Synthesis of the Water-Soluble, Electrically Conducting Poly(5-Aminonaphthalene-2-sulfonic Acid)

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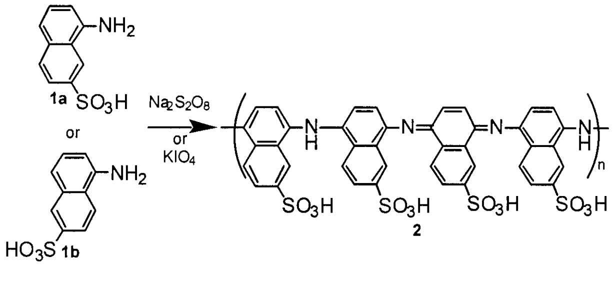
Poly(5-aminonaphthalene-2-sulfonic acid) 2 can be prepared by oxidative polymerisation of 5- or 8-aminonapthalene-2-sulfonic acid (1a, 1b) with $Na_2S_2O_8$ or KIO_4. This polymer is water soluble, electrically conducting and fluorescent.

Polyaniline (PANI) can be reversible doped to an electrically conductive state by external Brønsted acids.[1] Self-doped PANl derivatives, incorporating covalently attached acidic functional groups, offer greater thermal stability and solubility in water or dilute base.[2] Sulfonated polyaniline (SPANI), for example, has been synthesised by post-polymerisation treatment of PANI to afford up to a 75% sulfonated polyaniline with electrical conductivity of 1 S cm^{-1}.[3] Poly(3-amino-4-methoxybenzenesulfonic acid) has been prepared by oxidative polymerisation of the corresponding monomer[4] but the conductivity of this material is significantly less than that for partially sulfonated SPANI. This has been attributed to the larger twist of phenyl rings and increased interchain separation as a result of the steric requirements of the methoxy substituent.[4a] Some of us have previously reported the synthesis of 100% sulfonated SPANI by the high-pressure oxidative polymerisation of *o*-, or *m*-aminobenzenesulphonic acid.[5] This reaction is not possible at ambient pressure, presumably because of the inhibiting influence of the electron withdrawing sulfonic acid group on oxidation of the aromatic amine.

The deactivating influence of the sulfonic acid group would be minimised in an appropriately substituted poly (aminonaphthalenesulfonic acid) (Scheme 1). Poly(1-aminonaphthalene) and substituted derivatives have received some interest recently[6] because of the potential for a lower band gap as a result of the more extended π system.



Scheme 1.

Although not unambiguously determined, it would appear that poly(1-aminonapthylamines) consist of 1,4 linked monomers.[6] Analogy with polyanilines and some IR evidence also suggests the incorporation of naphthoquinone units in material prepared with hydrogen peroxide and an iron catalyst[6a] or electrochemically.[6b,c] Relatively modest conductivities have been observed (< 10^{-3} S cm^{-1}) and these polymers are only sparingly soluble in organic solvents.

We now report preparation of the potentially self-doping poly(5-aminonaphthalene-2-sulfonic acid), **2** by the oxidative polymerisation of the monomers **1a** and **1b**.[7] These monomers are sparingly soluble in water and can be polymerised in dilute solutions, but higher concentrations were achieved by first converting them to the corresponding sodium sulfonates with sodium hydroxide. Both $Na_2S_2O_8$ and KIO_4 were effective oxidants for polyerisation, with the latter providing higher yields, particularly with the addition of anilinium hydrochloride (5%). The resulting polymer **2** remained in solution and was purified by dialysis through a modified cellulose membrane with a molecular weight cut-off of 1000. Gel permiation chromatography revealed these samples to contain a bi-, tri- or tetramodal molecular weight distribution with each component of narrow polydispersity (Table 1). High molecular weights relative to neutral PEG and PEO standards were observed and these values changed only very little on conversion of the sodium sulfonates to the sulfonic acid ammonium chlorides with dilute HCl. These HCI doped samples exhibited modest electrical conductivity (Table 1).

Table 1. Summary of reactions and polymer characteristics.

M[a]	Oxidant[b]	Yield %	Mn[c] kDa	PD	peak area %	σ [d] S cm^{-1}
1a	$Na_2S_2O_8$	31	473	1.02	67	5 x 10^{-3}
			140	1.10	33	
1b	$Na_2S_2O_8$	25	508	1.01	7	2 x 10^{-4}
			212	1.03	17	
			124	1.01	22	
			52	1.01	54	
1a	KIO_4	71	405	1.05	70	1 x 10^{-5}
			100	1.01	20	
			51	1.02	10	
1b	KIO_4[e]	95	510	1.01	80	1 x 10^{-5}
			148	1.03	20	

[a]Converted to the sodium salt to aid solubility. [b]1.25 eq of $Na_2S_2O_8$, 1.5 eq KIO_4. [c]Determined by gpc on a Waters' Ultrahydrogel® 500 column in water relative to PEG and PEO standards. [d]Determined using the 4-point probe method on a compressed pellet. [e]Anilinium hydrochloride (5%) added.

The structure of these polymers has not been unambiguously determined, but literature precedence would suggest 1,4-head-to-tail linked naphthylamines (Scheme 1) and containing an unknown ratio of oxidised naphthoquinone units.[6] Infra-red spectra are consistent with this hypothesis but, unfortunately, the diagnostic region around 1640 cm^{-1} is broad with any C=N stretching vibrations overlaid by $C=C_{aromatic}$ stretches. The deactivating influence of the sulfonic acid group makes addition to the second aromatic ring unlikely.[6b] The colour and UV spectrum is also consistent with this structure.[6b] An aqueous solution of **2** is rosé in colour with absorptions at 220 nm, 290 nm, 350 nm and 500 nm which, surprisingly, are invariant over the pH range 1 to ca 10. More responsive to acidic doping, however, are the absorption spectra of films cast from methanol. Figure 1 consists of UV spectra of a sample of **2** which was doped with 1 M HCl and cast as a film on ITO glass. This film was then exposed to ammonia vapor that caused a color change from rosé to brown and a diminution of the benzenoid absorbance at 535 nm. The band gap for the π - π^* transition at 292.15 nm can be calculated from this spectrum to be 2.8 eV. Subsequent exposure of this film of HCl vapor caused a small red shift in the π - π^* transition to 277.49 nm and an increase in the absorbance at 535 nm to beyond the absorbance value of the original, 1 M HCl doped sample. Polymer **2** (Na salt) exhibited fluorescence, emitting at λ_{max} = 478 nm with a quantum efficiency,[8] φ = 0.08.

In conclusion, we have demonstrated that self-doped, electrically conducting polymer **2** can be conveniently prepared by the oxidative polymerisation of aminonaphthalene sulfonic acids **1a** and **1b**. The polymer can be of high molecular weight and is soluble in water. Films can be cast from methanol and doped by exposure to HCl vapour. This polymer exhibits fluorescence.

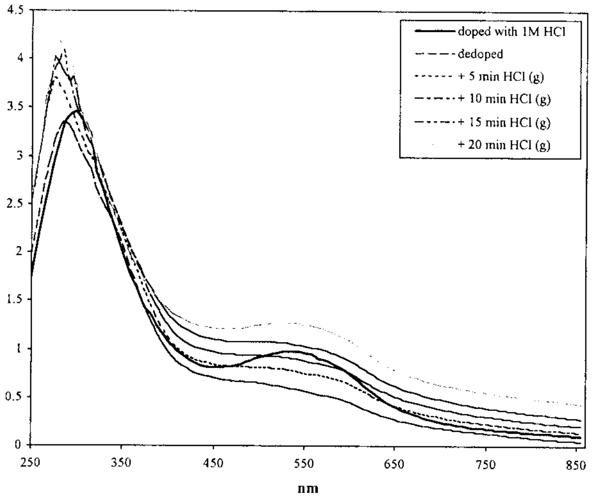


Figure 1. Absorption spectra of **2** doped with 1 M HCl and cast from a 0.02 M solution in methanol onto ITO glass. This film was dedoped with ammonia vapor and then redoped by exposure to HCl vapor with spectra acquired at 5 minute intervals during exposure.

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References and Notes

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7 Typical procedure for the polymerisation of **1a** and **1b**. Monomer **1** was converted to the sodium salt by titration with sodium hydroxide solution to a phenolphthalein end point and evaporated to dryness under high vacuum. This material (2.0 g, 8.16 mmol) was dissolved in distilled water (30 mL) and a solution of sodium persulfate (2.43 g, 10.2 mmol) in water (10 mL) added dropwise at room temperature. The stirred solution intensified in colour and, after 16 h, was sealed in Spectra/Por® dialysis tubing with a molecular weight cut-off of 1000. These sealed bags were stirred in doubly distilled water (2 L) over 20 h and the water replaced 4 times over this period. The contents of the dialysis tubing were then evaporated under high vacuum to provide an intensely coloured powder.

8 Determined by comparison with quinine sulfate using a value of (φ = 0.51 for a 10^{-3} M solution of quinine sulfate in 1N H_2SO_4. G. G. Guilbault “Practical Fluorescence,” 2nd ed, Marcel Dekker, New York (1990), pp. 14 - 16.