV) obtained for the anodically produced PANI-PSSA in dilute, aqueous PSSAH on the 26th cycle at a scan rate of 50 mV s<sup>-1</sup>. We observe two redox peaks: the first lies at  $E_{1/2} = 70$  mV; the second lies at 432 mV vs. SCE. After about ten cycles the first peak begins to drift to higher potentials at a rate of 2.73 mV per cycle. We attribute this drift to polysemiquinone instability arising from steric effects in accommodating the bulky polyanion. Moreover, the second redox peak shifts to lower potentials at about the same rate, suggesting that oxidation of the polysemiquinone occurs more readily with its increasing instability.

Titration of these PANI samples with standard aqueous NaOH solution at a rate of 1 pH h<sup>-1</sup>,<sup>7</sup> showed *pK<sub>a</sub>*s at 2.5 and 5.0, which we assign to -NH<sub>2</sub><sup>+</sup> and terminal -NH<sub>3</sub><sup>+</sup>, respectively. Based on these results and the observed potential shifts, we estimate that the degree of polymerization (DP) of these as obtained PANI samples is at least 25 -C<sub>6</sub>H<sub>4</sub>NH- units.† The DP varies mainly with the aniline : persulfate ratio. We also titrated a sample of chemically prepared product that we purified by ion exchange to remove potassium or ammonium ion, followed by dialysis to remove sulfate and other low molecular mass materials, followed by centrifugation to obtain the highest molecular mass material present. This material showed no perceptible end point for terminal -NH<sub>3</sub><sup>+</sup> end groups, which suggests that its molecular mass was beyond the limits of the titration. This material was water-

Table 1 Solubilities of PSSAH-doped PANI

Solvent	Reported <sup>a</sup> herein	Reported <sup>1</sup>
DMF	Sl. sol.	Sol.
Me <sub>2</sub> SO	Sl. sol.	Sol.
MeOH	Insol.	Sl. sol.
CHCl <sub>3</sub>	Insol.	Sl. sol.
Benzene	Insol.	Sl. sol.
Ethanol	Insol.	—
Acetone	Insol.	—
Acetonitrile	Insol.	—
CH <sub>2</sub> Cl <sub>2</sub>	Insol.	—
THF	Insol.	—
PSSAH (dil. aq.)	Sol.	Insol.
NaOH (dil. aq.)	Sol.	—
Water	Sol.	Insol.
H <sub>2</sub> SO <sub>4</sub> (conc.)	Insol.	Insol.
HCl (conc.)	Insol.	—

<sup>a</sup> Sl. sol. = slightly soluble; sol. = soluble; insol. = insoluble.

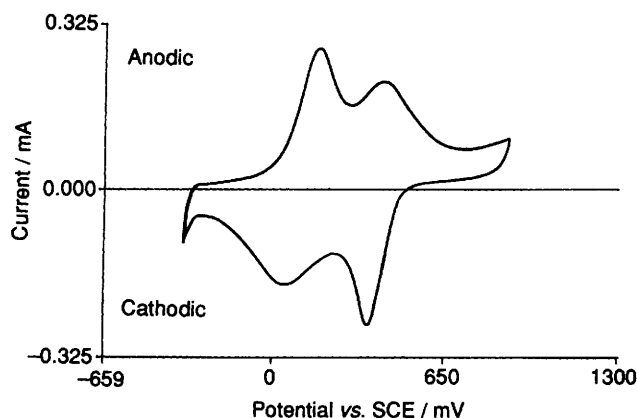


Fig. 1 CV of polyaniline in 0.256 mol dm<sup>-3</sup> PSSAH at 50 mV s<sup>-1</sup>

soluble. While we do not rule out differences in molecular mass as the cause of the discrepancy between our results and those of the cited<sup>1,2</sup> reports, we obtain an obviously different product than they merely by using carefully purified PSSAH.

The four-probe conductivity of these PSSAH-doped PANI samples is *ca.*  $10^{-2}$  s cm<sup>-1</sup>.

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#### Footnote

† We will describe our analysis of the acid–base properties of soluble PANI in a forthcoming publication.

#### References

- 1 S. Li, Y. Cao and Z. Xue, *Synth. Met.*, 1987, **20**, 141.
- 2 Y. Kang, M.-H. Lee and S. B. Rhee, *Synth. Met.*, 1992, **52**, 319 and papers cited therein.
- 3 P. M. Budd, *Polyelectrolytes*, in *Comprehensive Polymer Science: The Synthesis, Characterization, Reaction and Applications of Polymers*, ed. C. Booth, C. Price, Pergamon Press Inc., New York, 1989, vol. 1, pp. 215–217.
- 4 W. R. Carroll and H. Eisenberg, *J. Polymer Sci.*, 1966, **4**, 599.
- 5 J. C. Chiang and A. G. MacDiarmid, *Synth. Met.*, 1986, **13**, 193 and references cited therein.
- 6 A. F. Diaz and J. A. Logan, *J. Electroanal. Chem.*, 1981, **111**, 111.
- 7 W. W. Focke, G. E. Wnek and Y. Wei, *J. Phys. Chem.*, 1987, **91**, 5813.