Water-Soluble Self-Acid-Doped Conducting Polyaniline: Structure and Properties

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Abstract: The water-soluble self-acid-doped conducting polyaniline poly(aniline-*co*-*N*-propanesulfonic acid aniline) (PAPSAH) with an oxidation level of about 0.5 in aqueous solution and as a solid film has been characterized. Elemental analysis and spectroscopic data show that almost each amine nitrogen (approximately 50% of the total nitrogen) in the polymer is linked with a $-(CH_2)_3SO_3H$ group, in which the proton is capable of doping the quinoid unit of the polymer. Titration analysis and spectroscopic data of the polymer in aqueous solution and as a solid film, respectively, show that suprisingly the fractions of $-(CH_2)_3SO_3H$ groups that protonate (dope) the imine nitrogens to give semiquinone radical cations are equal in both cases, about 0.66 (equivalent to the doping level, 0.33). However, the free spins in the aqueous solution are more localized than those in the solid film. The fractions of proton, about 34%, that do not participate in the doping have no effect on the conductivity of the film. As the doping level is reduced by increasing the degree of neutralization, the conductivity drops by a factor of 10^4 at the doping level of zero. The conductivity, UV–vis spectroscopy, and X-ray diffraction pattern of the polymer, in comparison with those of HCl-doped polyaniline, exhibit that the decreases of polaron delocalization and structural order result from the steric hindrance imparted by the substituent alkanesulfonic acid. The conductivity of PAPSAH film (at 25 °C, 10^{-2} S/cm) increases with temperature from −50 °C (10^{-8} S/cm) to +110 °C (10^{-1} S/cm) due to thermal activation, and decreases with temperature from 110 to 170 °C (10^{-5} S/cm) due to thermal undoping accompanied by the loss of some polarons. After the heating scan, the conductivity at room temperature drops by a factor of 10^3. Cyclic voltammetry of the polymer coated on a platinum electrode in aqueous acid solutions shows two redox reactions between −0.2 and +0.8 V *vs* SCE. The two oxidation potentials are dependent on pH in the range −0.05 to +2.09. During the redox process, the PAPSAH film exhibits reversible color changes from pale yellow to green to blue as in the case of polyaniline.

Introduction

Polyaniline (PAn) is an important conjugated conducting polymer because of its good enviromental stability.[1,2] It is different from other conjugated conducting polymers in that it can be doped to a conducting form without changing the number of π-electrons through protonation by exposure to an appropriate protonic acid in an aqueous solution.[3] However, the conductive form of polyaniline is difficult to be processed because it is insoluble in common organic solvents and is unstable at melt processing temperatures; these limit its applications. Several substituted polyanilines soluble in organic solvents have been prepared such as alkyl-[4,5] and alkoxy-[6] ring-substituted and alkyl-N-substituted[7–9] polyanilines. The incoporation of the side groups to polyaniline has enhanced its solubility and processability and changed its properties. Although, alkyl- and alkoxy-ring-substituted polyanilines after acid-doping have a moderate conductivity of 10^{-1}–10^{-3} S/cm, their molecular weights are usually low, on the order of 10^3. While poly(*N*-alkylaniline)s have moderate molecular weight, their conductivities are low (10^{-3}–10^{-7} S/cm). The most successful approach toward soluble conductive polyaniline is to introduce sulfonic acid groups on PAn chains. Yue and Epstein[10,11] have synthesized the sulfonic acid ring-substituted PAn (SPAN) by a reaction of emeraldine base with fuming sulfuric acid, which is soluble in water only after conversion to the salt form (by undoping in basic aqueous solutions). SPAN is in the conductive form, "self-doped", and has a conductivity of about 0.1 S/cm. Since their SPAN is insoluble in water, a comparison of its electronic structures in aqueous solution and in a solid film was not possible. Genies et al.[12] also have attempted to synthesize a self-doped PAn by reaction of emeraldine base directly with propane- or butanesultone. However, the reaction product has a very poor solubility and low conductivity (~10^{-9} S/cm). So far, the reported self-doped PAns are insoluble in the conductive form, and thus their applications are limited. Dao and coworkers[13] have synthesized a water-soluble polyaniline by reaction of leucoemeraldine base (the fully reduced PAn) with propanesultone. However, the polymer is supposed to have no imine nitrogen to allow a self-acid-doping, although they have claimed the appearance of a strong absorption band at about

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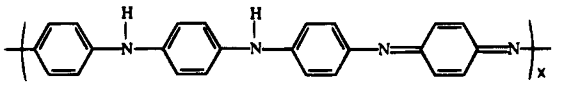
900 nm, which always appears for protonic acid-doped PAn. Another approach toward soluble conductive PAn is copolymerization of aniline with a suitable substituted aniline to produce copolymers. By this approach the copolymers produced have improved solubility in organic solvent[14,15] or aqueous NH_4OH solution.[16] Besides modifying the structure of PAn to make them inherently soluble, PAn has also been made to be soluble by an addition of acid-type dispersants.[17]

Very recently, the first water-soluble self-acid-doped polyaniline, poly(aniline-*co*-*N*-propanesulfonic acid aniline) (PAPSAH), was successfully synthesized by us,[18] which can be cast into free-standing film directly from its aqueous solution. PAPSAH has a conductivity of about 10^{-2} S/cm without external doping. In this paper, the structure and properties of this novel copolymer of aniline with *N*-propanesulfonic acid aniline in aqueous solution and in solid film form are investigated by use of titration, spectroscopic, electron spin resonance, conductivity, and electrochemical measurements. Effects of temperature variation and of the degree of neutralization on its conductivity are investigated. A comparison of the electronic structures of this polymer in aqueous solution and as a solid film is also made. Such a comparison for "self-doped PAn" or "self-acid-doped PAn" (by our terminology) is believed to appear in the literature for the first time.

Experimental Section

Synthesis. The detailed synthesis procedure was reported in our previous paper.[18] The dried emeraldine base form of polyaniline[3] (PAn, **I**) (2.26 g) was reacted with excess NaH (0.9 g) in dimethyl sulfoxide (DMSO) at about 45 °C under a dried nitrogen atomosphere for 6 h. The color of the solution changed from dark blue to green-black. The solution was subsequently reacted with excess 1,3-propanesultone (4.57 g) for 20 h at room temperature to give a blue-black solution. The resulting solution was precipitated with 1 M HCl aqueous solution, and the green precipitate after filtration was washed by a large amount of acetonitrile and then undoped with a NaOH aqueous solution to yield a blue solution, which was then purified 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 poly(aniline-*co*-sodium *N*-propanesulfonate aniline) (PAPSANa, **II**) aqueous solution so obtained was then converted to poly (aniline-*co*-*N*-propanesulfonic acid aniline) (PAPSAH, **III**) by dissolving it in DI water and then exchanging Na^+ for H^+ using a H^+-type ion exchange resin (IR 120H resin from Rohm and Haas Co.) to give a PAPSAH aqueous solution green in color. A conducting film green in color is formed by coating this green solution on various substrates. Films obtained in this way can be subject to structure characterization and property measurements. The nonprotonated sodium salt polymer PAPSANa (**II**) solution, blue in color, was reproduced by adding a stoichiometrically equivalent NaOH to a PAPSAH aqueous solution.



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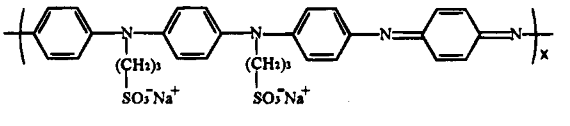

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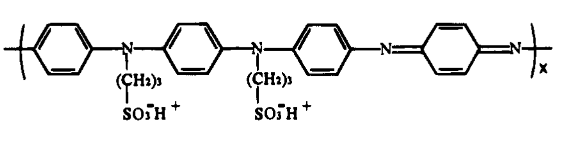

III

Characterization. A Suntex Model sp-7 digital pH meter was used to measure pH change during the titration of PAPSAH aqueous solution with NaOH aqueous solution. The NaOH aqueous solution prior to use was standardized with a primary standard of potassium hydrogen phthalate, using phenolphthalein as an indicator.

An infrared spectrophotometer (IR; Perkin-Elmer Model 983) was used to identify chemical structures of the polymers. Solid specimens of PAPSAH and PAPSANa were prepared by mixing their powders with KBr and then pressing the mixtures into tablets.

Electronic spectra of PAPSAH in aqueous solution and as a solid film and its sodium salts in aqueous solutions obtained by neutralization with NaOH aqueous solution at various extents were measured using an UV–vis–near-IR spectrophotometer (Perkin-Elmer Lambda 19) in the wavelength range 300–1300 nm. PAPSAH solid film coated on a glass plate was obtained by casting from its aqueous solution at ambient condition. PAn film was prepared by casting from the solution of PAn in *N*-methyl-2-pyrrolidone on a glass plate and then drying under dynamic vacuum at about 50 °C, while the HCl-doped PAn film was obtained by exposing the PAn film in HCl vapor for 24 h at room temperature.

Electron spin resonance (ESR) measurements of PAPSAH solid films were performed using an IBM Bruker 200 D 10/12 ESR spectrometer interfaced with an IBM computer for data acquisition and analysis. The solid films were dried under dynamic vacuum at 50 °C for at least 24 h prior to the measurements in order to remove residual moisture and adsorbed oxygen and then inserted in 3 mm outer diameter ESR tubes, which were immediately sealed with epoxy resin. 1,1′-diphenyl-2-picrylhydrazyl (DPPH) was used as the calibration standard. For the aqueous solution of PAPSAH, the sample was placed in a flat cell; no further treatment was made for removing the dissolved oxygen. Since the spin density of PAPSAH in the aqueous solution (7.5×10^{19} spins/g) is very close to that of the solid film (7.1×10^{19} spins/g), the trace amount of oxygen in the aqueous solution must have no appreciable effect (see ESR section below).

X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Perkin-Elmer Model 1905 spectrometer with a Mg Kα X-ray source (1253.6 eV). The PAPSAH solid film was cast on an Al substrate from its water solution, while the solid specimen of PAn was prepared by pressing the powder into a pellet. All core-level spectra were referenced to the C(1s) neutral carbon peak at 284.6 eV. The X-ray power supplier was run at 12 kV and 250 W. The pressure in the analysis chamber during the scans was approximately 10^{-8} Torr or less. All core-level spectra were deconvoluted into Gaussian component peaks.

An X-ray diffractometer (XRD; Rigaku Model D/Max-2B) was used to examine the ordering in polymer samples. The X-ray beam was nickel-filtered Cu Kα radiation from a sealed tube operated at 30 kV and 20 mA. Data from 5° to 35° (2θ) were obtained at a scan rate of 1 deg/min.

The four-probe[19] method was used to measure the conductivities from −50 to +170 °C at a heating rate of about 2 °C/min under dry nitrogen purging. During the measurements, an appropriate constant current in the range 0.01–60 μA was maintained on two outer probes. The voltage across two inner probes was measured to determine the conductivity. Both film and powdery samples were used for the measurement. For film samples, they were prepared by coating the PAPSAH aqueous solution (16 g/L of water) on a glass plate, allowing it to dry in air, drying it under dynamic vacuum for one day for removing the residual moisture at 90 °C, and then transferring it to the

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sample cell for the conductivity measurement. The film thickness was about 0.001 mm. The powdery samples were subjected to dynamic vacuum pumping for one day and then compressed into pellets for the measurement. In the measurement, film or pellet samples were first heated at 90 °C with dry nitrogen purging for 1 h for removing the moisture and then cooled to room temperature. The samples were then ready for conductivity measurement at various temperatures.

Cyclic voltammetry studies were carried out using a galvanostat/potentiostat (model 173/M 276 from Princeton Applied Research Co.) with a SCE as the reference electrode, a platinum (Pt) strip coated with PAPSAH as the working electrode, and a blank platinum strip as the counter electrode. Voltammograms were recorded on an *X*−*Y* recorder (YOKOGAWA 3025). The working electrode, PAPSAH coated on a Pt strip, was prepared by casting from an aqueous solution of the polymer at ambient condition. In order to obtain reproducible cyclic voltammograms, the cell was preconditioned by cyclic scanning between −0.2 and +0.4 V *vs* SCE for several cycles. For the in-situ spectroelectrochemical measurements, an indium tin oxide (ITO) glass and a platinum strip were used as the anode and cathode, respectively. Before each measurement, the potential was kept at the desired value for about 15 min.

Results and Discussion

A. Significance of the Proposed Synthesis Route for the Water-Soluble Self-Acid-Doped Polyaniline. In the synthesis procedure described above, several key points to make the polymer soluble in water are emphasized below. First, the blue-black solution, obtained from reactions of emeraldine base with NaH and then propanesultone, must be precipitated with protonic acid (such as HCl) aqueous solution to obtain powderlike HCl-doped PAPSAH, which is soluble in aqueous NaOH. However, when the blue-black solution is precipitated with a common organic solvent, such as tetrahydrofuran (THF), the precipitate becomes gumlike and has a very poor solubility in organic solvent or water, similar to that of PAn when treated with THF or NMP.[20] Second, a conversion of PAPSANa to PAPSAH must be *via* exchanging Na^+ for H^+ using a H^+-type ion exchange resin, so that a stable PAPSAH aqueous solution is obtained. The self-acid-doped PAn free-standing film can be obtained by casting from the green solution; however, this film is, after removal of residual moisture by dynamic vacuum pumping, insoluble in water but soluble in aqueous alkaline solution.

Although it is reasonable to think that the present water-soluble self-acid-doped polyaniline can also be prepared by a copolymerization of aniline with *N*-propanesulfonic acid aniline, this process would result in lower molecular weight copolymers due to a steric hindrance imparted by the bulky $-(CH_2)_3SO_3H$ group, as in the copolymerization of aniline with alkyl-N-substituted aniline or alkyl-ring-substituted aniline.[14−16] In general, copolymerization could also lead to a product with several different chemical structures, such as block copolymers and copolymers with various compositions and sequences resulting from the difference in reactivity ratios of the two comonomers.

B. Structure Characterization. In the previous work,[18] the structure characterization of PAPSAH so prepared by use of infrared spectroscopy, ^1H NMR, elemental analysis, electronic spectroscopy, conductivity measurements, and electron spin resonance was found to be consistent with its chemical structure in that each amine nitrogen is linked with a propanesulfonic acid and it is a self-acid-doped conducting polymer both in aqueous solution and as a solid film.[18] This polymer can be regarded as that it first represents polymer **III** and then is 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.[3] Owing to the fact that polymer **III** is water soluble, its self-doped structure can be further investigated *via* neutralization at various extents as depicted below.

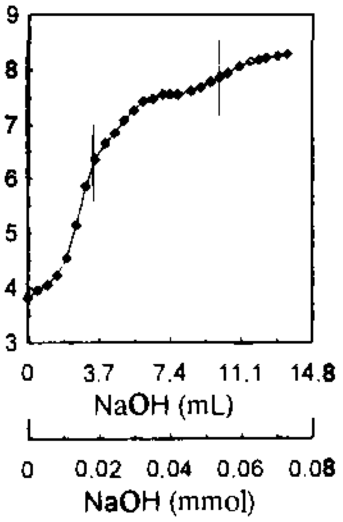

Figure 1. Titration curve of PAPSAH aqueous solution with aqueous NaOH.

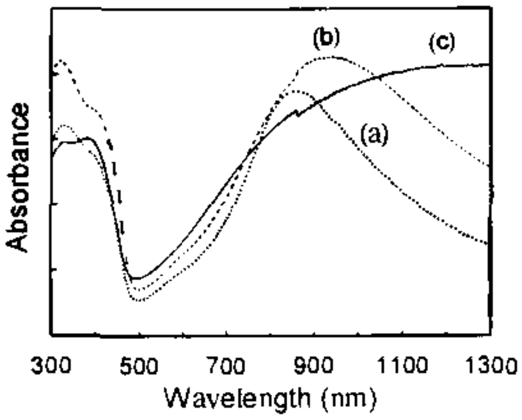

Figure 2. UV−vis spectra at room temperature of (a) PAPSAH aqueous solution, (b) PAPSAH film cast from its water solution, and (c) HCl-doped PAn film obtained by doping PAn film (cast from its solution in NMP) with 1.0 M HCl.

1. Titration Analysis. Elemental analysis for PAPSAH gives a S/N atomic ratio of 0.48, which implies that almost each amine nitrogen (about 50% of the total nitrogen) in the polymer is linked with a side chain of propanesulfonic acid.[18] In order to understand the doping phenomenon, the PAPSAH aqueous solution was titrated with aqueous NaOH. Titration with 5.4×10^{-3} N aqueous NaOH on 5.3×10^{-5} equiv of $-(CH_2)_3-SO_3H$ of aqueous PAPSAH 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 already protonated (doped) the imine nitrogens (H_p^+) as to be confirmed in the next section by the changes of the electronic spectra of the aqueous PAPSAH during the titration. The fractions of H_f^+ and H_p^+ calculated from the two end points (at which the slopes are maximum) marked on the pH titration curve in Figure 1 are 34% and 66%, respectively. In other words, the doping level of the polymer in the aqueous solution is about 0.33, although it contains 0.5 propanesulfonic acid molecule per ring.

2. Electronic Spectroscopy. The electronic spectra of PAPSAH aqueous solution and solid film and HCl-doped PAn solid film are shown in Figure 2. Three absorption bands are observed for each case. The absorption at 310−330 nm ($\pi-\pi^*$ transition[21]) and that at 380−410 nm (polaron band[22]) for

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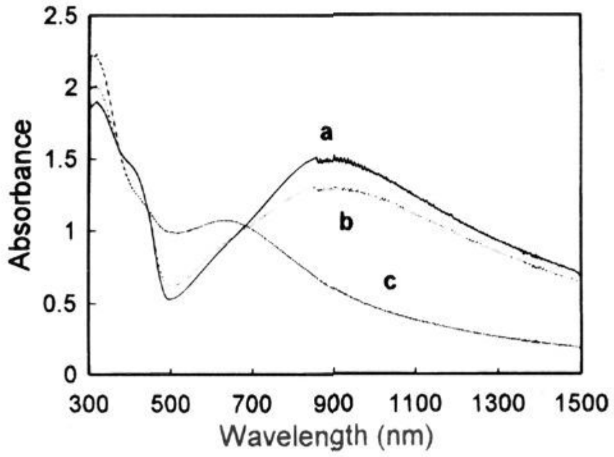

Figure 3. UV−vis spectra at room temperature of (a) PAPSAH film and that after heating at 90 °C (indistinguishable), (b) at 150 °C, and (c) at 250 °C each for 30 min.

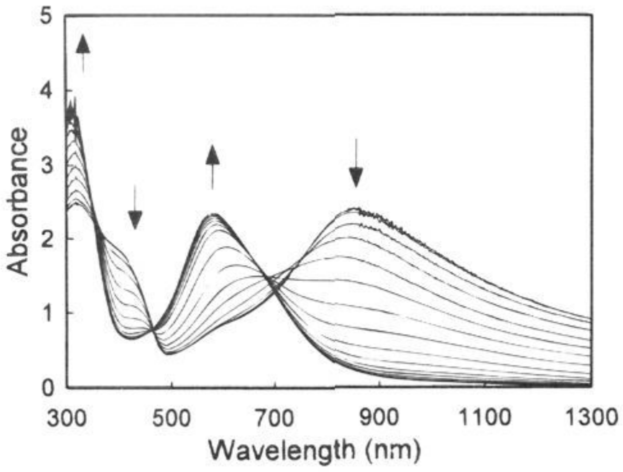

Figure 4. UV−vis spectra of PAPSAH aqueous solution during titration with various amounts of aqueous NaOH as in the titration shown in Figure 1.

these systems are similar. While the absorption peak at about 860 nm (polaron band[22]) for PAPSAH aqueous solution shows a bathochromic shift (red shift) to 910 nm and about 1200 nm for PAPSAH solid film and HCl-doped PAn, respectively. Furthermore, for this absorption peak, the PAPSAH as a film is broader than that in solution form, but narrower than that of the HCl-doped PAn. This result would indicate that the polarons in the solid film are more delocalized than in the aqueous solution, but are more localized than in the HCl-doped PAn.

For an understanding of the effects of thermal treatment on the electronic structure of PAPSAH, 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 3. As can be observed, the polaron band transitions at 400−410 and 860 nm disappear gradually and a strong absorption due to exciton transition of the quinoid rings at about 600 nm grows. This implies that a partial permanent thermal undoping occurs, and the conductivity would decrease as will be described later.

In order to explore the variation in electronic structure during the titration of aqueous PAPSAH, the electronic spectra at various pH values were recorded. Electronic spectra of aqueous PAPSAH (5.3×10^{-5} equiv of $-(CH_2)_3SO_3H$) before and after neutralization with 0.493 N aqueous NaOH were recorded as shown in Figure 4. Before neutralization, the aqueous PAPSAH is in the doped state as reflected in the presence of polaron band transitions[22] at about 400−410 and 856 nm, in addition to $\pi-\pi^*$ transition of the benzenoid rings[21] at 312 nm. As the levels of neutralization of PAPSAH increase, the polaron bands disappear gradually and a strong absorption due to exciton transition of the quinoid rings[23] at 600−570 nm grows at the same time.

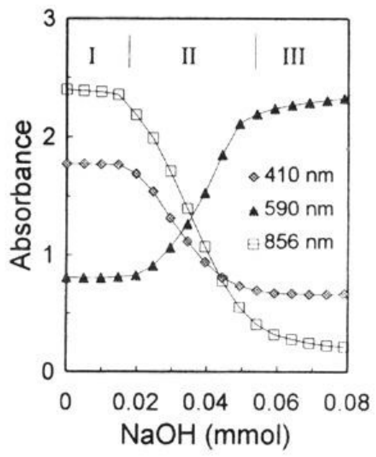

Figure 5. Absorbances of PAPSAH neutralization with NaOH at 410, 590, and 856 nm.

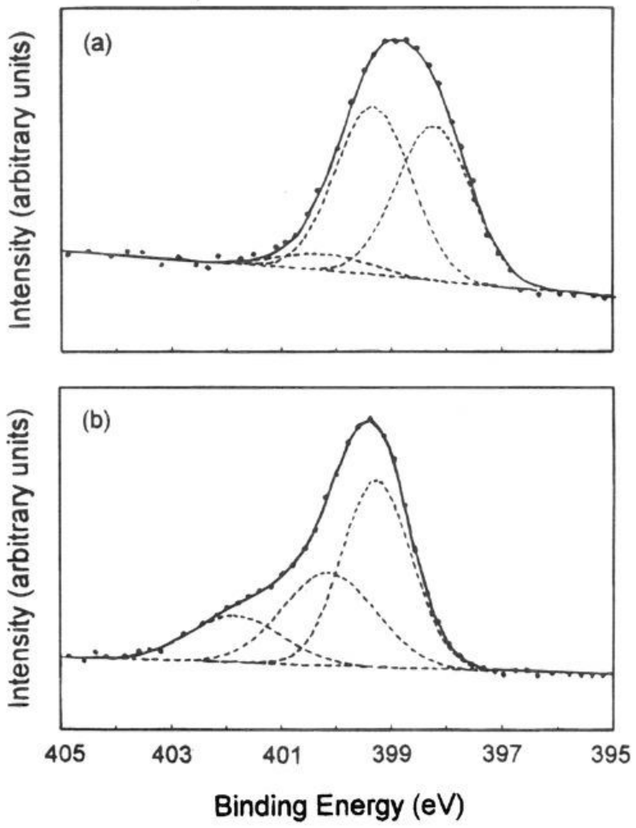

Figure 6. N(1s) XPS core-level spectra of (a) emeraldine base powder and (b) PAPSAH film.

The absorbances at 856, 410, and 590 nm for the above system against the amount of NaOH added are plotted in Figure 4. These variations of absorbances can be divided into three regions: I, II, and III, with the two end points of titration as the boundaries as shown in Figure 5. All 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, while the decreases of the 856 and 410 nm bands and the increase of the 590 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 results of titration analysis above.

3. X-Ray Photoelectron Spectroscopy (XPS). The XPS N(1s) spectrum of the emeraldine base has a simple nearly symmetric curve centered at 399.0 eV as shown in Figure 6a. This N(1s) spectrum can be deconvoluted into two major peaks, one centered at 398.2 ± 0.1 eV and the other at 399.3 ± 0.1 eV. Both have a fwhm (full width at half-maximum) of 1.6 eV. The former can be assigned to the imine nitrogen,[24] while the latter to the amine nitrogen.[24] The area fractions of the two

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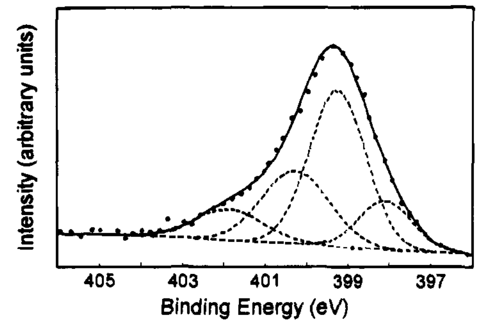

Figure 7. N(1s) XPS core-level spectrum of HCl-doped PAn.

major components are 0.46 and 0.49, respectively, indicating that about equal amounts of imine and amine units are present in the emeraldine base. The slightly lower content of imine units is compensated by the trace amount of positively charged nitrogen at higher binding energy (BE) centered at about 400.3 eV. For PAPSAH, the N(1s) spectrum (Figure 6b) changes to asymmetric, due to the presence of propanesulfonic acid linked on the amine nitrogen and the protonation of the imine nitrogen atoms; it can be deconvoluted into three component peaks, centered at 401.8 ± 0.1 eV with a fwhm of 2.0 eV, at 400.2 ± 0.1 eV with a fwhm of 2.0 eV, and at 399.3 ± 0.1 eV with a fwhm of 1.5 eV. The area fractions of these three peaks are about 0.17, 0.33, and 0.50, respectively. In comparison to the emeraldine base, the amount of nitrogen of the uncharged amine located at 399.3 ± 0.1 eV remains about the same, while the imine nitrogen component, centered at 398.2 ± 0.1 eV in the emeraldine base, disappears completely. The peak centered at 400.2 ± 0.1 eV is attributed to the radical cation nitrogen and is about 33% of the total nitrogen atoms, implying that the PAPSAH as a solid film has the same content of radical cation nitrogen (or same doping level) as in the aqueous solution. The peak centered at 401.8 ± 0.1 eV (17% of the total area) can be assigned to the generated iminium ions ($-\mathrm{NH}^{+}=$) of the PAPSAH solid film. This part of the protons is thus 34% of the total protons, which is also equal to the presence of the H_f^+ determined in the aqueous solution. For comparison purposes, the XPS N(1s) spectrum of the HCl-doped PAn has also been recorded as shown in Figure 7. After a deconvolution, the spectrum gives four component peaks at 398.2 ± 0.1 eV (14% of the total area), 399.3 ± 0.1 eV (48%), 400.2 ± 0.1 eV (27%), and 401.8 ± 0.1 eV (11%). The binding energies of the latter three peaks are identical to those of PAPSAH, and that of the first one is due to the unprotonated imine nitrogen, resulting from a partial undoping by dynamic vacuum pumping to below 10^{-8} Torr during the XPS measurement. The doping level is about 0.27 which is lower than that of the PAPSAH, 0.33.

The above XPS result is different from that of SPAN. The N(1s) spectrum of SPAN has been deconvoluted into two peaks, one following the Gaussian function and centered at 399.1 eV (with fwhm 1.5 eV) and the other following the Lorentzian function and centered at 400.7 eV (with fwhm 1.8 eV).[25] The former was assigned to the amine nitrogen, and the latter to the radical cation nitrogen. Since the area ratio is 1:1, it was claimed that the doping level is 0.5, which is higher than that of the PAPSAH, 0.33. However, the latter peak might involve two types of protons as in the present PAPSAH, one forming iminium ion ($-\mathrm{NH}^{+}=$) and the other forming radical cation nitrogen ($\cdot\!\!\!-\mathrm{NH}^{+}\!\!\!-\!\cdot$), both with the imine nitrogen, which is in need of further investigation. If this is the case, then the doping level of SPAN would be lower than 0.5.

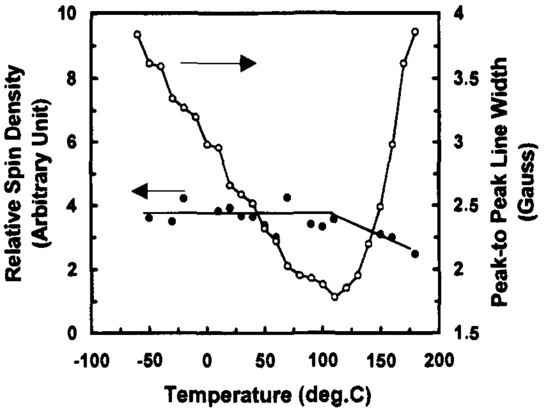

Figure 8. ESR measurement on the solid film of PAPSAH in the temperature range from −50 to +180 °C.

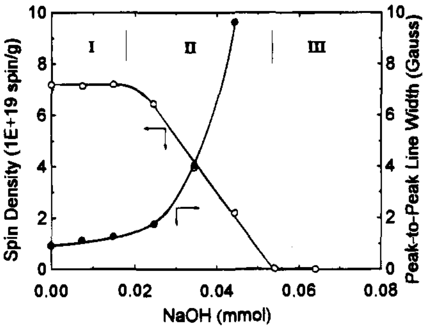

Figure 9. ESR measurements of PAPSAH solid films at room temperature cast from the aqueous solutions after neutralization with various amounts of aqueous NaOH: ○, spin density; ●, peak-to-peak line width.

4. Electron Spin Resonance. The ESR measurement at room temperature on the 0.14 wt % aqueous solution of PAPSAH gives an asymmetric ESR signal with a peak-to-peak line width $\Delta H_{pp} = 10.8$ G, a spin density of 7.5 × 10^{19} spins/g, and $g = 2.0042$, and that on the solid film of PAPSAH gives a symmetric ESR signal with $\Delta H_{pp} = 2.5$ G, a spin density of 7.1 × 10^{19} spins/g, and $g = 2.0029$. These two spin densities are nearly equal, which also indicates 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 propanesulfonic acid bound on the side chain attached to the amine nitrogen does protonate ("dope") the imine nitrogen atom to give the polymer in the semiquinone radical cationic state,[3] both in aqueous solution and as a solid film at the same doping level.

The ESR measurement on the solid film of PAPSAH in the temperature range from −50 to +180 °C was also carried out, and the characteristic values, relative spin density and peak-to-peak line width (ΔH_{pp}), are plotted in Figure 8. Here, there is no attempt to separate the contributions of Curie and Pauli spins. As can be seen, the relative spin density is almost unchanged up to about 90−100 °C and then decreases slowly with temperature up to 180 °C, but the ΔH_{pp} decreases with increasing temperature in the range from −50 to +110 °C and increases from 110 to 180 °C. This would indicate that the increase in polaron delocalization (as reflected in the decrease of ΔH_{pp}) with temperature from −50 °C up to about 100−110 °C is due to the thermal activation, while the decrease of polaron delocalization (as reflected in the increase of ΔH_{pp}) with temperature from 110 to 180 °C is due to the overcompensation of the thermal activation effect by the effect due to the loss of some polarons.

Figure 9 shows the changes of the spin density and line width of the ESR signal (ΔH_{pp}) of the solid films at room temperature

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[25] Yue, J.; Epstein, A. J. *Macromolecules* **1991**, *24*, 4441−4445.

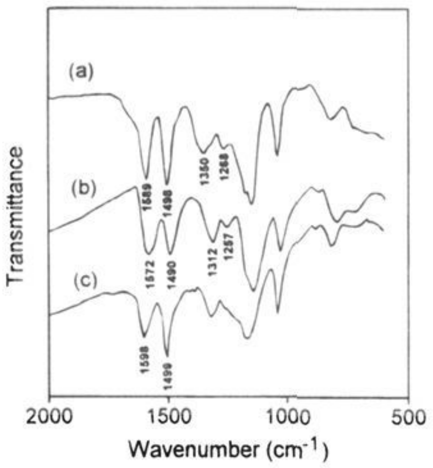
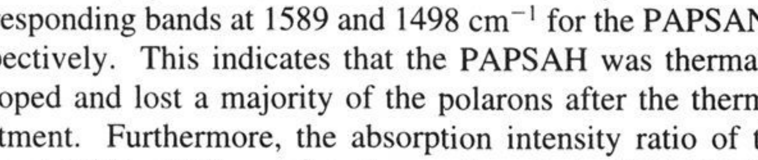


Figure 10. IR spectra of (a) PAPSANa, (b) PAPSAH, and (c) PAPSAH after thermal treatment by heating at 150 °C for 30 min under a nitrogen atmosphere.

cast from the PAPSAH aqueous solutions (5.3×10^{-5} equiv of $-(CH_2)_3SO_3H$) 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, while 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. Infrared spectra of PAPSANa and PAPSAH are shown in Figure 10. Figure 10a shows that PAPSANa with an oxidation level of about 0.5 has sodium propanesulfonate groups linked on the amine nitrogens as reported in our previous work.[18] As PAPSANa was converted to PAPSAH (Figure 10b), the bands at 1498 and 1589 cm^{-1} due to the benzeneoid ring and quinoid ring, respectively, shift to lower frequencies at 1490 and 1572 cm^{-1}, and the absorption at about 1350 cm^{-1} due to the $C_{aromatic}-N$ stretching shifts to lower frequency by about 38 cm^{-1}, both similar to those observed in the PAn before and after HCl-doping.[26] Furthermore, the absorption peak at 1268 cm^{-1} characteristic of the $C_{aliphatic}N$ group also shifts to lower frequency by 11 cm^{-1}, which implies that the self-acid-doping also undergoes a polaron separation to yield a polaron lattice (**IV**) after a disassociation of bipolaron into two polarons, similar to the HCl-doping of PAn.[23]



IV

As the solid film of PAPSAH was subjected to the thermal treatment by heating at 150 °C for 30 min under nitrogen atmosphere, the 1572 and 1490 cm^{-1} bands shifted to 1598 and 1499 cm^{-1} (Figure 10, curve c), which are very close to the corresponding bands at 1589 and 1498 cm^{-1} for the PAPSANa, respectively. This indicates that the PAPSAH was thermally undoped and lost a majority of the polarons after the thermal treatment. Furthermore, the absorption intensity ratio of the peak at 1598−1499 cm^{-1} is lower than that of PAPSANa, indicating the occurrence of a cross-linking reaction through a conversion of quinoid rings (including those from thermal undoping) to benzenoid rings.[27]

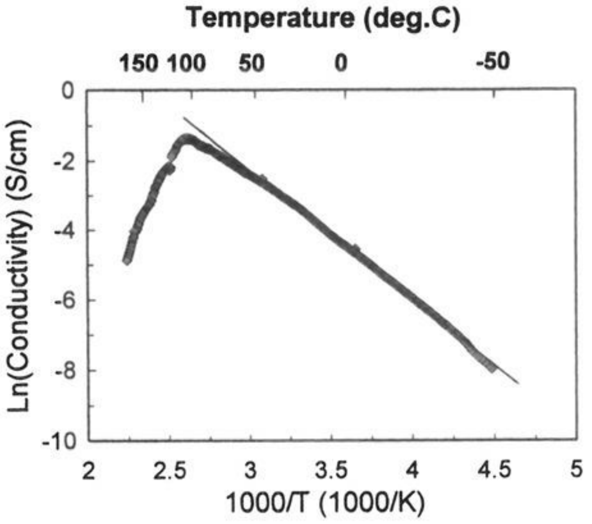


Figure 11. Temperature dependence of the conductivity of PAPSAH.

C. Electrical Properties. For PAPSAH at room temperature, the compressed pellets have conductivities of 2.2×10^{-2} S/cm under ambient conditions and 1.5×10^{-2} S/cm under a dry nitrogen atmosphere, while the thin films coated on a glass plate have conductivities of 3.6×10^{-2} S/cm under ambient conditions and 3.0×10^{-2} S/cm under a dry nitrogen atmosphere. These results would indicate that the moisture can increase the conductivity only very slightly. These conductivities are 2−3 orders of magnitude 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 propanesulfonic acid substituent on the basis of the studies of alkyl-ring-substituted polyanilines.[28] The bulky substituent on nitrogen in PAPSAH can be expected to induce an additional ring twisting along the polymer backbone due to the increased steric hindrance. 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} (2.5 G) in the ESR signal than the ΔH_{pp} of HCl-doped PAn (0.3 G)[29] and in the narrower polaron bands in electronic spectra than those stated above.

Another factor that could affect the conductivity is the chain packing. Contrary to the HCl-doped PAn (50% crystallinity),[30] PAPSAH is basically an amorphous substance (as was found from its X-ray diffraction pattern) due to the steric hindrance of the bulky propanesulfonic acid groups, which is analogous to that of the sulfonic acid ring-substituted polyaniline (SPAN).[31] This lower crystallographic order of the polymer chains causes the increased separation of the polymer chains and the decreased conductivity. An amorphous structure is also observed for the nonprotonated sodium salt PAPSANa.

The temperature dependence of the conductivity for PAPSAH was measured as shown in Figure 11, in which the measured ln(conductivity) is plotted against the inverse temperature 1000/*T* from −50 to +170 °C. In the range from −50 to about +50 °C, the plot is linear, indicating that the charge transport follows the polaron hopping model (i.e., the conductivity variation with

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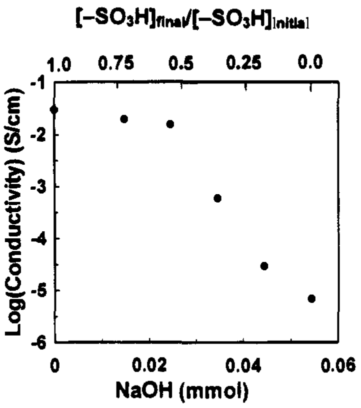

Figure 12. Conductivity changes of the PAPSAH films at room temperature cast from aqueous PAPSAH (5.3×10^{-5} equiv of $-(CH_2)_3-SO_3H$) before and after neutralization with various amounts of 0.493 N aqueous NaOH.

temperature follows the Arrhenius law).[32] According to this model, the activation energy calculated from the slope is 0.315 eV. As the temperature increases further, the conductivity also increases up to 110 °C but slightly departs from the linear relationship. After 110−170 °C, the conductivity drops with temperature. The increase in conductivity with temperature from −50 to +110 °C can be attributed to the increase in polaron delocalization due to thermal activation as revealed in the ESR section above, while the decrease in conductivity in the range 110−170 °C is due to the occurrence of thermal undoping as revealed in the ESR, UV, and IR sections above. After the heating scan from −50 to +170 °C, the conductivity at room temperature was found to drop by a factor of 10^3.

Figure 12 shows the conductivity changes of the PAPSAH films cast from aqueous PAPSAH (5.3×10^{-5} equiv of $-(CH_2)_3SO_3H$) before and after neutralization with various amounts of 0.493 N aqueous NaOH in order to control the degree of protonation. When the added amount of NaOH is less than 0.018 mmol, the conductivity remains at the same level (or only slightly decreases with the added amount of NaOH by about 0.3 order of magnitude). This is due to the fact that only free protons are neutralized in this range (the first stage) and the doping level remains at about 0.33 as determined from titraton, UV−vis, XPS, and ESR measurements mentioned in the above sections. However, when the added amount of NaOH is more than 0.018 mmol, the conductivity decreases with increasing added amount of NaOH due to the successive decrease of the doping level. This result is in excellent agreement with that of ESR above. In comparison with the partly HCl-doped emeraldine base,[33] the changes of conductivity with doping level in both cases are similar. The conductivity of the protonated emeraldine base exhibits a slight decrease in conductivity (within about 0.5 order of magnitude) as the doping level drops from 0.5 to about 0.33, and then a rapid decrease with decreasing doping level. This might indicate that its real doping level is probably only about 0.33 rather than 0.5 as determined from elemental analysis. A confirmation of this doping level, 0.5, by XPS is not possible, since partial elimination of the dopant HCl occurs during the measurement under high vacuum. Actually the XPS measurement on the fully protonated emeraldine base gives the doping level as only about 0.27 as indicated in the XPS section above.

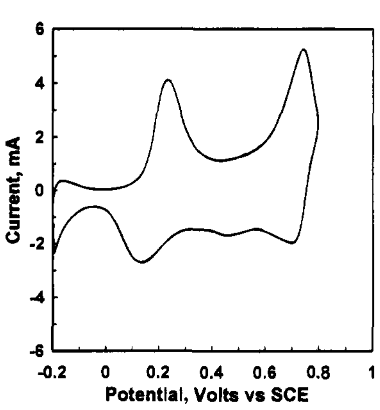

Figure 13. Cyclic voltammogram (50 mV/s) of PAPSAH film in 1.0 M HCl.

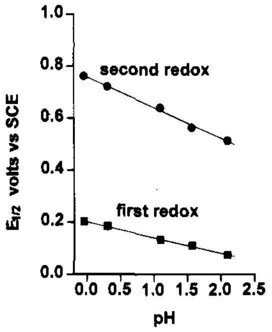

Figure 14. Linear plots of $E_{1/2}$ (50 mV/s) versus pH of the PAPSAH film in aqueous HCl solutions: ■, the first redox process; ●, the second redox process.

D. Redox Properties. 1. Cyclic Voltammetry. A typical cyclic voltammogram of PAPSAH in 1 M HCl is shown in Figure 13. As in the voltammogram of polyaniline,[1] it also consists of two well-resolved peaks corresponding to the two redox processes at $E_{1/2} = 0.19$ and 0.72 V *vs* SCE at a scan rate of 50 mV/s.

Analogous to that observed in the sulfonic acid ring-substituted polyaniline,[10] the $E_{1/2}$ values of both redox processes for PAPSAH are dependent on the pH values in the electrolytic solutions; the $E_{1/2}$ value of the first redox peak shifts at the rate of −0.059 V/pH and the second at −0.118 V/pH in the pH range −0.02 (2 M HCl) to ~+2.09 (0.01 M HCl) (Figure 14). According to the Nernst equation for the pH-dependent redox process

$$AH_m^{(m-n)+} \rightleftharpoons A + mH^+ + ne^-$$

MacDiarmid and co-workers[1] have proposed that in a system with a given fixed ratio of $[A]/[AH_m^{(m-n)+}]$, a plot of $E_{1/2}$ *vs* pH is linear with a slope of $-0.059m/n$ V/pH unit. Hence, the first redox reaction involves a loss of one proton per electron (i.e., $m = n$), and its electrochemical process can be given as Scheme 1. The second redox peak involves a loss of two protons per electron (i.e., $m/n = 2$), and its electrochemical process can be given as Scheme 2.

PAPSAH has a higher potential for the first redox process and a lower potential for the second redox process, in comparison to PAn ($E_{1/2} = 0.13$ and 0.75 V *vs* SCE in 1 M HCl, respectively).[5] Such a phenomenon was already observed for several cases in polyanilines[4,5] and has been associated with the steric and electronic effects of the substituents. The bulky alkanesulfonic acid substituent will induce additional deformations along the polymer backbone due to an increase in steric hindrance and hence a reduction in chain conjugation, which

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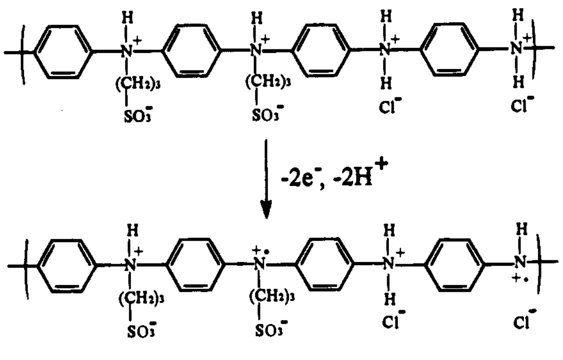
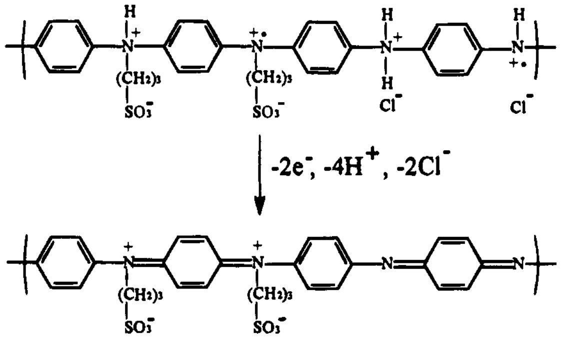
(32) Epstein, A. J. AC Conductivity of Polyacetylene: Distinguishing Mechanisms of Charge Transport. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1985; Vol. 2, p 1050.

(33) MacDiarmid, A. G.; Chiang, J. C.; Richter, A. F.; Epstein, A. J. *Synth. Met.* **1987**, *18*, 285−290.

Scheme 1



Scheme 2



will reduce the stability of the generated polysemiquinone radical cations, leading to a higher oxidation potential for the first redox process. The electron-donating effect of the alkanesulfonic acid group can be expected to stabilize the radical cation and thus lead to a lowering in the oxidation potential.

The stability of potential cycling of PAPSAH is similar to that of polyaniline.[34] The voltammograms of a film in 1.0 M HCl remain almost the same after 1000 cycles in the range 0.0–0.6 V *vs* SCE at 50 mV/s. Furthermore, the peak current for the first redox process is found to vary linearly with the square root of the scan rate, indicating that the first redox process is a reversible process.[35] However, once the potential is raised to 0.8 V, irreversible degradation begins to occur, and a third set of peaks appear between the two original peaks due to the hydrolysis of the imine to form benzoquinone;[36] these were also found in the parent polyaniline.[34]

2. Spectroelectrochemistry. The optical property of a thin film of PAPSAH coated on ITO glass is studied in situ by spectroelectrochemistry in 1.0 M hydrochloric acid, as shown in Figure 15. At −0.2 V, the polymer film is pale yellow with one main absorption band at about 310 nm. When the potential increases to 0.2–0.4 V, an absorption band appears at about 400–420 nm. Meanwhile, a growing absorption band is observed at above 800 nm, and the film turns green. These new bands at 400–420 nm and above 800 nm are assigned to the electronic transition of the radical cation.[22] At higher potential (0.6–0.8 V), the polymer becomes blue while a significant hypsochromic shift (blue shift) of the absorption band at above 800 nm occurs. These color changes are identical to those of polyaniline when subjected to an electrochemical redox process.

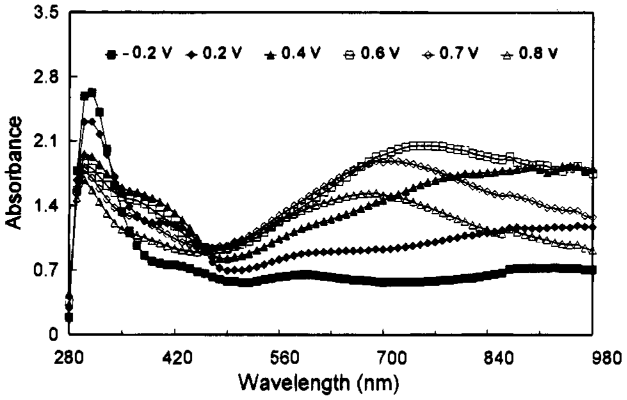


Figure 15. UV–vis spectra of PAPSAH film coated on ITO glass in 1.0 M HCl at various applied potentials.

Conclusion

The water-soluble self-acid-doped conducting polyaniline PAPSAH with intermediate conductivity (about 10^{-2} S/cm) is synthesized by a chemical reaction of the emeraldine base form of polyaniline with propanesultone; approximately each amine nitrogen (about 50% of the total nitrogen) in the polymer is linked with a propanesulfonic acid. The doping level of the polymer (i.e., imine nitrogens being protonated to give semiquinone radical cations) is about 0.33, both in its aqueous solution and as a solid film, and the protons that do not participate in the doping have no effect on the conductivity of the film. As the doping level is reduced by increasing the degree of neutralization, the conductivity at room temperature drops by a factor of 10^4 at the doping level of zero. The self-acid-doping undergoes a polaron separation to yield a polaron lattice after a dissociation of the bipolaron to two polarons, similar to those in the case of HCl-doped PAn. The cyclic voltammograms of PAPSAH consist of two pairs of well-resolved redox peaks corresponding to the formation of the semiquinone radical cation and to the formation of the fully oxidized form of the polymer. During the redox process, the PAPSAH films exhibit reversible color changes from pale yellow to green to blue. The conductivity of the PAPSAH film increases with temperature from −50 to +110 °C due to thermal activation, and decreases with temperature from 110 to 170 °C resulting from thermal undoping. After the heating scan, the conductivity at room temperature drops by a factor of 10^3 due to the loss of some polarons.

The incoporation of the propanesulfonic acid substituent causes increases of the electron localization and structural disorder, which result in a decrease in conductivity. The self-acid-doping nature allows the polymer to become a water-soluble Zwitterionic polymer.

Acknowledgment. We wish to thank the National Science Council of the Republic of China for financial aid through Project No. NSC 84-2221-E007-023.

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