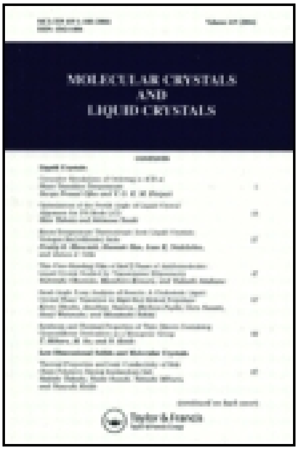

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

X-ray Photoelectron Spectroscopy Studies of Some Polyaniline-Halogen Complexes

E. T. Kang [a] , K. G. Neoh [a] , K. L. Tan [b] , M. H. Kuok [b] & B. T. G. Tan [b]

[a] Department of Chemical Engineering, National University of Singapore, Kent Ridge, Singapore, 0511

[b] Department of Physics, National University of Singapore, Kent Ridge, Singapore, 0511

Version of record first published: 04 Oct 2006.

To cite this article: E. T. Kang , K. G. Neoh , K. L. Tan , M. H. Kuok & B. T. G. Tan (1990): X-ray Photoelectron Spectroscopy Studies of Some Polyaniline-Halogen Complexes, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 178:1, 219-230

To link to this article: http://dx.doi.org/10.1080/00268949008042720

Mol. Cryst. Liq. Cryst., 1990, Vol. 178, pp. 219–230
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

X-ray Photoelectron Spectroscopy Studies of Some Polyaniline-Halogen Complexes

E. T. KANG and K. G. NEOH
Department of Chemical Engineering, National University of Singapore, Kent Ridge, Singapore 0511

and

K. L. TAN, M. H. KUOK AND B. T. G. TAN
Department of Physics, National University of Singapore, Kent Ridge, Singapore 0511

(*Received June 21, 1989; in final form September 1, 1989*)

Changes in the structure and oxidation state of polyemeraldine (PEM) and polyleucoemeraldine (PLM) upon "doping" by iodine and bromine were studied by x-ray photoelectron spectroscopy (XPS). The charge transfer interaction with the halogens resulted in a decrease in imine repeating units in the case of PEM. In the case of PLM, interaction with halogens resulted in a nitrogenonium ion structure analogous to that of the protonated imine nitrogen in PEM. In both polymer structures involving iodine, the presence of I_3^- and I_5^- species was suggested by the I3d5/2 XPS core-level spectrum. For complexes involving bromine, the ratio of covalent to ionic bromide content increases with increasing bromine to monomer ratio during the "doping" process.

Keywords: XPS, polyemeraldine, polyleucoemeraldine, halogens, oxidation states

INTRODUCTION

Electrically conducting polymers have attracted a great deal of research interest in recent years.[1] This has resulted in renewed interest[2–4] in the century-old[5] aniline family of polymers. The electrical conductivity of polyaniline can be varied from about 10^{-11} S/cm to over 1 S/cm by acid protonation[2] or by electrochemical doping.[6,7] Furthermore, the oxidation state of the polymer can be varied from the fully reduced poly(paraphenyleneamine) or "leucoemeraldine" to the fully oxidized poly(paraphenyleneimine) or "pernigraniline." The 50% oxidized polymer has been termed "emeraldine base." The structures of the polyaniline complexes have been studied by various analytical techniques.[8–12] A number of oligomeric model compounds of aniline has also been investigated.[13–15]

Most of the studies on the structural changes associated with chemical "doping" of polyaniline have been centered on the protonation of polyemeraldine (PEM).

Much less work has been devoted to the doping of polyleucoemeraldine (PLM) as well as the use of other dopants.[9,10,16,17] Traditionally halogens, iodine and bromine in particular, have been used to enhance the electrical conductivity of conjugated polymers, such as polyacetylene[18] and Polypyrrole.[19] Recently, Ray *et al.* have also reported on the doping of PLM by chlorine and a number of other electron acceptors.[20] Accordingly, it should be interesting to carry out a detailed study on the structural changes associated with various degree of "doping" of PEM and PLM by halogens. It was also demonstrated that x-ray photoelectron spectroscopy (XPS) provided a convenient tool for such purpose.

EXPERIMENTAL

Polymer samples

Polyemeraldine hydrochloride was prepared by the oxidative polymerization of aniline by ammonium persulfate in 1M aqueous HCl at 0–5°C and under a N_2 atmosphere according to the published method.[2,3] It was converted to the emeraldine base polymer (PEM) by treatment with excess 0.5 M aqueous NH_4OH and dried by pumping under reduced pressure. Elemental analysis suggests a C:H:N mole ratio of 24.0:18.2:4.02 for the present PEM base. This composition is consistent with an approximately 50% oxidized polymer structure. Some of the polymer base was further converted to the polyleucoemeraldine (PLM) by treatment with excess phenylhydrazine accoding to the method of Green and Woodhead.[5] Complex formation with the halogen, I_2 or Br_2, was carried out by dispersing with vigorous agitation the finely ground PEM or PLM in dry acetonitrile solution of the halogen at various concentrations. The solvent was then allowed to evaporate off at room temperature. The residual solvent in the sample was removed by pumping under reduced pressure. The final uptake of the halogen (bulk composition) was determined gravimetrically.

Polymer characterization

Electrical conductivity of the polymer-halogen complexes was measured using both the standard collinear four-probe and two probe techniques on compressed pellets. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a VG ESCALAB MkII spectrometer with a MgKα x-ray source (1253.6 eV photons). The samples in fine powder form were mounted on sample studs by means of double sided adhesive tapes. The pressure in the analysis chamber was maintained below 10^{-8} mbar. The x-ray source was operated at 120 W (12 kV and 10 mA). All core-level spectra were referenced to the C1s neutral carbon peak at 284.6 eV. Experimentally determined sensitivity factors were used to obtain the elemental compositions from the peak area ratios and may be subjected to ±10% error. All spectra were fitted with Gaussian component peaks. The full width at half maximum (f.w.h.m.) for each peak component in a particular spectrum was maintained constant during spectral deconvolution. The Raman spectra were obtained using the 514.5 nm excitation line of a Spectra-Physics 2030 argon-ion laser. As the samples were black, the laser beam was incident on them at a glancing angle. The scattered light, collected at 90° to the incident beam, was analyzed with a Spex 1403 double monochromator and a photon-counting detection system.

RESULTS AND DISCUSSION

Interaction with Iodine

Figure 1(a) and Figure 1(b) show the respective N1s XPS core-level spectrum of PEM base and PLM. Our earlier studies[21,22] suggested that the N1s core-level spectrum of PEM base can be deconvoluted into two peak components of about equal sizes with binding energies (B.E.) of 399.3 ± 0.1 eV and 398.1 ± 0.1 eV. The peaks have been assigned to the benzoid amine and quinoid imine nitrogen, respectively. The presence of about equal amounts of imine and amine repeating units is consistent with the PEM structure proposed by MacDiarmid *et al.*[3] The presence of a trace amount of positively charged nitrogen (see below) in the present PEM base, as suggested by the weak high-B.E. tail, is probably associated with some surface oxidation products and/or incomplete deprotonation. The present

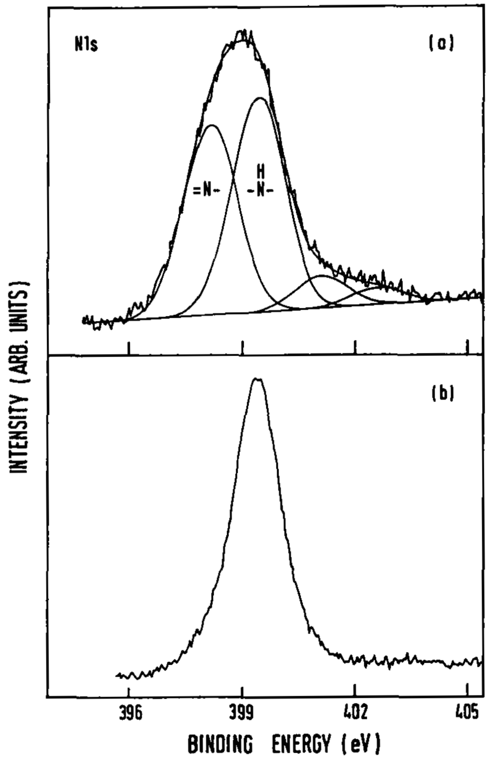

FIGURE 1 Curve-fitted N1s XPS core-level spectrum of (a) polyemeraldine base and (b) polyleucoemeraldine.

peak assignments are further supported by the fact that PLM which consists entirely of reduced amine repeating units,[17] exhibits only a single N1s environment at 399.3 eV.

First, a blank test has been performed to ensure that the solvent used does not induce any structural changes in the polymer. For a PEM base powder that has been vigorously agitated in pure acetonitrile, the N1s core-level spectrum shows a close resemblance to that of Figure 1(a). Figure 2(a) to Figure 2(d) show the N1s and I3d5/2 core-level spectra for two PEM/I_2 complexes at different iodine levels. In each case, the I3d5/2 core-level spectrum consists of two major peak components at B.E. of about 618.5 and 620.0 eV and a high B.E. tail. In iodine doped conjugated polymers, such as polyacetylene[23,24] and Polypyrrole,[26] the peaks corresponding to about these B.E. have been assigned to the I_3^- and $I_2 + I_3^- = I_5^-$ species, respectively, while the high B.E. tail has been attributed to the shake-up structure[23] associated with the two major component peaks. The occurrence of I_3^- and I_5^- species in the present PEM/I_2 complex is further confirmed by the presence of intense Raman bands at about 108 cm^{-1} and 168 cm^{-1}, attributable to the respective triiodide and pentaiodide anions.[24,25] However, in the present PEM/I_2 complex, the high B.E. tail is more appropriately associated with the formation of a small amount of covalently bonded iodine. This is based on the fact that treatment of the PEM/I_2 complex with aqueous NaOH can result in the complete removal of the two major component peaks, but not the high B.E. peak at about 621 eV. Furthermore, the I3d5/2 XPS core-level spectrum of poly(iodoaniline), such as poly(2-iodoaniline), prepared chemically in the presence of HCl and ammonium persulfate, exhibits only a major component at about 621 eV.

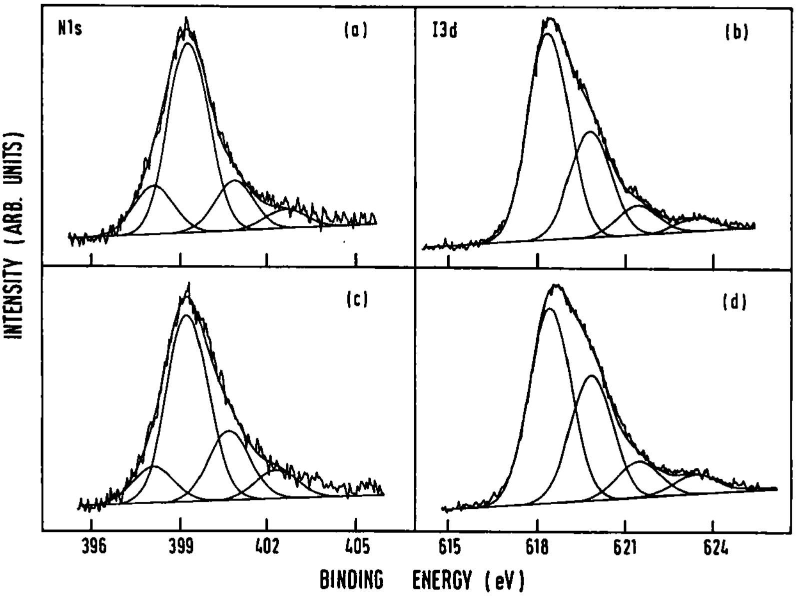

FIGURE 2 N1s and I3d5/2 XPS core-level spectra for two PEM/I_2 complexes with surface (and bulk) I/N ratios of (a) and (b), 0.60 (0.80); and (c) and (d), 0.84 (2.0).

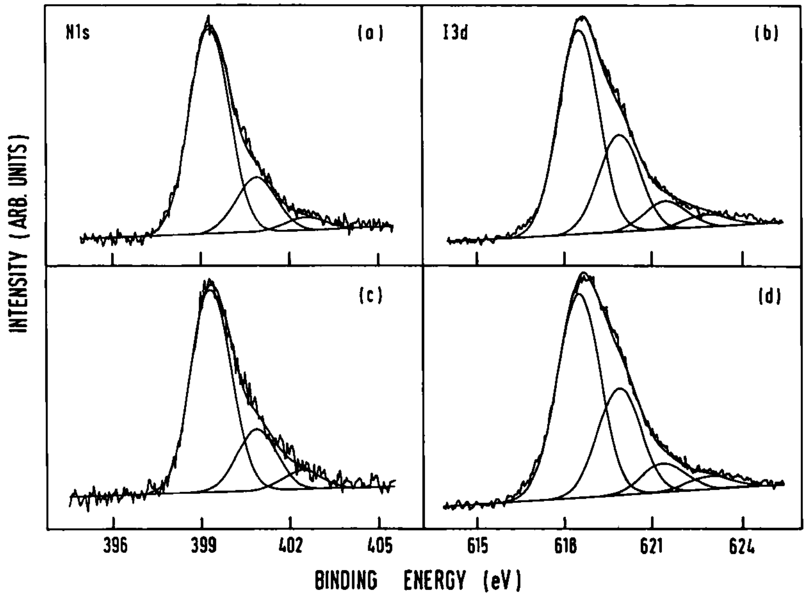

FIGURE 3 N1s and I3d5/2 XPS core-level spectra for three PLM/I_2 complexes with surface (and bulk) I/N ratios of (a) and (b), 0.66 (0.80); and (c) and (d), 1.14 (2.0).

The N1s core-level spectrum for the two PEM/I_2 samples shown in Figure 2 reveals that the proportion of peak component at 398.1 eV and attributable to the imine species decreases from the original value of about 0.5 in the PEM base upon increasing iodine loading. For instance, Figure 2 suggests that the proportion of imine species has decreased to about 0.16 and 0.10, respectively, for samples with surface I/N ratios of about 0.60 and 0.84. The decrease in imine structure is accompanied by a corresponding increase in the proportion of the positively charged nitrogen, represented by the high-B.E. tail above 401 eV.[28,29] The exact nature of the component at 402.5 eV is not clearly understood at present. However, the inclusion of this component as part of the positively charged nitrogens is required to maintain charge neutrality (see Figure 4 and Table I below). Thus, the interaction between PEM and iodine has resulted in a substantial decrease in the neutral imine repeating units, as in the case of protonation by acids.[3] Comparison of surface and bulk compositions reveals that for sample with initial I_2/monomer mole ratio greater than about 0.3, a significant amount of iodine is removed during prolonged pumping under reduced pressure. Thus, the iodine content at the surface, as revealed by XPS, is always substantially lower than that in the bulk for the moderately and highly doped samples. This makes the quantification of the structural changes of the polymer as a function of iodine concentration by XPS difficult. The gradual removal of iodine during prolonged pumping in the ultra-high vacuum environment of XPS has also been reported for the case of polyacetylene/I_2 complexes.[27]

Figure 3(a) to Figure 3(d) show the N1s and I3d5/2 core-level spectra for two PLM/I_2 complexes of about the same bulk iodine compositions as the two PEM/I_2 complexes shown in Figure 2. As in the case of PEM/I_2 complexes, the iodine in PLM/I_2 complexes exists mainly as I_3^- and I_5^- anions. Furthermore, a substantial amount of iodine is also removed from the sample surface, especially at high iodine loading. The N1s core-level spectrum of the complex, which consists of only a major component peak at 399.3 eV, is consistent with the presence of only amine nitrogen in PLM. The high B.E. tail is again attributable to the positively charged nitrogen. In this case, the positively charged nitrogen must have resulted from the removal of an electron from the amine nitrogen by the halogen acceptor.

The highest electrical conductivities achieved in the present PEM/I_2 and PLM/I_2 complexes are in the order of 5×10^{-3} and 5×10^{-1} S/cm, respectively, at a bulk I/N ratio of about 2.0. These conductivity values are comparable to that reported in the literature.[16] However, we wish to point out that at this high level of iodine loading, both complexes lose iodine, and thus conductivity, gradually in the atmosphere.

Interaction with bromine

Figure 4(a) to Figure 4(f) show the N1s and Br3d XPS core-level spectra for three PEM/Br_2 complexes at low, moderate and high bromine concentration. At low

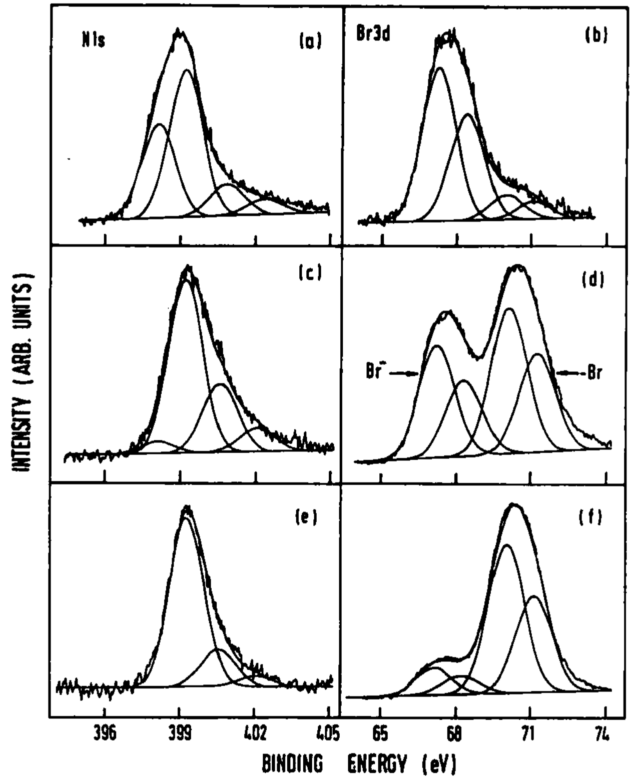

FIGURE 4 N1s and Br3d XPS core-level spectra for three PEM/Br_2 complexes with surface Br/N ratios of (a) and (b), 0.11; (c) and (d) 0.62; and (e) and (f) 1.3.

TABLE I

XPS results and stoichiometries of the various polyemeraldine/bromine complexes

Sample	Bulk Br/N	Surface stoichiometry[a]			Proportion of			Conductivity σ (S/cm)
		Br/N	$-$Br/N	Br^-/N	=N—[b]	—NH—	N^+	
1	0.05	0.05	—	0.05	0.35	0.50	0.15	9×10^{-7}
2	0.10	0.11	0.01	0.10	0.33	0.50	0.17	1×10^{-4}
3	0.30	0.28	0.08	0.20	0.17	0.56	0.27	3×10^{-2}
4	0.60	0.62	0.35	0.27	0.04	0.62	0.34	1×10^{-1}
5	1.0	0.87	0.64	0.23	0.07	0.64	0.29	2×10^{-2}
6	2.0	1.30	1.11	0.19	—	0.78	0.22	8×10^{-3}
7	4.4	1.48	1.30	0.18	—	0.78	0.22	4×10^{-3}

[a] Based on the corrected bromine to nitrogen core-level spectral area ratios.
[b] Neutral imine structure.

bromine loading, most of the halogen exists as bromide anions and the surface composition of the complex, as suggested by the total Br/N ratio, is similar to the bulk composition. However, upon increasing the bromine concentration, an increasing amount of bromine becomes covalently bonded to the polymer, as indicated by the increasing proportion of the high B.E. Br3d component, and the halogen content at the surface also falls substantially below that of the bulk. Table I summarizes the chemical states and amounts of the halogen in some PEM/Br_2 complexes at various bromine levels. Similar "doping" behavior are also observed in the case of PLM/Br_2 complexes. The nature of interactions between PLM and bromine are summarized in Table II. Figure 5(a) to Figure 5(f) show the N1s and Br3d core-level spectra for three typical PLM/Br_2 complexes with increasing halogen concentrations.

The data in Table I and Table II readily indicate that there exists an optimum doping level at which the Br^-/N ratio reaches a maximum. In the case of PEM/Br_2 complex, the maximum Br^-/N ratio also corresponds approximately to a max-

TABLE II

XPS results and stoichiometries of the various polyleucoemeraldine/bromine complexes

Sample	Bulk Br/N	Surface stoichiometry[a]			Proportion of			Conductivity σ (S/cm)
		Br/N	$-$Br/N	Br^-/N	=N—[b]	—NH—	N^+	
1	0.05	0.11	0.01	0.10	0.08	0.74	0.18	5×10^{-6}
2	0.10	0.15	0.02	0.13	0.07	0.70	0.23	2×10^{-3}
3	0.30	0.27	0.03	0.24	0.07	0.60	0.33	5×10^{-1}
4	0.60	0.55	0.19	0.36	0.06	0.56	0.38	7×10^{-2}
5	1.0	0.65	0.31	0.34	0.03	0.62	0.35	1×10^{-2}
6	2.0	1.0	0.74	0.26	0.04	0.63	0.33	8×10^{-3}
7	4.4	1.31	1.10	0.21	0.03	0.69	0.28	2×10^{-3}

[a] Based on the corrected bromine to nitrogen core-level spectral area ratios.
[b] Neutral imine structure.

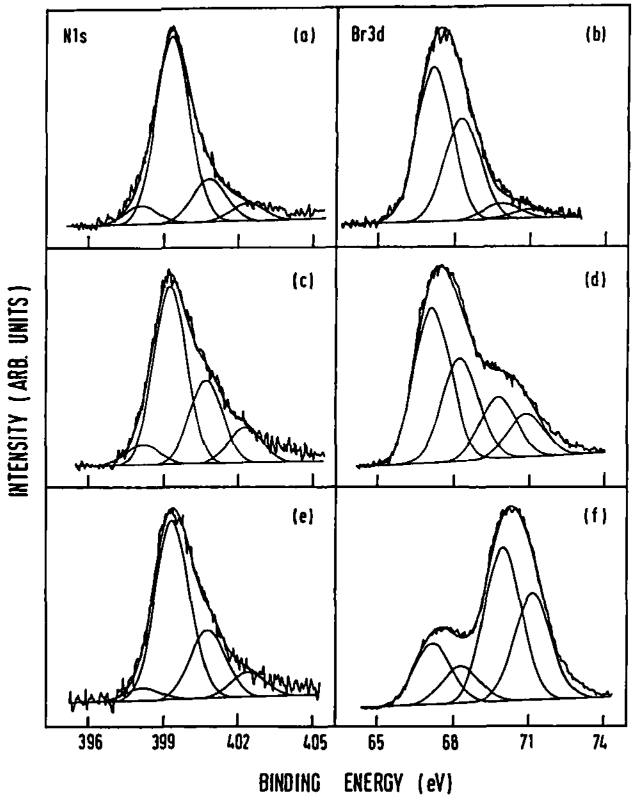

FIGURE 5 N1s and Br3d XPS core-level spectra for three PLM/Br_2 complexes with surface Br/N ratios of (a) and (b) 0.15; (c) and (d) 0.55; and (e) and (f) 1.0.

imum in the electrical conductivity (σ) of the complex. However, in the case of the PLM/Br_2 complex, maximum σ occurs somewhat below the maximum Br^-/N ratio. Comparison of the PEM/Br_2 and PLM/Br_2 complexes suggests that σ shows a strong dopant concentration dependence at low halogen levels. The decrease in σ in both complexes at high bromine content probably resulted from the increasing proportion of covalently bonded bromine. In the protonation of PEM by HCl, a decrease in σ has been associated with an increase in covalently bonded chlorine.[30] Although comparable $-$Br/N ratio is observed in both types of polymer complexes at high bromine content, the PLM complex exhibits, in general, a somewhat higher bromide anion ratio at low and moderate doping levels. Furthermore, the PLM/Br_2 complex also exhibits a significantly higher maximum electrical conductivity at a much lower halogen content than the PEM/Br_2 complex.

It would be of particular interest to elucidate the structural changes of the polymer resulting from the charge transfer interactions with bromine. Typical structural changes for some PEM and PLM complexes are revealed, respectively, by the N1s core-level spectrum of Figure 4 and Figure 5. Table I and Table II summarize the respective structural changes or changes in oxidation states for all the PEM/Br_2

and PLM/Br$_2$ complexes studied in this work. Again, in the case of PEM/Br$_2$ complex, interaction with bromine results in a gradual loss of the imine structure and the appearance of positively charged nitrogen. The latter reaches a maximum corresponding to the maximum Br$^-$/N ratio and conductivity. In all samples studied, a close balance between the number of bromide anions and the number of positive charged nitrogens is observed. The presence of localized unit positive charge on the nitrogen is consistent with the concept of nitrogenonium ion polymer proposed by MacDiarmid *et al.*[3] Thus, it is more appropriate to relate the electrical conductivity of the samples to the fraction of positively charged nitrogen. Good correlation has indeed been observed. This relation, however, should be regarded only as qualitative since the effect of varying degrees of covalent bromine formation on the electrical conductivity of the complex cannot be precisely determined. Finally, XPS data suggest that covalent bromine formation has also resulted in an increase in the proportion of the amine structure in PEM. This is probably analogous to the addition of the acid to the quinoid units, accompanied by a decrease in the quinoid/benzoid ratio, during PEM protonation.[9]

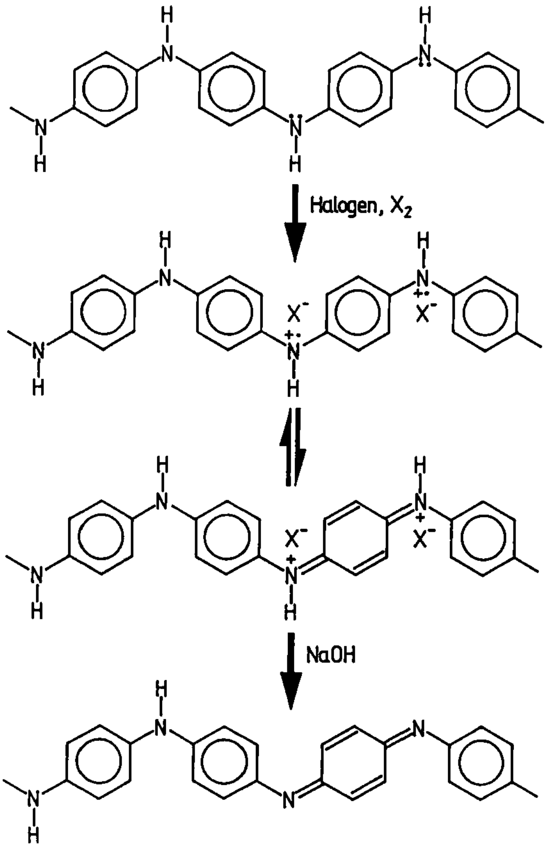

FIGURE 6 Oxidation of PLM by halogens and the possible structures involved.

In the case of the PLM/Br_2 samples, good correspondence between the amounts of positively charged nitrogen and the bromide anion is again observed. However, in these samples, maximum electrical conductivity is reached slightly below the maximum in bromide or nitrogenonium ion concentration. This can probably be attributed to a sharp increase in the proportion of the covalent bromine at a bulk Br/N ratio above 0.30. In all of the present PLM complexes, each sample contains only a small proportion of the residual imine structure. This is consistent with the predominantly amine structure of PLM.[17] Thus, the positively charged nitrogen must have originated from the oxidation of the amine nitrogen atoms. The oxidation process and the possible structures involved are depicted in Figure 6. The process involves first the formation of nitrogen radical cations in the presence of halogen anions. This is followed by the relaxation of the nitrogen radical cations to form a protonated diimine structure, similar to that which resulted from the protonation of imine repeating units of PEM base by protonic acids. In electrochemically synthesized polyaniline[31] and poly(alkylanilines),[32] two of the anodic peaks in the cyclic voltammograms have been associated with the oxidation of amine nitrogen atoms to form the respective radical cation and dications. It has also been suggested that PLM is transformed to PEM salt upon treatment with oxidizing agents such as chlorine.[20]

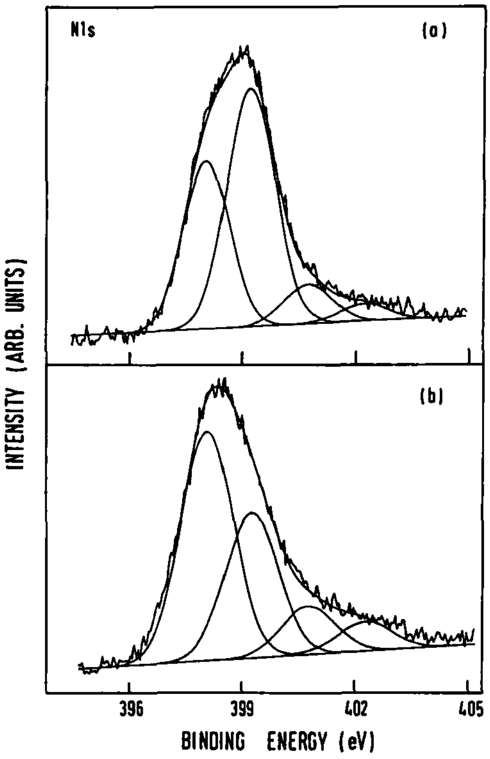

FIGURE 7 N1s XPS core-level spectrum of NaOH treated (a) PLM/Br_2 complex with initial bulk Br/N ratio of 0.60 and (b) PLM/I_2 complex with initial bulk I/N ratio of 2.0.

The mechanism for the oxidation of PLM by electron acceptors is further supported by the following XPS experimental evidence. Since the structure after halogen incorporation (Figure 6) is equivalent to that resulted from the protonation of PEM base, deprotonation of the PLM/halogen complexes should result in the appearance of the imine structure. Figure 7(a) shows the curve-fitted N1s spectrum of a NaOH (0.5 M) treated PLM/Br_2 sample with an initial bulk Br/N ratio of 0.60. The spectrum has broadened considerably from that of the pristine PLM and can be fitted with two peak components with B.E. and line width characteristic of the imine and amine nitrogen species of PEM.[21] Furthermore, the N1s XPS core-level spectrum of pristine PLM does not give rise to a significant amount of the imine structure upon treatment with NaOH. The presence of covalently bonded bromine in the present PLM/Br_2 complexes has limited the fraction of the imine nitrogen to the maximum Br^-/N ratio. However, in the case of PLM/I_2 complexes, most of the iodine exists in the form of iodide anions. Thus, deprotonation of a highly "doped" PLM/I_2 sample should give rise to a substantially higher proportion of the imine nitrogen. Figure 7(b) shows the curve-fitted N1s spectrum of a NaOH treated PLM/I_2 sample with an initial bulk I/N ratio of 2.0. In this case, the proportion of the imine structure at 398.1 eV has increased substantially above that of the amine structure. This is further substantiated by the presence of a substantially enhanced and broadened infrared absorption band at 1600–1580 cm^{-1}, attributable to the quinoid structure.[9,16] Thus, the present XPS results provide confirmation of the proposed mechanism.

CONCLUSION

It was demonstrated that XPS provided a convenient tool for the studying of changes in structure and oxidation state associated with the "doping" of polyleucoemeraldine (PLM) and polyemeraldine base (PEM) by halogens. In the case of the iodine complexes, a substantial amount of iodine was removed from the polymer surface under reduced pressure. In the case of bromine complexes, a substantial amount of bromine was incorporated as covalently bonded bromine, especially at high bromine loading. In complexes involving PEM, interactions with halogens resulted in the disappearance of the imine repeating units. However, charge transfer interaction of halogens with PLM resulted in a nitrogenonium ion structure analogous to that arising from the acid protonation of imine nitrogen in PEM.

References

1. See, for example, "Handbook of Conducting Polymers," Vol. I and II, T. Skotheim, Ed., Marcel Dekker, New York, N.Y. (1986).
2. J. C. Chiang and A. G. MacDiarmid, *Synth. Metals*, **13**, 193 (1986).
3. A. G. MacDiarmid, J. C. Chiang, A. F. Richter and A. J. Epstein, *Synth. Metals*, **18**, 285 (1987).
4. S. P. Armes and J. F. Miller, *Synth. Metals*, **23**, 385 (1988).
5. A. G. Green and A. E. Woodhead, *J. Chem. Soc.*, 2388 (1910).
6. A. F. Diaz and J. A. Logan, *J. Electroanal. Chem. Interfacial Electrochem.*, **111**, 111 (1980).
7. E. M. Genies, A. A. Syed and C. Tsintavis, *Mol. Cryst. Liq. Cryst.*, **121**, 181 (1985).

8. T. Ohsaka, Y. Ohnuki, N. Oyama, G. Katagiri and K. Kamisako, *J. Electroanal. Chem. Interfacial Electrochem.*, **161**, 399 (1984).
9. J. Tang, X. Jing, B. Wang and F. Wang, *Synth. Metals*, **24**, 231 (1988).
10. Y. K. Kim, C. Foster, J. Chiang and A. J. Heeger, *Synth. Metals*, **25**, 49 (1988).
11. T. Hjertberg, W. R. Salaneck, I. Lundstrom, N. L. D. Somasori and A. G. MacDiarmid, *J. Polym. Sci., Polym. Lett. Ed.*, **23**, 503 (1985).
12. T. Nakajima, M. Harada, R. Osawa, T. Kawagoe, Y. Furukawa and I. Harada, *Macromolecules*, **22**, 2644 (1989).
13. T. Hjertberg, M. Sandberg, O. Wennerstrom and I. Lagerstedt, *Synth. Metals*, **21**, 31 (1987).
14. R. H. Baughman, J. F. Wolf, H. Eckhardt and L. W. Shacklette, *Synth. Metals*, **25**, 121 (1988).
15. T. Hagiwara, M. Yamaura and K. Iwata, *Synth. Metals*, **26**, 195 (1988).
16. Y. Cao, S. Li, Z. Xue and D. Guo, *Synth. Metals*, **16**, 305 (1986).
17. C. Menardo, M. Nechtchein, A. Rousseau, J. P. Travers and P. Hany, *Synth. Metals*, **25**, 311 (1988).
18. A. G. MacDiarmid and A. J. Heeger, *Synth. Metals*, **1**, 101 (1979/80).
19. E. T. Kang, K. G. Neoh and H. C. Ti, *Solid State Commun.*, **60**, 457 (1986).
20. A. Ray, G. E. Asturias, D. L. Kershner, A. F. Richter, A. G. MacDiarmid and A. J. Epstein, *Synth. Metals*, **29**, E141 (1989).
21. K. L. Tan, B. T. G. Tan, E. T. Kang and K. G. Neoh, *Phys. Rev. B.*, **39(11)**, 8070 (1989).
22. E. T. Kang, K. G. Neoh, S. H. Khor, K. L. Tan and B. T. G. Tan, *Chem. Commun.* **11**, 695 (1989).
23. W. R. Salaneck, H. R. Thomas, R. W. Bigelow, C. B. Duke, E. W. Plummer, A. J. Heeger and A. G. MacDiarmid, *J. Chem. Phys.*, **72**, 3674 (1980).
24. S. L. Hsu, A. J. Signorelli, G. P. Pez and R. H. Baughman, *J. Chem. Phys.*, **69**, 106 (1978).
25. S. Lefrant, L. S. Lichtmann, H. Temkin, D. B. Fitchen, D. C. Miller, G. E. Whitwell II and J. B. Burlitch, *Solid State Commun.*, **29**, 191 (1979).
26. E. T. Kang, H. C. Ti, K. G. Neoh and T. C. Tan, *Polym. J.*, **20**, 399 (1988).
27. I. Ikemoto, M. Sakairi, T. Tsutsumi, H. Kuroda, I. Harada, M. Tasumi, H. Sirakawa and S. Ikeda, *Chem. Letter*, 1189 (1979).
28. W. R. Salaneck, I. Lundstrom, T. Hjertberg, C. B. Duke, E. Conwell, A. Paton, A. G. MacDiarmid, N. L. D. Somasiri, W. S. Huang and A. F. Richter, *Synth. Metals*, **18**, 291 (1987).
29. H. S. Munro, D. Parker and J. G. Eaves, *Springer Ser. Solid-State Sci.*, **76**, 257 (1987).
30. T. Hagiwara, M. Yamaura and K. Iwata, *Synth. Metals*, **25**, 243 (1988).
31. W. W. Focke, G. E. Wnek, Y. J. Wei, *J. Phys. Chem.*, **91**, 5813 (1987).
32. M. Leclerc, J. Guay and Le H. Dao, *Macromolecules*, **22**, 649 (1989).