X-ray photoelectron spectroscopic studies of H_2SO_4 protonated polyaniline

E. T. Kang*, K. G. Neoh, Y. L. Woo and K. L. Tan†

Department of Chemical Engineering and † Department of Physics, National University of Singapore, Kent Ridge, Singapore 0511

(Received 24 January 1992)

The protonation of polyaniline (PAN) by a non-volatile acid, H_2SO_4, has been studied by X-ray photoelectron spectroscopy. The amount of acid incorporated can be effectively varied by varying the synthesis conditions. At a sulphate/monomer ratio of >0.5, both the HSO_4^- anion and adsorbed molecular H_2SO_4 can be quantitatively differentiated in the S2p core-level spectrum. The N1s core-level spectrum indicates that the amine units of the emeraldine oxidation state of PAN are also susceptible to protonation in the presence of excess H_2SO_4.

(Keywords: polyaniline; H_2SO_4; X-ray photoelectron spectroscopy; protonation)

Introduction

The synthesis and characterization of electroactive polymers have become two of the most important areas of research in polymer science during the past decade[1]. Of these polymers, polyaniline (PAN) has been of particular interest because of its high electrical conductivity, environmental stability, interesting redox properties associated with the chain nitrogens[2,3], and more recently, its solution processibility[4] and partial crystallinity[5,6]. The ability of PAN to achieve its highly conductive state either through protonation of the emeraldine base (EM, containing 50% =N– units) or through oxidation of the fully reduced leucoemeraldine (LM, containing 100% –NH– units) has been used to illustrate the 'new concept'[2,3] in conducting polymers. Recently, it has been demonstrated that this 'new concept' can also be extended to polypyrrole[7].

A large number of X-ray photoelectron spectroscopy (X.p.s.) studies has been devoted to the investigation of protonation in PAN[8–14]. Our recent studies[15,16] have also demonstrated that the quinonoid imine, benzenoid amine and positively charged nitrogens in a PAN complex correspond, respectively, to peak components with binding energies at about 398.1, 399.3 and >400.5 eV in the properly curve-fitted N1s core-level spectrum. The majority of the protonation studies in PAN involves the use of HCl as the protonic acid. Relatively few studies[10,17] have been devoted to protonation by H_2SO_4, although PAN[18] has been found to be processible from concentrated H_2SO_4. An earlier study[19] has also suggested that the use of non-volatile acids, such as H_2SO_4, can result in the presence of an adsorbed acid film on the polymer surface. Accordingly, it should be important to carry out a careful study on the protonation of PAN by H_2SO_4, using X.p.s. as a primary surface analytical tool.

Experimental

The sulphate salts were prepared via the oxidative polymerization of aniline by ammonium persulphate in aqueous H_2SO_4 similar to the method reported[2,3] for the synthesis carried out in HCl. The total sulphate (both as the sulphate anion and as free H_2SO_4) incorporated into the complex was controlled by varying the H_2SO_4 concentration used during polymerization and the treatment of the complexes after polymerization. The EM base was obtained via the treatment of the complex with excess 0.5 M NaOH. The synthesis conditions for the samples studied in this work are summarized in *Table 1*.

X.p.s. measurements were carried out on a VG ESCALAB MkII spectrometer with a MgKα X-ray source (1253.6 eV photons). The X-ray source was run at a reduced power of 120 W (12 kV and 100 mA) and at a take-off angle of 75°. The samples in powder form were mounted on the sample studs by means of double-sided adhesive tape. All binding energies (BEs) were referenced to the C1s neutral carbon peak at 284.6 eV. In curve-fitting, the widths (full width at half maximum) of the Gaussian peaks were maintained constant for all components in a particular spectrum. Surface elemental stoichiometries were obtained from the peak area ratio corrected with the experimentally determined sensitivity factors and agreed to within $\pm 10\%$ with those obtained from chemical analysis.

Results and discussion

Since all of the present PAN/sulphate complexes are fairly conductive, no sample charging was observed and the main C1s component of the complexes appears at about 284.6 eV. *Figures 1a–h* show the respective N1s and S2p core-level spectra for the four PAN/sulphate complexes shown in *Table 1*. For complexes with S/N ratios of >0.5, the S2p core-level spectra are best resolved with at least two spin-orbit split doublets ($S2p_{3/2}$ and $S2p_{1/2}$), with BEs for the $S2p_{3/2}$ peaks at about

---

*To whom correspondence should be addressed

0032-3861/92/132857-03

Table 1 Synthesis conditions for the various PAN/sulphate complexes

Sample	Synthesis conditions	Complex composition (S/N ratio)[a]	Conductivity (S cm^{-1})
1	Synthesized with 1 M H_2SO_4, followed by partial deprotonation with 0.1 M NaOH	0.20	7×10^{-2}
2	Synthesized in 1 M H_2SO_4, washed with 0.1 M H_2SO_4	0.52	2
3	Synthesized in 2 M H_2SO_4, washed with 0.1 M H_2SO_4	0.74	1
4	EM base dissolved in conc. H_2SO_4 and reprecipitated from 0.5 M H_2SO_4	1.74	0.1

[a] Determined from the corrected S2p and N1s X.p.s. core-level spectral area ratios

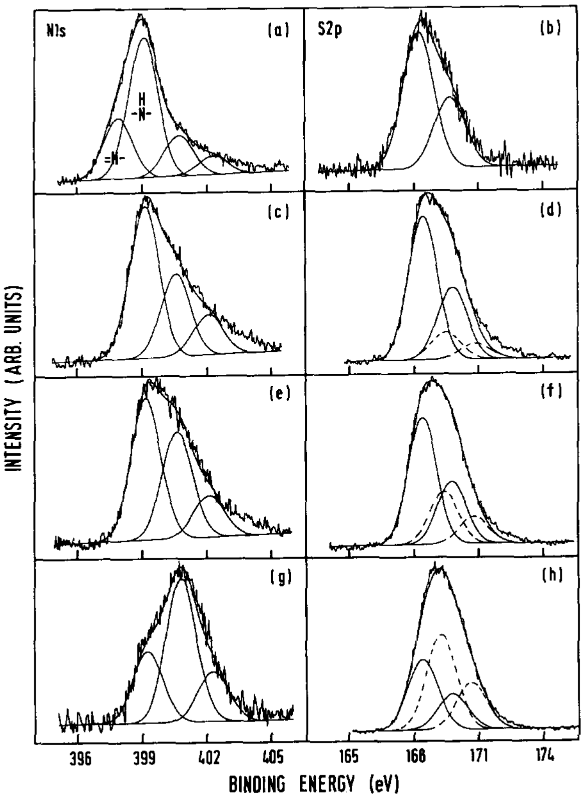

Figure 1 N1s and S2p X.p.s. core-level spectra of PAN/sulphate complexes with surface S/N ratios of: (a) and (b) 0.20; (c) and (d) 0.52; (e) and (f) 0.74; (g) and (h) 1.74

168.3 ± 0.1 and 169.3 ± 0.1 eV. The former is attributable to sulphate anions[10,20], and the latter, the proportion of which increases with increasing S/N ratio, is associated with the adsorbed molecular H_2SO_4 on the polymer surface. This is readily confirmed by the fact that for H_2SO_4 adsorbed on graphite, the S2p core-level spectrum reveals the presence of a single environment with a $S2p_{3/2}$ BE at about 169.4 eV. The assignment is also consistent with the observation that no appreciable amount of adsorbed H_2SO_4 is present for complexes with S/N ratios substantially below 0.5 and with a significant amount of the imine nitrogens remaining unprotonated (*Figures 1a* and *b*). Furthermore, for this partially deprotonated complex, the $S2p_{3/2}$ BE for the sulphate anion is shifted to a slightly lower BE of 167.9 eV. This is probably attributable to the fact that in the partially deprotonated sample the sulphate anions exist in a less positive environment.

The N1s core-level spectra suggest that the imine component with a BE of about 398.1 eV is observed only in the partially deprotonated sample. For complexes with S/N ratios of >0.5, all the imine components of the EM oxidation state have been protonated. The N1s core-level spectra reveal the presence of only the amine component at a BE of about 399.3 eV and a high BE tail attributable to the positively charged nitrogens. *Table 2* summarizes the proportions of the various sulphate and nitrogen species for the PAN/sulphate complexes shown in *Figure 1*. The data in *Table 2* readily indicate that after quantitative differentiation of the sulphate anion and molecular H_2SO_4, a fairly close balance between the sulphate anion/N ratio and the proportion of the positively charged nitrogens is observed for all samples studied. Thus, from charge neutrality considerations, the sulphate anion in the present PAN complexes must exist predominantly as monovalent sulphate species or the HSO_4^- species.

For complexes with moderate S/N ratios (samples 2 and 3 in *Table 2*), the proportion of positively charged nitrogens and the anion/N ratio remain relatively constant at around 0.5, despite the observations that all the imine units have been protonated and the complexes still contain excess molecular H_2SO_4. These are consistent with the general belief that protonation occurs preferentially through the imine repeating units[2,3]. However, for complexes with high S/N ratio, such as sample 4 in *Table 2*, the proportion of the amine nitrogens has decreased substantially below 0.5 and about three-quarters of the total nitrogens has become positively charged. This amount of positively charged nitrogens is consistent with an observed sulphate anion/N ratio of about 0.75 for the complex. These results readily suggest that at high H_2SO_4 loading, a substantial amount of the amine units must have also been protonated. The presence of protonated amine nitrogens is further supported by the following evidence. Treatment of sample 4 in *Table 2* with excess 0.5 M NaOH readily results in the removal of all the sulphate anions and molecular H_2SO_4. The N1s core-level spectrum of this NaOH treated sample is not unlike that of the EM base, with about equal amounts of the imine and amine units, as shown in *Figure 2*. Thus, the intrinsic structure or the oxidation state of the EM base is not significantly altered upon treatment with concentrated H_2SO_4 and the accompanying protonation of the amine units. An earlier study[18] has also suggested that the fully oxidized PAN is stable in concentrated H_2SO_4.

Most of the studies on the protonation of the EM base in PAN involved equilibrating the polymer base in a volatile acid medium, HCl in particular. In this case, protonation occurs preferentially at the imine units to give rise to a complex with a Cl/N ratio of about 0.5,

Table 2 X.p.s. results and compositions of the various PAN/sulphate complexes

		Proportion[b] of		Ratio of		Proportion[c] of		
Sample[a]	Total S/N ratio	HSO_4^-	H_2SO_4	HSO_4^-/N	H_2SO_4/N	=N–	–NH–	N^+
1	0.20	1.0	0.0	0.20	0.0	0.23	0.54	0.23
2	0.52	0.83	0.17	0.43	0.09	0.0	0.55	0.45
3	0.74	0.70	0.30	0.52	0.22	0.0	0.49	0.51
4	1.74	0.43	0.57	0.75	0.99	0.0	0.27	0.73

[a] The sample numbers correspond to those in *Table 1*
[b] From the curve-fitted S2p core-level spectra
[c] From the curve-fitted N1s core-level spectra

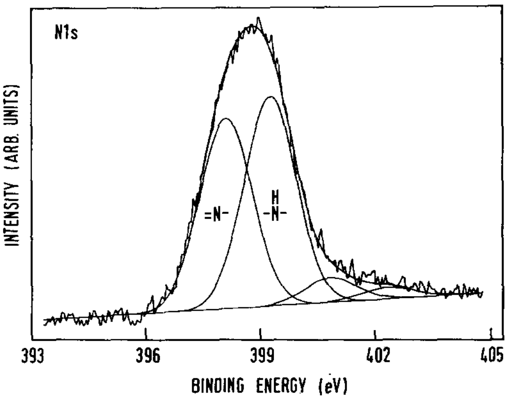

Figure 2 N1s core-level spectrum of an EM/sulphate complex (initial S/N = 1.74) after treatment with excess 0.5 M NaOH

leaving most of the amine units untouched. An earlier report[3] has predicted only a small proportion ($\sim$3.6%) of protonated amine sites at pH $\sim$ 0. Thus, it should be emphasized that protonation of the amine nitrogens in the EM base of PAN is likely to be observed only when the samples are loaded with excess amounts of non-volatile acids.

Protonation of the amine nitrogens in the polysemiquinone form of PAN would convert some of the –NH– groups to $-N^+H_2-$ groups. This would probably destabilize the polymer by reducing the extent of its π-conjugation[21]. Alternatively, the presence of the protonated amine structure may interfere with the formation of polarons and bipolarons and result in the interruption of the order of the polaron lattice[22]. As a result, the electrical conductivity of the complex with a high H_2SO_4 loading and a high proportion of the protonated amine units is substantially lower than that of the EM salt. A similar result has also been reported for the self-doped PAN when over half of the rings of the EM base are sulphonated[23].

Conclusions

It has been demonstrated that X.p.s. provides a convenient tool for the study of the surface adsorbed species in PAN arising from protonation by non-volatile acids, such as H_2SO_4. X.p.s. also provides direct evidence that the amine units of the EM oxidation state of PAN are also susceptible to protonation in the presence of a large excess of incorporated protonic acid.

References

1 Skotheim, T. (Ed.) 'Handbook of Conducting Polymers', Vols I and II, Marcel Dekker, New York, 1986
2 MacDiarmid, A. G., Chiang, J. C., Richter, A. F. and Epstein, A. J. *Synth. Met.* 1987, **18**, 285
3 Ray, A., Asturies, G. E., Kershner, D. L., Richter, A. F., MacDiarmid, A. G. and Epstein, A. J. *Synth. Met.* 1989, **29**, E141
4 Angelopoulos, M., Asturias, G. E., Ermer, S. P., Ray, A., Scherr, E. M., MacDiarmid, A. G., Akhtar, M., Kiss, Z. and Epstein, A. J. *Mol. Cryst. Liq. Cryst.* 1988, **160**, 151
5 Jozefowicz, M. E., Laversanne, R., Javadi, H. H. S., Epstein, A. J., Pouget, J. P., Tang, X. and MacDiarmid, A. G. *Phys. Rev. B* 1989, **39**, 12958
6 Phillips, S. D., Yu, G., Gao, Y. and Heeger, A. J. *Phys. Rev. B* 1989, **39**, 10702
7 Kang, E. T., Neoh, K. G., Ong, T. K., Tan, K. L. and Tan, B. T. G. *Synth. Met.* 1990, **39**, 69
8 Salaneck, W. R., Lundstrom, I., Hjertberg, T., Duke, C. B., Conwell, E., Paton, A., MacDiarmid, A. G., Somasiri, N. L. D., Huang, W. S. and Richter, A. F. *Synth. Met.* 1987, **18**, 291
9 Snauwaert, P., Lazzaroni, R., Riga, J. and Verbist, J. J. *Synth. Met.* 1987, **18**, 335
10 Munro, H. S., Parker, D. and Eaves, J. G. *Springer Ser. Solid-State Sci.* 1987, **76**, 257
11 Mirrezaei, S. R., Munro, H. S. and Parker, D. *Synth. Met.* 1988, **26**, 169
12 Hagiwara, T., Demura, T. and Iwata, K. *Synth. Met.* 1987, **18**, 317
13 Nakajima, T., Harada, M., Osawa, R., Kawagoe, T., Furukawa, Y. and Harada, I. *Macromolecules* 1989, **22**, 2644
14 Snauwaert, P., Lazzaroni, R., Riga, J. and Verbist, J. J. *J. Chem. Phys.* 1990, **92**, 2187
15 Kang, E. T., Neoh, K. G., Khor, S. H., Tan, K. L. and Tan, B. T. G. *J. Chem. Soc. Chem. Commun.* 1989, 696
16 Kang, E. T., Neoh, K. G., Tan, T. C., Khor, S. H. and Tan, K. L. *Macromolecules* 1990, **23**, 2918
17 Kang, E. T., Neoh, K. G. and Tan, K. L. *Polym. J.* 1989, **21**, 873
18 Cao, Y., Smith, P. and Heeger, A. J. *Synth. Met.* 1989, **32**, 263
19 MacDiarmid, A. G., Chiang, J. C., Halpern, M., Huang, W. S., Mu, S. L., Somasiri, N. L. D., Wu, W. and Yaniger, S. I. *Mol. Cryst. Liq. Cryst.* 1985, **121**, 173
20 Muilenberg, G. E. (Ed.) 'Handbook of X-ray Photoelectron Spectroscopy', Perkin-Elmer, Eden Prarie, MN, 1977, p. 56
21 Yue, J. and Epstein, A. J. *J. Am. Chem. Soc.* 1990, **112**, 2800
22 Tanaka, K., Wang, S. L. and Yamabe, T. *Synth. Met.* 1991, **36**, 129
23 Yue, J. and Epstein, A. J. *Macromolecules* 1991, **24**, 4441