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Synthesis and Properties of Novel Water-Soluble Conducting Polyaniline Copolymers

My T. Nguyen, Paul Kasai, James L. Miller, and Arthur F. Diaz*

Polymer Science & Technology, IBM Almaden Research Center, Department K92/801, 650 Harry Road, San Jose, California 95120

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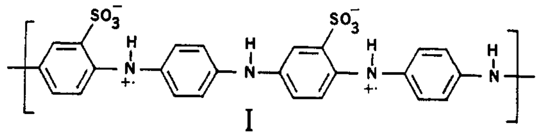
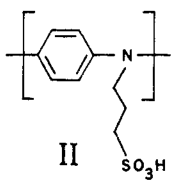
ABSTRACT: The chemical polymerization of aniline and sodium diphenylamine-4-sulfonate produces poly(aniline-*co*-*N*-(4-sulfophenyl)aniline) (PAPSA), copolymers which have high molecular weights and are recovered as a dark green powder. The PAPSA copolymers have a monomer composition like the composition in the reaction mixture. They have conductivities which range between the conductivities of the poly(*N*-(4-sulfophenyl)aniline) homopolymer (0.0035 S/cm) and polyaniline (5.2 S/cm). While the homopolymer poly(*N*-(4-sulfophenyl)aniline) is 10^3 times less conductive than polyaniline, it is still 10^6 times more conductive than other polyaniline polymers with sulfonate groups. The conductivity and the ESR signal both decrease with the phenylsulfonic acid content in the copolymer. The PAPSA copolymers are soluble in aqueous NH_4OH but not in aqueous HCl solutions. The color of the resulting solutions varies with the copolymer monomer composition. Films of the PAPSA copolymers on an electrode show two reversible redox reactions for the aniline units and one for the pendant phenylsulfonic acid groups between 0.2 and 0.8 V vs Ag/AgCl reference electrode, when immersed in aqueous acid solutions. During the redox process, the PAPSA films exhibit reversible color changes from pale yellow to green to dark blue.

Introduction

During the last decade, polyaniline has received considerable research attention owing to its high electrical conductivity (100 S/cm) and environmental stability.[1] However, the conductive form of polyaniline is difficult to process because it is insoluble in common organic solvents and is unstable at melt process temperatures. This limitation detracts from its usefulness of polyaniline but can be reduced by derivatizing the polymer. With the introduction of alkyl and aryl substituents, the polymer becomes soluble in solvents like *N*-methylpyrrolidone, dimethylformamide, tetrahydrofuran, etc.[2–4] The polymers retain their electrochromicity and electrical conductivity; however, the latter decreases dramatically to values between 10^{-3} and 10^{-7} S/cm. The most successful approach to a conductive polyaniline with solubility in aqueous solutions results from the introduction of sulfonic acid groups. This can be achieved by treating the polymer with the appropriate reagents after the polymerization or by polymerizing the substituted aniline derivatives. An example of the former approach is the sulfonation of the emeraldine base with fuming sulfuric acid, to produce a polymer (**I**) which is soluble in aqueous alkaline solutions.[5,6] The sulfonation introduces approximately one sulfonate group for every two phenyl rings and probably occurs on alternate rings. The sulfonated polymer is inherently in the conductive form, "self-doped", and has a conductivity of 0.1 S/cm. This polymer is also electroactive and resembles polyaniline in its properties. Likewise, treating the leucoemeraldine base with 1,3-propanesultone[7,8] and 1,4-butanesultone[8] in the presence of sodium hydride catalyst also produces polymers which are soluble in alkaline aqueous solutions. In this reaction, pendant propanesulfonic acid (**II**) and butanesulfonic acid (**III**) groups are attached to the nitrogen atoms in the polymer. These substituted polyanilines are electroactive and have conductivities between 10^{-5} and 10^{-9} S/cm.[7,8] Although these sulfonated polyanilines are processable and retain their electrical properties, the multistep syntheses to these materials are not viewed favorably for practical applications.



I



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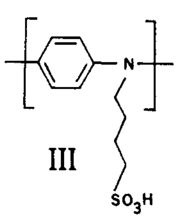
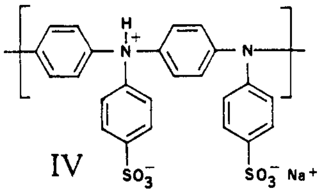


III



IV

The second approach was demonstrated by Armes and co-workers[9] by the chemical polymerization of sodium diphenylamine-*p*-sulfonate to produce a water-soluble polymer with an electrical conductivity of 0.006 S/cm. Half of the sulfonic acid groups in the polymer were neutralized to the Na^+ salt, and the polymer was proposed to have a head-to-tail coupled structure (**IV**) as was previously proposed for aniline.[1] The aqueous solution of this polymer undergoes color changes from red to green when the pH is varied from 6 to 4. The electrochemical response of the polymer in acetonitrile was poor and could not be measured in water. Another approach is copolymerization of aniline and a suitable substituted aniline comonomer to produce copolymers whose electrical conductivity and solubility can be varied by proper adjustment of the

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Table 1. Composition, Isolated Yields, and Conductivities of Poly(aniline-*co*-*N*-(4-sulfophenyl)aniline) Copolymers

PAPSA		atom wt % (elem anal.)				isolated yield, %	cond, S/cm
f_1[a]	F_1[b]	N	Na	S	Cl		
1.00	1.00[c]	5.18	0.77	10.96	0.61	19	0.0035
0.75	0.73	5.26	0.06	8.73	1.91	26	0.013
0.60	0.63	5.78	0.03	8.36	13.02	37	0.023
0.50	0.39	7.32	0.15	6.55	1.14	58	0.075
0.25	0.26	7.80	0.09	4.67	2.80	72	0.11
0.10	0.07	6.26	0.22	0.97	6.42	71	3.7
0.00	0.00	nd	nd	nd	nd	84	5.2

[a] f_1 = fraction of sodium diphenylamine-4-sulfonate in the reaction mixture. [b] F_1 = fraction of sodium diphenylamine-4-sulfonate in the copolymer. [c] The value 0.93 was corrected for NH_4^+ content in the polymer from the S/N molar ratio.

monomer ratio in the copolymer. This approach successfully produced copolymers with improved solubility in organic solvents,[4,10,11] and the conductivity of the copolymers usually responds monotonically with the monomer composition in the polymer. It should be mentioned that, besides modifying the polyaniline polymers to make them inherently soluble in aqueous solutions, polyaniline has also been solubilized by combining it with dispersants.[12,13]

In this paper we report the synthesis and characterization of poly(*N*-(4-sulfophenyl)aniline) and the poly(aniline-*co*-*N*-(4-sulfophenyl)aniline) copolymers (PAPSA). Although the homopolymer was recently reported,[9] in this paper we provide additional information on the polymer structure and properties. The PAPSA copolymers were obtained directly from the chemical polymerization of aniline and sodium diphenylamine-4-sulfonate. The monomer composition, and correspondingly the water solubility and conductivity, in the copolymer can be controlled.

Experimental Section

Materials. Aniline, sodium diphenylamine-4-sulfonate, ammonium persulfate, and hydrochloric acid were purchased from Aldrich Chemical Co. and used without further purification. Organic solvents methyl sulfoxide, *N*,*N*-dimethylformamide, *N*-methyl-2-pyrrolidinone, and tetrahydrofuran from Fisher were also used as received.

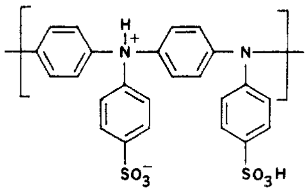
Polymerization. The poly(aniline-*co*-*N*-(4-sulfophenyl)aniline) copolymers and the corresponding homopolymers, i.e., polyaniline and poly(*N*-(4-sulfophenyl)aniline), were synthesized by chemical polymerization of the appropriate monomers in aqueous 1.2 M HCl using ammonium persulfate and a modified literature procedure.[9] The molar fraction of sodium diphenylamine-4-sulfonate in the reaction mixture (f_1) was varied from 0.10 to 0.75, and the resulting copolymers are referred to as PAPSA(f_1). Sodium diphenylamine-4-sulfonate is very reactive, as is evident by the immediate coloration of the reaction solution upon the addition of the oxidant, whereas with aniline, there is a ca. 3-min delay before coloration. The oxidant/monomer ratio was kept at a value of 1.5. The reaction yields were estimated to be 60–70%; however, the recovered yields decreased from 71 to 19% as the sodium diphenylamine-4-sulfonate content in the reaction mixture increased (Table 1). The loss occurred primarily in the centrifuging and washing step and was greater with the more soluble polymers. A typical polymerization of PAPSA-(0.5) copolymer is as follows: Aniline (0.93 g) and sodium diphenylamine-4-sulfonate (2.7 g) were dissolved in 50 mL of a 1.2 M HCl solution. A solution of 6.8 g of ammonium persulfate in 50 mL of 1.2 M HCl was then added slowly to the monomer solution with constant stirring at room temperature. A dark green color developed immediately, and the polymer eventually precipitated out of the solution. The reaction mixture was stirred for an additional 20 h at room temperature. The reaction mixture was then centrifuged, and the recovered dark green precipitate was washed 10–12 times with 1.2 M HCl. The polymer was isolated as a powder and dried to constant weight in vacuum at 20 °C. The yield was 58%.

Characterization. The polyaniline was analyzed as the base form, and the copolymers were analyzed in the doped form. The thermal gravimetric analyses of the PAPSA copolymers were measured in air with a heating rate of 20 °C/min using a Perkin-Elmer TGS-2. The ^1H NMR spectra of the PAPSA copolymers in DMSO-d_6 were obtained using a Bruker 250-MHz spectrometer. The ESR spectra were measured using dispersions of the PAPSA copolymers in ZnS (5% w/w) and were recorded using a Bruker ER080. The FTIR spectra of the polymer powders in KBr pellets were recorded using an IBM IR44 spectrometer. The UV–visible spectra were recorded using an HP-8452A diode array spectrophotometer. The elemental analyses were obtained from the Microanalytical Laboratory, University of California, Berkeley. The copolymers dissolve partially in tetrahydrofuran, and the average molecular weight of the soluble fraction, M_w, was determined by steric exclusion chromotography for each copolymer. Monodispersed polystyrene standards were used for calibration.

The room-temperature electrical conductivity of the polymer films and pressed pellets was measured by the conventional collinear four-probe technique using a Keithley 177 ampometer and an HP 3478A multimeter. For the electrochemical measurements, 30–50-nm-thick films of the PAPSA copolymers were coated on 2-cm² platinum foil electrodes and mounted in a one-compartment cell equipped with a gold wire counter electrode and an Ag/AgCl (3.8 N KCl) reference electrode. The cyclic voltammograms were recorded using an EG&G PAR potentiostat/galvanostat (Model 273) connected with an IBM *x*–*y*–*t* plotter (Model 7424 MT). For the in-situ UV–visible spectra, films of the copolymers were coated on the Nesa glass electrodes. The films were kept at the desired potential for 2 min before each measurement.

Results and Discussion

Poly(*N*-(4-sulfophenyl)aniline) (V). Poly(*N*-(4-sulfophenyl)aniline) was obtained from the polymerization of sodium diphenylamine-4-sulfonate in an aqueous HCl solution using ammonium persulfate as the oxidizing agent.[9] The recovered yield of the polymer is only 19%, and the loss occurs primarily in the washing step as evident by the coloration of the wash solutions. The yield of unpurified polymer is 50–60%. Even with the extensive washing, the sample still retains 1.4% (by weight) of sodium and chloride ions. This is seen in the elemental results listed in Table 1. Also seen is a S/N molar ratio of 0.93 rather than the expected value of 1.0. This difference results from the presence of 8% NH_4^+ ions from the oxidant which remain in the sample. This was determined by NMR and is discussed below. Therefore, the polymer has the expected S/N molar ratio of 1.0. It is worth mentioning that, unlike the case with other substituted anilines, with the present monomer the pendant group is not detached during the polymerization.[4,14] The amount of sodium ion in excess of chloride ion is only 1–2% of the sulfur content. Thus, the polymer recovered from our reaction has sulfonic acid groups as shown schematically in V. It is clearly not the half-neutralized polymer with sodium ions reported by Armes.[9] The molecular weight of the polymer could not be determined because the polymer is not soluble in tetrahydrofuran.



V

The ^1H NMR spectrum of V in DMSO-d_6 closely resembles the spectrum of the monomer. This is seen in

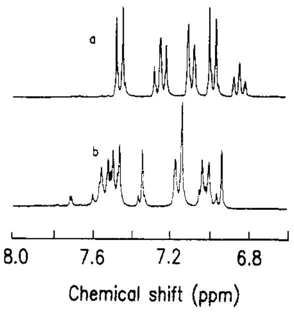


Figure 1. NMR spectra of sodium diphenylamine-4-sulfonate monomer (a) and polymer (b).

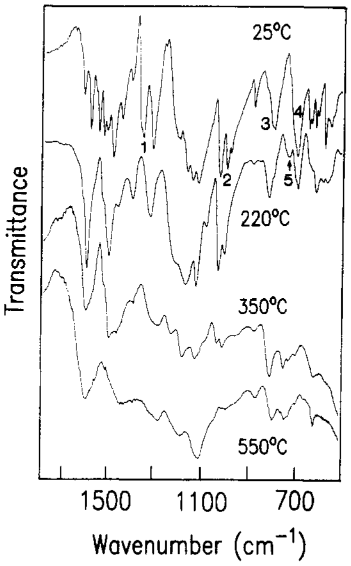


Figure 2. FTIR spectra of poly(*N*-(4-sulfophenyl)aniline) in KBr recorded after heating to 220, 350, and 550 °C.

Figure 1. The spectrum for V shows two doublets between 7.2 and 7.0 ppm for the protons on the pendant phenylsulfonic acid groups and quartets between 7.6 and 7.4 ppm for the aromatic protons in the polymer backbone. In addition, singlets appear at 7.34, 7.13, and 6.93 ppm for the protons of the NH_4^+ cation. This was confirmed by adding ammonium persulfate to the sample and observing the peak enhancements. The integration of the spectrum indicates 8% NH_4^+ ion in the sample. The XPS core-level spectrum of V shows a broad peak for N 1s. Deconvolution of the peak fits for the presence of three types of nitrogen atoms in the polymer (399, 400, and 401 eV) and the presence of 13% NH_4^+ (403 eV) in the sample. The peaks for the nitrogen atoms in the polymer were assigned to the unprotonated amine nitrogen (399 eV, 48%), the nitrogen atom bearing a radical cation (400 eV, 11%) and the protonated amine nitrogen (401 eV, 41%).[15,16] The data from the NMR and XPS analyses support structure V for poly(*N*-(4-sulfophenyl)aniline) which is internally protonated or "self-doped". It seems reasonable that the polymer in the solid state would not have all of the nitrogen atom protonated to minimize Coulombic interactions. Both measurements also indicate the presence of 8–13% NH_4^+ ion in the sample.

The FTIR spectra for V measured using KBr pellets are shown in Figure 2. The spectra show two strong aromatic C–N stretching bands at 1370 and 1125 cm^{-1}. The band at 1370 cm^{-1} (peak 1) is assigned to the C–N stretching of the phenylsulfonic acid substituent.[17] Several strong asymmetric and symmetric S=O stretching bands appear between 1176 and 1031 cm^{-1} (peak 2). The strong C–H out-of-plane bending vibration of the para-substituted benzene rings appears at 804 cm^{-1} (peak 3), indicating that the monomers in the polymer are bonded head-to-tail in agreement with previous reports.[9] A strong S–O stretching band is seen at 693 cm^{-1} (peak 4). Upon heating in air, V loses weight at three temperatures as seen in the thermogram in Figure 3a. At 180 °C the weight loss is probably due to the elimination of some free sulfonic acid groups as indicated by the decrease in intensity of the S=O and S–O stretching bands in the spectrum of the sample heated to 220 °C (Figure 2). The appearance of the C–H out-of-plane bending vibration at 745 cm^{-1} (peak 5) for the monosubstituted benzene rings is consistent with this interpretation. At 275 °C the remaining sulfonate groups are lost as indicated by the almost complete disappearance of the S=O and S–O stretching bands. These groups are the sulfonate groups which protonate the nitrogen atoms in the polymers. At 550 °C the polymer decomposes completely.

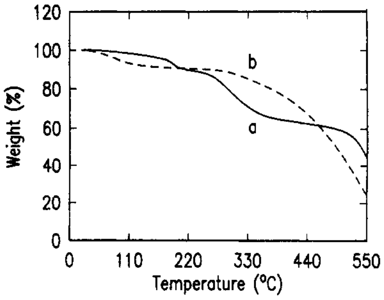


Figure 3. Thermograms of (a) poly(*N*-(4-sulfophenyl)aniline) and (b) PAPSA(0.50).

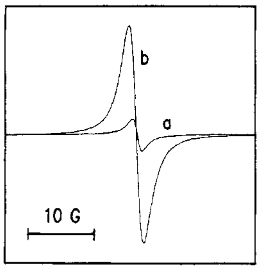


Figure 4. ESR spectra of (a) poly(*N*-(4-sulfophenyl)aniline) homopolymer and (b) PAPSA(0.39) powders in ZnS (5% by weight).

The ESR spectrum of the powder of V shows a small signal as seen in Figure 4a. This signal is $^1/_{20}$ the size of the signal produced by the copolymer containing 39% sodium diphenylamine-4-sulfonate. The relative peak sizes were estimated using (height) × $(\Delta H_{\text{peak-to-peak}})^2$. Therefore, the polymer has very little radical cation structure.

Dissolving V in a 1.0 M NH_4OH solution produces a red solution which displays three absorption bands at 320, 436, and 506 nm in the UV–visible spectrum as seen in Figure 5. The bands at 320 and 436 nm are assigned to the π–π^* electronic transition of the benzoid rings in the polymer backbone and in the phenylsulfonic acid pendant groups, respectively.[18,19] The shoulder at 506 nm probably corresponds to the exciton transition as in the assignment made for the sulfonated polyaniline (563 nm).[5] This suggests that the conjugation length in the poly(*N*-(4-sulfophenyl)aniline) is less than that in poly(*o*-anilinesulfonic acid).[5] The spectrum depends strongly on the solution pH as previously noted.[7-9] Dissolving V in water produces a green solution which absorbs at 320 and 415 nm. In addition, the exciton band disappears and a new band appears near 750 nm. This band is usually associated with the transition of a dication and again indicates that poly(*N*-(4-sulfophenyl)aniline) is internally protonated.

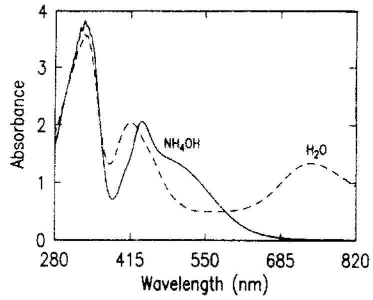


Figure 5. UV-visible spectra of poly(*N*-(4-sulfophenyl)aniline) in a 1.0 M NH$_4$OH aqueous solution and in water.

The electrical conductivity of **V** at room temperature as measured by the four-probe technique is 0.0035 S/cm (Table 1) and is not significantly different from the value of 0.006 S/cm reported for the half-neutralized form of the polymer (**IV**) with Na$^+$ ions.[9] **V** is approximately 10^3 times less conductive than polyaniline, and the lower conductivity probably reflects the reduced number of carriers plus reduced conjugation lengths and increased interchain distances which result from the presence of the pendant groups. On the other hand, **V** with the phenylsulfonic acid group and the corresponding copolymers are 10^2–10^6 times more conductive than polyaniline substituted with *N*-propanesulfonic acid (**II**) and *N*-butanesulfonic acid (**III**) groups which have conductivities between 10^{-5} and 10^{-9} S/cm.[7,8] The origin of this difference has not been investigated and may result from a variation in the number of carriers. The ESR results provide some indication of this. The size of the ESR signal decreases significantly when the diphenylamine-4-sulfonate monomer content in the copolymer is increased from 39% to 100% in the diphenylamine-4-sulfonate homopolymer, and it may be even smaller with the alkylsulfonic acid groups on the polymer as in **II** and **III**.

Poly(aniline-*co*-*N*-(4-sulfophenyl)aniline) Copolymers (PAPSA). The poly(aniline-*co*-*N*-(4-sulfophenyl)aniline) copolymers were synthesized by copolymerizing aniline and sodium diphenylamine-4-sulfonate in an aqueous HCl solution using ammonium persulfate as above.[9] The yields of the recovered polymer decrease with the phenylsulfonate content in the copolymer, and the loss occurs primarily in the washing step. The copolymers with the higher phenylsulfonate content are increasingly more soluble in water. The copolymers are partially soluble in tetrahydrofuran, and the molecular weights of these soluble fractions were determined by steric exclusion chromatography. Only one broad peak was observed in each case. The molecular weights found for these copolymer (F_1) fractions were 158 000 (0.0), 140 000 (0.10), 126 000 (0.25), 115 000 (0.50), and 74 000 (0.60). The copolymers with F_1 equal to 0.75 and 1.00 were not analyzed. The molecular weights of the insoluble portions were not determined. In contrast, the polyaniline homopolymer has a bimodal molecular weight distribution with values at 4300 and 158 300.

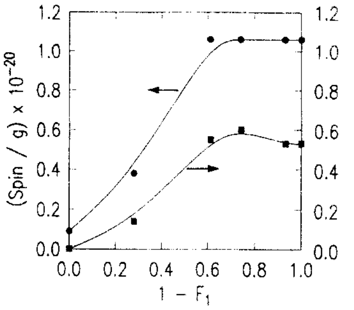


Figure 6. Plots of the spin per gram and the unprotonated nitrogens of the PAPSA copolymers versus the molar fraction of aniline in the copolymer.

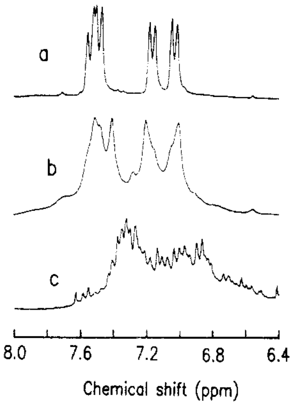


Figure 7. ^{1}H NMR spectra of (a) PAPSA(0.75), (b) PAPSA(0.50), and (c) PAPSA(0.25) copolymers in DMSO-d_6.

In this reaction, sodium diphenylamine-4-sulfonate appears to be more reactive than aniline, and this difference is probably related to the relative oxidation peak potentials (E_{pa}) which are 0.86 and 1.08 V (vs Ag/AgCl reference electrode). Because of the reactivity difference, sodium diphenylamine-4-sulfonate is consumed faster than aniline in the early stages of the copolymerization reaction. It is the predominant monomer in the copolymer and probably exists in short homopolymer segments. As the polymerization proceeds and sodium diphenylamine-4-sulfonate is depleted, the number and size of these segments decrease. The reciprocal architecture probably exists in the later stages of the copolymerization when most of sodium diphenylamine-4-sulfonate is consumed. Consequently, the PAPSA copolymers should have two somewhat homogeneous terminal *N*-(4-sulfophenyl)aniline and aniline segments containing short blocks separated by a heterogeneous segment of both monomers similar to that proposed for poly(aniline-*co*-*N*-butylaniline).[10]

The elemental analyses of these materials listed in Table 1 show that a small amount of Na$^+$ remains in all the samples. The Cl$^-$ content increases with the aniline content in the copolymer since it is protonated by HCl. From the S/N molar ratio it is seen that the copolymers produced under these conditions have a monomer composition which almost equals the molar composition in the reaction mixture. Thus both monomers react to the same extent during the 20-h reaction time. The fraction of the amine nitrogens which remain unprotonated in the copolymers was estimated by assuming that the sulfonate and chloride ions are a measure of the number of protonated nitrogens. This leads to the expression [1 − (S + Cl)/N] where S, Cl, and N are the atom mole fractions calculated from the elemental analysis data. As seen in Figure 6, the fraction of unprotonated nitrogens increases with the aniline content in the polymer ($1 - F_1$) and reaches a maximum value of 0.5. This maximum level of protonation has been previously noted for polyaniline.

The ^{1}H NMR spectra of the PAPSA copolymers dissolved in DMSO-d_6 are shown in Figure 7. The PAPSA(0.75) copolymer shows two doublets between 7.2 and 7.0 ppm for the protons on the pendant phenylsulfonic acid groups and quartets between 7.6 and 7.4 ppm for the aromatic protons in the copolymer backbone. A similar spectrum is observed for the PAPSA(0.50) copolymer; however, these resonances are broader and slightly shifted upfield possibly due to the higher molecular weight. The relative integrals of the two doublets and the quartet are

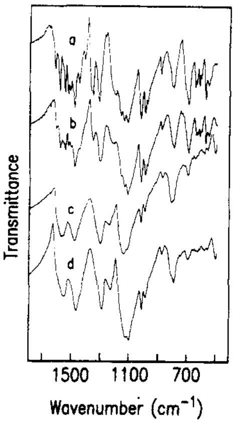


Figure 8. FTIR spectra in KBr pellets of (a) PAPSA(1.00), (b) PAPSA(0.75), (c) PAPSA(0.60), and (d) PAPSA(0.25).

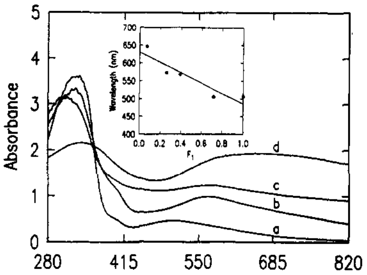
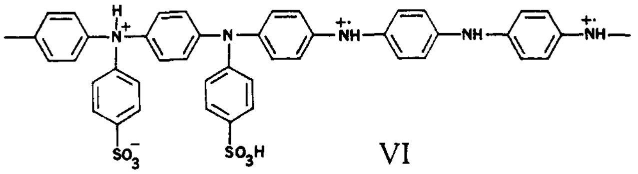


Figure 9. UV-visible of the poly(aniline-*co*-*N*-(4-sulfophenyl)aniline) dissolved in a 1.0 M NH_4OH aqueous solution: (a) PAPSA(0.75), (b) PAPSA(0.50), (c) PAPSA(0.25), (d) PAPSA(0.10). The inset is the plot of the absorption wavelength of the exciton band versus the molar fraction of the phenylsulfonic acid in the copolymers.

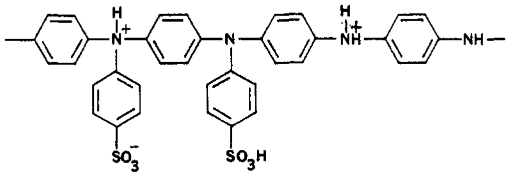
almost equal in both PAPSA(0.75) and PAPSA(0.50), suggesting that these resonances of the aromatic protons in the copolymer backbone belong to the diphenylaminesulfonate units only. This observation supports the block structure proposed for the copolymer. As with the unsubstituted polyaniline which has no ^1H NMR signal, the radical cations in the copolymer must reside in the unsubstituted aniline segments where the proton resonances are broadened beyond detection. The spectrum of the PAPSA(0.25) copolymer shows several new resonances between 7.5 and 6.3 ppm which are probably for the protons of the unsubstituted aniline units which are singly isolated by adjacent substituted aniline monomers.

The FTIR spectra of the PAPSA copolymers in KBr pellets are shown in Figure 8. The copolymers exhibit strong peaks due to different vibration modes of the benzene rings in the 1670–1500-cm^{-1} region. The bands at 1316 and 1031 cm^{-1} decrease with the *N*-(4-sulfophenyl)aniline content. In addition, the peak intensity ratio of the peak for the C–H out-of-plane bending vibration of the para-substituted benzene rings (804 cm^{-1}) and for the S–O stretching (693 cm^{-1}) is almost linear with F_1. Upon heating, the copolymers with F_1 less than 0.40 lose weight at around 300 °C probably due to the loss of the sulfonic acid groups and chloride[20] and again above 440 °C due to total decomposition.

The room temperature ESR spectra of the powders of the PAPSA copolymers show a strong Lorentzian peak with a 10-G peak-to-peak line width (Figure 4b). The polymers have different degrees of paramagnetism, and the number of spins/gram was estimated by comparing the size of the ESR peak with that of the peak from a 2,2-diphenyl-1-picrylhydrazyl hydrate standard. The number of spins increases with the molar fraction of aniline in the copolymer ($1 - F_1$) and reaches saturation when ($1 - F_1$) approaches 0.5 (Figure 6). This response nicely shows the relationship between the number of spins and the level of protonation of the copolymers. The radical cations in the copolymers probably have a structure like VIwhich resembles the structure proposed for the protonated emeraldine base.[21-23] The radical structures like **VI** arise from the internal redox reaction and polaron separation of the protonated diimine. Since the PAPSA copolymers are likely to have a block structure, the radical cations are probably formed preferentially in the aniline segments. The copolymers with the higher *N*-(4-sulfophenyl)aniline content are also more protonated and produce the stable diamine form (**VII**).



VI



VII

The UV–visible spectra of the PAPSA copolymers in 1.0 M NH_4OH are shown in Figure 9. These copolymers also display the π–π^* electronic transition for the benzoid rings in the polymer backbone at around 320 nm. The exciton band for these copolymers is broader than that for the poly(*N*-(4-sulfophenyl)aniline) homopolymer, and it shifts almost linearly from 646 to 436 nm as the *N*-(4-sulfophenyl)aniline content increases (inset in Figure 9). The color of the solutions correspondingly changes from blue to violet to purple to red as F_1 increases from 0.1 to 1.0. Since this transition has been shown to be sensitive to the polymer chain conformation,[18,19] the blue shift with increasing F_1 is presumably due to the steric effects of the phenylsulfonate substituents which produce torsional twists and shorten the conjugation lengths in the polymer.[18,19]

The electrical conductivity of the copolymers gradually increases with the aniline content in the polymer backbone (Table 1). This result is not surprising in view of the ESR results which show an increase in the radical cation content and the UV–visible results which indicate an increase in the conjugation lengths along the polymer. This result agrees with the literature reports which show a monotonic variation in the conductivity with the composition of the polymers.[10,11] However, the conductivity level is as much as 10^6 times higher than that reported for other substituted polyanilines.[8,10]

Electrochemistry. The PAPSA copolymer films which were cast on an electrode are stable in an aqueous 1.2 M HCl solution and could be used for electrochemical measurements. The films are electroactive, and as seen in the cyclic voltammograms for the PAPSA(0.10) and PAPSA(0.60) films in Figure 10, three oxidation–reduction peaks appear between 0.2 and 0.8 V vs Ag/AgCl (3.8 N

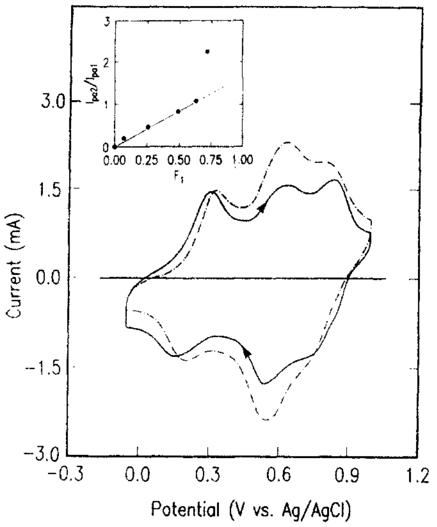


Figure 10. Cyclic voltammograms of PAPSA(0.10) (solid line) and PAPSA(0.60) (dashed line) films on a Pt electrode in a 1.2 M HCl aqueous solution at 100 mV/s. Inset: Plot of the second to first oxidation peak current ratio (I_{pa2}/I_{pa1}) versus the molar fraction of the phenylsulfonic acid in the PAPSA copolymers.

Table 2. Oxidation Potentials of Poly(aniline-*co*-*N*-(4-sulfophenyl)aniline) Films[a]

PAPSA(F_1)	E_{pa1}, V	E_{pa2}, V	E_{pa3}, V	I_{pa2}/I_{pa1}
1.00[b]		0.50[c]		
0.73	0.30	0.54	0.79	2.24
0.63	0.29	0.61	0.79	1.08
0.39	0.29	0.61	0.79	0.83
0.26	0.28	0.58	0.80	0.47
0.70	0.26	0.60	0.82	0.20
0.00	0.25		0.82	0.00

[a] Films on a Pt electrode immersed in 1.2 M HCl; 100 mV/s scan rate. [b] See above. [c] Measurement made with dissolved polymer.

KCl) reference electrode. The voltammograms of the copolymers which do not dissolve are stable and can be cycled repeatedly without change. The oxidation peak potentials of the PAPSA copolymer films are summarized in Table 2. The copolymers with the higher *N*-(4-sulfophenyl)aniline content produced broader peaks, and the first oxidation peak shifts to more anodic potentials, while the third oxidation peak shifts to less anodic potentials. The second oxidation peak at 0.59 V does not change position but does increase in size. The peak current ratio for the second and first oxidation peaks (I_{pa2}/I_{pa1}) increases almost linearly with F_1 as shown in the inset in Figure 10. These results suggest that the first and third oxidation peaks correspond to the stepwise oxidation of the nitrogen atoms in the aniline units to form radical cations and dications,[24] as shown in Scheme 1, while the second oxidation peak is probably due to the oxidation of the *N*-(4-sulfophenyl)aniline units to form dication species. Attempts to measure the voltammograms in neutral or slightly alkaline solution were unsuccessful because the films slowly dissolved. The copolymers with $F_1 > 0.63$ are soluble even in acid solution, and with $F_1 = 0.73$ the film dissolves off the electrode during the first scan. It is for this reason that the oxidation peak potential for the homopolymer was recorded for the polymer in solution and not as a film.

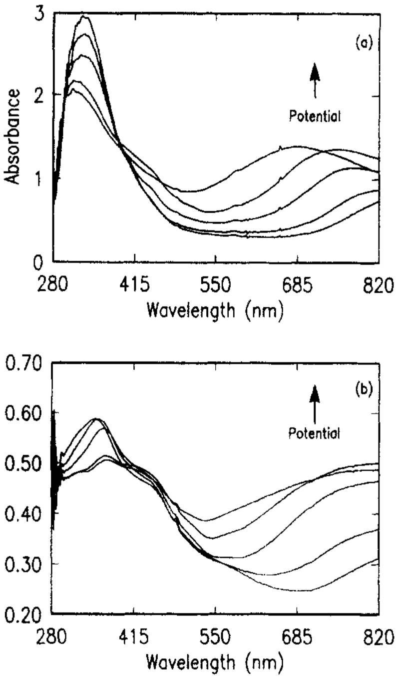
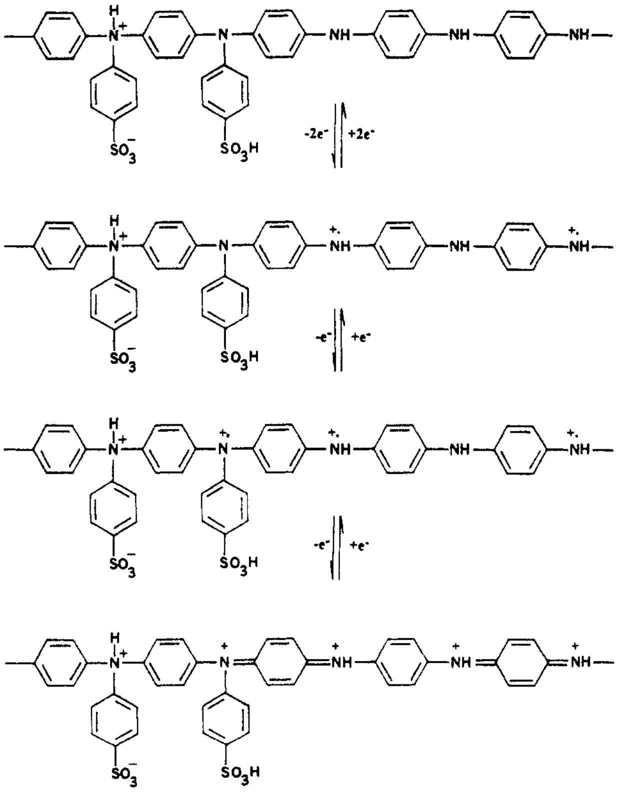


Figure 11. In-situ UV–visible spectra of (a) PAPSA(0.50) and (b) PAPSA(0.60) films on a NESA glass electrode, immersed in a 1.2 M HCl aqueous solution at 0.0, 0.4, 0.6, 0.8, and 1.0 V.

Scheme 1



Upon oxidation, the PAPSA copolymer films exhibit a reversible color change as normally seen with polyanilines.[7,8] Figure 11 shows the in-situ UV–visible spectra of the PAPSA(0.50) film on Nesa glass. At 0.0 V, this film has a pale yellow color with one main absorption band at 320 nm. When the applied potential is between 0.4 and 0.8 V, the film changes to a dark green color and two new absorption bands appear at around 420 and 800 nm. These new bands are assigned to the electronic transition of the radical cation.[2-4] At 1.0 V, the film turns blue and the band at 800 nm shifts to 685 nm, indicating the formation of the dication.[2-4] A similar behavior is seen with the PAPSA(0.60) film. The film of the PAPSA(0.60) in 1.2 M HCl changes color from green to blue when the applied potential is increased from 0.0 to 1.0 V. As seen in Figure 11, the PAPSA(0.60) film has a stronger absorption at 425 nm than does PAPSA(0.50), and this absorption band is almost unaffected by the applied potentials. This absorption band is similar to the band observed when emeraldine hydrochloride was treated with concentrated H_2SO_4.[25] At 1.0 V, the band at 800 nm again shifts to 685 nm.

Conclusion

In summary, water-soluble copolymers with intermediate conductivity were synthesized directly from aniline and sodium diphenylamine-4-sulfonate salt by a chemical polymerization. The monomer composition of these poly(aniline-*co*-*N*-(4-sulfophenyl)aniline) copolymers (PAPSA) can be controlled by varying the molar ratio of the monomers in the reaction mixture. The copolymers have a monotonic variation in their molecular weight, solubility in aqueous NH_4OH, and electrical conductivity with the monomer composition. The copolymers are proposed to have some short blocks in their structures. Upon heating the copolymers lose the sulfonic acid groups at two temperatures. The films of the copolymers are electrochromic and can be reversibly oxidized and reduced in aqueous acid solutions, and the color changes in the film are from yellow to blue.

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