Water-Soluble Conducting Copolymers of o-Aminobenzyl Alcohol and Diphenylamine-4-sulfonic Acid

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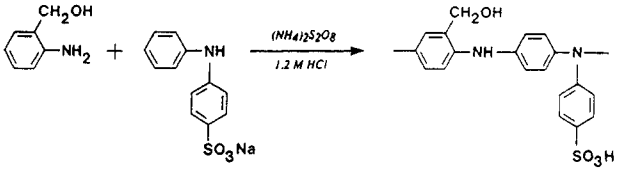
Conducting polymers which are soluble in water are more favorable for industrial applications than those soluble in organic solvents due to the environmental concerns with the latter. Several derivatives of polyaniline,[1-3] polythiophene,[4] and polypyrrole[5] have been reported to be soluble in the conductive form. However, the synthesis of these polymers involves multiple reaction steps, which makes them expensive and unattractive for practical applications. Recently, Armes and co-workers[6] reported the direct synthesis of a water-soluble conductive "polyaniline" from diphenylamine-4-sulfonic acid. The polymerization reaction produced low molecular weight polymers in a relatively low yield. In this Communication we report the first one-step chemical synthesis of poly(*o*-aminobenzyl alcohol-*co*-diphenylamine-4-sulfonic acid) (PADS) copolymers and describe their electrochemical, electrochromic, thermal, and conductive properties.

The PADS copolymers were obtained by polymerizing different mole ratios of *o*-aminobenzyl alcohol and diphenylamine-4-sulfonic acid sodium salt in 1.2 M HCl using ammonium persulfate as an oxidant. The oxidant to monomer ratio was kept at 1.5. The mole fraction of diphenylamine-4-sulfonic acid in the monomer mixture is f_1 and the resulting copolymer is PADS(f_1). The reaction was stirred at room temperature for 20 h. The polymeric product was collected by filtration or centrifugation, washed with a large amount of aqueous 1.2 M HCl solution, and dried under vacuum at 30 °C to constant weight. The yield of the recovered polymeric product decreased monotonically from 70 to 24% as the mole fraction of *o*-aminobenzyl alcohol in the reaction mixture was decreased from 1.0 to 0.3. This reflects the reaction characteristics of the diphenylamine-4-sulfonic acid polymerization where only a 19% yield of low molecular weight polymer is recovered.[7] Regarding the effectiveness of the washings, not much diphenyl-4-sulfonic acid homopolymer is expected to remain in the washed copolymer product because it is produced in low yields and is mostly removed with the 1.2 M HCl washings. On the other hand, some *o*-aminobenzyl alcohol homoplymer could remain in the products since it is highly insoluble and would not be removed with the 1.2 M HCl washings. In particular, the copolymer prepared with 0.1 mole fraction diphenylamine-4-sulfonic acid monomer appears to contain ca. one-third *o*-aminobenzyl alcohol homopolymer (see below). This material was removed by filtration prior to the spectroscopic and electrochemical analyses. At any rate, the polymer products are not simply a mixture of the homopolymers. The elemental compositions of the copolymers determined by XPS have been reported.[10] Thus, we chose not to repeat this analysis for all the copolymers; instead, one material was analyzed to establish a comparison. The elemental analysis of PADS(0.3) provides 57.84% C, 4.15% H, 7.49% N, 18.5% O, 5.45% S, and 0.90% Cl, and the calculated composition for $(C_7H_7NO)_{0.7}(C_{12}H_9NSO_3)_{0.3}Cl_{0.5}$ is 57.63% C, 4.29% H, 7.91% N, 14.46% O, 4.92% S, and 10.16% Cl. Thus, the agreement is reasonably good, except for the low Cl and high O content. The anion in the copolymer may be OH^-. The low molecular weight fraction of the copolymers in the product is soluble as the ammonium salt in tetrahydrofuran, and its average molecular weight was determined by steric exclusion chromatography. This fraction has an average molecular weight of ca. 160 000 based on the polystyrene standards and a very broad molecular weight distribution.

Scheme 1



Poly(*o*-aminobenzyl alcohol) has been reported.[10,11] We recovered this material as a black powder in 70% yield. The FTIR spectral characteristics of this homopolymer agree with those reported by Chan et al.[10] and are consistent with head-to-tail coupling of the rings in the polymer as previously suggested.[10,11] The elemental analysis for this polymer provides 57.66% C, 4.15% H, 7.49% N, 15.17% O, 9.58% Cl, and 0.22% S, and the calculated composition for $(C_7H_7NO)Cl_{0.5}$ is 60.52% C, 5.05% H, 10.04% N, 11.53% O, and 12.82% Cl. These calculated and measured percentages do not agree as well as with the PADS(0.3), and the discrepancy may result from the high level of O and S impurities. For comparison, Chan reports nonintegral atomic ratios for this polymer which correspond to weight percents of 69.9% C, 6.7% H, 10.5% N, and 12.7% Cl.[10]

The FTIR spectra of the PADS copolymers in KBr pellets show bands for the stretching modes of the aromatic carbons between 1592 and 1496 cm^{-1}. The C-N stretching band of an aromatic amine appears at 1105 cm^{-1}. The S=O asymmetric and symmetric stretching bands are seen between 1030 and 1006 cm^{-1}. The C-H out-of-plane bending vibrations corresponding to the 1,2,4- and 1,4-substited benzene rings[8] are seen at 870 and 818 cm^{-1}, respectively, indicating that the PADS copolymers have the head-to-tail coupling of the *o*-aminobenzyl alcohol and diphenylamine-4-sulfonic acid units (Scheme 1). This is similar to the proposed structure for polyaniline.[9] The relative peak intensities vary with the copolymer composition as expected. The ^1H NMR spectra of the PADS copolymers in DMSO-d_6 show two doublets between 6.99 and 7.16 ppm for the resonances of the protons on the phenylsulfonic acid pendant groups. The resonances for the aromatic protons on the polymer backbone appear between 7.26 and 7.54 ppm, for the proton of the alcohol group at around 4.0 ppm, and for CH_2 protons between 2.0 and 2.6 ppm. The integration of the NMR signals provides an *o*-aminobenzyl alcohol and diphenylamine-4-sulfonic acid monomer ratio for the copolymers from which F_1 values are calculated. These values agree well with the f_1 values and with the elemental analysis results for PADS(0.3). This comparison is shown in Table 1, where the diphenyl-4-sulfonic acid mole fractions for the reaction (f_1) and the product (F_1) are listed. This result resembles previous observations with the copolymerization of aniline and diphenylamine-4-sulfonic acid[7] and of aniline and *o*-aminobenzyl alcohol.[10] Although the elemental and NMR analyses indicate that the monomer composition in the copolymer reflects the composition in the reaction

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Table 1. UV–Visible Absorption, Electrical Conductivity, and Oxidation Data for the PADS Copolymers

f_1[a]	F_1[a]	λ_{max}, nm		σ, S/cm[b]	E_{pa1}/E_{pa2}, V[c]
0.00	0.00	320[d]	612[d]	2.6×10^{-3}	0.36/0.55
0.10	0.07	308	580	1.2×10^{-3}	0.37/0.55
0.20	0.22	310	570	2.8×10^{-4}	0.39/0.55
0.30	0.28	316	570	1.4×10^{-4}	0.40/0.56
0.50	0.55	318	562	6.9×10^{-5}	0.41/0.60
0.70	0.73	338	506	8.1×10^{-6}	0.52/0.73
1.00	1.00	320	506	3.4×10^{-3}	0.50[e]/—

[a] f_1 and F_1 are the mole fractions of diphenyl-4-sulfonic acid used in the reaction mixture and found in the copolymer by NMR, respectively. [b] Pressed pellet. [c] Film on Pt electrode immersed in 1.2 M HCl and using a Ag/Ag^+ reference electrode. [d] Poly(*o*-aminobenzyl alcohol) base in *N*-methyl-2-pyrrolidinone. [e] Polymer dissolved in 1.2 M HCl aqueous solution.

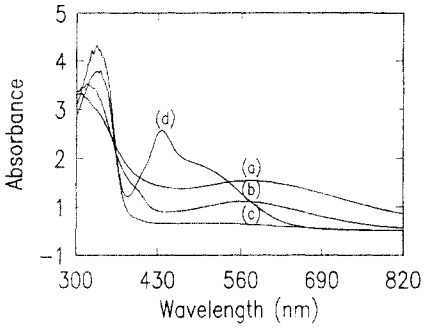


Figure 1. UV–visible spectra of the PADS copolymers dissolved in 0.1 M NH_4OH: (a) 0.1, (b) 0.3, (c) 0.7, and (d) 1.0 mole fraction of diphenylamine-4-sulfonic acid in the copolymer.

mixture, the recovered copolymers are most likely a mixture of copolymer chains with different monomer contents and with variations in the monomer homogeneity along the chain. The PADS copolymers have a thermal gravimetric behavior like those of polyaniline and other polyaniline copolymers.[7] Upon heating in air, the PADS copolymers display a weight loss starting at 200 and 450 °C in the thermograms. The FTIR spectra of the heated samples indicate that the weight loss at 200 °C corresponds to the elimination of water and chloride dopant, while at 450 °C it is related to the decomposition of the copolymers.

The PADS copolymers with more than 0.2 mole fraction of diphenylamine-4-sulfonic acid are completely soluble in an aqueous solution of NH_4OH and NaOH. Filtration of these solutions indicates that there are only trace amounts of insoluble material. The copolymer with 0.1 mole fraction of diphenylamine-4-sulfonic acid is the exception and had ca. one-third insoluble material which was not analyzed further but is presumed to be poly(*o*-aminobenzyl alcohol). The aqueous solutions are violet and display two absorption bands in their UV–visible spectra as shown in Figure 1. The π–π^* transition shows a bathochromic shift as the diphenylamine-4-sulfonic acid content in the copolymer increases (Table 1), suggesting an increase in the extent of conjugation as has been observed with other copolymers of aniline.[10,11] This is accompanied by a decrease in intensity of the broad "exciton" band.[2] Since the exciton band is related to the quinoid structure, it appears that the quinoid structure is only present in the *o*-aminobenzyl alcohol units after deprotonation. The aqueous solutions of the PADS copolymers were used to cast uniform and adherent films on electrodes.

The PADS copolymers are partially soluble in polar organic solvents such as *N*-methyl-2-pyrrolidinone (NMP), dimethyl sulfoxide (DMSO), and dimethylformamide (DMF). In these solvents, the low molecular weight

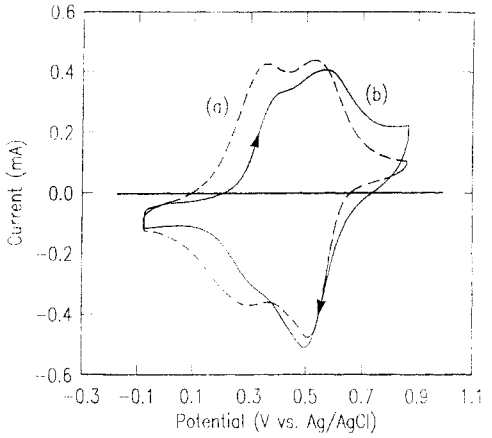


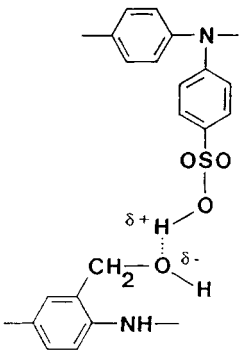
Figure 2. Cyclic voltammograms of the PADS films immersed in 1.2 M HCl aqueous solution at scanning rate 100 mV/s: (a) 0.1 and (b) 0.5 mole fraction of diphenylamine-4-sulfonic acid in the copolymer.

fraction is dissolved, leaving behind the high molecular weight fraction, and the amount of soluble material increases with the diphenylamine-4-sulfonic acid content in the polymer. The UV–visible spectra of poly(*o*-aminobenzyl alcohol) and of PADS(0.3) dissolved in NMP resemble the spectra measured in alkaline aqueous solution. These solutions show no additional absorption bands out to 2100 nm.

The thin films of the PADS copolymers coated on the platinum foil electrode exhibit two broad and overlapping oxidation peaks between –0.1 and 0.9 V in the cyclic voltammograms for electrodes immersed in 1.2 M HCl solution (Figure 2). The films are stable to the oxidation/reduction process and could be cycled repeatedly. The oxidation peaks correspond to the oxidation of the neutral nitrogen atoms in the polymer backbone to form the radical cation and dication and they compare well with the peaks for poly(*o*-aminobenzyl alcohol) and polyaniline films.[10,11] The peak currents (I_{pa}) vary linearly with the scanning rates. The oxidation peaks show a small anodic shift as the diphenylamine-4-sulfonic acid content in the copolymers increases, possibly reflecting conformational changes in the polymer chain. On the other hand, these shifts could result from local acidity changes since the peaks do shift with solution pH changes. For example, the peaks at 0.23 and 0.41 V for the PADS(0.7) film shift from 0.38 to 0.54 V when the pH of the HCl/KCl buffer solution changes from 2.0 to 0.5, respectively. The question is to what extent do the polymer compositional changes alter the pH in the films. The peak potentials for the homopolymers agree well with previous reports.[7,11] Concurrently with the redox reactions, the PADS films exhibit multiple and reversible color changes. These films are pale yellow and have only one absorption band at ca. 320 nm at 0.0 V. They became green at 0.3–0.6 V and have two new bands at ca. 430 and 820 nm due to the formation of the radical cation. At higher potentials, these films turn dark blue and have the absorption band of the dication at ca. 685 nm.

The electrical conductivity of the PADS copolymers recovered from 1.2 M HCl aqueous solution was measured on pressed pellets and using the conventional colinear four-probe technique. As seen in Table 1, the electrical conductivity of these copolymers is lower than for either homopolymer and varies with the composition. This result suggests that the polymeric products are copolymers and not a mixture of the homopolymers since this response is not expected for simple mixtures of two polymers. The lower electrical conductivity of the PADS copolymers may

Scheme 2



reflect a reduction in the number of carriers as evident by the decrease in the "exciton" band, as well as possible increases in the separation of the polymer chains caused by the hydrogen bonding between the sulfonic acid groups and alcohol groups[10,11] (Scheme 2). The relative importance of these effects remains to be determined. The σ value of PADS(0.1) is actually lower than the listed value because the sample has ca. one-third insoluble material, presumed to be the homopolymer. $\log(\sigma)$ for poly(*o*-aminobenzyl alcohol) and the five copolymers plot linearly with f_1. The slope of the plot is -4 ± 0.2. Thus the discontinuity in the plot occurs with materials with $f_1 > 0.7$. This result suggests that the diphenylamine-4-sulfonic acid polymer may have an unexpectedly high σ value due to the presence of a second transport process, possibly H^+ transport. The conductivities of the homopolymers agree well with previous reports.[7,10,11]

In summary, we have demonstrated the one-step chemical polymerization of high molecular weight poly(*o*-aminobenzyl alcohol-*co*-diphenylamine-4-sulfonic acid) copolymers. The monomer composition in the copolymers represents the monomer ratio used in the polymerization reaction. These copolymers dissolve in aqueous and polar organic solvents to form viscous solutions which can be used to cast films on various substrates. The PADS copolymers exhibit an electrical conductivity between 1.2×10^{-3} and 8.1×10^{-6} S/cm. The thin films of these copolymers immersed in aqueous acid media can be oxidized and reduced in the voltage range between -0.1 and 0.9 V. These reactions are accompanied by color changes in the film.

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