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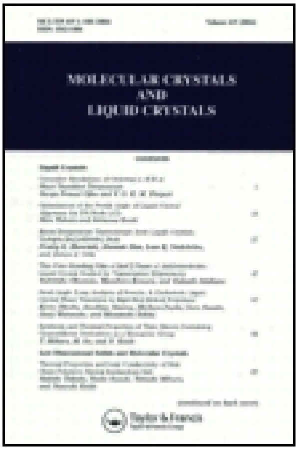

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Sulfonic Acid Ring-Substituted Polyaniline, A Self-Doped Conducting Polymer

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Sulfonic Acid Ring-Substituted Polyaniline, A Self-Doped Conducting Polymer

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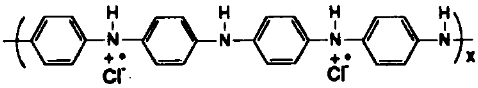
Sulfonic acid ring-substituted polyaniline has been synthesized and characterized by elemental analysis, FTIR, UV-vis and electron spin resonance spectroscopy. Approximately 50% of the total number of phenyl rings in the polymer are mono-substituted by $-SO_3^-$ groups. Without external doping, the ring-sulfonated polyaniline has a conductivity of ~0.03 S/cm; it is therefore a "self-doped" conducting polymer. The water soluble sodium salt of the ring-sulfonated polyaniline is an insulator and can be reversibly converted back to the self-doped conducting form by treatment with aqueous acid.

Polyaniline is a conducting polymer whose electronic properties can be reversibly controlled by both protonation and charge transfer doping (i.e., by changing the oxidation state of the polymer).[1,2] Sulfonic acid ring-substituted polyaniline, differs from the parent polyaniline in number of ways: (1) It is soluble in basic aqueous solutions due to the presence of $-SO_3^-$ groups on the phenyl rings. The sodium salt, formed by treating it with aqueous NaOH, is a water soluble insulating polymer that can be converted back to the self-doped conducting form by treatment with aqueous HCl. (2) The ring-sulfonated polyaniline is "self-doped," it differs from the parent (nonsubstituted) polyaniline in that its conductivity (~0.03 S/cm) remains unchanged when it is equilibrated with aqueous solutions of pH $\leq$ 7. In contrast, the parent polyaniline is converted to an insulator for pH $\geq$ 4.

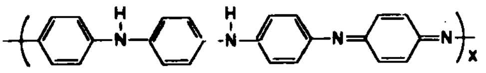
It is demonstrated here that the electronic properties of ring-sulfonated polyaniline and its sodium salt when compared with emeraldine hydrochloride and base show similarities due to the same backbone structure and differences because of $-SO_3^-$ groups on the phenyl rings.

EXPERIMENTAL

Synthesis of ring-sulfonated, protonated, polyaniline. Emeraldine hydrochloride powder, **compound I**

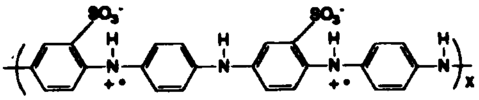


was synthesized from an aqueous solution of aniline, $(NH_4)S_2O_8$ and HCl; it was then converted to analytically pure (Table I) emeraldine base, **compound II**



using a previously described method.[3]

0.5 g of emeraldine base was sulfonated by dissolving it in 40 ml of fuming sulfuric acid (Fisher Scientific) with constant stirring at room temperature for ~2 hours. The solution was then slowly added during ~20 minutes to 200 ml of methanol to precipitate most of the product. The temperature was held between 10~20°C by an ice bath during this procedure. 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 at least 10 times with ~50 ml portions of methanol until the filtrate had a pH of 7 when tested by wet pH paper. It was then dried under dynamic vacuum for 24 hours. Elemental analyses (Table I) were consistent with the composition, assigned to **compound III**



viz., ring-sulfonated, protonated polyaniline in the emeraldine oxidation state.

TABLE I

Elemental Analyses[a] of Chemically Synthesized Sulfonic Acid Ring-Substituted Polyaniline

sample	C	H	N	S	O[b]	Total	Formula
PAN[c] (cal.)	79.54	5.00	15.46	—	—	100	$C_{12}H_9N_2$
PAN[c] (found)	79.14	4.96	15.16	—	—	99.26	
SPAN[c] (cal.)	51.67	3.96	10.04	11.49	22.84	100.00	$C_{12}H_9N_2SO_3(H_2O)_{0.98}$
SPAN[c] (found)	52.12	3.98	10.13	11.18	22.59	100.00	

[a] C, H, and N analyses were performed by Dr. R. Kohli at U. of Pennsylvania. Sulfur analysis was carried out by M-H-W Laboratories, Phoenix, AZ.

[b] Oxygen content is obtained by 100-(H% + C% + N% + S%).

[c] PAN refers to the emeraldine base form of polyaniline and SPAN to ring-sulfonated polyaniline.

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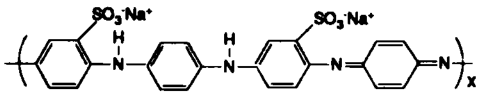
Synthesis of ring-sulfonated, non-protonated sodium polyaniline salt. 1.0 g of compound III was dissolved in 40 ml of 0.1 M NaOH solution. The color of the solution was blue-violet. After removing water from the solution, the ring-sulfonated, non-protonated sodium polyaniline salt, **compound IV**,



was obtained as a free flowing dark purple powder.

Electronic spectra. For taking electronic spectra compound III was dissolved in 0.1 M NH_4OH to form a homogeneous solution, which was then cast on a quartz substrate. Slow evaporation of the resulting aqueous solution of the polymer (ammonium salt; having an analogous constitution to the sodium salt) in air at room temperature resulted in spontaneous removal of the weak volatile base, NH_3 with reformation of compound III. Compound IV was dissolved in H_2O for taking the spectra.

Electron spin resonance. Temperature dependent (30 K to 295 K) electron spin resonance was measured for compound III using a Bruker 300 spectrometer and an Oxford 900 temperature control system.

Conductivity measurement. Conductivities of compound III and IV were measured at room temperature on compressed pellets of the powder by using four point probe techniques with a Keithley 220 constant current source, Keithley 181 digital voltmeter and 617 digital electrometer.

RESULTS AND DISCUSSION

Elemental analyses, infrared, electronic and electron spin resonance spectroscopy and conductivity studies are consistent with the sulfonation of emeraldine base with fuming sulfuric acid proceeding to give a self-doped, ring-sulfonated, protonated form of the emeraldine oxidative state of polyaniline, compound III. The absorption peaks at 1080, 700 and 620 cm^{-1} in the FTIR spectrum of the self-doped polyaniline, Figure 1, are consistent with the presence[4] of $-SO_3^-$ groups attached to the aromatic rings. The absorption maxima at 820 and 870 cm^{-1} are indicative of 1, 2, 4 trisubstitutents on the rings. These absorptions are not present in the 1, 2 disubstituted emeraldine base from which the compound III was synthesized.

The conductivity of compound III ($\sigma \sim 0.03$ S/cm) is lower than that of emeraldine hydrochloride measured under the same experimental conditions ($\sigma \sim 1-5$ S/cm; laboratory air).[5,6] The lower conductivity of compound III, as compared with that of emeraldine hydrochloride, can be rationalized by analogy with earlier studies of poly(o-toluidine)[7] and poly(o-methoxy aniline),[8] i.e., the lower conductivity is in accord with increased conduction electron localization induced by the increased separation of the polymer chains due to the presence of side groups or poorer alignment. However, the conductivity of compound III remains the same after it was equilibrated with H_2O indicating that the polymer is indeed "self-doped."

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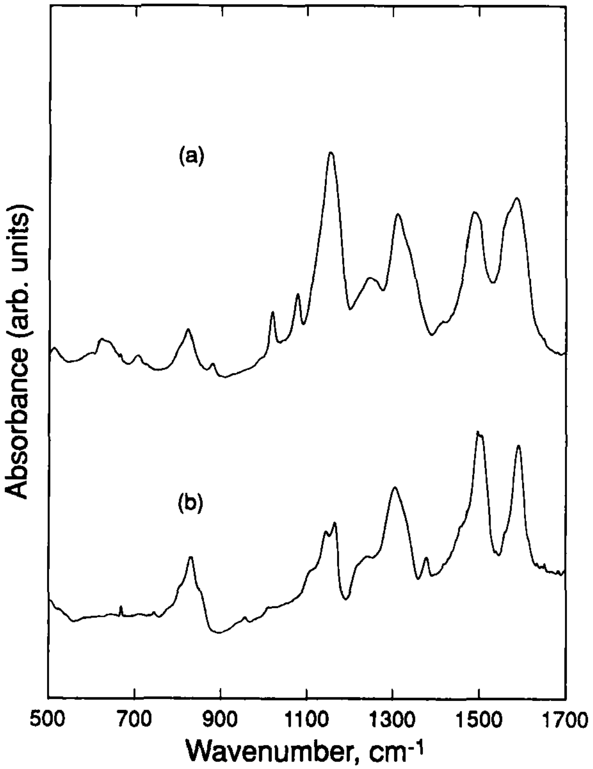


FIGURE 1 FTIR spectra of (a) self-doped, ring-sulfonated polyaniline; (b) emeraldine base (in wave numbers, cm^{-1}).

Compound IV which is in the structure as emeraldine base has the conductivity of $\sim 10^{-7}$ S/cm.

Comparisons of the electronic absorption spectra of compound III and emeraldine hydrochloride, and also of compound IV and emeraldine base provide insight into changes in the molecular geometry caused by the sulfonic acid group-substitution on the polyaniline backbone. Solid state ^{13}C NMR studies[9] have shown that adjacent phenyl rings of the emeraldine backbone are not coplanar. Introduction of sulfonic acid groups on phenyl rings of the polyaniline backbone can be expected to increase the torsional angle between adjacent rings even further to relieve steric strain[10] affecting the electronic absorption spectra and reducing the conductivity, i.e., poorer conjugation. The electronic spectra of compound III and emeraldine hydrochloride are given in Figure 2. The high energy absorption band at 320 nm (3.88 eV) and 326 nm (3.81 eV) for compound III and emeraldine hydrochloride, respectively, is assigned to the $\pi - \pi^*$ transition based on earlier experimental and theoretical studies.[1,11,12] The other two absorption bands at 435 nm (2.85 eV) and 850 nm (1.46 eV) for the compound III, 413 nm (3.00 eV) and 826 nm (1.50 eV) for emeraldine hydrochloride, have been assigned to the optical absorption of the metallic polaron band of the salt form.[13,14] The hypsochromic shift of the $\pi - \pi^*$ transition in going from emeraldine hydrochloride to compound III is in accord

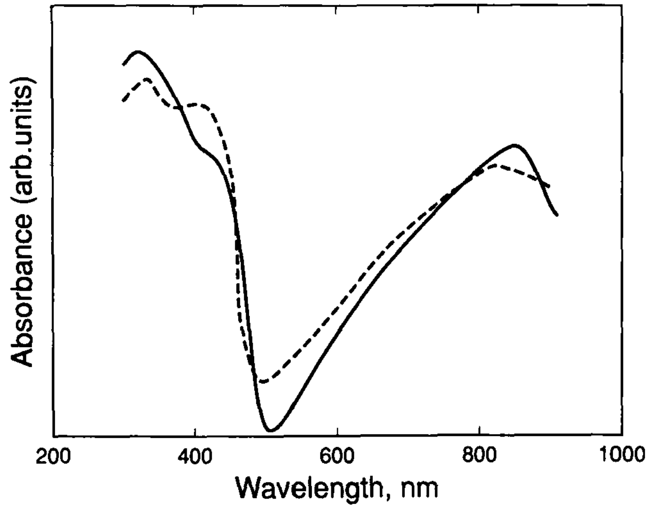
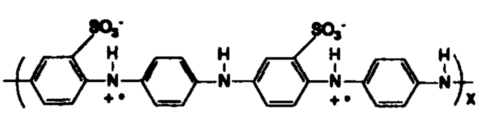


FIGURE 2 Electronic absorption spectra of (a) —— self-doped polyaniline film cast from an aqueous NH_4OH solution on a quartz substrate, then dried in air; (b) - - - - emeraldine hydrochloride film.

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 bathochromic shift of the polaron band transition is also in agreement with relative energy band shifts expected for increased ring torsion angles.[10]

Temperature dependent electron spin resonance studies show a ~0.4 G peak to peak linewidth for compound III similar in intensity to that of emeraldine hydrochloride.[15] This result supports the conclusion that compound III is in the polysemiquinone (polaron energy band) state.[13,15] The stabilization of the polysemiquinone form,



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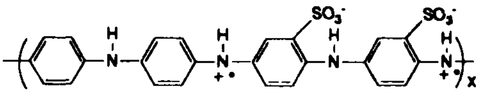

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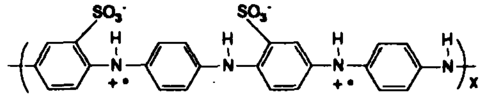
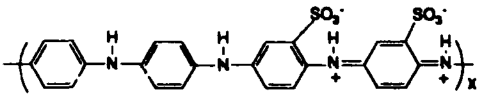


instead of the spinless diprotonated imine (bipolaron form),



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may occur regardless of whether the $-SO_3^-$ groups are on adjacent or alternating rings since it is as yet unknown if the $-SO_3^-$ groups added in ortho or meta, or random positions with respect to the radical cationic nitrogens.

The electronic spectra of compound IV and emeraldine base consist of two major absorption bands, Figure 3. The first absorption band at 320 nm (3.88 eV) and 330 nm (3.76 eV) for compound IV and emeraldine base, respectively, is assigned to the $\pi - \pi^*$ transition based on the earlier studies of polyaniline.[1,13] This absorption shifts somewhat with increasing oligomer length.[16] The $\pi - \pi^*$ transition band shows a hypsochromic shift from 3.76 eV for emeraldine base to 3.88 eV for compound IV. This blue shift implies a decrease in the extent of conjugation and an increase in the band gap, which is consistent with the adjacent phenyl rings of the polymer having larger torsion angles with respect to the plane of the nitrogens due to the presence of $-SO_3^-Na^+$ groups. The second absorption band at 563 nm (2.20 eV) and 630 nm (~2.00 eV) for compound IV in H_2O and emeraldine base in NMP (N-Methyl-2-Pyrrolidinone) respectively also has a substantial hypsochromic shift with sulfonation. This band has been assigned to an absorption from the highest occupied molecular orbital (HOMO) based band centered on the benzenoid units to the lowest unoccupied molecular orbital (LUMO) centered on the quinoid units. When the absorption is intrachain, the excitation leads to formation of a "molecular" exciton (with positive charge on adjacent benzenoid units bound to the negative charge centered of the quinoid),[14,17] while interchain charge transfer from HOMO to LUMO may lead to formation of positive and negative polarons.[14,18] The increase in this transition energy is also in accord with increased ring torsion angles due to the presence of $-SO_3^-Na^+$ groups on the phenyl rings. The increased torsional angle may mainly result from two effects: (1) steric repulsion between $-SO_3^-Na^+$ groups and hydrogens on the adjacent phenyl rings and (2) solvatochromic effect between NMP and H_2O. Based on earlier studies of poly(o-toluidine),[7] the steric effect of $-SO_3^-Na^+$ groups play an important role in increasing this transition energy.

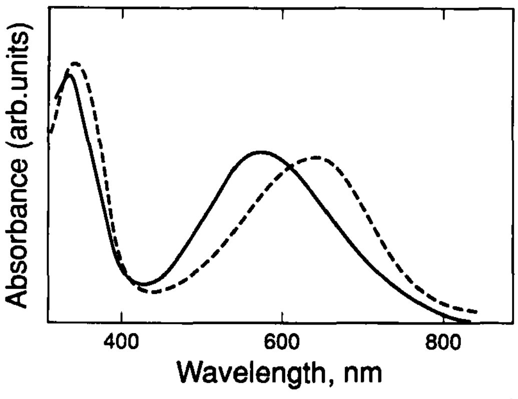

FIGURE 3 Electronic absorption spectra of (a) —— ring-sulfonated polyaniline in aqueous NaOH, maxima at 320 nm (3.88 eV) and 563 nm (2.20 eV); (b) - - - - emeraldine base in NMP, maxima at 330 nm (3.88 eV) and 630 nm (~2.00 eV).

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CONCLUSIONS

The present study demonstrates that sulfonic acid substituted polyaniline can be synthesized chemically and that it is a self-doped conducting polymer. Insulating salts of sulfonic acid ring-substituted polyaniline have been prepared by treating the self-doped polyaniline with bases such as NaOH. Elemental analysis and FTIR data suggest that approximately one $-SO_3H$ group is substituted for every two phenyl rings. The conductivity is independent of pH in the range of pH values smaller than or equal 7. Two effects, steric and electronic, are associated with the sulfonic acid substituent. The steric effect is largely responsible for: (1) the decrease in the conductivity through: (A) decreased interchain transport or (B) reduced conjugation of π system; (2) the hypsochromic shifts of the $\pi - \pi^*$ transition band in the UV-region. The electronic effect is mainly responsible for independence of the conductivity on pH in the range smaller than or equal to 7. It may also lead to greater localization of charge due to the proximity of the $-SO_3$ to the polyaniline backbone.

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