Structure Characterization of Self-Acid-Doped Sulfonic Acid Ring-Substituted Polyaniline in Its Aqueous Solutions and as Solid Film

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ABSTRACT: Self-doped sulfonic acid ring-substituted polyaniline (SPAN) reported so far is only slightly soluble in water. This work reports the synthesis route of SPAN in water with a solid content at least 50% by weight, which is stable (without precipitation) for more than 1 year and can be cast into free-standing films. The protons on the bound sulfonic acid groups can dope the imine nitrogens both in its aqueous form and as a solid film as evidenced by the presence of polaron absorption bands in its UV−vis spectra and of free spins from the ESR measurement. Titration analysis and spectroscopic data of the polymer in aqueous solution and as solid film, respectively, show that, surprisingly, the fractions of $-SO_3H$ groups that protonate (dope) the imine nitrogens to give semiquinone radical cations are equal in both cases, about 0.60 (equivalent to the doping level, 0.30). However, the free spins in the aqueous solution are more localized than those in the solid film. The thermostability of SPAN is also investigated. The conductivity of SPAN film (at 25 °C, 0.01 S/cm) increases with temperature from −10 (0.002 S/cm) to 190 °C (0.09 S/cm) and decreases with temperature from 190 to 225 °C (0.06 S/cm) due to thermal undoping accompanying a loss of some polarons as confirmed by the UV−vis, IR, and TGA analyses. After the heating scan, the conductivity at room temperature drops by a factor of 10^3.

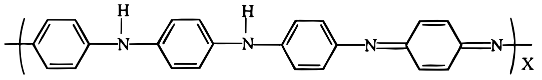
Introduction

Polyaniline (PAn) is the first conducting polymer that can be doped to a conducting form by external protonic acid without changing the number of π-electrons, in addition to the normal charge transfer process.[1] When acid groups are introduced to the polymer chain to make the polymer conducting, this type of doping is designated “self-doping”[2] or “self-acid-doping”.[3] Yue and Epstein[2] have synthesized the first protonic acid self-doped PAn by reaction of emeraldine base with fuming sulfuric acid to give a sulfonic acid ring-substituted PAn (SPAN) powder having a conductivity of about 0.1 S/cm. However, the as-prepared polymer is only slightly soluble in water. Since good solubility is essential for a polymer to facilitate postsynthesetic processing, the solubility of SPAN in water can be improved by dissolving it in aqueous basic solutions of NH_4OH due to the presence of the $-SO_3^-$ groups. When in the basic aqueous solutions, the SPAN polymer backbone is in the emeraldine base structure. 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.)[4] Similar cases were found in the recent studies by Diaz and co-workers[5,6] on aniline copolymers with phenylsulfonic acid groups bound on the amine nitrogens of the chains, which are soluble only in aqueous NH_4OH or alkali but not in pure water. Recently, the first water-soluble self-acid-doped conducting polyaniline, poly(aniline-*co-N*-propanesulfonic acid aniline) (PAPSAH), was successfully synthesized by us,[3] which can be cast into free-standing films directly from aqueous solutions. A comparison of the electronic structures of this polymer in aqueous solution and as solid film has been made.[7] Another type of self-acid-doped conducting polyaniline derived from *o*-aminobenzylphosphonic acid, poly(*o*-aminobenzylphosphonic acid), which is soluble in dilute aqueous NH_4OH but insoluble in water, has also been synthesized by Tan et al.[8]

The structural and electronic properties of SPAN in its solid film or powder have been studied.[4] However, the insolubility of SPAN in water restricts further studies about its electronic structure in aqueous solution. Here, we report a successful approach to prepare SPAN aqueous solution at a solid content at least above 50% by weight; a free-standing film of SPAN with a conductivity of 10^{-2} S/cm at room temperature can be obtained by casting from the aqueous solution. We also report the electronic structures of this polymer both in aqueous solution and as solid film as investigated by use of titration, electronic spectra, X-ray photoelectron spectroscopy, and electron spin resonance. The good environmental stability of SPAN afforded by the presence of $-SO_3^-$ groups on the phenyl rings, due to its strong electron-withdrawing properties is also proved. The conductivity of the SPAN film increases with temperature up to 190 °C, after which the conductivity drops as a result of thermal undoping.

Experimental Section

Synthesis. The emeraldine base form of PAn (**I**) was synthesized by use of the chemical oxidation method similar to that of MacDiarmid and co-workers.[1] It was then converted to SPAN by sulfonation of the emeraldine base as described by Yue and Epstein.[2] The emeraldine base (3 g) was sulfonated by dissolving in 240 mL of fuming sulfonic acid with constant stirring in an ice bath for 3 h. The resulting dark purple solution was then precipitated with methanol, the temperature being held between 10 and 30 °C by an ice bath. The precipitate was then washed by a large amount of methanol until the filtrate had a pH of 7. The resulting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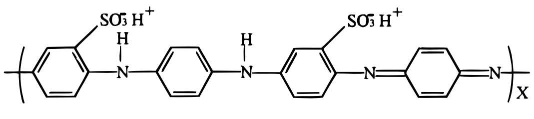
product, SPAN (**II**), can be dissolved in NaOH aqueous solution to give the sodium salt, SPANNa (**III**). The SPANNa aqueous solution was purified to remove excess NaOH by dialysis with a semipermeable membrane (Spectra/Por 3 membrane, molecular weight cutoff, 3500) in deionized (DI) water, which was replaced with fresh DI water frequently for 3 days. The resulting aqueous solution is blue in color. The SPANNa in the aqueous solution was then converted to SPAN by exchanging Na^+ for H^+ using an H^+-type ion-exchange resin (IR 120H resin from Rohm and Haas Co.) to give a stable SPAN water solution green in color.



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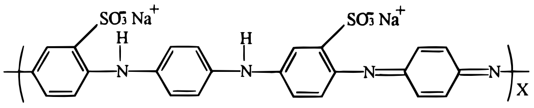


III

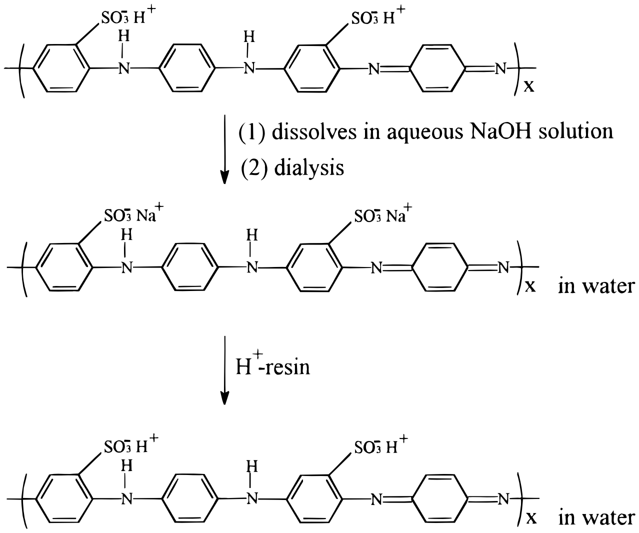
Characterization. The instruments used [pH meter, infrared spectrophotometer (IR), UV−vis−near-IR spectrophotometer, electron spin resonance spectrometer (ESR), X-ray photoelectron spectrometer (XPS) and conductivity measurement device] as well as sample preparations and measurement conditions were described in detail in our previous paper.[7] For the ESR measurement, the sample of aqueous solution of SPAN was placed in a flat cell; no further treatment was made for removing the dissolved oxygen. Since the spin density of SPAN in the aqueous solution (9.1×10^{19} spin/g) is very close to that as solid film (8.3×10^{19} spin/g), the trace amount of oxygen in the aqueous solution must have no appreciable effect (see Electron Spin Resonance).

A thermogravimetric analyzer (DuPont Model TGA 2950) was used to measure the weight loss of SPAN films under a nitrogen stream during a temperature scan from 30 to 500 °C with a heating rate of 10 °C/min. Prior to the temperature scan, each specimen was subjected to an isothermal heating at 90 °C for 1 h in the thermogravimetric analyzer to remove adsorbed moisture.

Results and Discussion

The precipitate cake of SPAN as prepared by Yue and Epstein[2] is soluble in aqueous basic solutions but only slightly soluble in water. To prepare the water solution of SPAN, we propose a two-step procedure for further treatment of the SPAN cake as described in Scheme 1. First, the SPAN was dissolved in water to give a SPANNa aqueous solution, which was then purified to remove excess NaOH by dialysis with a semipermeable membrane in DI water. The resulting aqueous solution is blue in color. Second, the SPANNa in the aqueous solution was then converted to SPAN by exchanging Na^+ for H^+ using an H^+-type ion-exchange resin to give a stable SPAN water solution green in color. This approach ensures that the SPAN has no external acid doping, and it has been also used successfully in our previous study for another self-acid-doped polyaniline derivative, poly(aniline-*co*-*N*-propanesulfonic acid aniline).[3,7] The aqueous solution can be concentrated to a solid content of at least 50% by weight, which is very stable for more than 1 year and was then used for various measurements and for preparation of solid film through casting. Normally, a polymer with limited solubility cannot be cast into a smooth continuous film from its solution. A SPAN free-standing smooth continuous film can be obtained directly by casting from this green solution. The film is hard and brittle, since it is in the doped state. Surprisingly, the solid film is insoluble in water even at the elevated temperature of 70 °C. It may be caused by the strong intermolecular Coulombic interaction. The pressed pellet and thin SPAN film coated on a glass plate have conductivities of 0.008 and 0.01 S/cm in vacuum at room temperature, respectively; both conductivities are lower than that of the SPAN prepared by Yue and Epstein (0.1 S/cm)[2] but close to that of the SPAN prepared by Jing et al. (0.023 S/cm).[9]

Scheme 1



The IR spectrum of the SPANNa shows absorption bands at 1500 and 1592 cm^{-1} due to the stretching modes of the benzenoid and quinoid rings, respectively. The $C_{aromatic}-N$ stretching band of an aromatic amine appears at 1303 cm^{-1}. The absorption peaks at 873 and 821 cm^{-1} are indicative of 1,2,4-trisubstitution of the ring, while those at 1182, 1081, 704, and 625 cm^{-1} are due to the $-SO_3^-$ function groups. Elemental analysis for SPAN gives a S/N atomic ratio of 0.48, indicating that approximately one $-SO_3H$ group is linked on the 2-position of the phenyl ring for every two phenyl rings. The SPAN can be regarded as polymer **II**; it self-doped immediately via protonation of the imine nitrogen atoms to make the polymer conducting in a manner analogous to that of PAn doped with strong acids such as HCl.[1] The availability of the SPAN aqueous solution allows us to study the difference in electronic structures in aqueous solution and in solid film. However, such study is not permitted for the SPAN prepared according to the procedure proposed by the others.[2]

1. Titration Analysis. The SPAN so prepared has a S/N atomic ratio of 0.48 as determined from elemental analysis, indicating that approximately one $-SO_3H$ group is linked on the 2-position of the phenyl ring for every two phenyl rings. For an understanding of the doping behavior, the SPAN aqueous solution was titrated with aqueous NaOH. Titration with 0.493 N aqueous NaOH on 6.5×10^{-5} equiv of $-SO_3H$ of aqueous SPAN at room temperature exhibits a two-stage variation in pH values, as shown in Figure 1. The first stage involves a neutralization with free protons (H_f^+), while the second stage involves the protons that were already protonated (doped) on the imine nitrogens (H_p^+), as will be confirmed in the next section by the changes of the electronic spectra of the aqueous SPAN during the titration. The fractions of H_f^+ and H_p^+

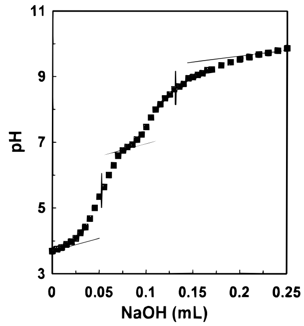


Figure 1. Titration curve of SPAN aqueous solution (contains 6.5×10^{-5} equiv of $-SO_3H$) with 0.493 N aqueous NaOH.

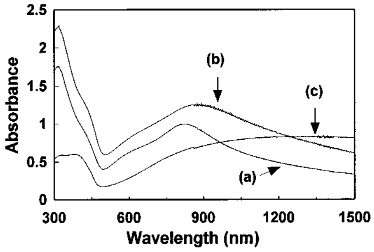


Figure 2. UV−vis spectra at room temperature of (a) SPAN aqueous solution, (b) SPAN film cast from its water solution, and (c) HCl-doped PAn film obtained by doping PAn film (cast from its solution in NMP) with 1.0 M HCl.

calculated from the two end points (at which the slopes are maximum) marked on the pH titration curve in Figure 1 are 39.4% and 60.6%, respectively. In other words, the doping level of the polymer in the aqueous solution is about 0.3, although it contains 0.5 sulfonic acid per ring.

2. Electronic Spectroscopy. The electronic spectra of SPAN aqueous solution, solid film, and HCl-doped PAn solid film are shown in Figure 2, in which each spectrum exhibits three absorption bands. For the aqueous solution of SPAN, an absorption peak due to $\pi-\pi^*$ transition of the benzenoid ring[10] at 313 nm and absorption peaks due to polaron band transitions[11] at 420 and 830 nm are observed, indicating that SPAN is in the doped state in its aqueous solution. The absorption at 310−330 nm and that at 380−420 nm for these systems are similar. The absorption peak at about 830 nm for the SPAN aqueous solution bathochromic shifts (red shifts) to 880 nm and about 1200 nm for SPAN solid film and HCl-doped PAn, respectively. Furthermore, this absorption peak for SPAN as solid film is broader than for solution form but narrower than for the HCl-doped PAn film. This result would indicate that the polarons in the solid film are more delocalized than in the aqueous solution but more localized than in the HCl-doped PAn. In comparison with the electronic spectra of PAPSAH in aqueous solution and as solid film reported in our previous work,[3,7] the intensity ratios of the peak at 830 nm to that at 313 nm of the SPAN in both forms are significantly lower. This can probably be attributed to the lower doping level by 0.03 (i.e., the doping level of PAPSAH is 0.33) and/or to the lower electron density in the backbone due to the electron-withdrawing capability of the $-SO_3^-$ group attached directly to the benzenoid ring.

For an understanding of variations in electronic structure at various levels of neutralization of the aqueous SPAN, the electronic spectra at various pH values during titration were recorded. Electronic spectra of the aqueous SPAN (7.6×10^{-5} equiv of $-SO_3H$) before and after neutralization with 0.493 N aqueous NaOH were recorded as shown in Figure 3. Before neutralization, the aqueous SPAN is in the doped state as reflected in the presence of polaron band transitions[11] at about 400−420 and 830 nm, in addition to $\pi-\pi^*$ transition of the benzenoid rings[10] at 313 nm. As the level of neutralization of SPAN increases, the polaron band disappears gradually and a strong absorption due to exciton transition of the quinoid rings[12] at 600−570 nm grows at the same time. The absorbances at 830 and 580 nm for the above system against the amount of NaOH added are plotted in Figure 4. These variations of absorbances, as in the case of PAPSAH,[7] can be divided into three regions, I, II, and III, with the two end points of titration as the boundaries as shown in Figure 4. All of the absorbances remain constant in region I, indicating that the first stage involves a neutralization of free protons H_f^+ which solvate with H_2O. The decrease of the 830 nm band and the increase of the 580 nm band in region II signify the transformation of the polarons into quinoid rings. This implies that the second stage involves the conversion of semiquinone radical cations to quinoid unit by the removal of the protons on imine nitrogen atoms. These results are in excellent agreement with the result of titration analysis above.

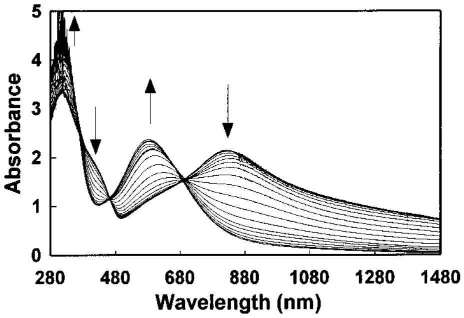


Figure 3. UV−vis spectra of SPAN aqueous solution (contains 7.6×10^{-5} equiv of $-SO_3H$) during titration with various amounts of 0.493 N aqueous NaOH.

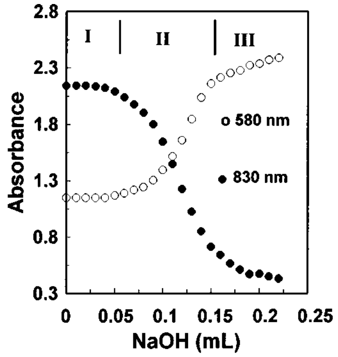


Figure 4. Absorbances of SPAN neutralization with NaOH at 580 and 830 nm.

For an understanding of the effects of thermal treatment on the electronic structure of SPAN, the solid samples were heated at 150 and 250 °C for 30 min and then their UV−vis spectra at room temperature were recorded as shown in Figure 5. As can be observed, the electronic spectrum of the SPAN is not changed even after heating at 150 °C for 30 min. The polaron band transitions at 420 and 880 nm disappear gradually, and a strong absorption due to exciton transition of the quinoid rings at about 656 nm grows when the SPAN was heated at 250 °C for 30 min. This implies that a partial permanent thermal undoping occurs, and the

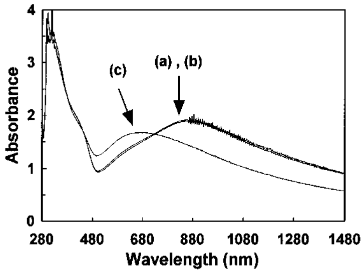


Figure 5. UV−vis spectra at room temperature of (a) SPAN film and that after heating at 90 °C (indistinguishable), (b) at 150 °C for 30 min, and (c) at 250 °C for 30 min.

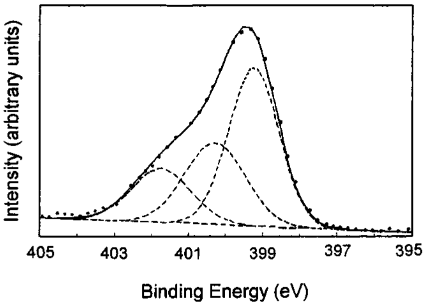


Figure 6. N(1s) XPS core-level spectrum of SPAN.

conductivity would decrease, as will be described later. This thermal undoping temperature is much higher than that in the case of PAPSAH[7] (i.e., the thermal undoping occurs at 110 °C for PAPSAH).

3. X-ray Photoelectron Spectroscopy (XPS). For SPAN, the N(1s) spectrum (Figure 6) changes from symmetric for the emeraldine base[7] to asymmetric, due to the presence of sulfonic acid linked on the phenyl ring and the protonation of the imine nitrogen atoms; it can be deconvoluted into three Gaussian component peaks, centered at 401.8 ± 0.1 eV with a fwhm of 1.9 eV, at 400.2 ± 0.1 eV with a fwhm of 1.9 eV, and at 399.3 ± 0.1 eV with a fwhm of 1.6 eV. The area fractions of these three peaks are about 0.20, 0.30, and 0.50, respectively. In comparison to the emeraldine base,[7] the amount of nitrogen of the uncharged amine located at 399.3 ± 0.1 eV[13−15] remains about the same, while the imine nitrogen component, centered at 398.2 ± 0.1 eV[13−15] in the emeraldine base, disappears completely. The peak centered at 400.2 ± 0.1 eV (about 30% of the total nitrogen atoms) is attributed to the radical cation nitrogen, implying that the SPAN as solid film has the same content of radical cation nitrogen (or same doping level) as the aqueous solution. The peak centered at 401.8 ± 0.1 eV (20% of the total area) can be assigned to the generated iminium ions ($-NH^+=$) of the SPAN solid film. This part of protons is thus 40% of the total protons, which is also almost equal to the presence of the H_f^+ determined in the aqueous solution. It is of interest to compare the intensities of the component peaks of SPAN with that of PAPSAH. The results show that the doping level (i.e., the amount of radical cation nitrogens) of SPAN (30%) is slightly lower than that of PAPSAH (33%).[7]

Yue and Epstein[16] have deconvoluted the N(1s) spectrum of the SPAN into two component peaks using Gaussian line shape with Lorentzian broading function. The one at higher binding energy attributed to radical cation nitrogen is centered at 400.7 eV with a fwhm of 1.8 eV, while the one at the lower energy side attributed to the amine nitrogen is centered at 399.1 eV with a fwhm of 1.5 eV (the core-level spectra were referenced to the C(1s) neutral carbon peak at 285.0 eV]. The ratio of amine nitrogen and cationic radical nitrogen atoms is 1:1, which led these authors to take the doping level as 0.5, higher than that determined in this work (0.3).

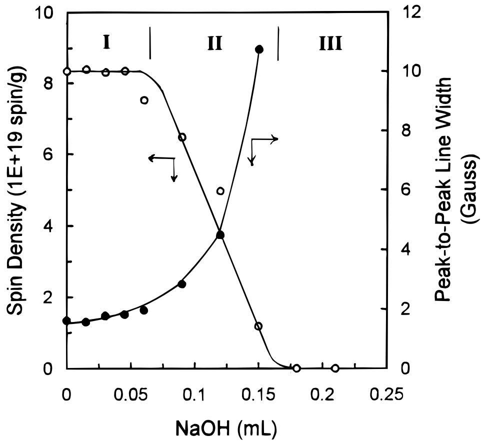


Figure 7. ESR measurements of SPAN solid films at room temperature cast from the aqueous solutions after neutralization with various amounts of aqueous NaOH: (○) spin density; (●) peak-to-peak line width.

4. Electron Spin Resonance. The SPAN in 0.1 wt % aqueous solution at room temperature has an asymmetric ESR signal with a peak-to-peak line width ΔH_{pp} = 2.88 G, a spin density of 9.1 × 10^{19} spin/g, and g = 2.0029; that as solid film has a symmetric ESR signal with ΔH_{pp} = 1.6 G, a spin density of 8.3 × 10^{19} spin/g, and g = 2.0029. These two spin densities are nearly equal, indicating the same doping level at both states; however, ΔH_{pp} of the solid film is lower than that of the aqueous solution, indicating that the polarons in the solution are more localized than those in the solid film. Thus, in the present self-acid-doped polymer the sulfonic acid group bound to the phenyl ring does protonate ("dope") the imine nitrogen atom to make the polymer in the semiquinone radical cation state, both in aqueous solution and in solid film at the same doping level.

Figure 7 shows the changes of the spin density and line width of the ESR signal (ΔH_{pp}) of the solid films at room temperature cast from the SPAN aqueous solutions (8.0 × 10^{-5} equiv of $-SO_3H$) having been neutralized with various amounts of 0.493 N aqueous NaOH. There is no attempt to separate the contributions of Curie and Pauli spins. It is quite clear that as the degree of neutralization (content of NaOH) increases, the spin density is almost unchanged in region I, but it decreases rapidly in region II. The line width of the ESR spectrum decreases with increasing spin density. The g factor is around 2.0029 and does not vary with the doping level. These results for the solid films are in excellent agreement with those of XPS and UV−vis−near-IR in that (i) the iminium ion is recovered to its original imine nitrogen in region I, which gives no effect on the doping level, and (ii) the doping level is determined by the fraction of imine nitrogen that has been protonated to yield radical cation in region II.

5. Infrared Spectroscopy. The infrared spectrum of the SPAN powder with KBr in tablet form is shown in Figure 8a. Strong asymmetric and symmetric S=O stretching bands appear at 1157 and 1071 cm^{-1}, respectively. A strong S−O stretching band is seen at 702 cm^{-1}. The C=C stretching of the benzene ring appears at 1480 cm^{-1} and the $C_{aromatic}$−N stretching at 1301 cm^{-1}, both lower than that of PAPSAH.[7] This can be attributed to the lower electron density in the backbone

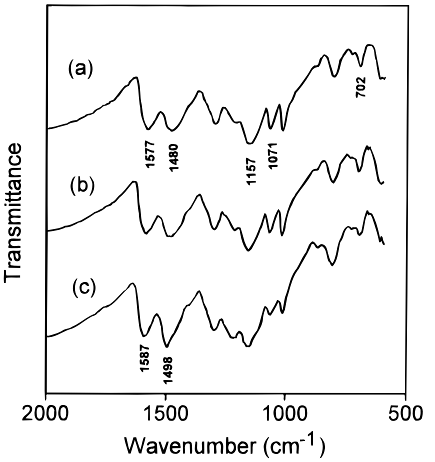


Figure 8. IR spectra of (a) SPAN and (b) SPAN after thermal treatment by heating at 150 °C and (c) at 220 °C each for 30 min under nitrogen atmosphere.

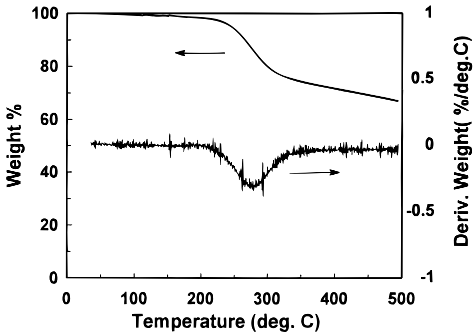


Figure 9. TGA thermogram of SPAN solid film.

due to the electron-withdrawing capability of the $-SO_3^-$ group attached directly to the benzene ring. The band at 1577 cm^{-1}, which is assigned to the C=C ring stretching of the radical cation of imino-1,4-phenylene,[17] is higher than that of PAPSAH.[7] This can probably be attributed to the lower doping level of the SPAN. SPAN was subjected to a thermal treatment by heating at 150 °C for 30 min under dry nitrogen atmosphere, but the absorption characteristics of the IR spectrum did not change (Figure 8b); heating at 220 °C for 30 min caused the intensities of the stretching bands at 1157, 1071, and 702 cm^{-1} to decrease, indicating an elimination of some sulfonic acid groups (Figure 8c). The 1577 and 1480 cm^{-1} bands shift to 1587 and 1498 cm^{-1}, which are very close to the corresponding bands at 1592 and 1500 cm^{-1} for SPANNa, respectively. This indicates that the SPAN was thermally undoped and lost a majority of the polarons after the thermal treatment at the higher temperature. Furthermore, the absorption intensity ratio of the peaks at 1587 and 1498 cm^{-1} is lower than that of SPANNa, indicating the conversion of quinoid rings to benzenoid rings.[18]

6. Thermogravimetric Analysis. The TGA thermogram of the SPAN in dry nitrogen atmosphere is shown in Figure 9. It shows a weight loss starting at about 190 °C (majority weight loss at 275 °C). The weight loss is probably due to the elimination of some sulfonic acid groups as indicated by the decrease in intensity of the S=O and S—O stretching bands in the IR spectrum of the sample after heating at 220 °C (Figure 8c).

7. Electrical Properties. For SPAN at room temperature, the compressed pellet and the thin film coated on a glass plate have conductivities of 0.008 and 0.01 S/cm, respectively, under dry nitrogen atmosphere. The conductivities are 2—3 orders smaller than that of the HCl-doped PAn compressed pellet ($\sigma \approx 1-10$ S/cm). The origin of the lower conductivity can be attributed to the steric effects of the sulfonic acid substituent.[2] The bulky substituent on the phenyl ring in SPAN can be expected to induce an additional ring twisting along the polymer backbone due to the increased steric hindrance and the lowering of the crystallographic order of the polymer chains and the decreased conductivity. Such induced ring twisting not only increases the energy barrier for charge transport but can also reduce the extent of polaron delocalization along the chain. The latter effect is reflected in the higher ΔH_{pp} (2.88 G) in the ESR signal than the ΔH_{pp} of HCl-doped PAn (0.3 G)[19,20] and in the narrower polaron bands in the electronic spectra stated above.

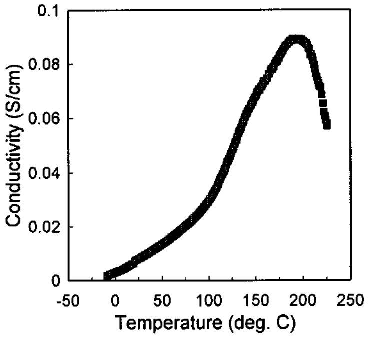


Figure 10. Results of conductivity versus temperature for SPAN solid film coated on glass plate.

The temperature dependence of the conductivity for SPAN solid film coated on a glass plate was measured as shown in Figure 10, in which the measured conductivity is plotted against the temperature from −10 to 225 °C. As can be seen, the conductivity increases with temperture from −10 to 190 °C and decreases from 190 to 225 °C. The drops of the conductivity above 190 °C can be attributed to the occurrence of thermal undoping as revealed in the discussions of UV—vis, IR, and TGA above. After the heating scan from −10 to 225 °C, the conductivity at room temperature is found to drop by a factor of 10^3.

Conclusion

According to the known synthesis method for SPAN, it is only very slightly soluble in water. To prepare an aqueous solution of SPAN, we propose a two-step procedure. A free-standing film can be obtained directly by casting from this solution. The thin film coated on a glass plate has a conductivity of about 0.01 S/cm. This new method not only improves the processibility but also allows detailed studies on the electronic structures of both the solid film and the aqueous solution. Similar to PAPSAH, the protons of sulfonic acid groups of SPAN in aqueous solution and as solid film exist in two forms: the free protons, $-SO_3^-H^+$, and the protons that protonated on imine nitrogens to form semiquinone radical cations. These two forms of acid both in aqueous solution and as solid film contain 39.4% and 60.6%, respectively; the latter implies a doping level of about 30%. The polarons in the SPAN solid film are more delocalized than in the aqueous solution but more localized than in HCl-doped PAn. SPAN has a higher thermal undoping temperature than PAPSAH; therefore, the temperature at which the conductivity of SPAN film is maximum (190 °C) is higher than that of PAPSAH (110 °C).

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