

Limitations of the X-ray Photoelectron Spectroscopy Technique in the Study of Electroactive Polymers

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Polyaniline (PAN) and polypyrrole (PPY) were analyzed by X-ray photoelectron spectroscopy (XPS) and bulk analytical techniques. A systematic comparison of the results was carried out to determine the effects of anion size, synthesis methods, and the nature of the polymer (powder or film) on the variation between the surface and bulk compositions. Good agreement between the XPS and bulk analytical results is generally obtained for chemically synthesized polyaniline (in powder form). However, these two methods may give substantial discrepancies in the analysis of anion concentration in as-cast polyaniline base films subjected to re-doping by acids. Such discrepancies are also found in the analysis of as-synthesized polypyrrole doped by large anions and polypyrrole base films and powders after re-doping by acids. In these cases the XPS technique tends to give anion concentrations that are significantly higher than the bulk values. In some of these cases the high surface anion concentration supports a high proportion of positively charged nitrogens (>50% for polyaniline, >30% for polypyrrole), which must involve the protonation of some amine units in addition to all of the imine units. However, in actuality, the re-doping process can only replenish the anions to less than half of the original bulk concentration in polypyrrole.

Introduction

Electroactive polymers have become the subject of numerous studies¹ due to their potential applications in devices such as sensors or batteries. Many continuing efforts have been spent on developing polymers with superior conductivity, stability, mechanical strength, and processability. In conjunction with these efforts, a better understanding of the physicochemical properties of the polymers is critical for improvement and optimization. Many investigators have found X-ray photoelectron spectroscopy (XPS) to be a particularly useful tool for obtaining information on the structure of the electroactive polymers and the charge distribution during charge transfer processes.² Examples of its recent applications include studying the intrinsic structure of polyaniline (PAN) and polypyrrole (PPY),^{3–8} the chemical states of the dopants in PAN,^{9–13} PPY,¹⁴ and polyacetylene,^{15–18} and the degradation mechanisms in these polymers.^{7,8,19–22} As the unique advantages of using XPS for studying electroactive polymers become more recognized, its popularity correspondingly increases. However, a number of discrepancies can be found in the published XPS results, due partly to the differences in spectra deconvolution and peak assignments. (For example, compare refs 3, 23, and 24). In addition, certain shortcomings of this technique have to be recognized.

The present study focused on the important limitations of the XPS technique when used in the study of electroactive polymers. PPY and PAN were chosen for this study in view of the extensive on-going research on these two polymers. It has generally been accepted that the aniline polymers possess the general formula $[(\text{--BNHBNH--})_y(\text{--BN=Q=N--})_{1-y}]_x$ in which B and Q denote the C_6H_4 rings in the benzoid and quinoid forms, respectively. The usual method of chemically synthesizing PAN in dilute HCl yields a 50% oxidized polymer (in powder form) termed emeraldine (EM, $y = 0.5$) in which the

imine nitrogens (--N=) are selectively protonated.^{23,24} The removal of the protons result in a transition to an insulating state. The heteroatoms of PAN and PPY show similarities in protonation/deprotonation and charge transfer processes, although the --N= groups only constitute about 20–25% of the total nitrogens in the deprotonated PPY.⁸ In this work, PPY and PAN in the form of films and powders were subjected to investigations using both XPS and bulk analytical techniques such as infrared (IR) absorption spectroscopy, and elemental analysis. The discussion will be centered on those instances where significant discrepancies existed between the results obtained from the surface and bulk techniques.

Experimental Section

Sample Preparation. Polyaniline was synthesized via the chemical oxidation of aniline by $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in 1 M acid, similar to the procedure published earlier.^{25,26} The acids used were HCl, HClO_4 , *p*-toluenesulfonic acid (TSA), and poly(styrenesulfonic acid) (PSSA). The as-synthesized PAN salts (denoted by PAN-HX, HX being the acid used) are in the form of powder. Conversion to the base form was carried out by equilibrating the salts in 1 M NaOH for 1 h, followed by rinsing with deionized water until neutral, and then by pumping dry under reduced pressure. Free-standing base films of $\sim 5 \mu\text{m}$ thickness were cast from a solution of the base in *N*-methylpyrrolidinone (NMP). The reprotonation of the base powders and films by the above-mentioned acids was also carried out. The effect of reprotonation time was investigated.

Polypyrrole in powder form was prepared from the chemical oxidation of pyrrole (0.2 M) by $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.42 M) in either water or 0.15 M TSA or the sodium salt of PSSA (NaPSSA). Since PPY is not soluble in the common organic solvents, PPY films were synthesized electrochemically using 0.2 M pyrrole and 0.05 M TSA, dodecylbenzenesulfonic acid (DBSA), NaPSSA, or the sodium salt of poly(vinylsulfonic acid) (NaPVSA) as electrolyte. The film was deposited galvanostatically at 2 mA/cm² on a stainless steel electrode under a N_2 atmosphere.

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The polymerization time was 10–15 min, depending on the electrolyte. The films were rinsed with a small amount of water, dried under vacuum, and scraped off the electrode. Films of about 5 μm thickness (denoted by PPY-HX, HX being the acid used) were prepared in this manner. PPY bases were obtained by treating either the powders or films with 1 M NaOH for 1 h, similar to the method used for PAN. For study of the reprotonation process, the PPY base powders and films were also treated with 0.5 M acids for varying periods of time.

Instrumentation. The Fourier transform infrared (FTIR) absorption spectra of the polymers were measured using a Shimadzu FTIR 8101M spectrophotometer. The absorption spectra of the films were measured directly, while powder samples were first dispersed in KBr and then pressed into pellets. Bulk analysis of C, H, N, and S was carried out using a Perkin-Elmer 2400 Series II CHNS/O analyzer, while Cl was determined using a titration technique. The XPS measurements were made on a VG ESCALAB MkII spectrometer with a Mg K α X-ray source (1253.6 eV photons). The films and powder samples were mounted on standard sample studs by means of double-sided adhesive tape. Unless otherwise stated, core-level spectra were taken at a take-off angle (α) of 75° (measured with respect to the sample surface). The X-ray source was run at a reduced power of 120 W (12 kV and 10 mA). Throughout the measurements, the pressure in the analysis chamber was maintained at 10^{-8} mbar or lower. To compensate for the surface charging effect, all binding energies (BE) were referenced to the C1s neutral carbon peak at 284.6 eV. In peak synthesis, the line widths (full width at half-maximum, fwhm) of the Gaussian peaks were maintained constant for all components in a particular spectrum. Surface chemical compositions were determined from peak–area ratios corrected with the appropriate experimentally determined sensitivity factors.

Results and Discussion

A review of the results indicates that substantial discrepancies between the XPS and bulk analyses may arise. These discrepancies are likely to be due to one of the following factors: dopant volatility, inability for the anions to migrate into the bulk, and the manner in which anions are incorporated during the synthesis of the polymers. The problem of dopant volatility is clearly illustrated by comparing PAN doped by HCl (volatile acid) and HClO₄ (nonvolatile acid) and has been highlighted in one of our earlier publications.²⁷ In the present work, the latter two issues are discussed. To avoid confusion, the PAN and PPY results are discussed separately below.

PAN Films. The consequence of anion diffusion limitation is most easily observed during the re-doping of PAN base films cast from NMP solutions. These films are purplish blue with a copper luster and have been reported to be near full density from helium pycnometry and bulk density measurements.²⁸ The treatment of 5 μm thick PAN base films by dilute HCl or HClO₄ results in a clear color change to blue green, and the electrical conductivity, σ , increases by more than 7 orders of magnitude to 5 S/cm. However, if acids with large anions such as DBSA are used, the films retain their original color even after 20 h of treatment, and σ increases only to 10^{-3} S/cm. A comparison of the FTIR absorption spectra of the films after treatment with either 0.1 M HClO₄ or 0.1 M DBSA for 20 h and that of the pristine base film in Figure 1 further illustrates the differences in the reprotonation behavior. The absorption spectrum of the DBSA-treated film (Figure 1b) closely resembles that of the base film (Figure 1a), with an absence of prominent bands due to the $-\text{SO}_3^-$ groups (between 1000 and 1050 cm^{-1} and at 670 cm^{-1} ²⁹). Thus, the visual observation, σ measurement, and

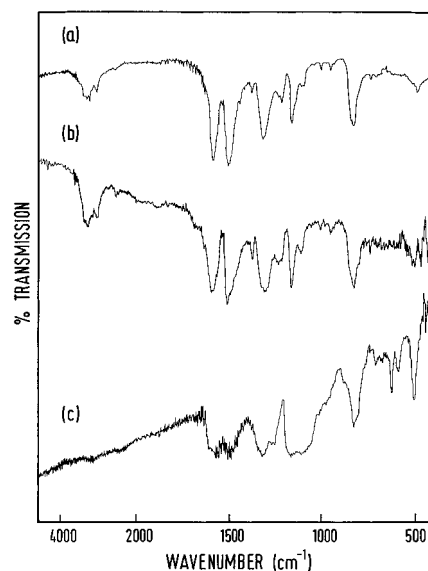


Figure 1. FTIR absorption spectra of (a) polyaniline base film cast from NMP solution, (b) base film after treatment with 0.1 M DBSA for 20 h, and (c) base film after treatment with 0.1 M HClO₄ for 20 h.

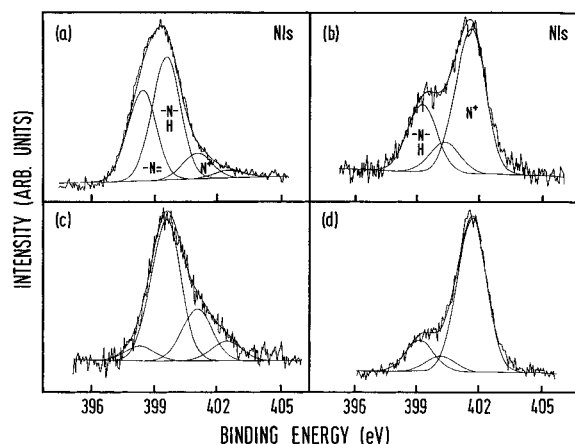


Figure 2. XPS N1s core-level spectra of (a) polyaniline base film cast from NMP solution and (b–d) base film after treatment with 0.1 M DBSA (b), 0.1 M HClO₄ (c), and 3 M HClO₄ (d).

FTIR absorption spectrum of the DBSA-treated film conclusively show that there is little penetration of DBSA anions into the bulk of the film. The spectrum of the HClO₄-treated film (Figure 1c), on the other hand, shows features characteristic of polyaniline salt, with a long absorption tail from 4000 to 1650 cm^{-1} , an intense and broadened 1140 cm^{-1} band,³⁰ and a prominent 630 cm^{-1} band attributable to ClO₄⁻ anions.³¹ If 0.01 M HClO₄ is used as the reprotonating acid, the FTIR absorption spectrum of the film after 1 h remains rather similar to that of the base film (Figure 1a). However, after 20 h, the intensity of the 630 cm^{-1} band increases and the 1140–1160 cm^{-1} band broadens. When the HClO₄ concentration is increased to 1 M, an absorption spectrum characteristic of a highly protonated PAN salt is obtained within an hour.

The XPS N1s core-level spectra of the pristine PAN base film and the film after re-doping with 0.1 M DBSA and 0.1 M HClO₄ are shown in Figure 2a–c, respectively. It is generally accepted that the amine ($-\text{NH}-$) nitrogens in PAN would give rise to a peak component at 399.4 eV, whereas the corresponding peak for the imine ($-\text{N}=\text{}$) nitrogens would be at 398.2 eV.^{6–8} From the XPS analysis, the fractions of $-\text{N}=\text{}$ and $-\text{NH}-$ species in the pristine base film are 0.37 and 0.50, respectively, with the balance being attributed to residual positively charged nitrogen (N^+). Thus, the fraction of $-\text{NH}-$ groups shows the

TABLE 1: Composition and Electrical Conductivity of Re-Doped PAN Powder

anions	re-doping time	XPS results				bulk results		
		$-\text{N}=\text{N}$	$-\text{NH}-$	N^+/N	A^-/N^a	A/N^b	$(\text{C}/\text{N})_{\text{PAN}}^c$	σ (S/cm)
ClO_4^-	1	0	0.53	0.47	0.57	0.53	6.23	1
TSA	1	0	0.59	0.41	0.59	0.55	6.30	0.1
TSA	20	0	0.58	0.42	0.48	0.49	5.77	1
PSSA	1	0	0.50	0.50	0.69	0.41	5.50	0.01
PSSA	20	0	0.51	0.49	0.69	0.39	5.91	0.05

^a A^- refers to ClO_4^- when HClO_4 is used and $-\text{SO}_3^-$ when TSA and PSSA are used. ^b A refers to Cl when HClO_4 is used and S when TSA and PSSA are used. ^c $(\text{C}/\text{N})_{\text{PAN}}$ refers to C/N of PAN after correcting for C in dopant.

PAN to be in the emeraldine state. The peak assignment for the positively charged nitrogens involved in electrostatic interaction with the anions is less clear. In Figure 2c, on the basis of the fixed fwhm approach, the high binding energy (BE) tail has been deconvoluted into two component peaks separated by 1.45 and 2.95 eV, respectively, from the $-\text{NH}-$ peak component. On the other hand, in Figure 2b, the N^+ component peaks are 1.10 and 2.25 eV from the $-\text{NH}-$ peak component. For ease of discussion, the type of N1s spectrum shown in Figure 2c will be denoted as type I, whereas that in Figure 2b with a prominent second N^+ peak, a weak first N^+ peak, and a smaller BE separation between the $-\text{NH}-$ peak and the N^+ components will be designated as type II. We propose that the type II spectrum occurs only when a substantial amount of $-\text{NH}-$ units are protonated (see below). This results in the positive charges being more localized in a bipolaron-type defect structure, whereas a polaron lattice results when only the imine nitrogens are protonated.^{4,23} Thus, the former will be represented by the major N^+ peak component in the type II spectrum. From the XPS spectra taken at $\alpha = 75^\circ$, the N^+/N ratio for the DBSA-re-doped PAN is 0.72, whereas the corresponding ratio for the HClO_4 -re-doped PAN is 0.34. At the more surface glancing angle of 20° , the N^+/N ratio for the DBSA-doped film increases to 0.83. The corresponding ratio for the HClO_4 -doped PAN does not show a significant change. As a direct consequence of the short mean free path of the photoejected electrons in the energy range of interest in XPS, the sampling depth is typically limited to the top ~ 5 nm of the material. Thus, from the XPS and FTIR absorption results, it can be interpreted that the DBSA anions are capable of protonating only the outermost region of the as-cast base film. However, in this region, a substantial fraction of the $-\text{NH}-$ units are protonated, in contrast to the HClO_4 -protonated film where even some $-\text{N}=\text{N}$ units remain unprotonated by the 0.1 M acid. This observed difference in the surface protonation levels between the HClO_4 - and DBSA-protonated films may be due to the higher propensity of DBSA to stick to the film surface. This results in the retention of an acid film on the surface of the PAN which is concentrated during drying under reduced pressure. With HClO_4 as the re-doping acid, the protonation of $-\text{NH}-$ units in the PAN film can only be achieved at high concentrations. When 1 M HClO_4 concentration is used, all $-\text{N}=\text{N}$ units are protonated and the N^+/N ratio is 0.45. When the HClO_4 concentration is increased to 3 M, the N^+/N ratio increases to 0.85 and a type II spectrum similar to Figure 2b is obtained (Figure 2d).

PAN Powders. Since the as-cast PAN base films possess only limited porosity, a comparison of the effect of anion size on the re-doping of PAN base powder was also carried out. Three 1 M acids of vastly different anion sizes, HClO_4 , TSA, and PSSA, were selected. The XPS results, bulk Cl/N or S/N ratios, and σ are given in Table 1. The XPS S/N ratio was calculated from the peak areas of the S (BE ~ 167 eV, characteristic of $-\text{SO}_3^-$) and N components, using experimentally determined sensitivity factors. From the XPS results, it can be seen that all three acids are capable of protonating all of

the imine units and protonation levels between 0.4 and 0.5 are obtained. The S/N ratios of samples subjected to re-doping by TSA for both 1 h and 20 h, obtained by XPS, agree well with those obtained from bulk analysis. With PSSA as the re-doping acid, although the bulk S/N ratios are significantly lower than values obtained from XPS, the former are only 20% lower than the value expected when all of the imine units in polyaniline (in the emeraldine oxidation state) are protonated by the $-\text{SO}_3^-$ groups. Comparing the TSA and PSSA re-doped samples, it can be seen from Table 1 that the latter possess a lower bulk S/N ratio but a higher surface $-\text{SO}_3^-/\text{N}$ ratio. Since the $-\text{SO}_3^-/\text{N}$ ratios of the PSSA re-doped samples are higher than the N^+/N ratio, the excess $-\text{SO}_3^-$ anions must be associated with H^+ rather than N^+ . Thus, the polymeric acid is inhibited to some extent (more than TSA) in doping the bulk of the PAN and tends to concentrate on the surface. It is interesting to note that although the S/N ratios obtained at 1 h doping time is either close to or larger than the corresponding value at 20 h doping time, σ is larger in the latter case for both TSA- and PSSA-doped samples. The σ of the 20 h TSA-re-doped sample is in fact similar to that of PAN synthesized in TSA. In Table 1, the C/N ratio of the PAN polymer is estimated from the elemental analysis after correcting for the C in the dopant (using the anion/N ratio to estimate the dopant content). The calculated C/N ratios are in most cases within 5% of the theoretical value of 6 expected for PAN polymer.

The bulk and surface S/N ratios of PAN synthesized (rather than re-doped) in TSA and PSSA have also been compared. Good agreement between the surface and bulk values was obtained with the PAN-TSA sample (0.46 from XPS and 0.54 from bulk analysis). The PAN-PSSA sample is largely soluble. The small amount of solid obtained is 1000 times less conductive than the PAN base re-doped with PSSA. Even after NaOH treatment, the XPS $-\text{SO}_3^-/\text{N}$ ratio remains at 0.50 compared to the bulk of S/N of 0.45. This indicates that the PSSA chains are well-distributed within the PAN matrix and are not removed even after base treatment. Thus, the results obtained with either re-doped or as-synthesized PAN powder show that, even with polymeric anions, the bulk anion concentration is close to that required to support the protonation of all $-\text{N}=\text{N}$ units.

PPY Films. The XPS N1s core-level spectra of electrochemically synthesized PPY-TSA film and this film after NaOH treatment are shown in Figure 3a,b, respectively. The main component peak at 399.7 eV is assigned to the neutral $-\text{NH}-$ nitrogens.⁶⁻⁸ The high BE tail has been deconvoluted into two component peaks, in a manner similar to that used in Figure 2c. Thus, Figure 3a may be considered a type I spectrum. In Figure 3b, the peak at 397.7 eV has been assigned to the $-\text{N}=\text{N}$ nitrogens. When the base film was subjected to re-doping by 0.5 M TSA, DBSA, and PSSA for 20 h, the XPS results showed that all of the imine nitrogens disappeared and the intensity of the high BE tail increased (Figure 3c,d). The XPS results of the redoped films are given in Table 2a together with the values of the bulk S/N ratio and σ . On the basis of the XPS results,

TABLE 2: Comparison of Re-Doped and As-Synthesized PPY Films

anions	XPS results				bulk results		
	$-\text{N}=\text{N}$	$-\text{NH}-/\text{N}$	N^+/N	$-\text{SO}_3^-/\text{N}$	S/N	$(\text{C}/\text{N})_{\text{PPY}}^a$	σ (S/cm)
(a) re-doped films							
TSA	0	0.75	0.25	0.36	0.13	3.99	8
DBSA	0	0.77	0.23	0.51	0.09	3.05	2
PSSA	0	0.74	0.26	0.47	0.10	3.81	10
(b) as-synthesized films							
TSA ^b	0 (0.19)	0.69 (0.65)	0.31 (0.16)	0.37 (0.04)	0.36 (0.05)	3.82 (4.12)	100
DBSA	0	0.50	0.50	0.83	0.37	3.10	50
PSSA	0	0.69	0.31	0.44	0.19	3.70	10

^a $(\text{C}/\text{N})_{\text{PPY}}$ refers to C/N of PPY after correcting for C in dopant. ^b Values in parentheses refer to results obtained from treatment of as-synthesized PPY-TSA with 1 M NaOH for 1 h.

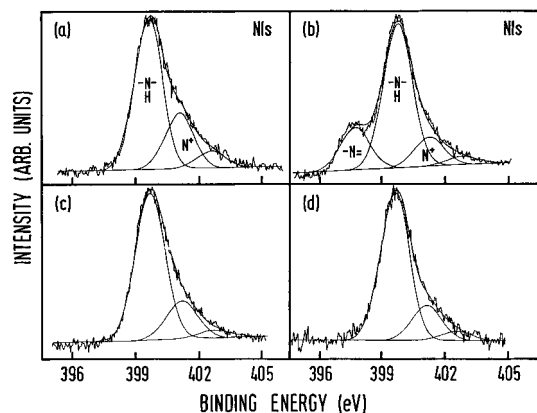


Figure 3. XPS N1s core-level spectra of (a) as-synthesized PPY-TSA film, (b) PPY-TSA film after treatment with NaOH, (c) base film after treatment with 0.5 M TSA, and (d) base film after treatment with 0.5 M DBSA.

one would be inclined to conclude that the undoping–re-doping process is reversible. However, in all cases the bulk S/N ratio is substantially lower than the XPS $-\text{SO}_3^-/\text{N}$ ratio. In contrast, the S/N ratios obtained by the two methods are very similar for the as-synthesized PPY-TSA film (Table 2b). When the as-synthesized PPY-TSA film was treated with NaOH for 1 h, there was an almost complete loss of the $-\text{SO}_3^-$ anions (S/N is 0.04 and 0.05 from XPS and bulk analysis, respectively). Thus, although the as-synthesized PPY-TSA film loses the anions readily (within 1 h) upon NaOH treatment, the re-doping process does not appear to be able to replenish similar or bigger anions in the bulk of the film even after 20 h. The deficiency in anions in the bulk of the re-doped PPY films may be one reason why there is a significant decrease in σ from the pristine value. Another important factor that causes σ to decrease is the loss of effective conjugation of the PPY film due to the reaction of the ring C with oxygen during the undoping process.³²

The above discussion was centered on the problems of anion migration into the bulk of the PPY film during the re-doping process. However, substantial differences in the surface and bulk anion concentrations also arise when DBSA and PSSA are used in the synthesis process. In the case of PPY-DBSA, the N1s core-level spectrum (Figure 4a) is distinctly different from that of PPY-TSA (Figure 3a), with the N^+ component peaks being only 1.15 and 2.05 eV from the $-\text{NH}-$ peak. The N^+/N ratio is also much higher. Thus, this spectrum may be considered type II. The undoping of the PPY-DBSA film gives rise to a N1s spectrum (Figure 4b) which is similar to Figure 3b. The higher N^+/N ratio in the PPY-DBSA film must be a result of the doping of all of the imine units and some amine units. However, the bulk S/N ratio of PPY-DBSA is similar to that of PPY-TSA (Table 2(b)) and supports the notion that about one-fourth to one-third of the PPY rings undergo doping by the anions. It is interesting to note that the as-synthesized PPY-

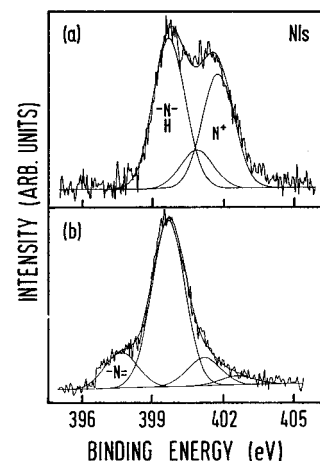


Figure 4. XPS N1s core-level spectra of (a) as-synthesized PPY-DBSA film and (b) PPY-DBSA film after treatment with NaOH.

DBSA film shows a type II spectrum (Figure 4a), whereas the PPY re-doped by DBSA film shows a type I spectrum (Figure 3c), even though a higher concentration of DBSA anions was present in the latter process (0.5 M vs 0.05 M in the former). The S/N ratio of the former is also correspondingly higher (Table 2). It would have been expected, on the basis of the results of the HClO_4 -re-doped PAN films (discussed earlier), that a higher concentration of anions would be more likely to give rise to a type II spectrum. However, the effect of anion concentration on the doping level is apparently not equivalent in the synthesis and re-doping processes.

In the case of the as-synthesized PPY-PSSA film, the bulk S/N ratio is about half of those of the PPY-TSA and PPY-DBSA films (Table 2b). Less than one-fifth of the PPY nitrogens in the bulk need to be positively charged to counterbalance the PSSA anions. However, the XPS results may lead one to conclude that the PPY-TSA and PPY-PSSA films are doped to the same degree ($\text{N}^+/\text{N} = 0.31$) and the excess $-\text{SO}_3^-$ anions in the latter are balanced by H^+ . A scanning tunneling electron micrograph study on PPY-PSSA film has suggested that the polymer has a helix chain configuration in which the polymeric anions are coated on the outside of the helical chains instead of being incorporated fully within the PPY matrix.³³ The large difference in the bulk and surface S/N ratios of PPY-PSSA (Table 2b) provides quantitative support of the postulate. In the case of the as-synthesized PPY-PVSA film, the bulk S/N ratio is higher than that of PPY-PSSA but lower than that of PPY-TSA. This is consistent with the postulate that the extent of anion incorporation into the PPY matrix is dependent on the bulkiness of the anions. It can be seen from Table 2 that the C/N ratio estimated for the PPY polymer is close to the theoretical value of 4, with the exception of the DBSA-doped polymers. In the latter, each dopant molecule accounts for 18

TABLE 3: Comparison of Re-Doped and As-Synthesized PPY Powders

anions	XPS results						bulk results			
	-N=N/-	-NH-/N	N ⁺ /N	(Cl/N) ^a	(Cl ⁻ /N) ^a	-SO ₃ ⁻ /N	Cl/N	S/N	(C/N) _{PPY} ^b	σ (S/cm)
(a) re-doped powders										
TSA	0	0.70	0.30	~0	~0	0.24	~0	0.08	3.92	0.01
PSSA	0	0.58	0.42	~0	~0	0.41	~0	0.12	3.85	10 ⁻⁴
(b) as-synthesized powders ^c										
Cl ⁻	0 (0.19)	0.73 (0.64)	0.27 (0.17)	0.25 (0.02)	0.22 (0.02)		0.30 (0.01)		4.00 (3.94)	10
TSA	0 (0.17)	0.69 (0.65)	0.31 (0.18)	0.13 (0.02)	0.11 (0.02)	0.15 (~0)	0.16 (0.03)	0.13 (0.01)	4.16 (4.00)	8
PSSA	0 (0.08)	0.68 (0.68)	0.31 (0.24)	0.06 (0.06)	0.04 (0.04)	0.61 (0.53)	0.05 (0.05)	0.34 (0.32)	3.87 (3.96)	1

^a (Cl/N) refers to the ratio of the total Cl to N, while (Cl⁻/N) includes the Cl* component. ^b (C/N)_{PPY} refers to C/N of PPY after correcting for C in dopant. ^c Values in parentheses refer to results obtained from treatment of as-synthesized PPY with 1 M NaOH for 1 h.

C, and hence small errors in the S/N ratio will greatly affect the calculation of the C/N ratio of the PPY polymer.

PPY Powders. PPY synthesized as a powder by the oxidative polymerization of pyrrole by FeCl₃ in water was converted to the base form by treatment with 1 M NaOH for 1 h. The -N=:NH-:N⁺ ratio in the base polymer is 0.19:0.64:0.17. Table 3a shows the XPS and elemental analysis results and σ for the base polymers after treatment with 1 M TSA and PSSA for 20 h. The XPS results show that the protonation levels obtained in the re-doped polymers are similar to (in the case of TSA) or higher (in the case of PSSA) than that of the polymer synthesized in water. However, the σ of the re-doped polymers are 100–10⁵ times lower. This magnitude of decrease in σ is even larger than that observed with the re-doped films (Table 2). The bulk analysis, revealed a S/N ratio which is much lower than that obtained from XPS. The XPS, bulk analysis, and σ results of the polymer re-doped for 20 h are not significantly different from those obtained with a re-doping time of 1 h. The inability of the bulk of the PPY polymer to undergo re-doping is consistent with the low σ of the re-doped PPY. These results are in direct contrast to the re-doped PAN powder results (Table 1) which show that even the polymeric PSSA anion can re-dope the bulk of the PAN to a very substantial degree and restore conductivity to a respectable value (0.05 S/cm). Thus, unlike the PAN powder, PPY powder and films must have undergone a transformation during the undoping process (NaOH treatment followed by water rinse and drying under vacuum) that impedes subsequent anion migration into the bulk during re-doping.

When 0.15 M TSA or PSSA is used instead of water in the chemical synthesis of PPY, the N1s core-level spectra of the resulting polymers are almost identical to those of the corresponding electrochemically synthesized films (compare Tables 3b and 2b). However, during chemical synthesis both Cl⁻ from the oxidant and the anions from the acid contribute to the doping of the polymer, although the effect of the former is much reduced when PSSA is the acid medium (Table 3b). The XPS Cl2p spectra of the PPY samples synthesized either in H₂O (Figure 5) or 0.15 M TSA show the presence of a small proportion (~10%) of covalently bonded Cl (Cl2p_{3/2} component at 200 eV). The Cl2p_{3/2} peak components at 197 and 198.5 eV are attributed to ionic chloride (Cl⁻) and chlorine species which have undergone partial charge transfer with the polymer (Cl*), respectively.^{3,34} The total Cl/N ratios as determined by XPS are lower than those from bulk analysis except when PSSA is used. In this case, the Cl⁻/N ratio is very small and the Cl/N ratios determined by both methods are similar in value. The lower Cl/N from XPS may be related to the volatility of the dopant, similar to the problem encountered with PAN doped with HCl.²⁷ The bulk analysis of all three as-synthesized PPY samples (Table 3b) show that one out of every three or four pyrrole rings would be associated with an anion (assuming that most of the Cl species in the bulk are also in the form of Cl⁻

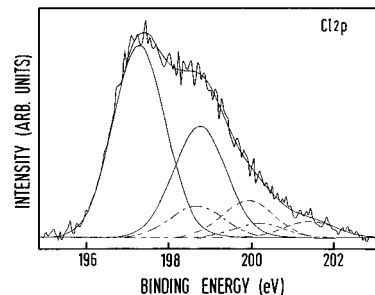


Figure 5. XPS Cl2p core-level spectrum of PPY chemically synthesized in H₂O using FeCl₃ as oxidant: (—) Cl⁻ component; (---) Cl* component; (- -) -Cl component.

and Cl* as shown by XPS for the samples synthesized in H₂O or 0.15 M TSA). The good distribution of the anions in the as-synthesized PPY powder contrasts sharply with the re-doped powders, and the large difference in σ 's of these two sets of samples can be largely attributed to this effect. It is interesting to note that although the polymeric PSSA anions are again concentrated on the surface (the -SO₃⁻/N ratio remains constant even after repeated washings with H₂O) similar to that observed in the electrochemically synthesized film (Table 2b), the bulk S/N in the powder is substantially higher. This reflects differences in the growth mechanism of the PPY chains and the manner in which the polymeric anions are incorporated during the growth process by the two different methods.

After treatment with NaOH for 1 h, the bulk and XPS analyses indicate an almost complete removal of the anions from the PPY powders synthesized in H₂O and TSA (Table 3b). This ease of movement of anions out of these polymers during the undoping process and the difficulty encountered by the anions in the re-doping process (Table 3a) are similar to the results of PPY films discussed earlier. The concentrations of the polymeric PSSA anions both on the surface and in the bulk decrease only slightly upon NaOH treatment, indicating that the polymeric anions cannot be easily disengaged from the PPY chains. For all of the as-synthesized, undoped, and re-doped samples listed in Table 3, the C/N ratios estimated for the PPY polymer are within 5% of the theoretical value of 4. Since each TSA molecule and PSSA repeating unit contribute seven and eight C atoms, respectively, the similarity between the calculated C/N ratio of the polymer matrix and the theoretical values for both PPY and PAN indicates that the bulk analysis results are of high accuracy.

Conclusion

A systematic comparison of the XPS and bulk analyses results of polyaniline and polypyrrole in the form of films and powders indicate that serious discrepancies between the surface and bulk anion concentrations may arise depending on the anion size, the nature of the polymer, and the manner in which the anions are introduced. In the case of chemically synthesized poly-

aniline (in powder form), the similarity in the XPS and bulk analyses results suggests that the anions, even the polymeric ones, are well-distributed. The polyaniline after conversion to the base form can be readily re-doped by acids with either small or polymeric anions. Although the latter tend to concentrate more on the surface, there is sufficient concentration in the bulk to support protonation of a substantial fraction of the imine units. However, for polyaniline base films cast from NMP solutions, the XPS results may indicate that a high protonation level is achievable with large acidic anions, when in actuality there is little migration of these anions into the bulk of the film. In the case of polypyrrole, the electrochemically synthesized films tend to possess an anion concentration on the surface (calculated from XPS analysis) that is much higher than the bulk concentration if large anions such as DBSA or PSSA are used. With the PSSA anions, less than 1 in 5 pyrrole rings in the bulk can be protonated compared to the 1 in 3 ratio achievable with the smaller anions. The size of the anions does not pose a problem in chemically synthesized polypyrrole which is in powder form. However, in the re-doping of both chemically and electrochemically synthesized polypyrrole base, although the N^+/N and anions/N ratios from XPS indicate substantial recovery of the doping level, this is not the situation in the bulk, even in the case of TSA anions. The extent of recovery of the conductivity of these polypyrrole samples is thus low compared to that observed in polyaniline powders.

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