

Electrochemical synthesis of fully sulfonated *n*-dopable polyaniline: poly (metanillic acid)[†]

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Electrochemical homopolymerization of metanillic acid has been achieved for the first time using a 4:1 acetonitrile–water mixture to get 100% sulfonated polyaniline which is soluble in both organic and aqueous solvents, electrically conducting, and is *n*-dopable.

Electrodes modified with conducting polymer films have shown promising applications in the field of biosensors and bio-electrochemistry by providing an active matrix with controlled morphology for immobilisation of biological materials as well as transduction of chemical to electrical signal. One of the easiest ways to modify an electrode with conducting films is by electropolymerization of the monomer on the electrode surface. Among various conducting polymers, polyaniline (PANI) has a unique position due to its easy synthesis, good environmental stability and reversible acid base chemistry in aqueous solution. Unlike polythiophene and polypyrrole, conductivity of polyaniline can be varied by non-redox doping.¹ This change in conductivity with change in pH has been effectively employed for the fabrication of biosensors.² Though the theoretical studies on *n*- and *p*-doping of polyaniline were done by Epstein and co-workers,³ experimental *n*-doping poses problems. However, very recently, the first successful chemical *n*-doping of polyaniline was reported by Hua *et al.*⁴ One of the major drawbacks of polyaniline is that it loses its electrochemical activity in solutions of pH greater than 4. Therefore, adaptation of polyaniline to neutral pH is an important problem. The first attempt in this direction was demonstrated by Epstein and co-workers⁵ by the introduction of a sulfonic acid group on the polyaniline to get self-doped polyaniline. This altered the acid base chemistry of the polymer and the polymer remained conducting up to pH 7. Sulfonated polyaniline prepared by the sulfonation of emeraldine base has potential application in rechargeable batteries with higher charge density and has also been used in LEDs.⁶ However, sulfonation of emeraldine base and leucoemeraldine lead to 50% and 75% sulfonation, respectively. Since post polymerization sulfonation has not been successful to achieve 100% sulfonation, various groups have tried to homopolymerize sulfonated aniline. Polymerization of ring sulfonated aniline was unsuccessful and was thought to be because of the electron withdrawing nature of sulfonate group and its bulkiness.⁷ Various research groups have employed different strategies to overcome this problem either by substituting with electron donating groups or by putting a spacer between the sulfonate group and the ring or by copolymerization.⁸ All these approaches lead to polymers with lower conductivities and lower degrees of sulfonation. The first chemical homopolymerization of metanillic acid was done by carrying out the reaction under high pressure.⁹ The yields in these high pressure homopolymerizations were only around 10%. Electrochemical homopolymerization has also been tried but resulted in the formation of soluble oligomers because the monomer and the polymer were found to be soluble only in water.¹⁰ Therefore, to date, there has been no report on the

successful homopolymerization of metanillic acid. The problem of water solubility for both the monomer and polymer encountered in the electrochemical homopolymerization, can be circumvented by a careful design of solvent where only the monomer is soluble and not the polymer. Electropolymerization carried out from such solutions will then result in the formation of an electroactive film. In this paper we report, for the first time, successful electrochemical homopolymerization of metanillic acid using a mixed solvent approach. Since the homopolymer of metanillic acid synthesized by us is electroactive in organic solvents, electrochemical *n*-doping was possible. In fact, this is the first report on electrochemical *n*-doping of polyaniline or its derivatives.

In order to carry out the successful electropolymerization of metanillic acid, we used the combination of organic (acetonitrile, ACN) and aqueous solvent (water). The first step was to find out the optimum composition in which only the monomer is soluble and not the polymer. This was achieved by the dropwise addition of water to a mixture of the monomer and 0.1 M tetraethylammonium tetrafluoroborate (TEAFB) in acetonitrile until it formed a clear solution. It was observed that an ACN–water ratio of 4:1 (vol/vol) was optimum to make a 0.01 M solution of metanillic acid. Therefore the electropolymerization was carried out at 1 V vs. Ag/Ag⁺ as the reference electrode from a 0.01 M solution of metanillic acid in 4:1 ACN–water in presence of 0.1 M TEAFB using Pt wire as the working electrode. This resulted in the formation of a very thin film at the electrode. In order to improve the electropolymerization process, we tried the polymerization at low temperature as this has been found to produce polymer of increased conductivity in the case of polyaniline.^{11,12} Indeed, polymerization carried out at 5 °C resulted in the formation of a thick conducting polymer film at the electrode. In order to study the effect of ACN–water composition on the rate of electropolymerization, different mixtures of acetonitrile and water (3:2 and 9:1) were chosen. Polymerization was carried out for 120 s, and the measured charge was taken as the measure of the efficiency of polymerization. The charge for 9:1 ACN–water solution was found to be significantly lower than that from 4:1 ACN–water mixture. The lower polymerization charge is attributed to the lower concentration of the dissolved monomer due to the lower water content in the polymerizing solvent. The polymerization charge in the case of 3:2 ACN–water mixture was found to be comparable to that of 4:1 ACN–water mixture. However, the redox current in this case was significantly lower, indicating that the polymer formed dissolved in the polymerization solution because of the high water content. Similarly, lower redox current was observed in case of 9:1 ACN–water solution because the polymerization charge was low. This clearly shows that the solvent ratio plays a critical role during electrochemical polymerization. Therefore, the polymerization was carried out at 5 °C from a 4:1 ACN–water solution for all further studies. The polymer formed was found to be soluble in water, dimethylformamide but was insoluble in acetonitrile, acetone, chloroform *etc.* For Size Exclusion Chromatography (SEC) analysis, the polymer was washed well with acetonitrile to remove supporting electrolyte. The SEC was carried out in DMF against polystyrene standards. The SEC analysis gave a

[†] Electronic supplementary information (ESI) available: CV, Scan rate, FT-IR and UV-Vis spectra of poly(metanillic acid). See <http://www.rsc.org/suppdata/cc/b1/b110157a/>

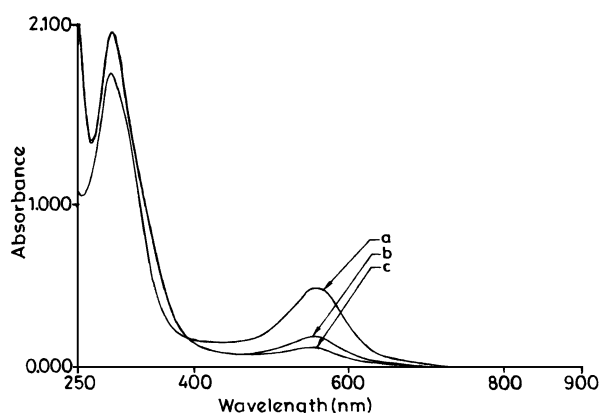


Fig. 1 Solution reduction of oxidized poly(metasilic acid) with increasing concentration of hydrazine hydrate in water; (a) without hydrazine hydrate, (b) and (c) after the addition of hydrazine hydrate.

weight average molecular weight of 39,000 with polydispersity of 1.4, confirming the polymeric nature of the electrochemically deposited film. The FTIR spectra gave the characteristic peaks due to sulfonate group at 1200 and 1040 cm^{-1} and a peak at 3450 cm^{-1} due to NH stretching.¹³ A strong aromatic C–N stretching vibration appears at 1117 cm^{-1} . The characteristic quinoidal stretching absorption was observed at 1599 cm^{-1} . In order to study the cyclic voltammetry, the polymer film was washed with monomer free solution and the scan rate dependence of the polymer redox process was investigated in the presence of 0.1 M TEAFB as the supporting electrolyte in ACN by cycling the potential between -0.2 V and $+0.5$ V. The polymer showed an anodic peak at $+0.15$ V and a cathodic wave at $+0.1$ V. A linear relationship was found between the peak current and scan rate, indicating that the electroactive polymer film is well adhered and the redox processes are nondiffusion limited.

The solution redox processes of the polymer were studied by UV–vis spectroscopy in water as a function of reductant concentration using hydrazine hydrate, as shown in Fig. 1. In the oxidized state, the polymer solution exhibited two peaks. The peak observed at 320 nm is attributed to π – π^* transition in benzenoid units and the peak at 560 nm is attributed to exciton-like transition (the conducting form) in quinoid diimino units. As the concentration of hydrazine hydrate is increased, the absorbance at 320 nm increases and that at 560 nm decreases indicating the reduction of the polymer. In order to study the effect of pH on polymer redox processes, the absorption spectra of the polymer was recorded in aqueous solutions of pH 1 and 7. No change in the absorbance spectra was observed on changing the pH from 1 to 7, indicating that the polymer remains conducting at neutral pH as was expected for the sulfonated polyaniline. Since the polymer is fully sulfonated and is redox active in organic solvents, studies were carried out to explore the *n*-doping. The polymer film was dried under vacuum and the cyclic voltammogram was recorded in 0.1 M TEAFB from -2 V to 0 V at a scan rate of 200 mV s^{-1} . The *n*-doping peak was observed at -1.5 V. This *n*-doping was further confirmed by measuring *in-situ* conductance of the polymer grown on a Pt twin wire electrode.¹² The polymer bridges the twin wire which further confirms that the homopolymer grows well on the electrode. The *in-situ* conductance (Fig. 2) of the polymer was found to be 4.4×10^{-4} S at -2.0 V. A decrease

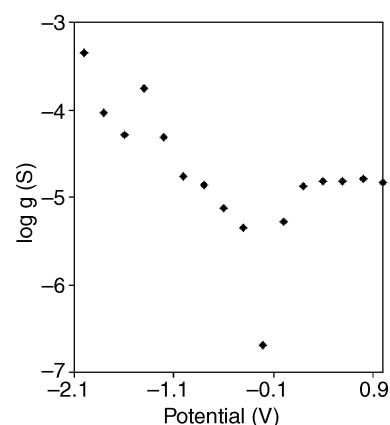


Fig. 2 *In-situ* conductance of poly(metasilic acid) as a function of applied potential.

in conductivity was observed on increasing the potential and was lowest at -0.2 V (2×10^{-7} S). Therefore, a three orders of magnitude change in conductivity was observed due to *n*-doping. Further increase in potential led to an increase in conductivity until $+0.4$ V (1.6×10^{-5} S) and there was no considerable change in conductivity after $+0.4$ V up to 1 V. The high conductivity at negative potential further confirms the *n*-doping process.

In summary, we have reported, for the first time, a facile preparation of high molecular weight fully sulfonated polyaniline by an electrochemical polymerization using a mixed solvent approach. The fully sulfonated polyaniline was found to be soluble in both organic and aqueous solvents, electrically conducting, and *n*-dopable. We are currently working on the detailed characterization of fully sulfonated polyaniline and also to extend this mixed solvent approach for other sulfonated heterocycles.

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