A novel N-substituted polyaniline derivative

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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, FTIR and 1H n.m.r. spectroscopy, scanning electron microscopy, cyclic voltammetry in non-aqueous media, room temperature d.c. conductivity measurements, photon correlation spectroscopy and thermogravimetry.

(Keywords: polyaniline; conducting polymer; water-soluble polymer)

INTRODUCTION

Polyaniline is generally recognized to be the only air-stable organic conducting polymer1. It can be synthesized either chemically2~4 or electrochemically5~7 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, the doped (conducting) form of polyaniline is insoluble in almost all solvents (except concentrated acids8) 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-substituents16~20.

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 diphenylamine monomer21. 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-dopants11~16.

EXPERIMENTAL

Chemicals

The sodium salt of diphenylaminesulphonic acid, 1, (NH₂)₂S₂O₅, KIO₃, FeCl₃, Cu(ClO₄)₂.2H₂O and N(C₄H₉)₄HSO₄ 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 (NH₄)₂S₂O₈ (0.782 g), KIO₃ (0.245 g) or FeCl₃ (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 (~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 rpm for 4 h using an L2-65B Beckman ultracentrifuge. This procedure produced a dark green

![Figure 1](Image)

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 ultrasonic.

The same synthetic methodology was used to polym-
erize tetrabutylammonium diphenylamine sulphonate
(1.34 g) using Cu(CIO4)2.6H2O (2.54 g) oxidant in aceto-
nitrile (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 (NH4)2S2O8 oxidant as
described previously4.

Polymer characterization

The n.m.r., visible absorption and FTIR 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 conducted 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 cm²). Films were grown under the following conditions: 5 mM tetrabutylammonium diphenylamine
sulphonate monomer; 0.10 M tetrabutylammonium tosylate supporting electrolyte; scan rate 100 mV s⁻¹;
potential range −0.50 to +0.50 V; 0.01 M Ag/AgNO₃
reference electrode.

RESULTS AND DISCUSSION

Our initial work focused on the spectroscopic character-
ization 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 homo-
polymer¹. 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)². 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 devices³. 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 polyaniline⁴
and sulphonated polyaniline⁵.

The FTIR spectrum (KBr disc) of the doped form of
2 is independent of the oxidant used for the poly-
merization. It is shown in Figure 3 together with the spectra
of the original diphenylaminesulphonate 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 group⁶,⁷. 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 pelleting 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-substi-
tuted polyaniline⁸,⁹. Thus we tentatively suggest that
the degree of 1,2 (ortho) coupling in 2 is relatively low
compared with 1,4 (para) coupling.

¹¹H n.m.r. spectrum of 2 redissolved in D₂O clearly
shows a broad signal due to the aromatic protons in
the polyaniline backbone at δ 6.5–8.5. This confirms
that 2 is solvated and, since it is a polyampholyte,
probably exists as colloidal multi-molecular aggregates
in solution²⁴. We wish to emphasize that the physical
state of 2 is rather different to the sterically stabilized
colloidal dispersions of polyvinylamine homopolymer which
have been previously described by several groups²⁵–²⁹.
In these latter systems there is no aromatic signal due
to the polyaniline protons in the n.m.r. spectrum³⁰, 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 redissolved
'solution' of 2 causes immediate and quantitative precipi-
tation, 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
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Figure 3 FTIR spectra of (A) polyaniline, (B) poly(N-substituted aniline) (2) and (C) the diphenylaminesulfonic 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. 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 × 10⁻³ S cm⁻¹. This is rather lower than that of polyaniline homopolymer but similar to that of poly(N-methylaniline). 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 polyanilophosphate 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-toluenesulfonic acid in order to acidify the solution did not result in any change in the voltammogram. Even polyanilino 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,
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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 cm² 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 7 Scanning electron micrograph of 2 synthesized with the (NH₄)₂S₂O₈ oxidant which suggests the existence of solvated, colloidal aggregates of polyanilophyte 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 (NH₄)₂S₂O₈ as an oxidant might be expected to contain some NH₄⁺ cations, whereas 2 synthesized using KIO₃ 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 (NH₄)₂S₂O₈ 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 NH₄⁺ ions (originating from the oxidant) as well as Na⁺ cations as counterions for the pendant sulphonate groups.

CONCLUSIONS

We have confirmed that the diphenylamininesulphonate (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 tetraethylammonium 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 polyanilophyte 2 probably exists as solvated, colloidal aggregates in aqueous media. Our spectroscopic, electrochemical, morphological and thermogravimetric data for 2 are significantly different to that of the unsubstituted polyaniline homopolymer. The solid-state conductivity of 2 is ~6 x 10⁻³ S cm⁻¹.

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