

CHAPTER VI

SURFACE DEGRADATION OF α -NAPHTHALENE SULFONATE DOPED POLYPYRROLE DURING XPS CHARACTERIZATION

Surface Degradation of α -Naphthalene Sulfonate Doped Polypyrrole during XPS Characterization

Abstract

The surface compositions of non-aging chemically synthesized polypyrrole samples doped with α -naphthalene sulfonate (PPy/ α -NS⁻) were investigated by X-ray photoelectron spectroscopy (XPS). The power of the X-ray source used was 300 W. Employing liquid nitrogen cooling of the sample holder, the spectra in the regions of C 1s, O 1s, N 1s, and S 2p were found to be reproducible with a gradual change in S 2p spectrum when the accumulated X-ray exposure time was less than 1050 min. Beyond this accumulated X-ray exposure time, dramatic changes were observed in all spectral regions. The decreases in the amount of dopant and HSO₄⁻ or SO₄²⁻ co-dopant species correspond to the decrease in the amount of polaron charge carrier species of PPy (-NH⁺-). We found increases in the amount of the imine-like nitrogen (=N-) and hydrocarbon and the presence of new sulfur-containing species. These results suggested the deprotonation of the polaron by the dopant and the desulfonation of the protonated dopant. After desulfonation, these new sulfur-containing species were removed whereas the carbons of the naphthalene rings were still adhering to the surface of the PPy pellet. This degradation became more severe when the liquid nitrogen cooling system of the spectrometer was not used. The results indicate that the degradation was mainly induced by heat from the X-ray beam.

Key words: polypyrrole, α -naphthalene sulfonate, polymer degradation, XPS, X-ray exposure

1. Introduction

Since the 1960s, the X-ray photoelectron spectroscopy (XPS) technique has found wide application in studying surface compositions [1] of metals, non-conducting polymers, and semiconductors. For the widely studied conductive polymer, polypyrrole (PPy), pioneering works in the 1980s [2-5] have been followed up with several extensive studies of chemical surface compositions. Many fruitful pieces of information can be obtained from XPS, e.g. the determination of doping level in terms of N^+/N ratio [5]; the determination of the intrinsic oxidation state [5-7]; the degree of branching and cross-link structure [3,8,9]; the valence band spectrum [3,10]; the environmental stability [11]; and structural changes induced by systematic chemical modifications [5,12], and upon chemical exposure [4,13].

Even though XPS is considered as a relatively non-destructive surface analysis technique, there have been several reports on polymer degradations caused by the X-ray flux in XPS [14-17]. The non-monochromatic Mg $K\alpha$ caused dehydrochlorination of polyvinylchloride after 20 hours of exposure [14]. It caused changes in the C 1s XPS spectra of polymethylmethacrylate within less than 1 hour of exposure [15]. The monochromatized Al $K\alpha$ was used by Boulanger *et al.* [16]. They found that the C 1s XPS spectrum of hydrocarbon contaminants on polyoxymethylene sample became larger and broader after the overnight XPS experiment. The chemical reduction of other C components in the sample was suggested to be caused by the interaction with the electrons emitted by the sample under irradiation rather than the heating effect from the X-ray beam. However, for the non-monochromatic X-ray source, a possible heat-induced degradation on the polymers was suggested by Buncick *et al.* [17] and Briggs [18] due to the vicinity of anode and sample. Moreover, the presence of Bremsstrahlung radiation when a non-monochromatic X-ray source is used creates a more serious damage [18]. Nevertheless, this type of X-ray source is commonly available. Some researchers have suggested that XPS experiments of PPy films or PPy layers should be

performed using reduced X-ray power, 120 W [7,12] or 200 W [19], to avoid the possible degradation.

We report here the results of X-ray flux induced degradation of the non-aging chemically polymerized α -naphthalene sulfonate doped PPy (PPy/ α -NS⁻), during XPS experiments with a non-monochromatic Mg K α source. PPy/ α -NS⁻ is one of the PPys having the best electrical and mechanical properties amongst other PPys doped with six other types of dopants [20]. A liquid nitrogen cooled sample holder was utilized aiming to minimize the degradation induced by the heat of the X-ray source tip. These results were compared with the degradation that occurred without the cooling outfit.

2. Experimental

2.1 Materials

Pyrrole monomer, Py (AR grade, Fluka) was purified by distillation under reduced pressure prior to use. Ammonium persulphate, (NH₄)₂S₂O₈ (AR grade, Aldrich) was used as the oxidant. The dopant used was α -naphthalene sulfonic acid, sodium salt (AR grade, Fluka). It was commercially available and used without further purification.

2.2 The Polymerization Procedure

The PPy/ α -NS⁻ was chemically synthesized by *in situ* doped polymerization according to the method of Shen *et al.* [21]. A solution of 0.6846 g (3.0 mmole) (NH₄)₂S₂O₈ in 10.0 ml deionized water was slowly added to a mixture of 1.2 mmole of α -naphthalene sulfonic acid and 1.0 ml (14.5 mmole) Py in 20.0 ml deionized water. The reaction was carefully maintained at 0 °C (\pm 0.5 °C) for 2 hours. The obtained PPy was precipitated by pouring the reaction mixture into a large excess amount of deionized water. The PPy powder was washed several times with

deionized water and methanol before drying under vacuum at room temperature for 2 days. The synthesized PPy was aged in dry air (40-50 % relative humidity) at atmospheric pressure for 9 months, before XPS experiments. Over these 9 months, PPy became non-aging: its specific conductivity reached a constant and reproducible level. The powder was then pressed into pellets, with a diameter of 1.3 cm and a thickness of ~0.5 mm, for XPS experiments.

2.3 The XPS Experiment

XPS characterization of the surface composition of PPy pellets was carried out using a Perkin Elmer / PHI 5400 XPS. As X-ray source, the non-monochromatic MgK α with photon energy of 1253.6 eV was selected. The X-ray source power was 300 W (15 kV x 20 mA). The pass energy used was 17.90 eV. The aperture number 4 was selected. The pressure in the load lock position of the XPS instrument was in the range of 10^{-5} Pascal. By utilizing a liquid nitrogen cooling kit, the pressure in the XPS analyzing chamber could be kept in the range of 6.6×10^{-7} to 2.6×10^{-6} Pascal. When there was no cooling kit used, the pressure was in the range of 1×10^{-6} to 2.6×10^{-6} Pascal. Samples were mounted with two copper clips on sample holders made of stainless steel. The sample stage was aligned to be perpendicular to the incident X-ray beam and to be at a 45° angle with respect to the analyzer (the so called take-off angle).

The pellets of PPy/ α -NS $^-$ and the α -naphthalene sulfonic acid dopant were placed in the load lock position and evacuated for 24 hours before loading into the XPS analyzing chamber to remove moisture. The C 1s, O 1s, N 1s and S 2p XPS spectra of both samples were taken at 5 sweeps, 6 cycles. The XPS experiments for PPy/ α -NS $^-$ were repeated for 12 times after the first experiment. The total X-ray exposure time for each experiment was 150 min. The samples remained fixed in the XPS chamber during this experiment and the introduction of any new samples into the XPS chamber was prohibited while the samples were mounted in the XPS chamber.

The neutralizer to prevent charging effects on insulating specimens was not utilized. The shifts in binding energies in C 1s, O 1s, N 1s and S 2p regions of both insulating α -naphthalene sulfonic acid dopant and conducting PPy spectra were corrected by setting the main C peak as 284.6 eV [22]. All spectra were deconvoluted into the well-defined components based on a linear baseline subtraction and the Gaussian assumption [3,5,7]. The full widths at half-maximum (FWHM) were fixed to be the same for all Gaussian components in any particular envelope, except those in the C 1s envelope of α -naphthalene sulfonic acid dopant where the proportions of all C components are known. The quantitative estimations were carried out using the sensitivity factors suggested by the manufacturer for the Omni-Focus Lens A. These sensitivity factor values are 0.296 for C 1s, 0.477 for N 1s, 0.711 for O 1s, and 0.570 for S 2p spectra.

3. Results and Discussion

3.1 XPS Spectra of α -Naphthalene Sulfonic Acid Dopant and the Fresh PPy/ α -NS

The C 1s and O 1s core level XPS spectra of α -naphthalene sulfonic acid dopant give an idea how to extract intrinsic proportions of C and O in the PPy backbone from the C 1s and O 1s XPS spectra of PPy-dopant complex. They are shown along with the XPS spectra of PPy/ α -NS⁻ in Figures 1a – 1d.

The deconvolution of the C 1s core level spectrum (Figure 1a) of α -naphthalene sulfonic acid, sodium salt gave four Gaussian components. The main C peak at 284.6 eV (corrected from the raw data: 285.6 eV) arises from the α - and β -carbon of the naphthalene ring. The small peak at the lower binding energy, 283.3 eV arises from the fused C in the naphthalene ring. The smaller peak at the higher binding energy, 286.5 eV arises from C-S. The clearly separated peak at 290.3 eV can be attributed to the π - π^* satellite, which is commonly found in the aromatic system [23]. It has a 5.7 eV higher binding energy than the main C peak.

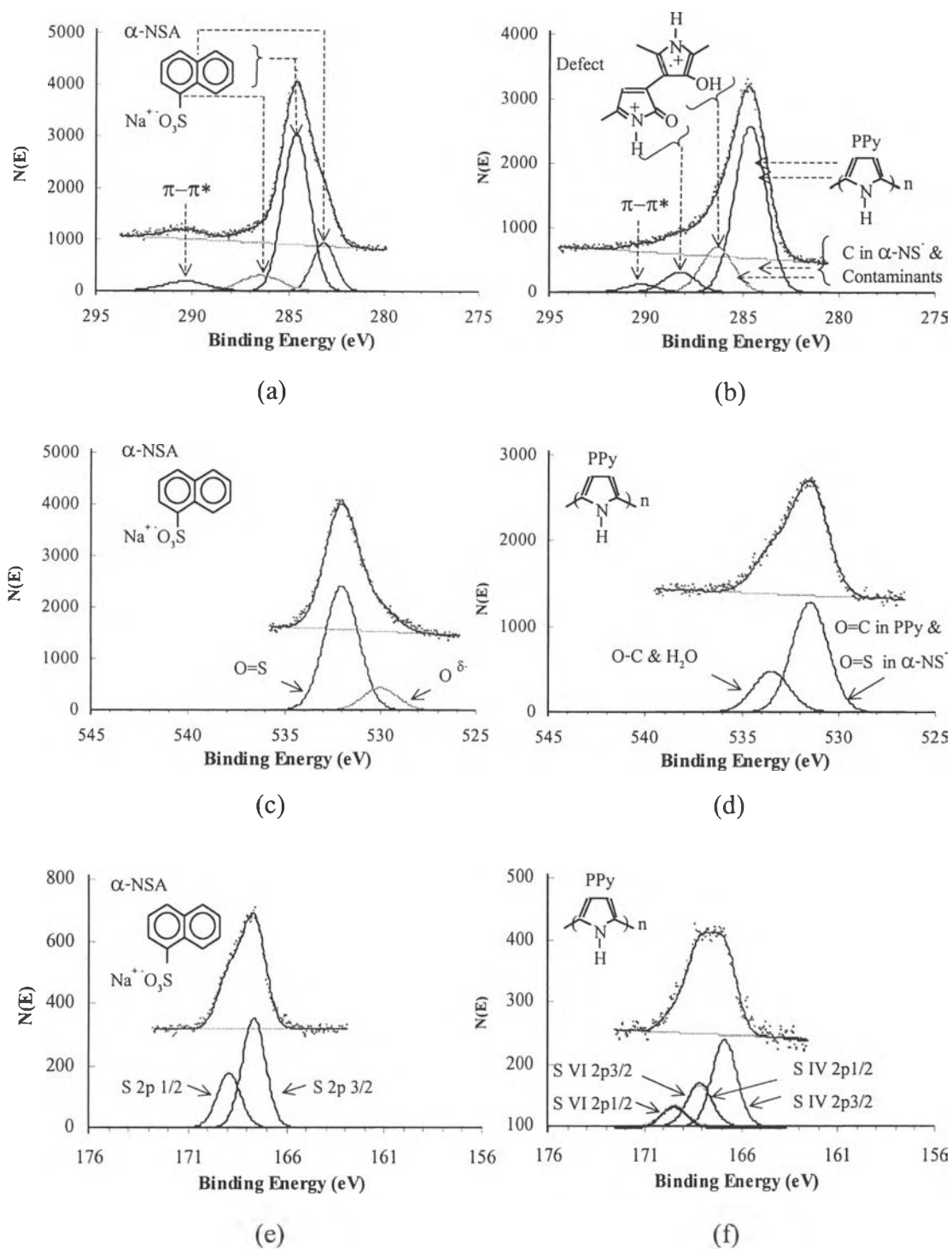


Figure 1 The XPS core level spectra of α -naphthalene sulfonic acid, sodium salt in the regions of: a) C 1s, c) O 1s, and e) S 2p, comparing with the spectra of PPy/ α -NS' in the regions of: b) C 1s, d) O 1s, and f) S 2p, with their deconvolution results underneath.

By discarding the contribution of this satellite peak, the ratio of C at the fused position to the C at α - and β - position to the C-S becomes 2:7:1. This corresponds well to the ratio calculated from the chemical structure and also indicates the absence of significant hydrocarbon contaminants in the XPS experiment and the specimen surface after evacuation in the load lock position for 24 hours. The intensity of the satellite peak relative to the other three C components is 4.85 %. The theoretically expected percentage is up to 10 % [23].

The C 1s core level XPS spectra of the fresh PPy/ α -NS⁻ (Figure 1b) is more complex due to the presence of disordered structures in PPy as well as the incorporation of dopant molecules. The main C peak of PPy/ α -NS⁻ at 284.6 eV (corrected from 284.1 eV) is attributed to α - and β - carbon in Py rings [2,3,5]. This peak also contains α - and β - carbon of the naphthalene ring of the dopant as well as its C at the fused ring position, and other inevitable contaminants.

The two C components at the higher binding energies belong to the defects in doped PPy. The peak at 286.2 eV can be attributed to the branching carbon [3], C-OH [24], C=N [25], and =C-NH⁺ (polaron) defects [24]. This peak also includes C-S from the dopant. The other carbon peak is located at 288.1 eV. It is derived from C=O [24] and -C=N⁺ (bipolaron) defects [26]. The highest binding energy peak at 290.0 eV, 5.4 eV higher than that of the main C peak, can be attributed to the π - π^* satellite in aromatic PPy. Its percentage is 3.46 % relative to the other three carbon peaks. This low percentage indicates the presence of contaminants, as will be discussed later as the ratio of observed C to N in PPy/ α -NS⁻.

The O 1s spectrum of the dopant anion (Figure 1c) is located at 531.9 eV with a tail at the lower binding energy side. The main peak is simply attributed to O=S in the dopant whereas its shoulder can be attributed to oxygen atoms with partial negative charges.

In the envelope of the O 1s spectrum of PPy/ α -NS⁻ (Figure 1d), there are the peaks of O=C [27] and O=S located at 531.6 eV (SD = 0.01 eV), and the peak of HO-C [24], branching carbon and bound water [28] located at 533.6 eV (SD = 0.1 eV). It should be noted that the non-uniform distribution of negative charge on O in the dopant is absent in the conducting PPy/ α -NS⁻ system.

Turning now to the S 2p core level XPS spectra of dopant (Figure 1e), it is known that the p valence is split upon ionization into 2p 1/2 and 2p 3/2. This leads to a doublet peak with an area ratio of 1:2. The split in binding energy was found to be ~1.28 eV (SD = 0.6 eV) in α -naphthalene sulfonic acid dopant. This splitting value was used for curve fitting purpose for the S 2p envelope of PPy/ α -NS⁻.

By using the splitting value of 1.28 eV and trying to keep the FWHM close to that found in dopant, the S 2p of PPy/ α -NS⁻ (Figure 1f) can be decomposed into two S components. The binding energies of 2p 3/2 are located at 167.0 eV (SD = 0.1 eV) and 168.9 eV (SD = 0.2 eV). According to the study of the oxidation state in S and the shift in binding energy of S 2p core level [29], these two peaks can be attributed to S having the oxidation states of IV and VI, respectively. The S IV can be attributed to the S of dopant, C₁₀H₇-SO₃⁻ whereas the S VI can be attributed to the S from co-dopant, HSO₄⁻ and SO₄²⁻. These co-dopants were generated from the oxidant, (NH₄)₂S₂O₈, used in the polymerization. The existence of these co-dopants was reported by many researchers [30-31], including our group [32], based on the elemental analysis of undoped PPy. The intensity ratio of S VI from co-dopants toward S IV from α -naphthalene sulfonate dopant is about 1:3.

The N 1s core level XPS spectra of PPy/ α -NS⁻ is solely derived from N of PPy itself, due to the absence of N in dopant used. From Figure 2, the main N peak centering at 399.4 eV (S.D. = 0.01 eV) is attributed to the neutral N at the pyrrole ring (-NH-) [2-5]. This peak is not symmetric. The small shoulder at the lower binding energy side can be defined as a structural defect in the form of imine-like nitrogen, =N- [33], its binding energy is about 2 eV lower than that of the main -NH-

peak. The other shoulders at the high binding energy side of the main -NH- peak can be attributed to the positively charged N in different environments. Comparing to the position of the main -NH- peak, the shoulder having about 1.5 eV higher binding energy (401.0 eV: SD = 0.01 eV) can be attributed to -NH^+ in the polaron charge carrier species [34]. The shoulder having about 3.1 eV higher binding energy (402.6 eV: SD = 0.01 eV) can be attributed to =NH^+ , which is a bipolaron charge carrier species [34].

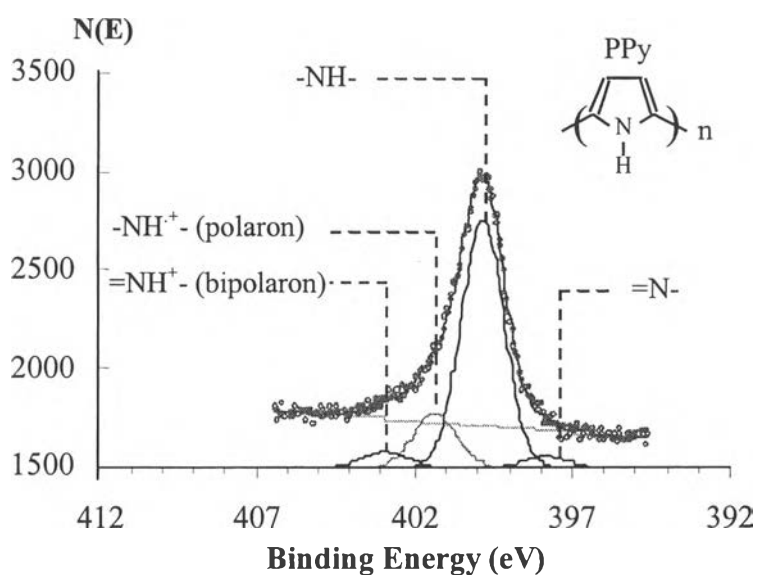


Figure 2 The N 1s XPS spectra of PPy/ $\alpha\text{-NS}^-$ with its deconvolution results underneath.

3.2 Quantitative Estimations of the Surface Elemental Components in PPy/ α -NS

Based on the information obtained from the XPS spectra of dopant described above, the quantitative estimations of the surface elemental components in PPy/ α -NS⁻ in terms of ratios referenced to N were obtained as follows:

1. (α - and β - carbon)/N

$$= [(I_{C\ 284.6} / C_{sf}) - (I_{S\ 167.0} / S_{sf}) * 9] / (I_N / N_{sf}) \dots \dots \dots (1)$$

2. (C-O and branching C) / N

$$= [I_{C\ 286.2} / C_{sf} - (I_{S\ 167.0} / S_{sf}) * 1 - (I_{-NH^+ - 401.0} / N_{sf}) - (I_{=N- 397.8} / N_{sf})] / (I_N / N_{sf}) \dots \dots \dots (2)$$

3. C=O / N

$$= [(I_{C\ 288.1} / C_{sf}) - (I_{-NH^+ - 402.6} / N_{sf})] / (I_N / N_{sf}) \dots \dots \dots (3)$$

4. O=C /N

$$= [(I_{O\ 531.6} / O_{sf}) - (I_{S\ IV\ 167.0} / S_{sf}) * 3 - (I_{S\ VI\ 168.9} / S_{sf}) * 4] / (I_N / N_{sf}) \dots \dots \dots (4)$$

5. (O-C and bound water) / N

$$= (I_{O\ 533.6} / O_{sf}) / (I_N / N_{sf}) \dots \dots \dots (5)$$

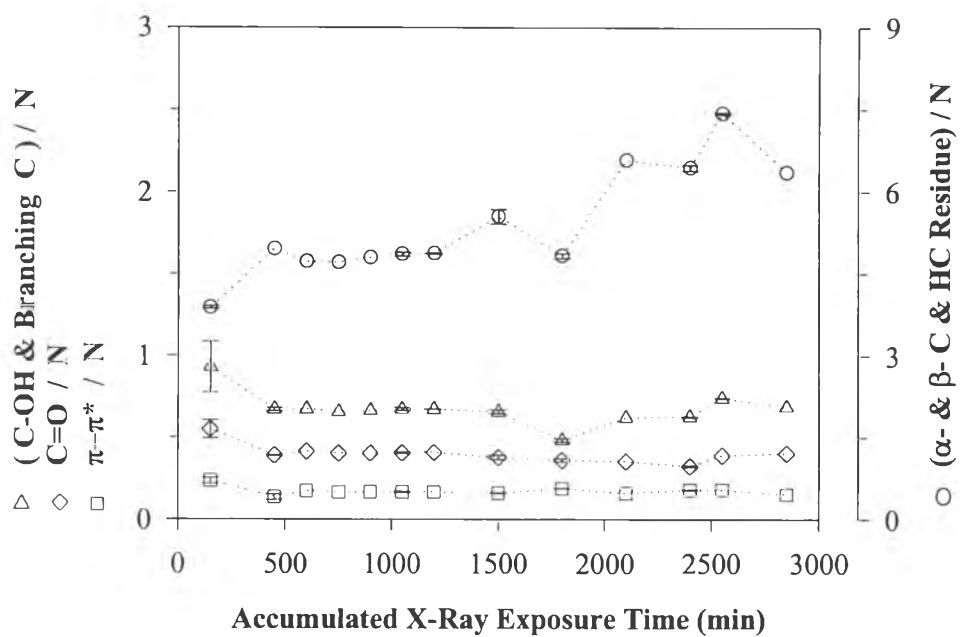
The calculations for other species are straightforward, using their intensities and sensitivity factors (sf) as given above. All the plots of components reported here are shown in terms of atomic ratio referenced to N.

3.3 Effect of the Accumulated X-Ray Exposure Time in XPS Experiment on the Surface Compositions of PPy/ α -NS

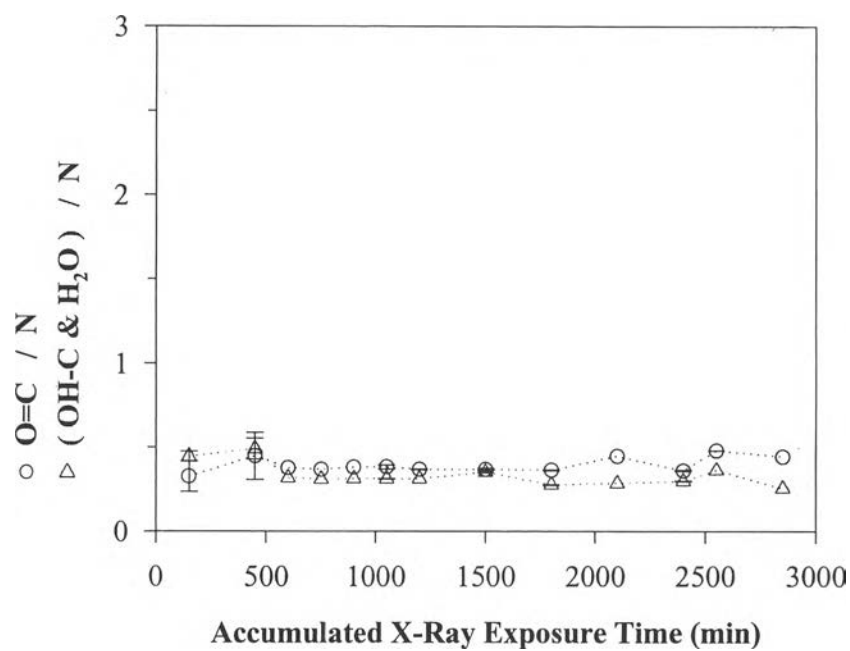
Figures 3a - 3d show the changes of all components in PPy/ α -NS⁻ in C 1s, O 1s, N 1s, and S 2p envelopes, respectively, as functions of accumulated X-ray exposure time. These data are expressed in terms of atomic ratios referenced to N.

They show slight but gradual changes from the first scan on as can be noticed in the case of S (Figure 3d) which is the most sensitive element in this work [35]. The changes become very significant also for other elements besides S after the accumulated X-ray exposure time of 1050 min. The data was extracted and is discussed here as before and after the accumulated X-ray exposure time of 1050 min.

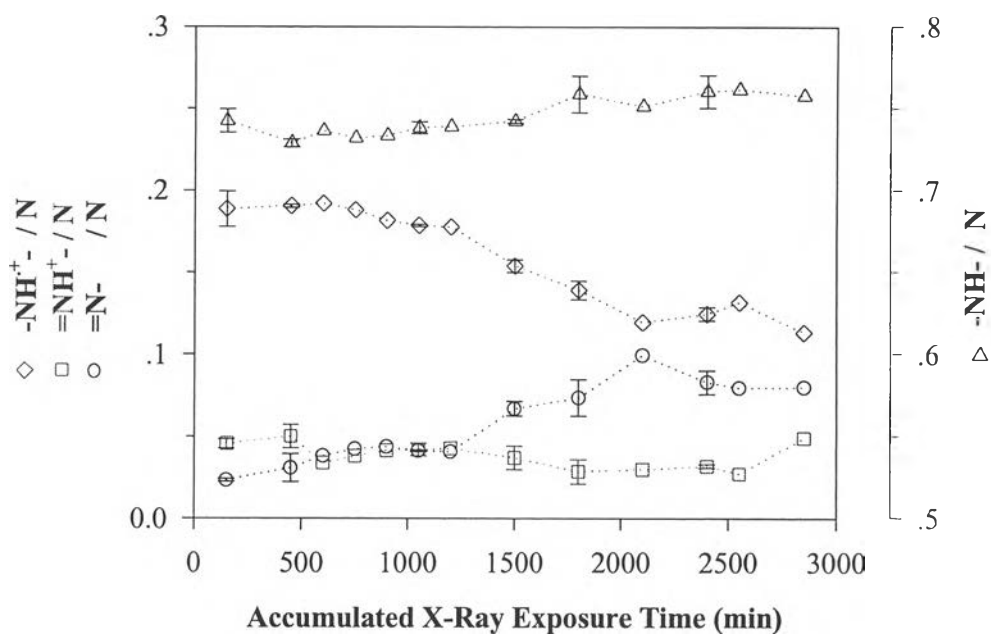
Figure 4a shows the ratio of $\underline{\text{C}}=\text{O}$ to $\underline{\text{O}}=\text{C}$ (the underlined atoms in each species denote the envelope from which that species was dissolved): the initial value is 1.46 (SD = 0.01). The excess amount over unity shows the presence of oxygen containing contaminants. After the removal of these contaminants by evacuation, this ratio became consistently close to unity.



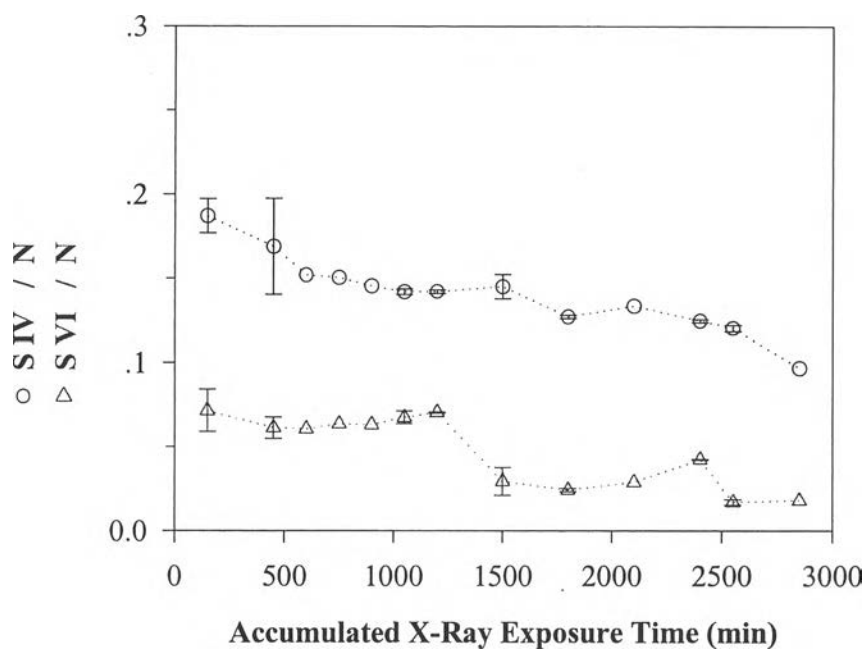
(a)



(b)



(c)

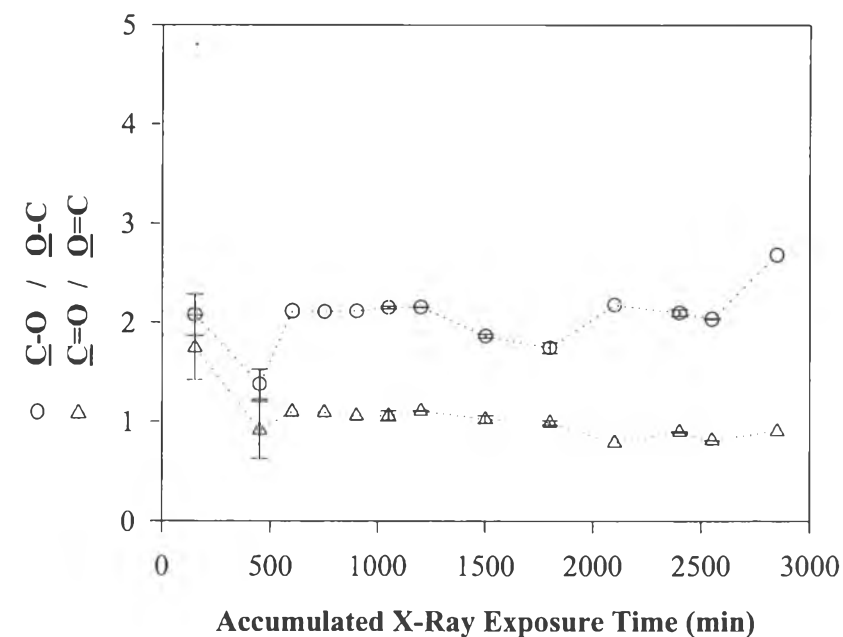


(d)

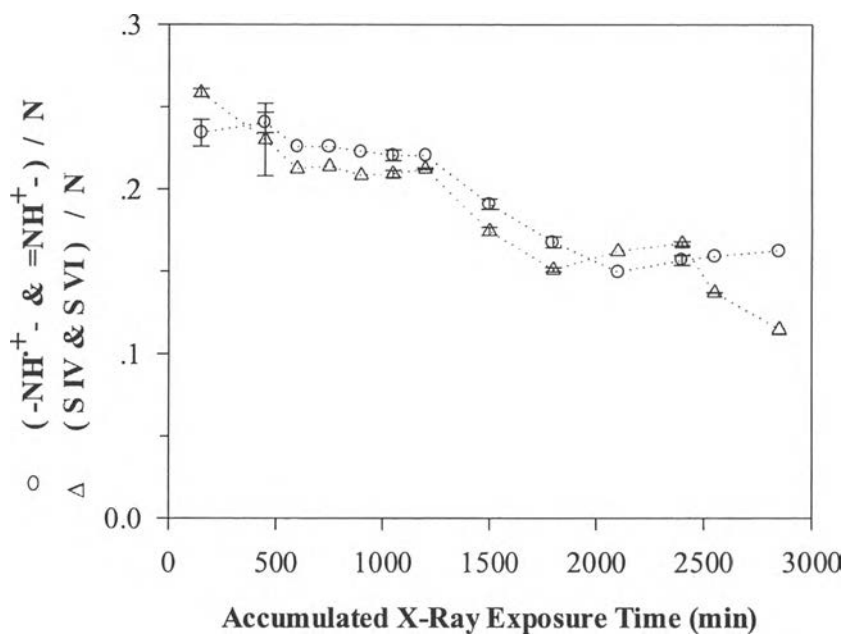
Figure 3 The calculated results of elemental compositions of the PPy/ α -NS⁻ in the envelopes of: a) C 1s; b) O 1s; c) N 1s; and d) S 2p, expressed in terms of atomic ratios referenced to N, as functions of accumulated X-ray exposure time in the XPS experiment.

The ratio of ($\underline{\text{C}}\text{-OH}$ and branching $\underline{\text{C}}$) to (HO-C & HOH) is also shown in Figure 4a. After the removal of bound water in the load lock, the excess value of this ratio is an attribution of branching carbon. A $\underline{\text{C}}\text{-O}/\underline{\text{O}}\text{-C}$ ratio of 1.1 ± 0.3 for oxidized PPy and of 3.6 ± 1.2 for PPy, was reported by Malitesta *et al.* [34], where the excess $\underline{\text{C}}\text{-O}$ was attributed to the presence of a satellite component at low binding energy. Comparing with the ratio of $\underline{\text{C}}=\text{O}$ to $\underline{\text{O}}=\text{C}$, the $\underline{\text{C}}\text{-OH}$ to HO-C ratio fluctuated more with values in the range of 1.6- 2.5. However, under a very high vacuum and heat from the X-ray source, it is possible that residual moisture in the bulk migrated to the surface. This should cause an increase in the term ($\text{HO-C} + \text{H}_2\text{O}$). In fact, in Figure 4a, there is a dip in the C / O ratio at 450 min (Fig. 4a). It is conceivable that this dip is caused by water migrating from the bulk to the surface of the sample. With increasing time of X-ray exposure, the water that had migrated to the surface might get removed causing the C / O ratio to recover its original higher value.

Figure 4b shows the ratio of all N^+ and all S containing species toward N as functions of the accumulated X-ray exposure time. This confirms that the critical accumulated X-ray exposure time for this system is 1050 min.



(a)

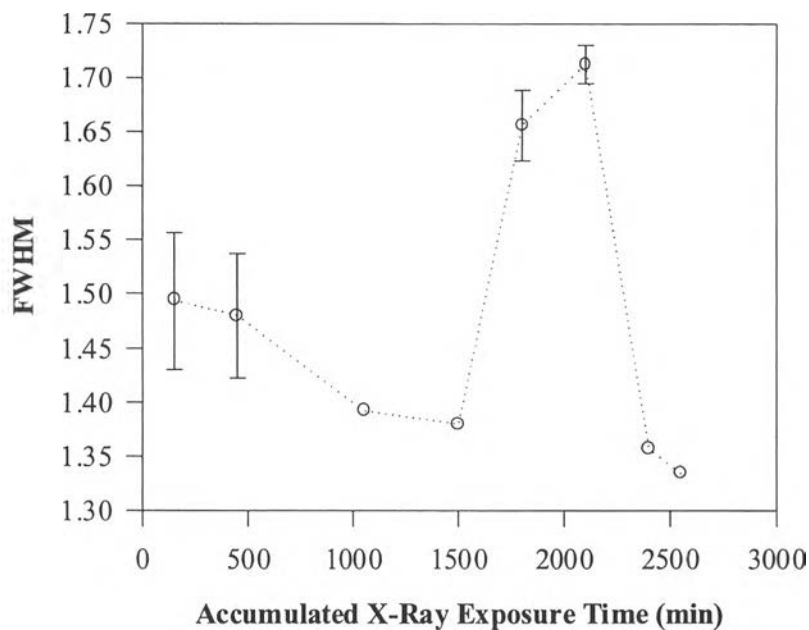


(b)

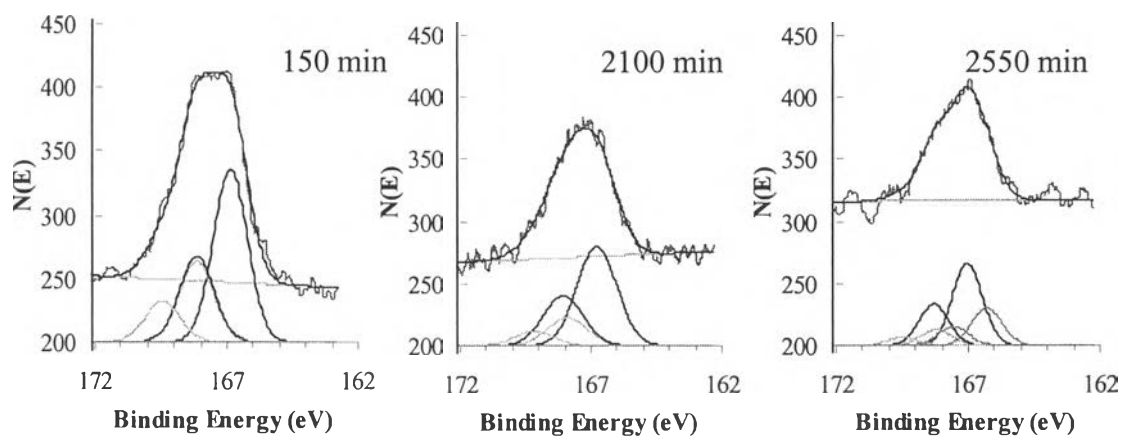
Figure 4 The comparison of the calculation results for: a) the ratio of $\underline{\text{C}}\text{-O}/\underline{\text{O}}\text{-C}$ and the ratio of $\underline{\text{C}}=\text{O}/\underline{\text{O}}=\text{C}$ and b) all charge carrier species and all sulfur containing dopants.

Beyond the accumulated X-ray exposure time of 1050 min, there were many changes as listed here: (i) the hydrocarbon residues increased whereas both S IV and S VI decreased. (Figure 5); (ii) $-\text{NH}^+$ species in polaron decreased whereas the neutral $-\text{NH}-$ and $=\text{N}-$ increased (Figure 3a); (iii) the FWHM values of the deconvoluted peaks in the S 2p envelope showed an unusual increase (Figure 5a). These FWHM values can be reduced by considering a new sulfur-containing species arising at ~ 166 eV (Figure 5d). Some additional changes were observed after the accumulated time of 2500 min: (iv) $\text{C}-\text{OH}$ and $\text{HO}-\text{C}$ slightly increased (Figure 3a), whereas their ratio still varied between 1.6- 2.5 (Figure 4a); (v) $\text{O}=\text{C}$ fluctuated with a trend to increase whereas $\text{C}=\text{O}$ remained constant (see Figure 4a for their ratio); those species were unstable and were not shown in Figure 3d.

In addition to the loss of S VI which corresponded to the decrease of $-\text{NH}^+$ species in the polaron and the increase of $-\text{NH}-$ species, these results indicate the deprotonation of polaron which decreases the $-\text{NH}^+$ species in the polaron and increases the amount of $=\text{N}-$. The hydrogen scavenger can be the naphthalene sulfonate dopant. After H abstraction, the protonated dopant was desulfonated, i.e. the C-S bond was broken. The possible new sulfur-containing species are SO_3^{2-} and SO_2 . The appearance of these species corresponded to the new peak found in the S 2p envelope. Their signals in the region of O 1s cannot be distinguished from the signal of $\text{O}=\text{C}$. This corresponded to the trend of the increase in the $\text{O}=\text{C}$ peak. These new species were removed whereas naphthalene rings and/or their derivatives were still sticking to the surface of the PPy pellet, corresponding to an increase of the hydrocarbon residue peak.



(a)



(b)

(c)

(d)

Figure 5 a) The FWHM of the deconvoluted Gaussian peaks in S 2p XPS spectra at various accumulated X-ray exposure times; and S 2p XPS spectra (moving average of 9 data points) with their deconvolution results underneath at: b) 150 min; c) 2100 min where the deconvoluted results became broader; and d) 2550 min, where the new S containing species could be dissolved.

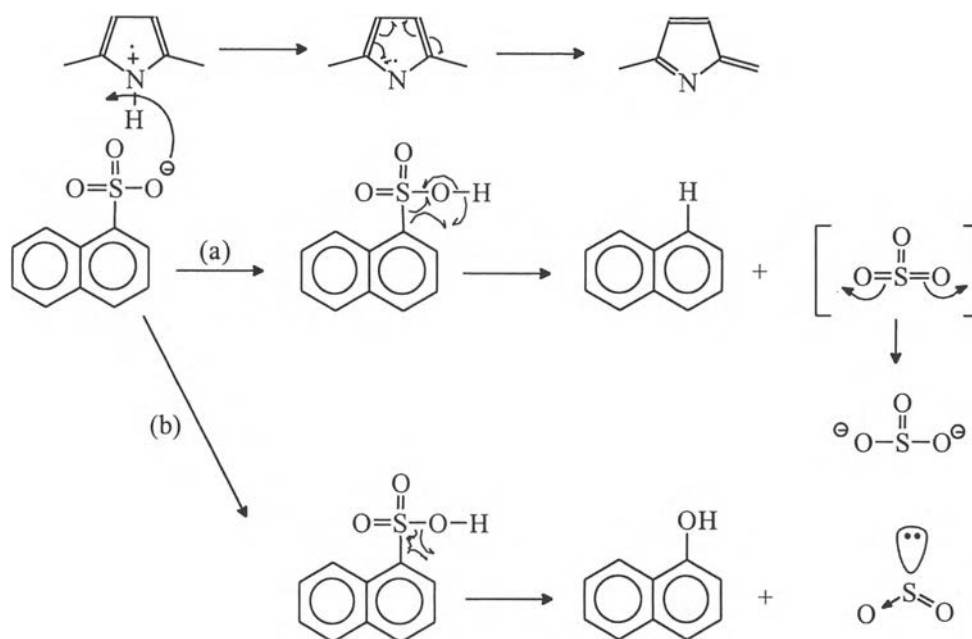


Figure 6 Possible deprotonation of PPy and desulfonations of α -naphthalene sulfonate dopant under the prolonged exposure to the X-ray flux in XPS.

All of these proposed reactions are schematically drawn in Figure 6. From the evidence that the \underline{C} -OH and \underline{HO} -C species were slightly increased, route (b) in Figure 6 is more likely.

When there was no liquid nitrogen cooling kit used, these observed degradation results became even more serious. As can be seen in Figure 7, a sharp decrease of S IV in the α -NS $^-$ dopant was observed when the accumulated X-ray exposure time was as short as 450 min, and the damage was two times larger. A more serious degradation at higher temperature indicates that the surface degradation of PPy/ α -NS $^-$ was mainly induced by heat from the X-ray source as also suggested by Buncick *et al.* [17] and Briggs [18].

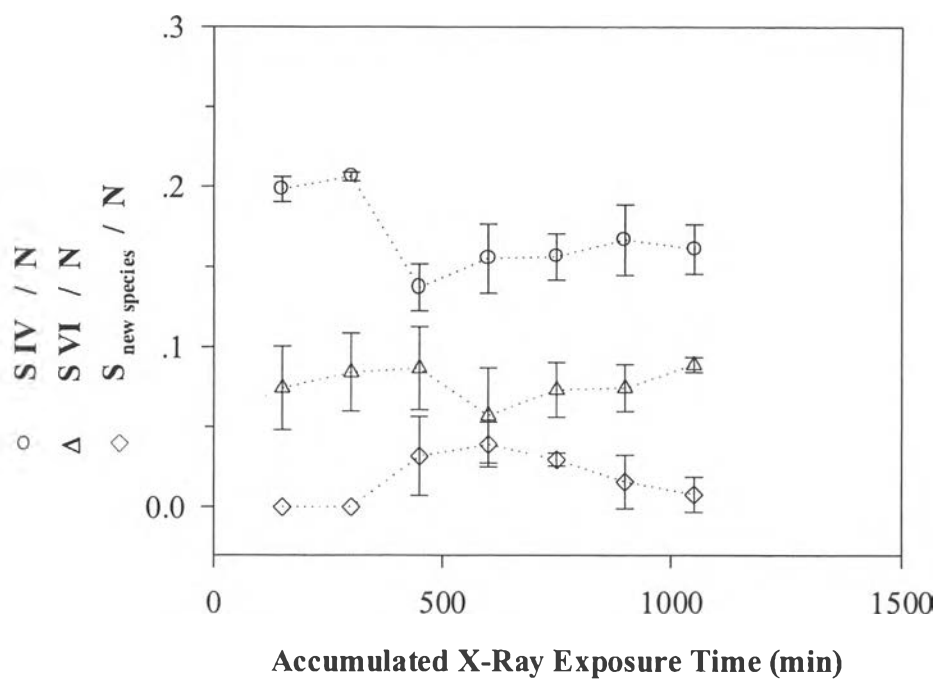


Figure 7 The calculated results of elemental compositions of the PPy/ α -NS⁻ in the envelopes of S 2p, expressed in terms of atomic ratios referenced to N, as functions of accumulated X-ray exposure times in the XPS experiment when there was no liquid nitrogen cooling outfit used.

4. Conclusions

When the liquid nitrogen cooling kit was utilized, reproducible XPS spectra of the non-aging chemically synthesized PPy/ α -NS⁻ was obtained under the high-power X-ray source with accumulated X-ray exposure time up to 1050 min. Beyond this time, further X-ray exposure can lead to progressive deprotonation of polaron charge carrier species in PPy and the desulfonation of α -NS⁻ dopant. The gradual formation of sulfur-containing species was observed. Without utilization of a cooling kit in the XPS instrument, this degradation became even more severe, indicating that these degradations were mainly induced by heat from the X-ray source.

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