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Effect of Sulfonic Acid Group on Polyaniline Backbone

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Abstract: This paper, aimed at delineating the significant changes in polyaniline (PAN) upon going from external protonic doping to internal doping, describes results on preparation and characterization of a self-doped conducting polymer: sulfonic acid ring-substituted polyaniline (SPAN). This polymer has a wide range of solubility, which improves the processibility of the polymer. Elemental analyses and spectroscopic data show that approximately 50% of the total number of phenyl rings in the polymer are monosubstituted by $-SO_3^-$ groups. SPAN has an intrinsic acid that is capable of doping the polyaniline backbone. Little correlation between the conductivity and pH is observed, the conductivity of ~0.1 S/cm being independent of pH for pH less than 7.5. Transport, magnetic, and electrochemical properties of SPAN provide insight into both the structural and electronic properties and the role that $-SO_3^-$ and $-SO_3^-Na^+$ groups play in affecting the solubility, doping mechanism, and charge transport in the polyaniline system. Comparative studies of SPAN and PAN show similarities due to the same backbone structure and differences because of the $-SO_3^-$ groups on the phenyl rings.

Introduction

Polyaniline (PAN) is the first conducting polymer whose electronic properties can be reversibly controlled by protonation.[1] Important issues within the polyaniline family of polymers include the relative effect of oxidative versus protonic doping,[1] the effects of derivatization at ring[2] and nitrogen sites,[3] the effect of the torsional degrees of freedom on the electronic and optical properties,[4] and the effect of localization on transport[2c–f] and magnetic phenomena.[5,6]

The motivation of this study is based on the fact that polyaniline (in the emeraldine base oxidation state) can be converted from an insulator to a conductor by external protonic doping.[1] Our approach is to introduce an acid group on the polymer chain to make the polymer a self-doped conducting polymer.

Introducing a $-SO_3H$ group on the polyaniline chain affects the properties of parent polyaniline without substantially sacrificing conductivity and is of specific interest for several reasons: (A) It brings new acid–base chemistry within a polymer system; such acid–base equilibrium can be changed externally by either an electrochemical or a chemical method. Protonation of the parent emeraldine base[1] leads to the emeraldine salt and a reorganization of the electronic structure to form a polaronic metal.[1c,6] Since benzenesulfonic acid is a strong acid, sulfonic acid ring-substituted polyaniline (SPAN) is capable of self-doping. The conductivity of SPAN is independent of external protonation in a broad pH range. The self-protonation of sulfonic acid ring-susbstituted polyaniline (in the emeraldine oxidation state) differs from the "self-doping" mechanism of poly(3-(4-butanesulfonato)thiophene)[7] in that the latter system requires an electrochemical force to drive the doping process. (B) It is generally accepted that PAN is insoluble in aqueous solvents and most common organic solvents. Good solubility is essential for a polymer in order to facilitate postsynthetic processing. The solubility of PAN is greatly improved by the presence of the $-SO_3^-$ groups. Specifically, SPAN dissolves in basic aqueous solutions, in contrast to polyaniline, which converts to the insoluble insulating form when treated with basic aqueous solutions. (C) The good environmental stability of the parent polyaniline is further improved by the presence of the $-SO_3^-$ groups on the phenyl rings due to its strong electron-withdrawing properties. (D) The chemical, electrochemical, electrical, and optical properties of SPAN differ from those of the parent polyaniline, reflecting the crystallographic, steric, and electronic effects of the $-SO_3^-$ groups. Theoretical studies of polyaniline[4,8] and other polymers[9a] indicate that the bandgap and bandwidth are affected by the torsion angle (dihedral angle) between adjacent repeating units of the polymer chain. For example, the small reduction of π-conjugation in alkyl derivatives of polyaniline (for example, poly(*o*-toluidine)) is caused primarily by steric effects.[2b–f,4b,c] (E) Being able to dope itself, the polymer may have enhanced optical and electrical response to electrochemical potential as compared with the parent polyaniline. Orata and Buttry[10] showed that the first redox process for polyaniline involves the insertion of anions that neutralize the charge change associated with the redox process. Since the solid-state diffusion of counterions in and out of a polymer during the electrochemical process is often the rate-controlling step in the kinetics, it limits the speed of both the optical and electrical response of the

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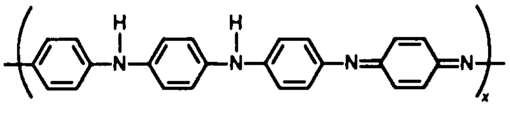
polymer.[11] In a self-doped conjugated polymer, the counterions are not necessarily from the medium in which the polymer is immersed; rather, they originate from moieties covalently bound to the polymer.[11d] Thus, only protons need move,[11d-f] leading to a faster kinetic process.

In the present paper, we focus on the investigation of this novel copolymer of aniline and *o*-aminobenzene- or *m*-aminobenzenesulfonic acid as well as comparative studies with the parent polyaniline. Results of spectroscopic, temperature-dependent dc conductivity, thermopower, susceptibility, electron spin resonance, and electrochemical studies are presented. (A) We demonstrate that SPAN possesses intrinsic protonic-doping ability and that when SPAN is in the emeraldine oxidation state, its conductivity (~0.1 S/cm) remains unchanged upon equilibration with aqueous solutions of pH ≤ 7.5. (B) The solubility of SPAN is improved by the presence of the $-SO_3^-$ groups; i.e., the polymer dissolves in aqueous basic solutions and other common solvents. The alkali-metal salts of SPAN are water-soluble insulating polymers that can be converted back to the self-doped conducting form by treatment with acidic media. Films and powders of the insulating ammonium salt of SPAN spontaneously revert to the self-doped conducting form through dissociation of NH_4^+ into NH_3 (which dissociates as a gas) and H^+ (which protonates the imine units). (C) Absorption spectra of SPAN are highly solvatochromic in homogeneous solutions. The self-protonated SPAN is in the polysemiquinone (polaron electronic) configuration. Greater electron localization in SPAN compared to that in polyaniline is induced by the $-SO_3^-$ groups. (D) The first redox process in cyclic voltammetry is dependent on pH for pH less than 7 due to the active protons on the polymer backbone. (E) Comparative studies of the doping mechanism, as well as electronic, charge transport, and electrochemical properties of SPAN with those of PAN show similarities due to the same backbone structure and present differences because of the sulfonic acid groups on the phenyl rings.

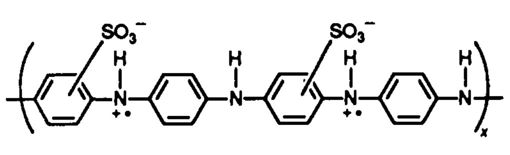
Experimental Section

Synthesis of Ring-Sulfonated, Protonated Polyaniline. The detailed synthetic procedure was reported in a previous paper.[2a] Only a brief description of the synthesis is presented here.

Emeraldine base[12] (0.5 g) was sulfonated by dissolving it in 40 mL of ~30% fuming sulfuric acid (Fisher Scientific) with constant stirring at 5 °C. The color of the solution changed from dark purple to dark blue during ~2 h. The solution was then slowly added to 200 mL of methanol to precipitate most of the product, the temperature being held between 10 and 20 °C by an ice bath. Precipitation was completed by the addition of 100 mL of acetone. The green powder was then collected on a Buchner funnel, and the precipitate cake was washed sufficiently with methanol and then dried under dynamic vacuum for 24 h. FTIR and elemental analyses[13] were consistent with the composition of polymer I, which is ring-sulfonated, protonated polyaniline in the emeraldine oxidation state.



Synthesis of Ring-Sulfonated, Nonprotonated Alkali-Metal Polyaniline Salts. Polymer I (0.5 g) was dissolved in 20 mL of 0.1 M NaOH or KOH solutions stoichiometrically. The color of the solutions was blue-violet. Water was removed by slowly evacuating the vessel containing the polymer solutions at room temperature. The polymers were then dried under dynamic vacuum for 24 h. The ring-sulfonated, nonprotonated sodium (or potassium) polyaniline salt polymer II was obtained as a free-flowing dark purple powder.



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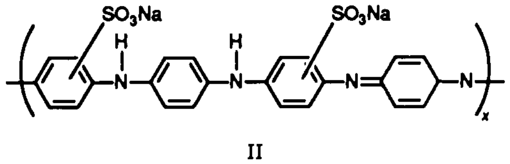

II

Electronic Spectra. Electronic spectra of polymer I were taken on films cast on quartz substrates from 0.1 M NH_4OH solution. Slow evaporation of the resulting aqueous solution of the polymer (ammonium salt, having an analogous constitution to polymer II) in air at room temperature resulted in spontaneous removal of the weak volatile base NH_3 with re-formation of polymer I. Polymer II was dissolved in H_2O and NMP (*N*-methyl-2-pyrrolidinone) solution before spectra were recorded.

Magnetic and Charge-Transport Measurements. Magnetic susceptibility was measured with use of a previously described Faraday technique.[6] Temperature-dependent (30–295 K) electron-spin resonance was measured for polymer I with a Bruker 300 spectrometer and an Oxford 900 temperature-control system. Measurements of the pH dependence of conductivity were carried out by equilibrating polymer I (250 mg) with 500 mL of different pH buffer solutions for 48 h, subsequently drying them under dynamic vacuum for a minimum of 40 h. Conductivities were measured at room temperature on compressed pellets of the powder by using a four-probe technique with a Keithley Model 220 constant-current source, Keithley Model 181 digital nanovoltmeter, and Keithley 617 digital electrometer. Gold wires were attached to the sample surfaces with use of Acheson 502 Electrodag. For the temperature-dependent measurements, the temperature was controlled by a Lake Shore DRC 82C temperature controller. The transport probe was enclosed in a Janis Supervaritemp dewar with He exchange gas.

A similar probe was used for thermoelectric power measurements. The sample was mounted between two single crystal quartz blocks controlled at different temperatures. A copper–constantan thermocouple was also mounted to monitor the temperature difference between the two blocks. During the measurement, the temperature difference is slowly increased to 1 K in 10 min. The thermovoltages of the samples and copper–constantan thermocouple were measured by Keithley 181 nanovolmeters and plotted on the *X* and *Y* axes of a HP 7004B X-Y recorder. The slope of the trace yields the thermopower after correction for the thermovoltage of the gold contacts.[2f]

Cyclic Voltammetry Studies. Cyclic voltammetry studies were carried out with a Hokto Corp. (HC) Model HA-301 potentiostat/galvanostat with an HC HC-201 digital Coulomb meter. An HC HB-111 universal programmer was used for the generation of the sweep signals, which were fed into the HA-301. Voltammograms were recorded on a Hewlett-Packard Model 7046B XYY′ recorder with an optional time base function. A standard three-electrode system was enclosed within a dual-compartment cell with a fine-porosity glass frit separating the working and reference electrodes from the counter electrode. Platinum disks (1.0 cm^2) were used as working and counter electrodes. A Ag/AgCl-saturated KCl electrode was used as a reference electrode throughout the experiment. All cyclic voltammogram studies were performed at a sweep rate of 50 mV/s. Since preliminary observations indicated that air did not have any effect on the cyclic voltammograms, all operations were carried out in the presence of air.

Polymer I was cast on a Pt electrode by evaporating a polymer solution of 0.1 M ammonium hydroxide and subsequently drying it in air. In order to obtain reproducible cyclic voltammograms, the electrode was preconditioned by cycling between −0.2 and +0.4 V for ~10 min (25 cycles), which may involve complete permeation of the electrolyte into the polymer. The cyclic voltammograms for the parent polyaniline were obtained for films cast on Pt electrodes from NMP solution.

Results and Discussion

As synthesized, polymer I is a green powder and polymer II is a purple powder. The conductivities are ~0.1, 10^{-7}, and 10^{-9}

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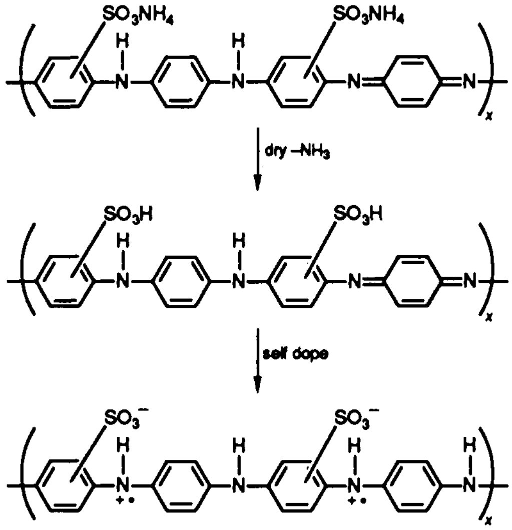
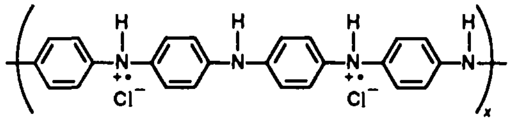
(13) Elemental analyses found for polymer I: C, 52.12; H, 3.98; N, 10.13; S, 11.18; O, 22.59 (oxygen by difference). Calcd for $C_{12}H_9N_2SO_3(H_2O)_{0.98}$: C, 51.67; H, 3.96; N, 10.04; S, 11.49; O, 22.83. FTIR data show absorption maxima at 820 and 870 cm^{-1}, indicative of 1,2,4-trisubstitution, and 1080, 700, and 620 cm^{-1}, which are absorptions of the $-SO_3^-$ function groups.

Scheme I. Conversion of Ammonium Salt of Polymer I to Its Self-Doped Conducting Form



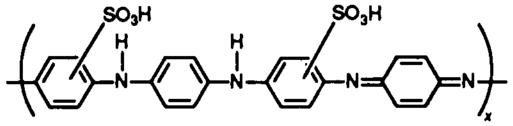
S/cm for polymer I and sodium and potassium salts of polymer I, respectively. The larger conductivity of the sodium salt as compared with that of the potassium salt may be due to a contribution from ionic conductivity of the less massive Na^+. The solubilities of these polymers differ markedly from those of the corresponding parent polyaniline polymers. Polymer I dissolves completely in aqueous 0.1 M NH_4OH or NaOH to form a homogeneous, blue-violet solution with solubility of ~23 mg/mL; in contrast, the analogous emeraldine hydrochloride treated with such solvent only converts to the insoluble base form.[1] When in the basic aqueous solvent, the SPAN polymer backbone is in the emeraldine base structure. The anionic $-SO_3^-$ groups present in the polymer chain probably are responsible for its solubility. Polymer I partially dissolves in NMP to form a dark blue (characteristic[14] of emeraldine base) solution and moderately in DMSO (dimethyl sulfoxide), having a green color (characteristic[14] of protonated emeraldine hydrochloride).



It is of interest to note that when polymer I dissolves in 0.1 M NH_4OH, it forms a homogeneous, blue-violet solution. However, when the polymer is cast on a substrate, the ammonium salt of sulfonated polyaniline dissociates into sulfonic acid and volatile NH_3 gas. A green, shiny conducting film is formed during the drying process. This is a clear indication that, with the removal of NH_3 the dedoped polymer turns back to its polaronic, conducting form as shown schematically in Scheme I. Films obtained in this way can be employed for studies of UV–vis, cyclic voltammetry, etc. Polymer II dissolves in water, yielding a blue-violet solution. It also partially dissolves in NMP and DMSO, resulting in a blue color.

A. Strategy for Synthesis of Sulfonated Polyaniline. It is reasonable to think of the synthesis of self-protonic-doped polyaniline by polymerizing monomers such as *o*-aminobenzene- or *m*-aminobenzenesulfonic acid. However, attempts to polymerize these monomers were neither chemically nor electrochemically successful. Two factors are possibly responsible for this: (1) The strong electron-withdrawing properties of the $-SO_3H$ lowers electron density on the amino groups; therefore under the present synthetic conditions (with use of $(NH_4)_2S_2O_8$, with standard reduction potential of 2.0 V, as an oxidizer), the monomers could not be oxidized. (2) Electrochemistry can certainly elevate the oxidation potential; however, considering the polymerization process, the presence of the bulky group of $-SO_3H$ on the phenyl rings affects the reactivity of two cationic radical monomers for head–tail coupling to form a relatively stable intermediate complex. In agreement with this possibility, recent theoretical calculations on the unsubstituted polyaniline[4b,c] have shown a strong steric interaction between the hydrogen atoms on adjacent rings. Therefore, substitution of the hydrogen atoms by bulky substituents like $-SO_3H$ leads to an increase of the steric hindrance, which is likely to limit the polymerization process. However, on the basis of studies of the electrochemical polymerization of polyaniline by Park et al.,[15] once the polymerization starts, an autocatalytic reaction takes place; therefore, copolymerization of aniline and *o*-aminobenzene- or *m*-aminobenzenesulfonic acid can be achieved. Once again, due to the bulky and electron-withdrawing properties of $-SO_3H$, the copolymerization process can be easily terminated by *o*-aminobenzene- or *m*-aminobenzenesulfonic acid at the end of the polymer chain, resulting in a low molecular weight polymer. In fact, copolymerization leads to a product with conductivity of $\sim 10^{-4}$ S/cm, although the copolymerization gives a chemical composition similar to that of SPAN.

B. Structure Characterization. Elemental analyses, infrared and electronic spectroscopy, conductivity, electron-spin resonance, and cyclic voltammetry studies (see below) are consistent with the sulfonation of emeraldine base with fuming sulfuric acid, yielding the self-protonated polymer I in the emeraldine oxidation state. This polymer can be regarded as being formed hypothetically via the initial formation of the strong acid polymer III, which then immediately protonates the imine nitrogen atoms to form the conducting polymer in a manner analogous to that of strong acids such as HCl.[16]



III

It is implict in the above structure that sulfonation occurs preferentially at alternate rings and that, under the present experimental conditions, only half the rings are sulfonated. This is consistent with the resulting increased stability of the semiquinone form.[1e] Further sulfonation and consequent protonation of amine nitrogen atoms would convert some of the $-(NH)-$ to $-(NH_2^+)-$ and hence reduce conjugation in the polymer. X-ray photoelectron spectroscopy (XPS) studies have confirmed the composition of polymers I and II.[17] XPS[17] and thermogravimetric[18] studies have shown increased stability in vacuum and at elevated temperatures for sulfonated polyaniline as compared with those for emeraldine hydrochloride. X-ray diffraction experiments[19] of both polymers I and II (Na salt of SPAN) show little structural order, similar to that of emeraldine base I but in contrast to the up to 50% crystallinity for emeraldine salt I, emeraldine salt II, and powders of emeraldine base II.[20]

C. Electronic Spectra. Figure 1 shows the electronic spectra of polymer I and emeraldine hydrochloride in film form. There is an absorption band at 320 nm (3.88 eV) and two other absorption bands at 435 nm (2.85 eV) and 850 nm (1.46 eV) for polymer I.[2e] Comparative studies of the electronic absorption spectra of polymer I and emeraldine hydrochloride, and also of polymer II and emeraldine base, provide insight into changes in the molecular geometry caused by the sulfonic group substitution

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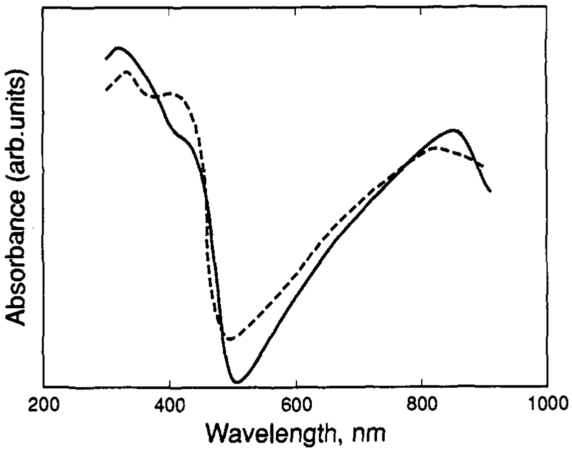

Figure 1. Electronic absorption spectra: —, ring-sulfonated polyaniline film cast from an aqueous NH_4OH solution in a quartz substrate and then dried in air; ---, emeraldine hydrochloride film.

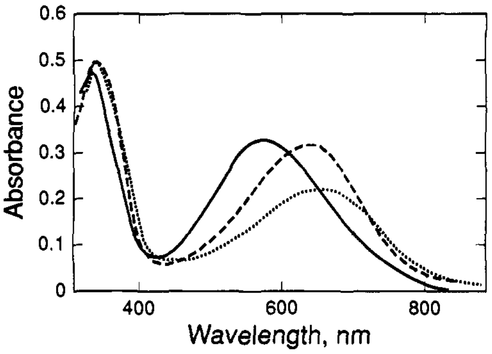

Figure 2. Electronic spectra: —, sodium salt of ring-sulfonated polyaniline in H_2O ([NaSPAN] ≈ 2 × 10^{-3} M), maxima at 320 nm (3.88 eV) and 563 nm (2.20 eV); ···, sodium salt of ring-sulfonated polyaniline in H_2O and NMP ([NaSPAN] ≈ 8 × 10^{-3} M), maxima at 329 nm (3.76 eV) and 620 nm (2.00 eV); ---, emeraldine base in NMP ([EB] ≈ 2 × 10^{-3} M). All spectra were obtained with a cuvette with a 1-mm path length through the solutions.

on the polyaniline backbone.[2e] Solid-state ^{13}C NMR studies[21] have shown that adjacent phenyl rings of the emeraldine backbone are not coplanar. Sulfonation of the phenyl rings on the polyaniline backbone can be expected to increase the torsional angle between adjacent rings even further to relieve steric strain.[4b,c] This affects the electronic transitions of the polymer. The absorption at 320 nm (3.88 eV) for polymer I is assigned to the π–π^* transition based on earlier experimental and theoretical studies[4,8] on the polyaniline system. The other two absorption bands at 435 nm (2.85 eV) and 850 nm (1.46 eV) of polymer I have been assigned to the optical absorption of the metallic polaron band of the conducting form.[4,8] The hypsochromic shift of the π–π^* transition on going from emeraldine hydrochloride (3.81 eV) to polymer I (3.88 eV) and the bathochromic shift of the polaron band transition are in accord with decreased extent of conjugation caused by increased phenyl ring torsion angle, which results from steric repulsion between the $-SO_3^-$ groups and hydrogens on the adjacent phenyl rings.

The electronic spectra of polymer II in H_2O, H_2O and NMP, and emeraldine base in NMP consist of two major absorption bands (Figure 2). The first absorption band is at ~320 nm (3.88 eV), and the second peak is ~620 nm (~2.0 eV). The first absorption band at 320 nm (3.88 eV) for polymer II is assigned to the π–π^* transition based on earlier studies of polyaniline.[4,8] This absorption shifts somewhat with increasing oligomer length.[22] The π–π^* transition band shows a hypsochromic shift from 3.76 eV for emeraldine base to 3.88 eV for polymer II, implying a decrease in the extent of conjugation and an increase in the band gap. From this, it is inferred that the adjacent phenyl rings of the polymer have larger torsion angles with respect to the plane of the nitrogen atoms due to the possible steric repulsion between the $-SO_3^-Na^+$ groups and hydrogens on the adjacent phenyl rings. The second absorption band at ~2 eV for polymer II is assigned to the "exciton" transition.[8] When the absorption is intrachain, the excitation leads to formation of a "molecular" exciton (positive charge on adjacent benzenoid units bound to the negative charge centered on the quinoid),[1c,4b,c,8b] while interchain charge transfer from the HOMO to LUMO may lead to the formation of positive and negative polarons.[1c,8,23] These local changes, reflected by the exciton transition, are sensitive to a chain conformation related process since strong solvatochromism is observed for the exciton transition. When polymer II is dissolved in water, the solution shows a 2.20-eV absorption. However, the transition is changed from 2.20 to 2.00 eV by adding NMP into the solution. As mentioned above, polymer II, which is soluble in water and partially in NMP, interacts readily with water to increase the degree of freedom and therefore the entropy of solvation. We suggest that the loss of the planarity of the chain (more "coil-like" conformation) decreases the conjugation of the polymer system; as a consequence, the exciton transition is shifted to higher energies. However, when NMP is added to the polymer II water solution, the less polar solvent promotes a thermodynamically more stable chain conformation and restricts the polymer to lower energy, high-planarity states. Such stiffness increases the conjugation of the system, which yields a lower energy transition, i.e., a red shift. An alternative explanation is that addition of NMP promotes some degree of counterion (Na^+) condensation to cause a global polymer configurational transition to an expanded form.[9b]

D. Charge Transport. 1. pH Dependence of Conductivity. It is known that ideal emeraldine base consists of a 1:1 copolymer of diamine and diimine alternating repeating units.[1] When it is treated with Brönsted acids, the imine nitrogen atom is protonated to form radical cations by an internal redox reaction.[1] This transition is known as the instability of diamine and diprotonated diimine toward reorganization of the electronic structure and formation of two semiquinone radical cations,[1c,6] i.e., the polaron metallic state. The degree of protonation and resulting conductivity are controlled by changing the pH of the Brönsted acid doping solutions.[1a] At pH greater than 4, the emeraldine polymer is essentially undoped and is an insulator. Its conductivity reaches the maximum value when it is treated at pH less than 1; i.e., the protonation of quinone diimine units is complete only at low pH. In this protonation process, the insertion of anions to ensure electrical neutrality is involved.[1a] There is a striking difference in the pH dependence of the conductivity for polymer I and that for polyaniline. For polymer I, there are intrinsic Brönsted acid groups (assuming volume of 1000 Å^3 for the two-ring polymer repeat unit (an effective diameter of ~11 Å for the polymer chain), the proton concentration due to the sulfonic acid groups is ~1.5 M) on the polymer backbone. Hence, its conductivity is independent of pH for values smaller or equal to 7.5 (Figure 3). This clearly shows that the internal acid–base equilibrium of SPAN is not affected by the external medium in this pH range.

Undoped imine nitrogen atoms and the associated quinoid groups are expected to behave as barriers for electron conduction along a chain as well as between chains.[2c,24] Hence, if the imine nitrogen atoms of I were not fully doped, the conductivity would depend on pH in the range of 0–7.5. Thus, the pH independence of the conductivity of polymer I in this range shows that the

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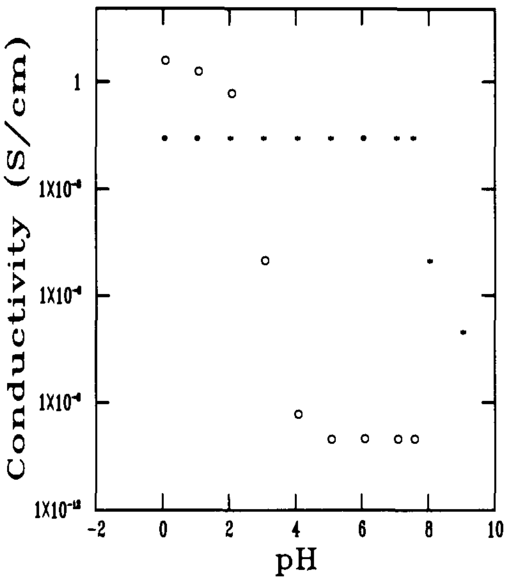


Figure 3. pH dependence of conductivities for ring-sulfonated polyaniline (*) and the emeraldine hydrochloride form of polyaniline (O).

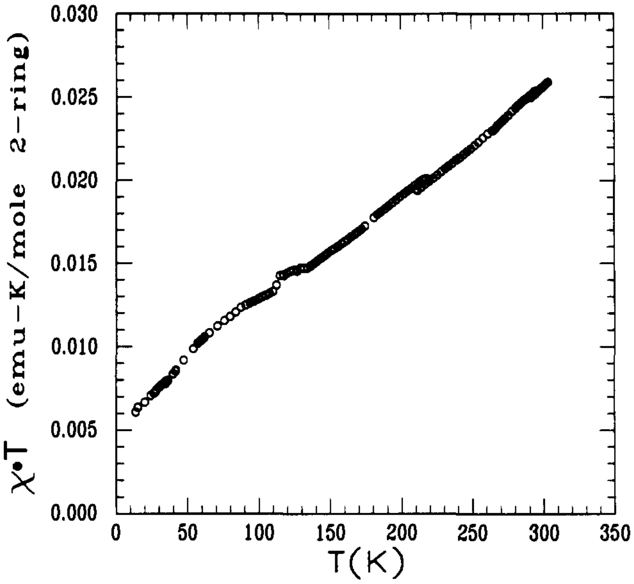
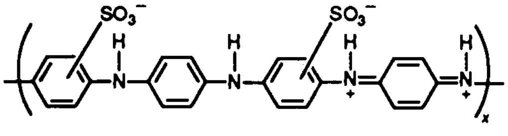


Figure 4. Spin susceptibility times temperature as a function of temperature of ring-sulfonated polyaniline. A core diamagnetism of -1.45×10^{-4} emu/mol-two rings was utilized to convert total susceptibility to spin susceptibility. This was determined with the experimental core diamagnetism of the emeraldine backbone[6] plus the Pascal constant value for the sulfonic group.

polymer is fully (50%) self-protonated.

2. Magnetic Properties. If the fully self-doped polyaniline was in the bipolaron configuration



it would be diamagnetic. However, magnetic susceptibility and ESR data demonstrate the presence of both "Curie-like" susceptibility and temperature-independent "Pauli-like" susceptibility. The plot of spin susceptibility times temperature (χT) vs temperature (Figure 4) yields an effective Pauli susceptibility for each sign of spin (from the slope) of ~0.8 state/eV-two rings and an effective Curie spin concentration (from the $T = 0$ intercept) of 0.02 spin/two rings.

The Pauli susceptibility is consistent with significant electron delocalization upon addition of protons from $-SO_3H$ to the imine

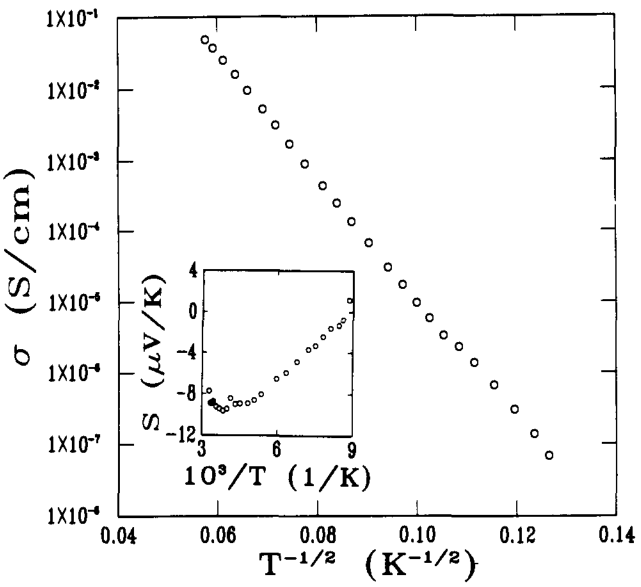


Figure 5. Temperature dependence of the conductivity ring-sulfonated polyaniline. The inset shows the thermopower vs reciprocal temperature for I.

sites. It was proposed[1c,6] that, upon protonation of imine, the resulting doubly positive bipolaron-type structure is unstable to formation of a nearly ordered array of polarons, which are essentially equally spaced along the emeraldine chain. This is also the case for polymer I. ESR data show that the polymer is strongly paramagnetic and has an ~0.3-G peak to peak line width at room temperature with an intensity similar to that of emeraldine hydrochloride.[6,25] This result supports that polymer I is in the polysemiquinone radical-cation (polaron energy band) state.[1c,6,8d] It is noted that the ESR line width of SPAN is much less sensitive to the presence of oxygen than is the case for emeraldine hydrochloride.

3. Temperature and Electric Field Dependence of Conductivity. The conductivity of polymer I is 1 order of magnitude smaller ($\sigma \approx 0.1$ S/cm vs 1–5 S/cm at room temperature in laboratory air for pressed pellets) and has a much stronger temperature dependence than that of emeraldine hydrochloride, indicating greater electron localization[2c,d,f] in SPAN. The best fit for the temperature dependence of the conductivity is $\sigma \approx \exp[-(T_0/T)^{1/2}]$ as shown in Figure 5 with $T_0 = 39000$ K. There are several models[2c,f,26] for this kind of temperature dependence: quasi-one-dimensional variable-range hopping (q1d-VRH),[26a,b] 3d-VRH with a Coulomb gap,[26c] and charging energy limited tunneling (CELT) for granular metals.[26d] In order to understand the conduction mechanism, we also measured the electric field dependence of the conductivity ($\sigma(E)$) at low temperatures[27] and the thermoelectric power (inset, Figure 5). The results show $\sigma(E) \propto \exp(E/E_0)$ at high fields, which eliminates the CELT model as the proper model (CELT predicts $\sigma \propto \exp(E_0'/E)$, where E_0' is a constant) for charge conduction in I.[2d,26d] The functional behavior of $\sigma(E) \propto \exp(E/E_0)$ is in accordance with variable-range hopping. Thermopower experiments show $S(T) = S_0 + B/T$ (S_0 and B constants) (inset of Figure 5), which is consistent with q1d-VRH[2c,f] but contrary to the Coulomb gap model for which S is a constant. $\sigma(E)$ and $S(T)$ data suggest q1d-VRH is the appropriate model for conduction.[2c,f] For q1d-VRH, interchain hopping contributes $S(T)$ = constant and intrachain hopping $S(T) \propto 1/T$ to the thermopower. Within the framework of the q1d-

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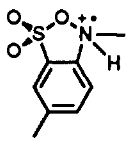
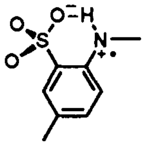
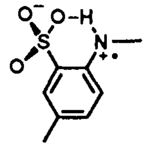
VRH, T_0 is defined[2c,26b] as $T_0 = 8\alpha/(N(E_F)Zk_B)$, where k_B is the Boltzmann constant, $N(E_F)$ is the density of states at the Fermi energy (~0.8 state/two rings for each sign of spin, nearly the same as for poly(*o*-toluidine) hydrochloride[2c]), Z is the number of the nearest-neighbor chains (~4), and α^{-1} is the localization length. Although this temperature dependence is similar to that of emeraldine hydrochloride, T_0 for polymer I is 39 000 K, much larger than 6000 K for unoriented emeraldine hydrochloride. The larger T_0 implies that there is a much greater localization of charge carriers in polymer I as compared with that in emeraldine hydrochloride,[28] or even that in its methyl ring derivative poly(*o*-toluidine) hydrochloride.[2c] Utilizing this expression for T_0, we obtain an effective localization length of α^{-1} = 6 Å, less than that of poly(*o*-toluidine) hydrochloride (α^{-1} = 8 Å[2c,f]) and much smaller than that of emeraldine hydrochloride ($\alpha^{-1} \approx$ 20 Å perpendicular to the chain and ~40 Å parallel to the chain[28]).

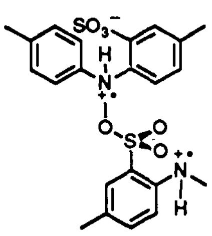
The origin of the lower conductivity and greater electron localization of polymer I can be attributed to several factors. First, by analogy with earlier studies of poly(*o*-toluidine),[2c] the lowered conductivity is caused by the decreased interchain diffusion of the charge carriers. This is induced by increased separation of the polymer chains due to the presence of side groups and lower crystallographic order (hence the reduced coherence) between the chains. Second, $-SO_3^-$ is likely to force the chain out of planarity by twisting the phenyl rings relative to one another to lower the overlap of orbitals along the conjugated system.[2b] As a consequence, the conduction electron wave functions in I are expected to be substantially more localized than those in emeraldine hydochloride, leading to a lower mobility for the charge carriers both along the polymer chain and between polymer chains. The XPS data[17] show that the positive charge carriers are much more localized on the nitrogen atoms in SPAN than those in emeraldine hydrochloride. This may be caused by a strong electrostatic interaction between the $-SO_3^-$ function groups and cationic radical nitrogen atoms or H bonding through space to form five- or six-member rings, which are in energetically favorable configurations

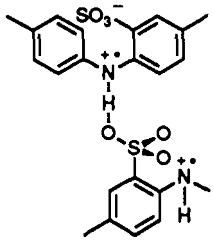






Such configurations can effectively localize the positive charge around the nitrogen atoms. Finally, interaction between the $-SO_3^-$ function groups and cationic radical nitrogen atoms or amine hydrogens may also take place between two adjacent chains





in addition to the intrachain interaction described above. This type of interchain interaction may play an important role in increasing the three-dimensionality of the charge and spin motion. The detailed origins of localization are under continuing investigation.

E. Redox Properties. Cyclic voltammograms of polymer I in 1 M HCl and pH 3 buffer solution are shown in Figure 6. For the one in 1 M HCl, it consists of two redox peaks: the first peak has an $E_{1/2}$ = 0.28 V vs Ag/AgCl (saturated) and the second an $E_{1/2}$ = 0.77 V. The cyclic voltammogram is essentially identical with that of parent polyaniline,[29] except that the two sets of redox peaks are closer together. Its cyclic voltammogram is similar to that of poly(*o*-toluidine)[2b] in which the two sets of redox peaks are also closer together than they are in the parent polyaniline.

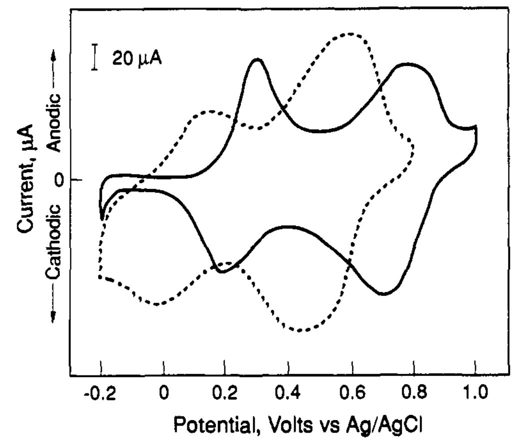


Figure 6. Cyclic voltammograms (50 mV/s) of ring-sulfonated polyaniline in 1.0 M HCl (—) and pH 3 buffer solutions (- - -).

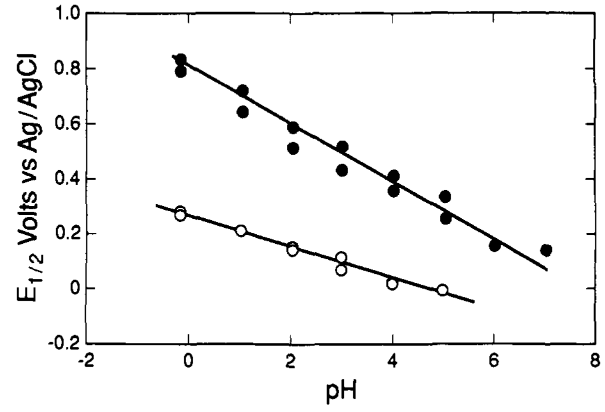
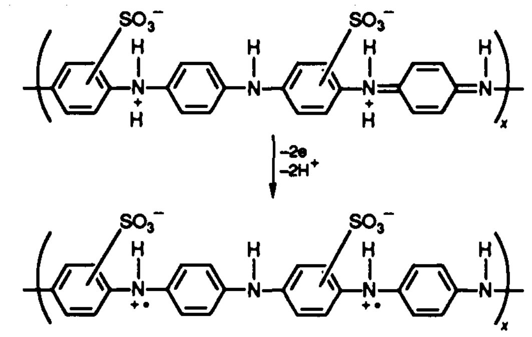


Figure 7. Relationship between $E_{1/2}$ (50 mV/s) and pH: open circles indicate the first and closed circles the second redox process of ring-sulfonated polyaniline in pH range 1–7.

Scheme II



The electrochemical process associated with the first peak is consistent with the equation given as Scheme II. It is analogous to that observed in parent polyaniline at pH values below zero;[29] the $E_{1/2}$ value of the peak shifts at the rate of 59 mV/pH (Figure 7), indicating the loss of an equal number of protons and electrons. This is caused by the high local concentration of protons associated with the $-SO_3^-$ groups in the vicinity of the polyaniline backbone.

The electrochemical equation consistent with second redox peak is given as Scheme III. The $E_{1/2}$ value changes at rate of 118 mV/pH (Figure 7). This is consistent with the loss of two protons per electron.[29]

When the potential was scanned between 0.0 and 0.9 V, the color of polymer I changed from transparent yellow at 0.0 V

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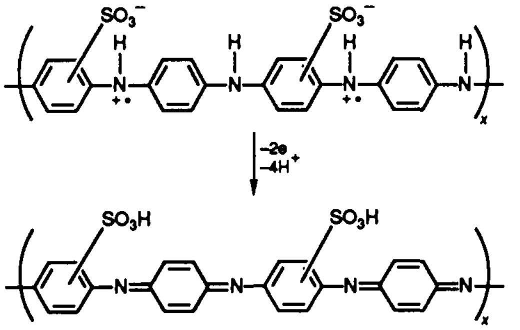
Scheme III



(reduced state), to green at 0.5 V (emeraldine oxidation state) and to blue at 0.8 V (fully oxidized state) in a manner similar to that of polyaniline.[29]

The $E_{1/2}$ of the first redox process in 1 M HCl occurs at a higher potential than that observed in parent polyaniline ($E_{1/2}$ = 0.23 V vs Ag/AgCl (saturated)). This has also been observed in the case of poly(*o*-toluidine)[2b] and has been ascribed to the fact that the bulky substituent of the ring will cause ring twisting and hence a reduction in chain conjugation, which will result in reduced stability of the polysemiquinone radical cation formed during the first redox process. Since the polysemiquinone radical cation is less stable than in the parent polyaniline, it will require a higher potential for its formation.

For both polymer I and poly(*o*-toluidine), the second redox peak occurs at a lower potential than in the parent polyaniline ($E_{1/2}$ = 0.79 V is Ag/AgCl (saturated)) in 1 M HCl. This shows that the oxidation of the polysemiquinone with simultaneous deprotonation occurs more easily in polymer I and poly(*o*-toluidine) than in the parent polyaniline. This may be caused by formation of imine nitrogens with a wider angle to release the steric strain,[30] leading to a lower $E_{1/2}$ for the second redox process.

It was found by Kobayashi et al.[31] that, in a potential scan range between 0.0 and 0.6 V vs SCE in 1.0 M HCl, polyaniline films are fairly stable and the shape of the voltammograms changed little during 5×10^3 cycles. A similar stability was observed for polymer I; the voltammograms of a film in 1.0 M HCl remained almost the same after a 48-h scan in the range of 0.0 and 0.6 V at 50 mV/s (approximately 5000 cycles). However, once the potential is taken up to 0.8 V, irreversible degradation begins to occur, as indeed found in parent polyaniline,[31] and a third set of peaks appears between the two original peaks due to the hydrolysis of the imine to form benzoquinone.[10]

Conclusion

The present study demonstrates that sulfonic ring substituted polyaniline can be synthesized chemically and that it is a self-doped conducting polymer. Insulating salts of the polymer have been prepared by treating polymer I with bases such as NaOH and KOH. Elemental analyses and spectroscopic data suggest that approximately one $-SO_3H$ group is substituted for every two phenyl rings. The solubilities of polymer I and its sodium salt changed markedly from those of the parent polyanilines. The conductivity is independent of pH in the range of equal to and smaller than 7.5. The transport studies show that the charge is more localized in polymer I than in the polyaniline system. This localization is caused most likely by the substituent and electronic effects of the $-SO_3^-$ groups. The cyclic voltammograms consist of two pairs of well-resolved redox peaks corresponding to the formation of the semiquinone radical cation and to the formation of the deprotonated, fully oxidized pernigraniline form of the polymer, respectively.

Two effects (steric and electronic) are associated with the sulfonic substituent. The steric effect is largely responsible for (1) the decrease of the conjugation in the π system, (2) the hypsochromic shifts of the π–π^* transition band in the UV region, and (3) the decreased stability of polysemiquinone radical cation as compared to that of the parent polyaniline. The electronic effect is mainly responsible for (1) solubility in basic aqueous solutions, (2) independence of the conductivity on pH in the range equal to and smaller than 7.5, (3) charge localization, and (4) the pH dependence of the potential of the first redox process.

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