Macromolecules 1991, *24*, 4441-4445

XPS Study of Self-Doped Conducting Polyaniline and Parent Systems

J. Yue[†] and A. J. Epstein*[,†,‡]

Departments of Chemistry and Physics, The Ohio State University, Columbus, Ohio 43210-1106

Received November 9, 1990; Revised Manuscript Received December 14, 1990

ABSTRACT: The structure and protonation level of sulfonated polyaniline as well as the chemically synthesized emeraldine base and its chloride salt have been investigated by X-ray photoelectron spectroscopy (XPS). The results indicate that ~50% of the phenyl rings of the sulfonated polyaniline have a hydrogen atom substituted by a $-SO_3H$ group. Approximately 50% of the nitrogen sites are protonated in this self-doped conducting polymer. The protonation level remains unchanged upon exposure to high vacuum at room temperature. In contrast, emeraldine hydrochloride undergoes partial deprotonation and probably reduction as well under high-vacuum conditions. The N 1s lines show there is greater charge localization in the sulfonated polyaniline system than in emeraldine hydrochloride due to the presence of $-SO_3^-$ groups. The results of the XPS study are in agreement with data obtained by other techniques.

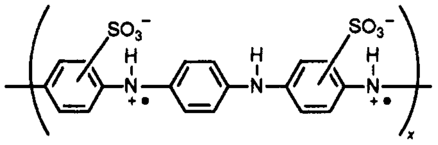
Introduction

The polyaniline family of polymer has been under intense study because of its facile chemistry and its ability both to be protonic acid and to be oxidatively or reductively doped to a highly conducting state.[1,2] The ideal emeraldine base (EB) oxidation state of polyaniline contains an equal number of alternating amine and imine repeat units (Figure 1a).[2-4] When EB is doped by a protonic acid, the protonation occurs preferentially on the imine nitrogen sites,[2] as, for example, shown for the emeraldine hydrochloride salt (ES) in Figure 1b. Recently, sulfonated polyaniline (SPAN), the first self protonic acid doped polyaniline, was reported.[5] Transport studies on this self-doped polymer show that there is greater charge localization present in SPAN than in ES.[6] In order to gain insight into the differences in structural and electronic properties among doped, undoped, and externally and internally doped emeraldine, a systematic study using X-ray photoelectron spectroscopy was undertaken.

The results reported here demonstrate that the stoichiometry of SPAN indeed is 0.5 $-SO_3^-$ group/phenyl-nitrogen unit, that the doping level is stable under vacuum (in contrast to a reduced surface doping level for ES), and that there is greater charge localization in SPAN as compared with ES. The origins of these differences are discussed.

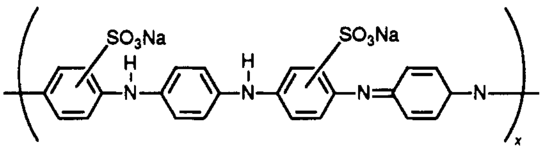
Experimental Techniques

Emeraldine base (EB; Figure 1a) and emeraldine hydrochloride powder (ES; Figure 1b) were synthesized by using a previously described method.[7] The resulting ES was then in the partially crystalline ES-I form and EB in the amorphous EB-I form.[8,9] The self protonic acid doped polyaniline was synthesized by sulfonation of EB-I.[5] In a typical procedure, 0.5 g of EB-I was sulfonated by dissolving it in 40 mL of fuming sulfuric acid with constant stirring at ~5 °C. After ~2 h, the solution was slowly added to methanol to precipitate the product. The green powder was then collected and washed completely with methanol. The filter cake was dried under dynamic vacuum for 24 h. The self-doped conducting polyaniline[10]



thus is obtained.

The sodium salt of sulfonated polyaniline (Na-SPAN)



was synthesized by stoichiometrically dissolving 0.5 g of SPAN in 20 mL of 0.1 M NaOH solution and subsequently removing water.

The vacuum-dried sample powders were mounted onto a standard sample holder by using double-sided adhesive tape. Core level spectra were obtained by a Perkin-Elmer Physical Electronics Model 550 ESCA system with a Mg Kα X-ray source (1253.6 eV). The X-ray powder supply was operated at 12 kW and 10 mA. The pressure in the analysis chamber during scans was kept below 10^{-8} Torr. The peak area ratios for various elements were corrected by experimentally determined instrumental sensitivity factors. N 1s and Cl 2p spectra, after background subtractions, were decomposed into suitable components consisting of a Gaussian line shape with a Lorentzian broadening function. All fitting parameters, including the number of components, widths, and intensities, were freely adjustable and determined for each spectrum with an iterative, least-squares fitting routine.

Occasionally, small differences were found in the binding energies determined for the same species in different samples. Thus during attempts to overlay binding energy spectra of supposedly identical samples, it was accordingly necessary to make a small energy adjustment to achieve good overlap. In every case these adjustments produced complete overlay of all peaks, indicating that these shifts are due to sample-dependent charging effects. Other possible chemical and physical causes cannot be precluded.

The binding energy of C 1s was adjusted to 285.0 eV based on the studies of polyaniline[11-13] in order to compensate the charging effects for each sample; it was taken as the reference for the other core level peaks. C 1s spectra were smoothed by a three-point averaging routine.[12]

Experimental Results

N 1s of emeraldine base: The XPS spectra for the polyaniline bases and salts vary systematically. EB-I has

---

[†] Department of Chemistry.
[‡] Department of Physics.

0024-9297/91/2224-4441$02.50/0

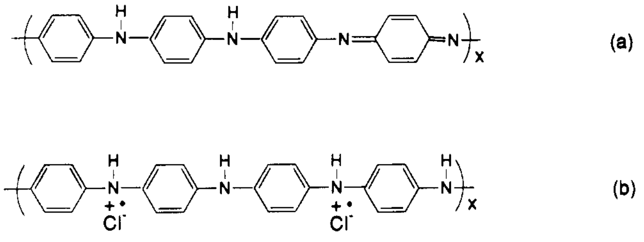


Figure 1. Schematic illustration of idealized structures for (a) emeraldine base and (b) emeraldine hydrochloride.

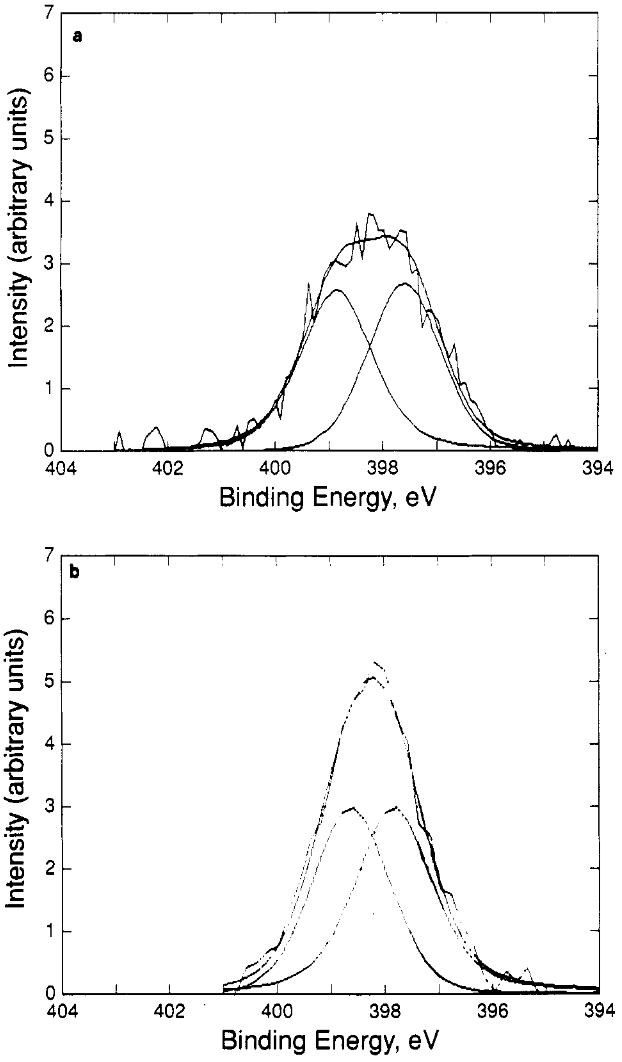


Figure 2. N 1s XPS core level spectra of (a) emeraldine base and (b) the sodium salt of sulfonated polyaniline. The solid lines are the fits to the data (see text).

a simple nearly symmetric N 1s line centered close to 398.6 eV (Figure 2a). This N 1s core spectrum level of the line can be deconvoluted into two peaks with equal intensity, one centered at 398.9 eV, the other located at 397.5 eV. Both have a fwhm (full width at half-maximum) of 1.6 eV.

N 1s of SPAN: The nearly symmetric N 1s peak in EB-I changes to asymmetric in SPAN (Figure 3a). As analyzed for EB-I, the N 1s core level of SPAN also can be decomposed into two components. The one at higher binding energy is centered at 400.7 eV with a fwhm of 1.8 eV, while the one at the lower energy side is centered at 399.1 eV with a fwhm of 1.5 eV. The ratio of the integrated areas of these two peaks is 1:1.

N 1s of emeraldine hydrochloride: Figure 3b shows the N 1s line of ES-I. The peak envelope obviously does not originate from a single component or two equal components. It can be decomposed into three peaks, one located at 402.2 eV with a fwhm of 2.0 eV, one centered at 400.4 eV having a fwhm of 1.8 eV, and the last one positioned at 399.1 eV with a fwhm of 1.6 eV. The ratio of the integrated area of these three peaks is 1:3.3:8.8.

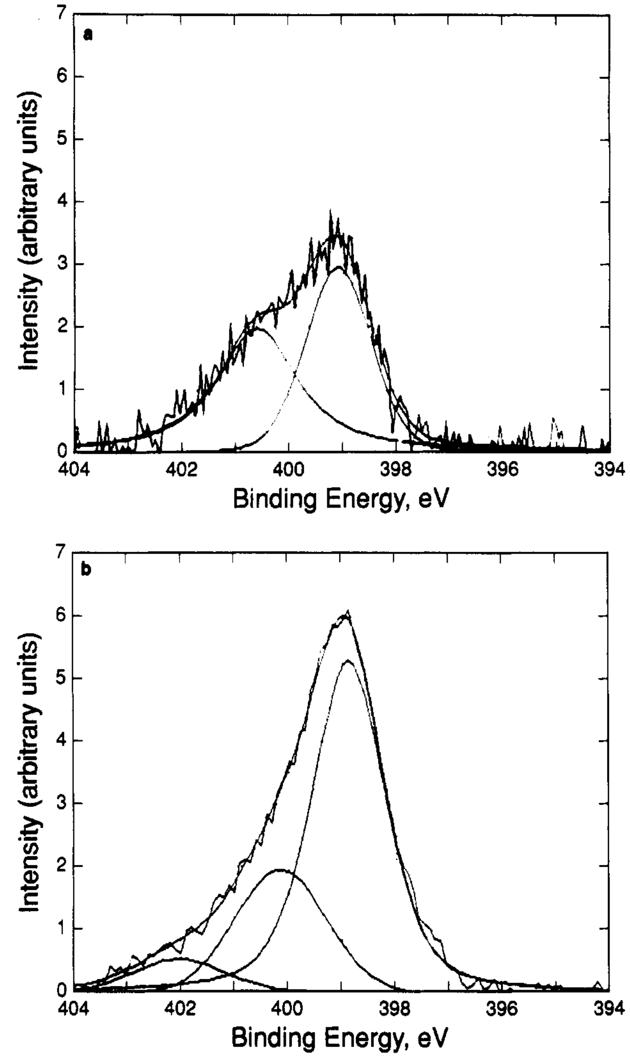


Figure 3. N 1s XPS core level spectra of (a) sulfonated polyaniline and (b) emeraldine hydrochloride. The solid lines are the fits to the data (see text).

N 1s of sodium salt of sulfonated polyaniline: The N 1s line of Na–SPAN (Figure 2b) has features almost identical with that of EB-I. However, the main envelope shifts slightly (0.5 eV) toward higher energy as compared to that of EB-I. The XPS spectrum is decomposed into two peaks, the ratio of which is 1:1.

S 2p of sulfonated polyaniline: The S 2p line of SPAN is shown in Figure 4. The N/S ratio is measured to be 2, the same as the theoretical value. Thus for every two phenyl rings of the polyaniline backbone there is a sulfonic group. The S 2p line of Na-SPAN is similar to that of SPAN with a somewhat narrower line width (fwhm(SPAN) $\sim$ 2 eV; fwhm(Na-SPAN) $\sim$ 1.75 eV).

Cl 2p of emeraldine hydrochloride: The Cl 2p line of ES-I (Figure 5) can be decomposed into Cl 2p$_{1/2}$ and Cl 2p$_{3/2}$ lines with an intensity ratio of 1:2 as expected. Cl 2p$_{1/2}$ is at 199.2, and Cl 2p$_{3/2}$ is at 197.1 eV, respectively.

C 1s of sulfonated polyanilines: The C 1s lines of Na-SPAN and SPAN are shown in Figures 6 and 7, respectively. Due to multiple carbon-bonding environments in the sulfonated polyanilines, it is difficult to carry out unambiguous decomposition of the C 1s signal. However, the envelope of the C 1s line of the conducting

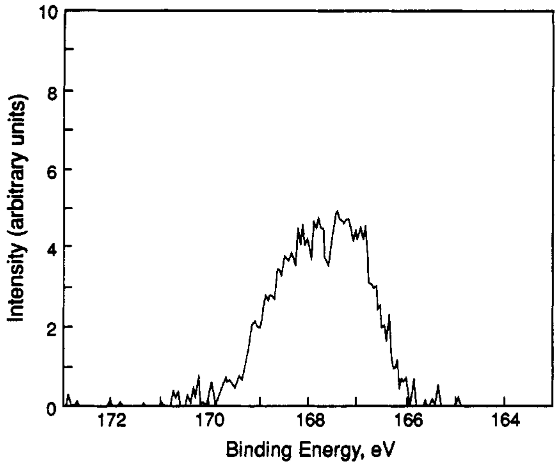


Figure 4. S 2p core level spectrum of sulfonated polyaniline.

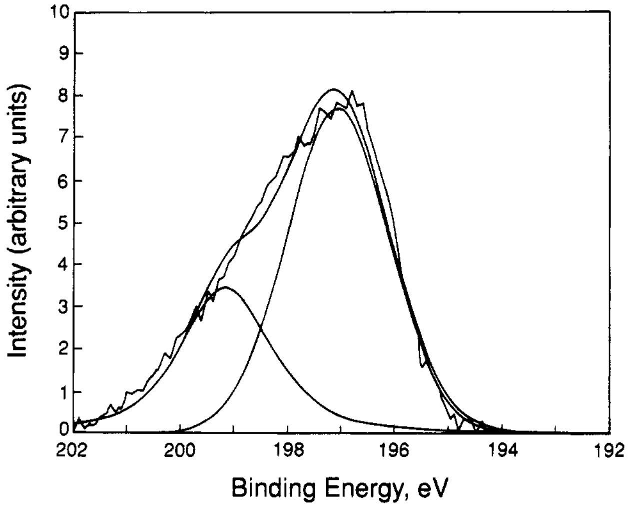


Figure 5. Cl 2p core level spectrum of emeraldine hydrochloride. The solid lines are the fits to the data (see text).

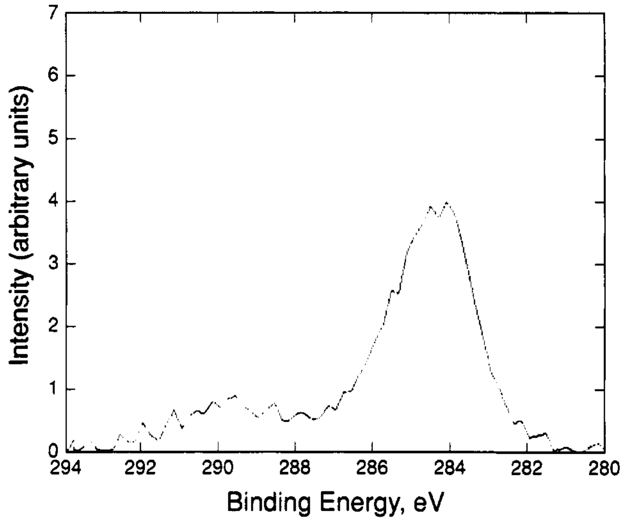


Figure 6. C 1s XPS core level spectrum of the sodium salt of sulfonated polyaniline.

form is skewed toward the high-energy side while satellites are seen in the C 1s spectrum of the insulating form of sulfonated polyaniline.

O 1s lines: The O 1s spectrum of EB and Na-SPAN have a single line of fwhm ~ 2 eV centered at 532.2 and 531.2 eV, respectively. For ES-I the line width increases to nearly 3 eV centered at 532.3 eV. In contrast, for SPAN two species of oxygen are observed. One is centered at 533.5 eV (fwhm ~ 1.5 eV), and another is at 531.3 eV (fwhm ~ 2 eV).

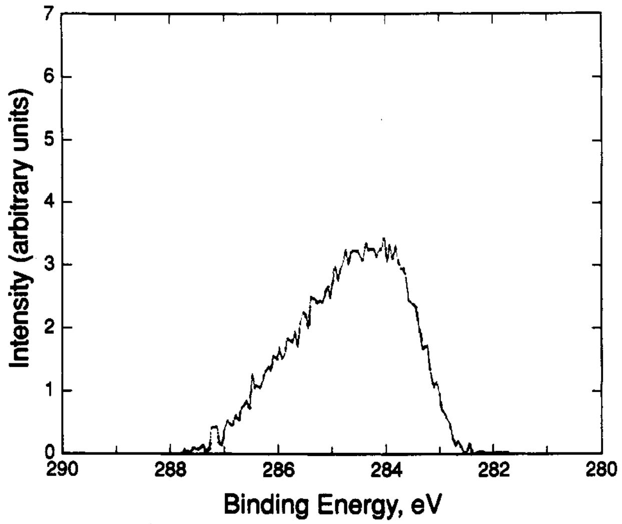


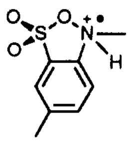
Figure 7. C 1s XPS core level spectrum of the sulfonated polyaniline.

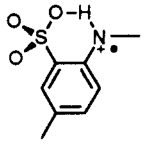
Discussion

N 1s of EB-I. Emeraldine base has a simple, symmetric N 1s line centered close to 398.6 eV, shown in Figure 2a. This is expected from the idealized structure of the emeraldine base backbone. The peak centered at 398.9 eV is assigned to the amine nitrogen.[14] The other located at 397.5 eV is attributed to imine nitrogen atoms.[14] The nearly 1 to 1 ratio of amine and imine nitrogen is consistent with the idealized EB structure.[2-4] The slight difference in imine and amine nitrogen ratio from that reported by Tan et al.[14] is likely due to differences in sample synthesis and handling.[3]

N 1s and S 2p of SPAN. A dramatic change in the N 1s line shape is observed when EB-I is sulfonated by fuming sulfuric acid, $H_2SO_4(SO_3)$ (Figure 3). The peak at higher binding energy (centered at 400.7 eV) is assigned to the radical cationic nitrogen atoms, while the one at the lower energy side (centered at 399.1 eV) is characteristic of uncharged amine sites. In all sulfonated samples investigated, the positively charged radical cationic nitrogen atoms have a slightly larger fwhm than that of the amine nitrogen atoms. This higher energy peak is also asymmetric. This is consistent with the environment of the positively charged nitrogen atoms being less homogeneous than that of amine nitrogen atoms. This inhomogeneity may be caused by deviations from the average angle between phenyl rings and the planes of the nitrogen sites due to the steric effect of $-SO_3^-$.

As compared with the N 1s line of EB-I, the imine nitrogen peak at 397.5 eV of EB-I (Figure 2a) disappears completely and the cationic radical nitrogen peak[14] (shoulder) appears at 400.7 eV (Figure 3a). Hence, these XPS spectra show that the imine nitrogen atoms are completely protonated by the intrinsic acid $-SO_3H$. The shoulder is believed to arise from the polarons in SPAN. By comparing N 1s lines, we concluded that the polaron in SPAN is more localized than that in EB-I doped by HCl (see below). The localization may be caused by a strong electrostatic interaction between the $-SO_3^-$ function groups and cationic radical nitrogen atoms or amine hydrogen through space to form five- or six-membered rings with energetically favorable configurations





Furthermore, the larger torsion angle introduced by an interaction between $-SO_3^-$ and hydrogens on the adjacent phenyl ring can somewhat break the π electron conjugation and tends to localize the positive polarons. In light of the above, variation in the local environment of the positive polarons may then be the origin of the enhanced asymmetry at the higher binding energy side of the XPS peak. This is consistent with conclusions based on the studies of the electric field and the temperature dependence of the conductivity of SPAN[6] and X-ray structural studies, which show that SPAN is nearly amorphous[15] in contrast to ~50% crystallinity for ES.[8,9] Despite the protonation of the imine nitrogen, the original structure of the amine nitrogen centered at 399.1 eV remains almost unchanged. In other words, half of the nitrogen atoms do not undergo protonation.

The ratio of the amine nitrogen and cationic radical nitrogen atoms (Figure 3a) is 1:1, indicating that the doping level reaches its maximum, i.e., $[SO_3^-]/[N] = 0.5$, consistent with the structure proposed previously.[5] Figure 4 shows a sulfonic S 2p signal at 167.5 eV, from which it was determined that there is one sulfur atom for every two nitrogen atoms. This result again supports the hypothesis that essentially half of the phenyl rings are monosubstituted by a sulfonic group,[5] leading to a self-doped state. The results demonstrate that the SPAN remains self-doped even under vacuum conditions.

N 1s of Emeraldine Hydrochloride. Although the N 1s main peak of ES-I in Figure 3b does not show clear splitting, the peak envelope obviously does not originate from a single component. The absence of a distinct shoulder at the higher binding energy side indicates that there is no unique difference between the amine and cationic radical nitrogen atoms in binding energies. On comparison with SPAN, the positive charge in ES-I is more delocalized. It appears that the N 1s core level line shape of ES-I can be decomposed into contributions from three inequivalent nitrogen species. The peak centered at 402.2 eV is attributed to the most positively charged nitrogen sites, perhaps in the vicinity of chloride ions. The peak located near 400.4 eV is attributed to nitrogen atoms with delocalized positive charge. It should be noted that the chloride ions with charge *e* are located between polymer chains. They produce an electric field locally at or near half of the nitrogen sites, causing those nitrogen atoms to appear "more" positive than the others. X-ray crystal structure studies of ES-I[8,9] show that the polymer is at most ~50% crystalline, with a coherence length of up to 100 Å. Hence, the N 1s lines of doped polyaniline are expected to be inhomogeneously broadened. In addition, correlated magnetic studies[8] have shown that the protonated sites of the amorphous region of ES-I have a much lower spin while the crystalline regions have Pauli susceptibility, leading to the expectation of a wider range of energy level for protonated N sites.[8]

It is of interest to compare the integrated intensities of positively charged nitrogen atoms (with a core level binding energy above 400.7 eV) with that of uncharged amine sites at 399.1 eV. The results show that the ratio of positively charged to neutral amine nitrogen atoms is 33:67. This 33% positively charged nitrogen is substantially lower than that of 50% obtained by chemical analyses in fully doped bulk ES-I[2,7] and surface (XPS) analysis for SPAN. The ratio of the counterions (Cl^-) to the total nitrogen atoms in the polymer chains can be employed to determine the doping level of the emeraldine system.[7] The 33% doping level obtained by analysis of N 1s XPS spectra is supported by $[Cl]/[N] = 0.29$ obtained from integrating the Cl 2p and the N 1s XPS spectra. The reduced surface doping level of ES-I at high vacuum likely arises from desorption of HCl or Cl_2 after the sample was pumped at room temperature. The substantially higher amine content (67%) is also consistent with the removal of Cl_2. A comparison with a measured ~50% doping level for the SPAN system supports that the protonation level at high temperatures[16] or in vacuo can be stabilized via self-protonation.

It is noted that our $[Cl]/[N] = 0.29$ is significantly less than the $[Cl]/[N] = 0.4$ reported by Tan et al.[14] from XPS studies on doped EB. The close agreement of the doping level determined by the charged nitrogen to total nitrogen and the chlorine to total nitrogen ratios supports the idea that there is no significant covalent chlorine[14] in our samples. This is consistent with the chloride ions being associated with emeraldine salt in ionic form and the emeraldine salt being reversibly converted to base by washing with NH_4OH aqueous solution.[7]

The argument of no significant covalent chlorine in ES-I is also supported by the Cl 2p core level spectrum (Figure 5). The spectrum reveals the presence of Cl $2p_{3/2}$ and Cl $2p_{1/2}$ peaks at 199.2 and 197.1 eV, respectively, corresponding to those for ionic chlorine only.[17]

The proposed structure for nitrogens is also consistent with the fwhm of the different components. The component at 402.1 eV, which is believed to be the most influenced by the presence of the chloride ions, has a fwhm of 2.0 eV, while the fwhm of 400.2 eV, which is less affected by the chloride ion, is 1.8 eV. The least influenced amine nitrogen atoms have a fwhm of 1.6 eV, which is essentially the same as that of EB-I. The more delocalized positive charge for ES-I as compared with SPAN is consistent with the former's higher conductivity.

N 1s of Na-SPAN. The N 1s line of Na-SPAN (Figure 2b) has features almost identical with that of EB-I. The 1:1 ratio of the imine and amine sites unambiguously suggests that this self-doped polymer, which has intrinsic acid–base equilibrium between $-SO_3H$ and imine nitrogen atoms, can be converted to its undoped insulating form by treating it with NaOH aqueous solution.

The N 1s peak shifts slightly (0.5 eV) toward higher energy for Na-SPAN as compared with EB-I. This is consistent with the primary substituent effect[18] of $-SO_3$-Na on phenyl rings. This energy shift indicates that the steric effect has dominant influence on the spectrum even though $-SO_3Na$ is a strong electron-withdrawing group.

C 1s Satellites. A small peak about 4 eV above the main peak is observed on the high binding energy side of the C 1s peak of Na-SPAN (Figure 6). The separation of this peak from the main peak is characteristic of shake-up satellites in aromatic systems.[19] In polymers[20] the satellite structures can arise from simultaneous core electron photoionization and valence electron excitation (shake-up). It has been found that such satellite structures are most prominent in polymer systems for which backbones are unsaturated, especially for those containing aromatic rings.[18] For most unsaturated polymeric systems, the shake-up satellites are located 6–8 eV above and have ~10% of the intensity of the main peak. The satellites have been assigned to π–π^* transitions involving two of the highest occupied orbitals and one lowest unoccupied orbital.[21] The ~4 eV shake-up line is consistent with the π–π^* absorption observed from optical studies.[22] The absence of shake-up satellites in conducting SPAN is in accord with the presence of a partly filled energy band as detected by magnetic susceptibility[6] (see below).

C 1s. The multiple inequivalent carbon-bonding states in both pure and sulfonated polyanilines make it difficult to carry out unambiguous analysis of the C 1s signal. Nevertheless, it is noted that the main peak of C 1s of SPAN (Figure 7), as well as N 1s of ES-I and SPAN, is skewed toward to the high-energy side; that is, both C 1s and N 1s line shapes change from symmetric for the insulating forms to asymmetric for conducting forms. The shake-up satellites are absent in the conducting forms, and ultraviolet photoelectron spectroscopy (UPS) data[12] show an increase in electron density toward the Fermi level after EB-I is doped. This is in accord with a finite density of states at the Fermi level determined by magnetic susceptibility studies of both emeraldine hydrochloride salt[23] and sulfonated polyaniline systems.[6]

The existence of a finite density of states at the Fermi level indicates a distribution of unoccupied orbitals immediately above the Fermi level. They are available for shake-up events to occur after emission of the core electron. In this case, the line shape for the core level is expected to be accompanied by a low kinetic energy tail. We therefore attribute the skewing mainly due to excitation of the Fermi surface electrons[24] rather than disorder.[25] This is consistent with the fact that excitation of the Fermi surface electrons produces asymmetric line shapes in metals.[26]

Oxygen Stoichiometry. Comparison of line intensities for oxygen and sulfur gives a ratio of 6:1 and 7:1 for SPAN and Na-SPAN, respectively. Values of the ratio are higher than expected. One possible explanation is the presence of three H_2O molecules associated with each repeat unit of the polymer chain. This is consistent with our observation of some oxygen, presumably associated with H_2O, in ES-I (one H_2O molecule for every two rings) and EB-I (one H_2O molecule for every six rings). Furthermore, oxygen contamination is present in virtually every XPS spectrum. It is noted that a possible anisotropy in the sample, i.e., a preferential stacking of the molecules, could also lead to deviations of the experimental stoichiometry values from those expected for homogeneous materials.[27] The presence of two distinct oxygen species for SPAN is in accord with the presence of distinct SO_3^- and H_2O units[17] in a ~2:1 ratio. The absence of a distinct contribution from these two species in Na-SPAN likely reflects the electrostatic effects of the Na^+ ions.

Conclusion

The first XPS experimental study of core level spectra of self-doped conducting polyaniline has been presented. Through use of the XPS technique, differing influences of $-SO_3^-$ and Cl^- on the N 1s core level have been demonstrated. The protonation occurs preferably on imine nitrogen atoms. The fitted widths of the excitation peak of doped nitrogen sites were generally 0.2–0.3 eV larger than those of amine sites. This difference is attributed to inhomogeneities in the bonding environment of the doped nitrogen sites. For the self-doped samples, the protonation is stabilized by the binding of the $-SO_3^-$ groups to the polymer backbone. In contrast, loss of some Cl_2 or HCl at high-vacuum conditions causes deprotonation of ES-I. There is greater charge localization in the SPAN system than in ES-I. This is attributed to the proximity of the $-SO_3^-$ groups on the polymer chain and absence of significant crystallinity. The agreement between the results of the present investigation using XPS and results from other means strongly supports the structure proposed for self-doped conducting SPAN. Almost identical features are observed for EB-I and the sodium salt of sulfonated polyaniline, indicating that the $-SO_3Na$ has less influence on the nitrogen core level than $-SO_3^-$ does.

Acknowledgment. This research has been supported in part by the Defense Advanced Research Projects Agency through a contract monitored by the U.S. Office of Naval Research. J.Y. thanks Mr. R. S. Tucker for technical assistance with the XPS experiment.

References and Notes

(1) See, for examples: Proceedings of the International Conference on the Science & Technology of Synthetic Metals, Tübingen, Germany, Sept 2–9, 1990, *Synth. Met.* **1991**, in press; Sante Fe, NM, June 25–July 2 1987, *Synth. Met.* **1989**, 27–29.

(2) MacDiarmid, A. G.; Epstein, A. J. *Faraday Discus. Chem. Soc.* **1989**, *88*, 317.

(3) Asturias, G. E.; MacDiarmid, A. G.; McCall, R. P.; Epstein, A. J. *Synth. Met.* **1989**, *29*, E157.

(4) Masters, J. G.; Sun, Y.; MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1991**, *41*, 715.

(5) Yue, J.; Epstein, A. J. *J. Am. Chem. Soc.* **1990**, *112*, 2800.

(6) Yue, J.; Wang, Z. H.; Cromack, K. R.; Epstein, A. J.; MacDiarmid, A. G. *J. Am. Chem. Soc.* **1991**, *113*, 2665.

(7) MacDiarmid, A. G.; Chiang, J. C.; Richter, A. F.; Somasiri, N. D. L.; Epstein, A. J. In *Conducting Polymers*; Alcacer, L., Ed.; Riedel: Dordrecht, Holland, 1987; p 105.

(8) Józefowicz, M. E.; Laversanne, R.; Javadi, H. H. S.; Pouget, J.-P.; Epstein, A. J.; Tang, X.; MacDiarmid, A. G. *Phys. Rev. B.* **1989**, *39*, 12958.

(9) Pouget, J.-P.; Józefowicz, M. E.; Epstein, A. J.; Tang, X.; MacDiarmid, A. G. *Macromolecules* **1991**, *24*, 779.

(10) Typical elemental analysis for SPAN. 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. Found: C, 52.12; H, 3.98; N, 10.13; S, 11.18; O, 22.59 (oxygen by difference).

(11) Snauwaert, P.; Lazzaroni, R.; Riga, J.; Verbist, J. J. *Synth. Met.* **1987**, *16*, 245.

(12) Nakajima, T.; Harada, M.; Osawa, R.; Kawagoe, T.; Furukawa, Y.; Harada, I. *Macromolecules* **1989**, *22*, 2644.

(13) Chan, H. S. O.; Munro, H. S.; Davies, C.; Kang, E. T. *Synth. Met.* **1988**, *22*, 365.

(14) Tan, K. L.; Tan, B. T. G.; Kang, E. T.; Neoh, K. G. *Phys. Rev. B* **1989**, *39*, 8070.

(15) Józefowicz, M. E.; Pouget, J.-P.; Yue, J.; Epstein, A. J., unpublished results.

(16) Yue, J.; Epstein, A. J.; Zhong, Z.; Gallagher, P. K.; MacDiarmid, A. G. *Synth. Met.* **1991**, *41*, 765.

(17) Wagner, C. D.; Riggs, W. M.; Davis, L. E.; Moulder, J. F.; Muilenberg, G. E. *Handbook of X-ray Photoelectron Spectroscopy*; Perkin-Elmer Corp.: Eden Prairie, MN, 1979.

(18) Briggs, D. In *Practical Surface Analysis*; Briggs, D., Seah, M. P., Eds.; John Wiley & Sons: New York, 1983; p 359.

(19) Briggs, D.; Riviere, J. C. In *Practical Surface Analysis*; Briggs, D., Seah, M. P., Eds.; John Wiley & Sons: New York, 1983; p 87.

(20) Briggs, D.; Riviere, J. C. In *Practical Surface Analysis*; Briggs, D., Seah, M. P., Eds.; John Wiley & Sons: New York, 1983; p 359.

(21) Clark, D. T.; Adams, D. B.; Dilks, A.; Peeling, J.; Thomas, H. R. *J. Electron Spectrosc.* **1976**, *8*, 51.

(22) Yue, J.; Epstein, A. J.; MacDiarmid, A. G. *Mol. Cryst. Liq. Cryst.* **1990**, *189*, 255.

(23) Ginder, J. M.; Richter, A. F.; MacDiarmid, A. G.; Epstein, A. J. *Solid State Commun.* **1987**, *63*, 97.

(24) Salaneck, W. R.; Erlandsson, R.; Prejza, J.; Lundstrom, I.; Inganas, O. *Synth. Met.* **1983**, *5*, 125.

(25) Pfluger, P.; Street, G. B. *J. Chem. Phys.* **1984**, *80*, 544.

(26) Citrin, P. H.; Wertheim, G. K.; Baer, Y. *Phys. Rev. B* **1977**, *16*, 4256.

(27) Lamb, R. N.; Baxtex, J.; Grunze, M.; Kong, C. W.; Unertl, W. N. *Langmuir* **1988**, *4*, 249.