# A novel *N*-substituted polyaniline derivative

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(*Received 31 January 1992; revised 7 April 1992*)

We report the chemical synthesis of an *N*-substituted water-soluble polyaniline derivative. This novel processable conducting polymer has been characterized by a wide range of techniques including visible absorption, *FT*i.r. and [1]H n.m.r. spectroscopy, scanning electron microscopy, cyclic voltammetry in non-aqueous media, room temperature d.c. conductivity measurements, photon correlation spectroscopy and thermogravimetry.

## INTRODUCTION

Polyaniline is generally recognized to be the only air-stable organic conducting polymer[1]. It can be synthesized either chemically[2–4] or electrochemically[5–7] as a bulk powder or film. Although it is soluble in various solvents such as tetrahydrofuran, dimethylformamide or *N*-methyl-2-pyrrolidone in the undoped state[8], the doped (conducting) form of polyaniline is insoluble in almost all solvents (except concentrated acids[9]) and is therefore an intractable and unprocessable material. Various groups have attempted to improve the processability of polyaniline, usually by modifying the polymer chain with various ring or *N*-substituents[10–20].

In this paper the chemical synthesis of a novel *N*-substituted water-soluble polyaniline derivative is described (*Figure 1*). We anticipated that the sulphonic acid substituent at the 4 position of 1 would effectively block any polymerization via 4,4' C–C coupling as reported by Guay *et al.* for the unsubstituted diphenyl-amine monomer[21]. Thus, chemical oxidation of 1 was expected to lead to the polymeric product 2. Furthermore, we believed that the pendant aromatic sulphonic acid groups would both solubilize the conjugated polyaniline backbone and possibly also act as self-dopants[11,16].

## EXPERIMENTAL

### Chemicals

The sodium salt of diphenylaminesulphonic acid, 1, $(NH_4)_2S_2O_8$, $KIO_3$, $FeCl_3$, $Cu(ClO_4)_2 \cdot 6H_2O$ and $N(C_4H_9)_4HSO_4$ were all purchased from Aldrich and were used as received.

### Monomer synthesis

The sodium salt of the diphenylaminesulphonic acid (1, 7.5 g) was mixed with an equimolar amount of tetrabutylammonium hydrogen sulphate (9.4 g) in water (25 ml). The resulting white precipitate was filtered, washed with water and recrystallized from dichloromethane in order to obtain the tetrabutylammonium salt of 1.

### Polymer synthesis

The monomer (1, 0.744 g) was dissolved in 15 ml of 1.2 M HCl and the oxidant [either $(NH_4)_2S_2O_8$ (0.782 g), $KIO_3$ (0.245 g) or $FeCl_3$ (1.11 g)] was dissolved in a further 10 ml of 1.2 M HCl. The oxidant solution was then poured into the stirred monomer solution at room temperature ($\sim 20°C$). A dark green colour developed immediately and no macroscopic precipitate was observed. The reaction was allowed to proceed for 16 h after which the reaction mixture was centrifuged at $50\,000\,\text{rev min}^{-1}$ for 4 h using an L2-65B Beckman ultracentrifuge. This procedure produced a dark green
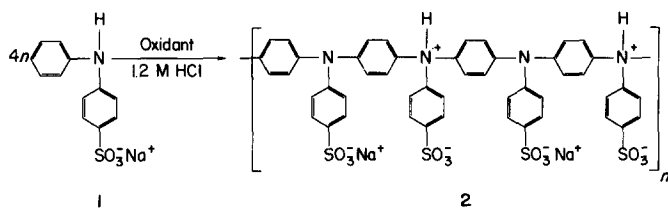


**Figure 1** Reaction scheme for the polymerization of monomer 1 and proposed structure of resulting polymer 2

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sediment and a dark green supernatant, which was decanted off. The sediment was washed five times with 1.2 M HCl and then redissolved in 1.2 M HCl by agitation and ultrasonics.

The same synthetic methodology was used to polymerize tetrabutylammonium diphenylamine sulphonate (1.34 g) using $Cu(ClO_4)_2.6H_2O$ (2.54 g) oxidant in acetonitrile (25 ml). This procedure immediately produced a dark green precipitate, which was filtered off, washed with acetonitrile and dried under dynamic vacuum at 6.7 Pa for 30 min.

Polyaniline homopolymer was prepared as a bulk powder in 1.2 M HCl using the $(NH_4)_2S_2O_8$ oxidant as described previously[4].

*Polymer characterization*

The n.m.r, visible absorption and *FT*i.r. spectra were recorded using 250 MHz Bruker AC250SY, Philips PU 8720 and Perkin-Elmer 1710 instruments, respectively. Scanning electron microscopy (SEM) studies were made on film fragments of **1** which were cast from 1–2 w/v% aqueous solutions at ambient temperature. These samples were sputter-coated with gold (two sputter cycles at 18 mA for 60 s) to prevent sample-charging and examined using a Philips 505 microscope. Thermogravimetric analyses were carried out in air at a scan rate of 20°C min$^{-1}$ using a Perkin-Elmer TGA-7 instrument. Photon correlation spectroscopy (p.c.s.) measurements were made using a Malvern 4700 series spectrometer in dilute, aqueous solution. Room temperature conductivity measurements were made on thin films or compressed pellets using conventional four-point probe methods. Cyclic voltammetry studies were made in acetonitrile using a platinum working electrode (electrode area ~0.030 cm$^2$). Films were grown under the following conditions: 5 mM tetrabutylammonium diphenylamine sulphonate monomer; 0.10 M tetraethylammonium tosylate supporting electrolyte; scan rate 100 mV s$^{-1}$; potential range −0.50 to +0.50 V; 0.01 M Ag/AgNO$_3$ reference electrode.

RESULTS AND DISCUSSION

Our initial work focused on the spectroscopic characterization of the chemically synthesized polymeric product **2**. The visible absorption spectrum of the doped form of **2** in acidic media is similar to that of polyaniline homopolymer[1]. The undoped, deprotonated form of **2** is red (shoulder at 500 nm, see *Figure 2*) rather than blue for polyaniline homopolymer (absorption peak at 600–650 nm[1]. This suggests that the degree of conjugation in **2** is less than that of the polyaniline homopolymer. Presumably the steric effects of the bulky aromatic sulphonate substituents produce torsional twists in the polymer backbone. This would reduce its coplanarity (and therefore its average electron delocalization length) resulting in lower conductivity than that seen for polyaniline. As far as we are aware this red-to-green doping-induced colour transition is unique amongst conducting polymers and may have applications in electrochromic display devices[6]. Aqueous solutions of **2** remain green in colour up to pH 4, whilst at pH > 6 these solutions become red. At intermediate pHs there appear to be some hysteresis effects. Thus the pH behaviour of **2** appears to be intermediate between that of polyaniline[2] and sulphonated polyaniline[16].
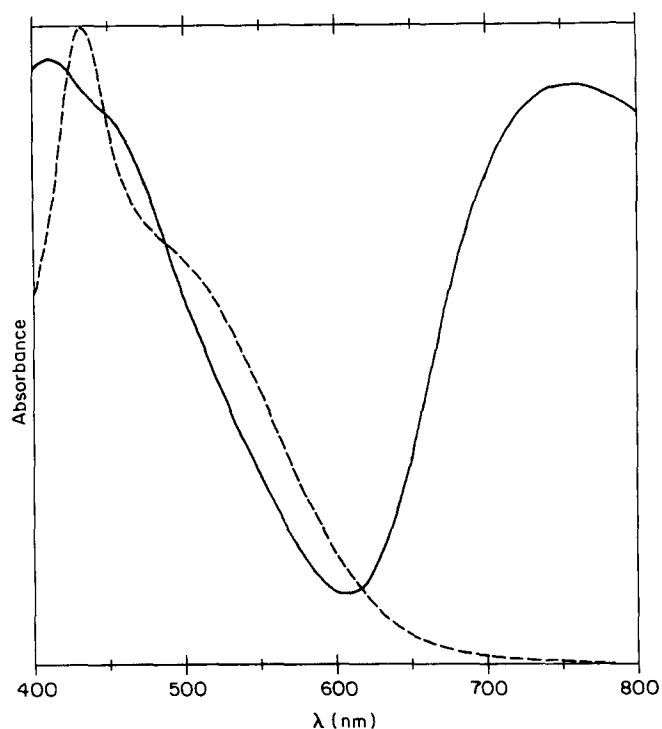


Figure 2 Visible absorption spectra of aqueous solutions of (——) doped and (— —) undoped **2**

The *FT*i.r. spectrum (KBr disc) of the doped form of **2** is *independent* of the oxidant used for the polymerization. It is shown in *Figure 3* together with the spectra of the original diphenylaminesulphonic acid monomer (**1**) and chemically synthesized doped polyaniline. There are various peaks at 1316, 1168, 1144, 1121 and 1031 cm$^{-1}$ in addition to those found in polyaniline, indicating the presence of the sulphonate group[22,23]. All of these bands are also present in the monomer spectrum, although some of them are shifted by up to 10 cm$^{-1}$ due to the pelletization process in the sample preparation. There are no peaks at 870 or 820 cm$^{-1}$ (not shown), which previous workers have attributed to 1,2,4-substituted polyaniline[11,16]. Thus we tentatively suggest that the degree of 1,2 (*ortho*) coupling in **2** is relatively low compared with 1,4 (*para*) coupling.

A $^1H$ n.m.r. spectrum of **2** redispersed in $D_2O$ clearly shows a broad signal due to the aromatic protons in the polyaniline backbone at $\delta$ 6.5–8.5. This confirms that **2** is *solvated* and, since it is a polyampholyte, probably exists as colloidal multi-molecular aggregates in solution[24]. We wish to emphasize that the physical state of **2** is rather different to the sterically stabilized colloidal dispersions of polyaniline homopolymer which have been previously described by several groups[25-29]. In these latter systems there is no aromatic signal due to the polyaniline protons in the n.m.r. spectrum[30], which indicates that the polyaniline component exists as non-solvated solid particles that are stabilized by adsorbed, solvated macromolecular surfactants.

Addition of a barium chloride solution to a redispersed 'solution' of **2** causes immediate and quantitative precipitation, producing a fine green precipitate. We believe that the colloidal micellar aggregates are destabilized by the formation of insoluble barium sulphonate salts.

Our preliminary p.c.s. studies on **2** in dilute acidic solution confirm the aggregated colloidal nature of this polymer, with time-dependent submicronic structures
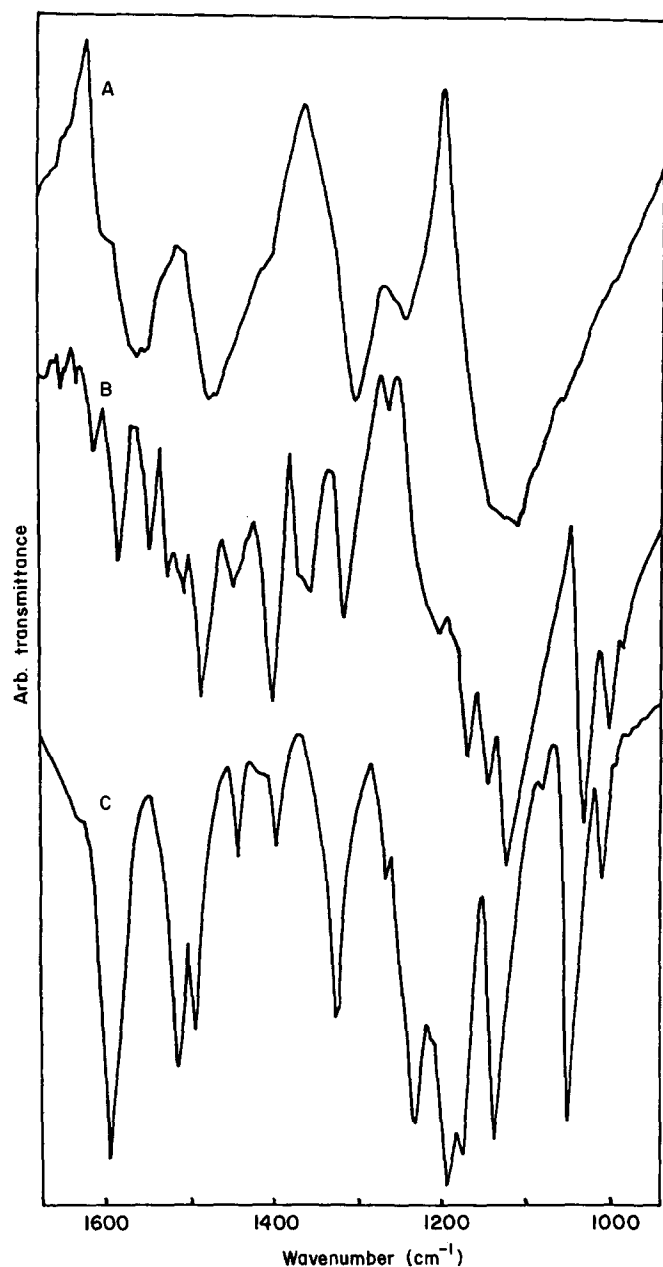
Figure 3 *FT*i.r. spectra of (A) polyaniline, (B) poly(*N*-substituted aniline) (2) and (C) the diphenylaminesulphonic acid monomer (1)



Figure 4 Cyclic voltammogram of 1 at an initial concentration of 5 mM using a 0.020 cm² platinum disc electrode in a solution of 0.1 M tetraethylammonium *p*-toluenesulphonate in acetonitrile (scan rate: 100 mV s⁻¹)



Figure 5 First three sequential cyclic voltammograms of 5 mM aniline in a solution of 0.1 M tetraethylammonium *p*-toluenesulphonate in acetonitrile (scan rate: 100 mV s⁻¹)

(600–800 nm) being observed[31]. Further experiments are currently in progress.

Room temperature four-point probe measurements on compressed pellets or solvent-cast films indicate that the doped form of 2 has a conductivity of up to $6 \times 10^{-3}$ S cm⁻¹. This is rather lower than that of polyaniline homopolymer but similar to that of poly(*N*-methylaniline)[1]. It is also consistent with the reduced conjugation length of 2, as indicated in *Figure 2*.

We selected acetonitrile as the non-aqueous solvent for our electrochemical experiments since we anticipated that the polyampholyte product (2) would be insoluble in this medium and thus it would be deposited as a thin film on the surface of the electrode. Our cyclic voltammogram studies confirm that 1 may be electropolymerized in this solvent (see *Figure 4*). A polymeric thin film is formed on the electrode surface and colour changes with potential scan are discernible after a few cycles (~10). In the anodic scan the film is blue at 0.4 V, turns yellow at 0.2 V during the reverse scan and is colourless
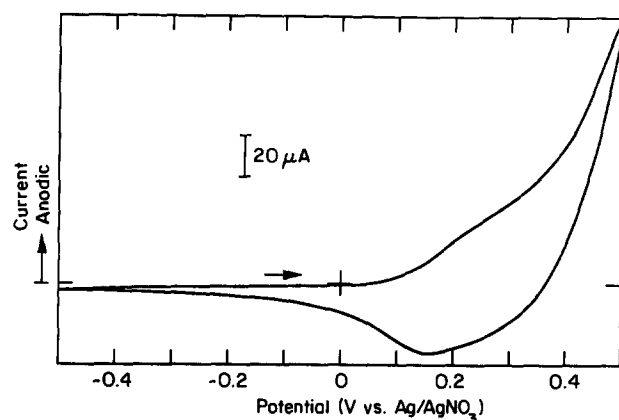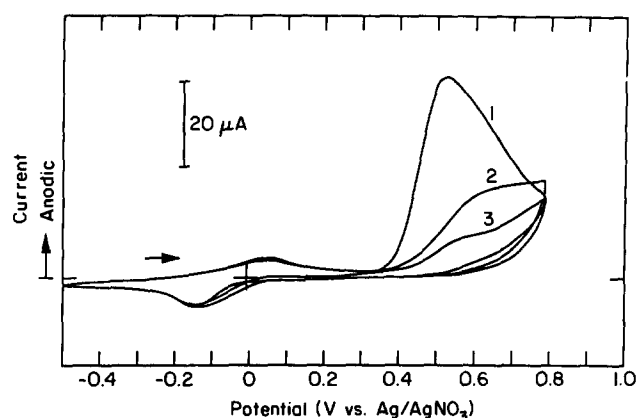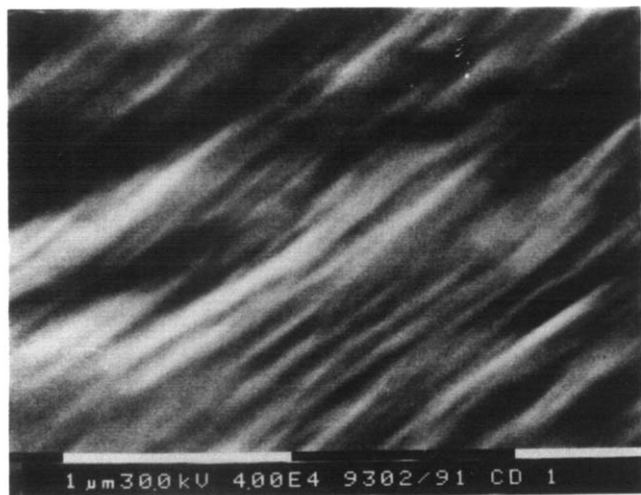
at −0.3 V. Upon consecutive cycles (between −0.5 V and +0.5 V) both anodic and cathodic currents increase consistently, indicating continuous growth of the polymer. However, after cycling for ~30 min no further film growth is observed. At this point visual inspection of the electrode reveals a powdery thick film which adheres poorly to the metal electrode surface.

The electrochemical behaviour of unsubstituted aniline under identical conditions to those described above is quite different from that of 1. As shown in *Figure 5*, aniline exhibits restricted electroactivity in an acetonitrile solution of tetraethylammonium *p*-toluenesulphonate. In the first scan an anodic product appears to form on the electrode surface. This product is *not* electroactive as indicated by the drop in current upon subsequent sequential cycles. Addition of *p*-toluenesulphonic acid in order to acidify the solution did not result in any change in the voltammogram. Even polyaniline films synthesized in aqueous solution lose their electroactivity when transferred into a solution of tetraethylammonium *p*-toluenesulphonate in acetonitrile, as shown in *Figure 6*. In this case no colour changes in the polymer film upon potential cycling are detected.

Our SEM studies on solution-cast film fragments of 2 indicated a smooth, featureless morphology even at high magnification (*Figure 7*). The *absence* of submicronic particulates is consistent with our other observations,
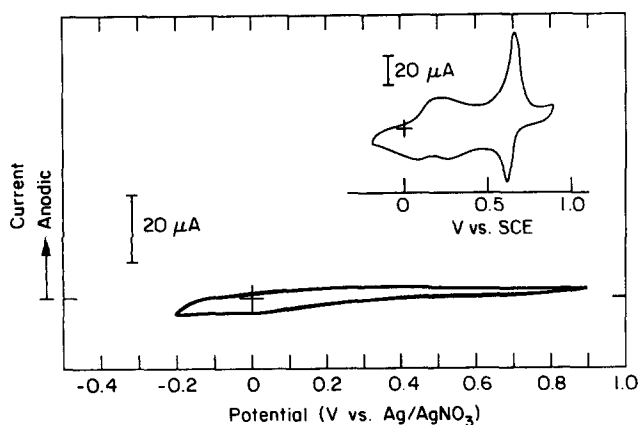
**Figure 6** Cyclic voltammogram of a polyaniline film in a solution of 0.1 M tetraethylammonium *p*-toluenesulphonate in acetonitrile (scan rate: $100\,mV\,s^{-1}$). This film was grown on a $0.020\,cm^2$ platinum disc electrode in an aqueous solution containing 50 mM aniline and 0.2 M *p*-toluenesulphonic acid. The inset shows a cyclic voltammogram recorded during the film preparation in aqueous solution
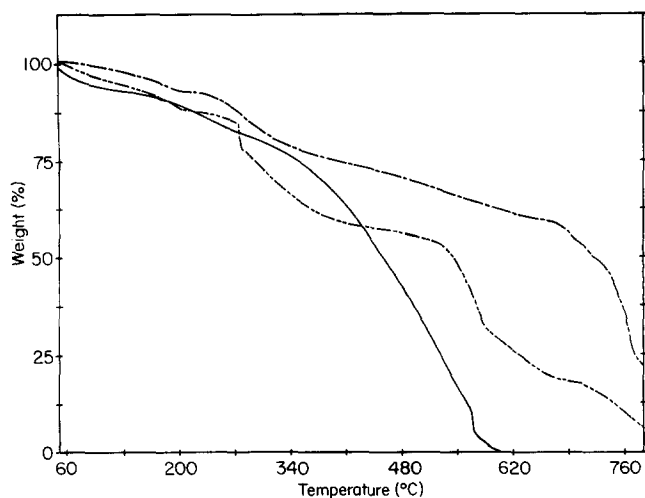


**Figure 8** Typical thermograms run in air at a scan rate of 20°C min$^{-1}$ of (— —) bulk polyaniline, (— — —) **2** synthesized using $(NH_4)_2S_2O_8$ and (——) **2** synthesized using $KIO_3$



**Figure 7** Scanning electron micrograph of **2** synthesized with the $(NH_4)_2S_2O_8$ oxidant

which suggest the existence of solvated, colloidal aggregates of polyampholyte structures in aqueous acidic media.

The thermal stability of the doped form of **2** in air was compared to that of bulk polyaniline powder (*Figure 8*). All thermograms of **2** were all markedly different from that of bulk polyaniline. There were also significant differences between samples of **2** synthesized using different oxidants. We believe that these latter variations in thermal stability are most likely to be due to the different cations incorporated as counterions to the pendant sulphonate groups. For example, **2** prepared using $(NH_4)_2S_2O_8$ as an oxidant might be expected to contain some $NH_4^+$ cations, whereas **2** synthesized using $KIO_3$ would probably contain some $K^+$ cations. It is well known that the presence or absence of metal cations within a polymer matrix can strongly affect the thermal stability behaviour of the polymer. This interpretation is consistent with the changes in the 'residues' mass between these samples (presumably due to the formation of involatile inorganic salts such as NaCl, KCl, etc.) observed at elevated temperatures.

Elemental microanalyses of **2** prepared using the $(NH_4)_2S_2O_8$ oxidant give the following results: C, 40.4;

H, 4.25; N, 7.9; S, 15.1%. These data correspond to a S/N mole ratio of 0.84 rather than the expected value of 1.00. We believe that this discrepancy is probably due to the incorporation of some $NH_4^+$ ions (originating from the oxidant) as well as $Na^+$ cations as counterions for the pendant sulphonate groups.

## CONCLUSIONS

We have confirmed that the diphenylaminesulphonate (sodium salt) monomer (**1**) can be chemically polymerized in its sodium salt form in aqueous acid using various oxidants to produce a 'soluble' *N*-substituted polyaniline derivative, whose chemical structure is likely to be **2**. Alternatively, **1** may be chemically or electrochemically polymerized in its tetrabutylammonium salt form in acetonitrile to produce an insoluble precipitate or thin film, respectively.

On the basis of our $^1H$ n.m.r. spectra and p.c.s. studies we believe the polyampholyte **2** probably exists as solvated, colloidal aggregates in aqueous media. Our spectroscopic, electrochemical, morphological and thermogravimetry data for **2** are *significantly* different to that of the unsubstituted polyaniline homopolymer. The solid-state conductivity of **2** is $\sim 6 \times 10^{-3}\,S\,cm^{-1}$.

## ACKNOWLEDGEMENTS

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