

## Water-soluble Conducting Poly(aniline) Polymer

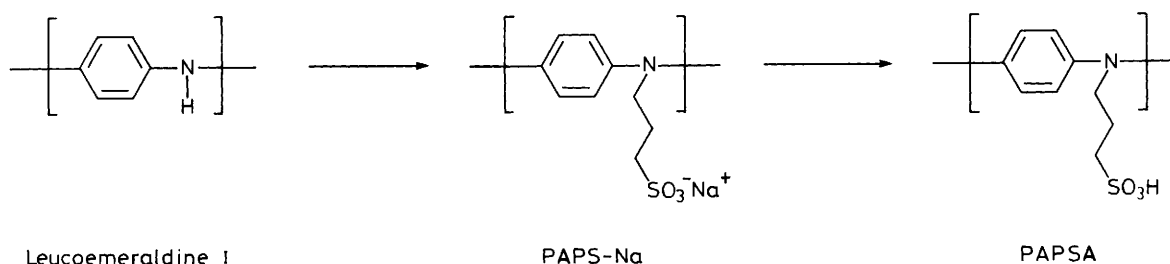
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Water-soluble conducting poly(aniline propane sulphonic acid) and its sodium salt have been synthesized by derivatization of polyaniline; multiple and reversible colour changes were observed for polymer films on indium–tin oxide coated glass dipped in a LiClO<sub>4</sub>/acetonitrile solution between –0.4 and 1.2 V vs. Ag/AgCl, and for aqueous polymer solutions between pH 1 and 10.

Conjugated conducting polymers, such as polyacetylene, polypyrrole, polythiophene, and polyaniline, have been the subject of intensive research due to their particular and intriguing opto-electric properties. However, their insolubility has made their characterization very difficult and their intractability has limited severely their applications. Recently, several organic solvent-soluble,<sup>1,2</sup> and even water-soluble<sup>3</sup> 3-substituted polythiophenes have been prepared. Analogous

soluble polyaniline derivatives have been more elusive, although several organic solvent soluble alkyl ring- and *N*-substituted-poly(anilines) have been prepared recently.<sup>4–7</sup> Contrary to alkyl ring-substituted polyanilines which are limited to low molecular mass polymers (<10 000),<sup>4</sup> high molecular weight (>100 000) polymers soluble in the doped and undoped states in common solvents [tetrahydrofuran (THF), acetonitrile, chloroform, *etc.*] can be obtained with



Scheme 1

*N*-alkyl substituents<sup>6,7</sup> [alkyl = benzyl, C(1)—C(18)]. We report here the first synthesis of an electroactive polyaniline which is soluble in water in the doped and undoped states.

Water-soluble sodium salt of poly(aniline propane sulphonate) (PAPS-Na) was obtained by a derivatization of the leucoemeraldine form I of polyaniline (Scheme 1). The perchlorate salt of polyaniline was first prepared by oxidation of 1 equiv. of aniline with 2 equivs. of  $\text{Cu}(\text{ClO}_4)_2$  in acetonitrile under argon at room temperature according to a published procedure.<sup>8</sup> After extensive extraction with acetonitrile, the vacuum-dried powder was successively treated with 0.2 M  $\text{NH}_4\text{OH}$  and phenylhydrazine to give the leucoemeraldine base I. Gel permeation chromatography (GPC) analysis with *N*-methylpyrrolidone (NMP) eluent showed a large band with molecular masses between 200 000 and 10 000 compared to polystyrene standards. The leucoemeraldine base I (11g) was reacted with 1.5 equiv. per repeat unit of NaH in dimethyl sulphoxide (DMSO) at 40–50 °C under argon for 4 h. The green viscous solution was subsequently treated with 1.5 equiv. of 1,3-propane sultone for 18 h at room temperature. PAPS-Na (1.3g) was isolated by precipitation into THF, followed by extensive washing and vacuum drying.

Electron dispersive spectrometry (EDS) analysis of PAPS-Na powder indicated a ratio S:Na = 1, suggesting that the sodium sulphonate form PAPS-Na was obtained (Scheme 1). The blue PAPS sodium salt is insoluble in THF, acetonitrile, acetone, or chloroform, soluble in DMSO and NMP, and very soluble in water. PAPS-Na shows only one absorption band at 630 nm in  $\text{H}_2\text{O}$  or NMP. UV-VIS spectra of aqueous solutions of PAPS-Na followed the Beer-Lambert law implying that real solutions were obtained. GPC analysis of PAPS-Na in NMP showed a trimodal distribution with average molecular mass of 250 000, 83 000, and 42 000. The transmission FTIR spectrum of PAPS-Na in KBr shows peaks at 1354 and 1198  $\text{cm}^{-1}$  characteristic of asymmetric and symmetric  $\text{SO}_2$  stretching vibrations, and 1045  $\text{cm}^{-1}$  characteristic of the sulphonic acid sodium salt. The FTIR spectrum also shows strong quinoid rings at 1592  $\text{cm}^{-1}$  compared to weak benzenoid absorption at 1503  $\text{cm}^{-1}$ , indicating that PAPS-Na is in the fully oxidized form.<sup>9</sup> An electrical conductivity value of  $1 \times 10^{-5} \text{ S cm}^{-1}$  was obtained on a compressed pellet by van der Pauw's four-probe method.

PAPS-Na salt could be cast from NMP solution as a film on various substrates, principally Pt and ITO glass (indium-tin oxide coated glass, 20 ohm/square). Typical cyclic voltammograms of a platinum-cast PAPS-Na film dipped in 0.1 M  $\text{LiClO}_4/\text{acetonitrile}$  solution at various scanning rates are shown in Figure 1. The voltammogram of PAPS-Na shows a large anodic wave near 0.65 V corresponding to 2 overlapped peaks at 0.45 and 0.7 V vs. Ag/AgCl. These peaks can be related to polaron and bipolaron formation.<sup>4</sup> In correlation with these anodic processes, PAPS-Na films show multiple and reversible colour changes. Visible absorption spectra of PAPS-Na film coated on an ITO electrode dipped in 0.1 M  $\text{LiClO}_4/\text{acetonitrile}$  are presented in Figure 2. PAPS-Na film

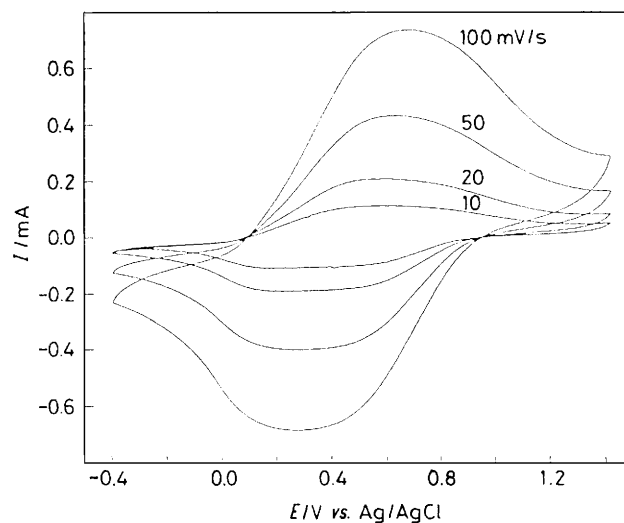


Figure 1. Cyclic voltammograms of PAPS-Na film on Pt dipped in 0.1 M  $\text{LiClO}_4/\text{acetonitrile}$  solution at various scanning rates.

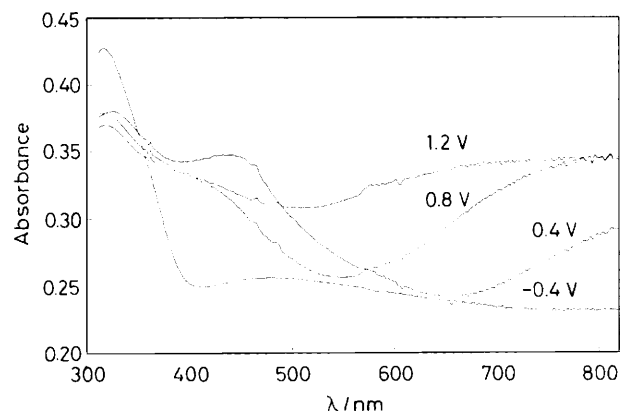


Figure 2. Absorption spectra of PAPS-Na film on ITO glass in 0.1 M  $\text{LiClO}_4/\text{acetonitrile}$  solution at various applied voltages (reference electrode Ag/AgCl).

changes colour from colourless to yellow to green to dark blue as the potential is swept between -0.4 and 1.2 V vs. Ag/AgCl. Increasing the potential from -0.4 to 0.4 V, two new absorption bands appear at 420 and 820 nm. These bands are associated with polaron transitions.<sup>4,10</sup> Above this potential, a simultaneous decrease and increase in the intensity of the absorbances at 420 and 820 nm, respectively, were observed. Increasing the potential above 0.8 V, the 820 nm band is shifted to a shorter wavelength (<700 nm).

As observed before for poly(aniline),<sup>10</sup> 'protonic acid doping' also involves optical changes. Transformations in the absorption spectra of an aqueous solution of PAPS-Na were

observed when the pH was changed from 1 to 10. A solution of 1% PAPS-Na in water had a pH of 8.0 and showed a strong absorption band at 630 nm. At pH 5, the band at 630 nm decreased strongly and two new bands appeared at 420 and 820 nm. The intensity of these two bands increased rapidly when the pH was lowered to 1. These transformations are reversible. When the pH was gradually increased from 1 to 10, there was a simultaneous decrease in the intensity of the bands at 420 and 820 nm, and increase of the band at 630 nm. Two well focused isosbestic points were observed at 460 and 700 nm. Similar results were observed when a thin film of poly(aniline) on ITO glass was titrated *in situ* in a spectrometer with aqueous solutions of varying pH.<sup>11</sup>

Poly(aniline propane sulphonic acid) PAPSA was obtained when an aqueous solution of PAPS-Na was exchanged through a Dowex 50W-X8-H<sup>+</sup> column (Scheme 1). PAPSA is very soluble in water and NMP, and an aqueous solution shows a strong absorption band at 900 nm.

This work is supported by operating and strategic grants from the N.S.E.R.C. of Canada. J. Y. B. is grateful to INRS for a post-doctoral fellowship and J. W. C. to FCAR for a graduate fellowship.

Received, 10th October 1989; Com. 9/04362D

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