Synthesis of fully sulfonated polyaniline: a novel approach using oxidative polymerisation under high pressure in the liquid phase

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The oxidative polymerisation of *o*- and *m*-aminobenzenesulfonic acid has been achieved for the first time at high pressures to yield fully sulfonated polyaniline (SPANI) which is self-doping, water soluble and electrically conducting.

Polyaniline (PANI) has received considerable attention over the past few decades on account of its high electrical conductivity, environmental stability and capacity for reversible doping to an electrically conductive state by external Brønsted acids.[1] More recently, the development of 'self-doped' PANI derivatives incorporating *N*-alkylsulfonic acid,[2] methylphosphonic acid[3] or sulfonic acid[4] moieties have been reported, of which the latter displayed the highest conductivity. This sulfonated polyaniline (SPANI) was synthesised by post-polymerisation treatment of PANI emeraldine base or pernigraniline base with fuming sulfuric acid[4a–d] to achieve 50% sulfonation, or by treatment of PANI leucoemeraldine base with fuming sulfuric acid[4e] to afford a 75% sulfonated polyaniline with electrical conductivity of *ca.* 0.1 and 1 S cm⁻¹ respectively. The production of 100% sulfonated SPANI has hitherto not been reported but would be predicted to have even greater water solubility and possibly higher conductivity.[4e] The oxidative polymerisation of *o*-aminobenzenesulfonic acid **1** or *m*-aminobenzenesulfonic acid **2** would obviously provide fully sulfonated SPANI but attempts so far by both chemical or electrochemical methods[4b,5] have been unsuccessful, presumably due to steric hindrance and the strongly deactivating influence of the electron withdrawing sulfonic acid moiety. Incorporation of an electron donating methoxy group onto the monomer does, however, allow oxidative polymerisation and poly(3-amino-4-methoxybenzenesulfonic acid) has been prepared in this way[5,6] and has found applications for electron device fabrication[5] and in a novel polymer complex.[7] The room temperature conductivity of this methoxy-SPANI is, however, significantly less than that for 50 or 75% sulfonated SPANI[5,6] which has been attributed to the larger twist of the phenyl rings and increased interchain separation.[6] We now present the first report of a facile preparation of fully sulfonated SPANI by oxidative polymerisation of **1** and **2** under the influence of high pressures in the liquid phase (Scheme 1).
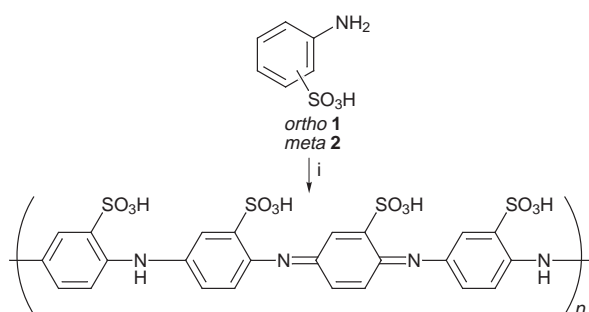
Scheme 1 *Reagents and conditions*: i, $Na_2S_2O_8$, high pressure, catalyst

Monomers **1** and **2** were polymerised at 19 kbar with $Na_2S_2O_8$ (1.25 equiv.) in aqueous LiCl (1.0 or 5.0 M) and with 5% $FeSO_4$ for 18 h at 20 °C. The usual requirement for added HCl to solubilise the monomer was not necessary and so the conductivity of the resulting polymers was exclusively due to self doping. After this period, the dark-green solution was freeze-dried, dissolved in a minimum amount of water and dialysed through cellulose acetate dialysis tubing with a molecular weight cut-off of 1000 g mol⁻¹. The yield of the polymers after dialysis and evaporation of the water was 10%. The addition of a small amount of aniline has been shown to facilitate the polymerisation of anilines bearing electron withdrawing nitro[8] or cyano[9] substituents. In combination with high pressure, the addition of 10% aniline had a dramatic effect on yield with essentially quantitative recovery of SPANI (Table 1) and no noticeable effect on the water solubility of the resulting polymer.

While the conductivity of polymers **3**–**8** was less than that reported for SPANI prepared by post-polymerisation sulfonation, these conductivity values are for 'as-synthesized' polymer (*i.e.* without addition of external dopant) and are comparable to externally doped *N*-alkylsulfonated polyaniline[2] and methoxy-SPANI.[5,6] The UV–VIS spectra of **3**–**8** gave three absorption bands. The band with λ_{max} at 306–324 nm is attributed to $\pi_B \to \pi^*$ and low lying $\pi_B \to \pi_Q$ transitions; the second with λ_{max} at 448–450 nm is consistent with low-lying π_B–π_S excitation to the polaron band whilst the third with λ_{max} at 565–624 nm is attributable to π_B–π_Q transition.[3b] Upon dedoping by addition of base, the absorption band at 448–450 nm was greatly diminished, showing the decreased contribution of the low-lying $\pi_B \to \pi_S$ transitions. The FTIR spectra gave the characteristic absorption bands for quinoidal and benzenoid stretchings at 1590 and 1500 cm⁻¹ respectively, as well as absorption bands of the sulfonic acid group at 1200 and 1020–1072 cm⁻¹.

The bulk *S*/*N* ratios (Table 1) indicate 100% sulfonation for polymers **3**, **4**, **6** and **7** and a lower degree of sulfonation for polymers **5** and **8** for which 10 mol% aniline was used to assist initiation. We ascribe the higher than expected bulk hydrogen and surface oxygen content to the extremely hygroscopic nature of these zwitterionic polymers. The C1s XPS signals of the polymers can be deconvoluted into three components, each with a FWHM (full width at half maximum) of 1.6 eV; C–C or C–H at 285 eV, C–N or C=N at 286 eV and C–O at 287 eV. The N1s signals can be deconvoluted into four environments each with a FWHM of 1.6 eV; –NH– at 399.7 eV, –⁺NH– at 401.2 eV, –⁺NH₂– at 402.5 eV and an unidentified component at 400.7 eV. This last environment was also reported by Yue and Epstein.[4c]

In conclusion, we have demonstrated for the first time that high pressure in the liquid phase facilitates the direct oxidative polymerisation of **1** and **2** which is otherwise not possible at ambient pressure. The polymer yield is substantially increased by the addition of a small amount of aniline. The resulting SPANI is highly water soluble. Despite a higher degree of sulfonation than is possible by post-polymerisation sulfonation

Table 1 Summary of reaction conditions and polymer characterisation data

Monomer	SPANI	Reaction conditions	Yield (%)	Bulk atomic ratio (surface at. ratio)	σ^a/S cm^{-1}
1	**3**	1.0 M LiCl 0.05 equiv. FeSO$_4$	10	$C_{6.9}H_{8.9}N_{1.0}S_{1.0}$	10^{-4}
1	**4**	5.0 M LiCl 0.05 equiv. FeSO$_4$	10	$C_{7.1}H_{10.0}N_{1.0}S_{1.1}$ ($C_{18.1}N_{1.0}S_{0.8}O_{6.9}$)	10^{-3}
1	**5**	5.0 M LiCl 0.05 equiv. FeSO$_4$ 0.1 equiv. aniline	98	$C_{6.3}H_{8.1}N_{1.0}S_{0.8}$ ($C_{8.1}N_{1.0}S_{1.0}O_{17.0}$)	10^{-3}
2	**6**	1.0 M LiCl 0.05 equiv. FeSO$_4$	10	$C_{6.8}H_{9.6}N_{1.0}S_{1.0}$	10^{-5}
2	**7**	5.0 M LiCl 0.05 equiv. FeSO$_4$	10	$C_{6.2}H_{8.6}N_{1.0}S_{1.0}$ ($C_{16.0}N_{1.0}S_{0.9}O_{6.7}$)	10^{-4}
2	**8**	5.0 M LiCl 0.05 equiv. FeSO$_4$ 0.1 equiv. aniline	100	$C_{6.4}H_{8.4}N_{1.0}S_{0.7}$	10^{-3}

[a] As determined using the four-point probe method.

of PANI,[4] the conductivity of the 'as-synthesised', high pressure SPANI is less than that of the latter and suggests the possibility of pressure induced defects. While these reactions were conducted at 19 kbar, we have observed that polymerisation of **1** will occur at pressures down to *ca.* 15 kbar, while **2** polymerises down to *ca.* 10 kbar. These reactions were catalysed with 5 mol% Co^{2+}. This difference in the reactivity of *ortho* and *meta* isomers has been reported for the oxidative polymerisation of cyanoanilines and ascribed to the relative effect of the electron withdrawing substituent on the spin densities at N and C4 in the oxidised monomers.[9] We are currently attempting to quantify the effect of pressure on reaction rate for the polymerisation of anilines. Preliminary rate measurements at different pressures for the ammonium persulfate oxidation of 2-methoxyaniline[10] conducted in a high pressure spectrophotometric cell[11] indicate a large, negative activation volume (ΔV^* of the order of -60 cm^3 mol^{-1}). Such a value would be consistent with charge development (and associated electrostriction of solvent) in the transition state[12] for the rate determining oxidation of aniline[13] and equates to a substantial rate enhancement (by a factor of *ca.* 12 at 1 kbar and a factor of *ca.* 10^{13} at 10 kbar, assuming a linear dependence of ln k on pressure[14]). This large effect suggests that the polymerisation of other unreactive aniline monomers may be viable at elevated pressures.

Notes and References

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