X-ray photoelectron spectroscopic characterization of protonation of polyaniline films by polymeric acids

E. T. Kang* and K. G. Neoh
Department of Chemical Engineering, National University of Singapore, Kent Ridge, Singapore 0511

and K. L. Tan
Department of Physics, National University of Singapore, Kent Ridge, Singapore 0511
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The protonation behaviour of emeraldine (EM) films by two polymeric acids, poly(acrylic acid) (PAAc) and poly(styrenesulfonic acid) (PSSAc), was studied by X-ray photoelectron spectroscopy (X.p.s.). The EM–PAAc films were prepared by direct protonation of EM films in aqueous PAAc medium, by blending of EM and PAAc in *N*-methylpyrrolidinone (NMP) and by near-ultra-violet light-induced surface graft copolymerization of EM film with acrylic acid. EM–PAAc salts were also prepared by direct polymerization of aniline in PAAc solutions. Relatively weak charge-transfer interactions or low protonation levels were observed in all cases, even in the presence of a large excess of PAAc units. However, in the presence of a strong acid such as PSSAc, almost all the amine nitrogens in the surface region of the EM film, in addition to the imine nitrogens, were susceptible to protonation. Furthermore, deprotonation of the PSSAc protonated EM film, but not the PAAc protonated EM film, was accompanied by a substantial increase in the intrinsic oxidation state of the EM film, leading to the 75% intrinsically oxidized nigraniline state. Lower extent of surface hydrolysis reaction was also observed during protonation by the polymeric acid than by mineral acids.

(Keywords: X-ray photoelectron spectra; polyaniline films; protonation by polymeric acids)

INTRODUCTION

The century-old[1,2] aniline family of polymers has been the subject of recently renewed interest because of their high electrical conductivity, environmental stability, solution processability and interesting redox properties associated with the chain nitrogens[3–8]. The aniline polymers have the general formula $[(\text{-B-NH-B-NH-})_y(\text{-B-N=Q=N-})_{1-y}]_x$, in which B and Q denote the C_6H_4 rings in the benzenoid and quinonoid forms, respectively. Thus, the aniline polymers are basically poly(*p*-phenyleneimineamine)s, in which the intrinsic oxidation states can range from that of the fully reduced leucoemeraldine (LM, $y=1$), though that of the 50% oxidized emeraldine (EM, $y=0.5$), to that of the fully oxidized pernigraniline (PNA, $y=0$). The polymer can achieve its highly conductive state either through the protonation of the imine nitrogens (=N–) in its EM oxidation state, or through the oxidation of the amine nitrogens (–NH–) in its fully reduced LM state. Recent studies[9,10] have also shown that the amine nitrogens of the EM and LM oxidation states of the polymer are also susceptible to protonation, especially in the presence of a strong, non-volatile acid. Strong acid treatment, followed by deprotonation, can also increase the intrinsic oxidation of the EM film to that of the 75% oxidized nigraniline (NA) base[9]. Furthermore, protonic-acid-induced processability of polyaniline (PAN) has been a subject of great interest[11,12]. Thus, the intrinsic structure of PAN is affected by the type and nature of the acid used for protonation. Relatively few studies have been devoted to the use of polymeric protonic acids[13,14]. Accordingly, it should be interesting to assess more quantitatively the effect and extent of protonation of PAN by polymeric acids.

EXPERIMENTAL

Materials preparation

The emeraldine (EM) sulfate salt was prepared via the oxidative polymerization of aniline by ammonium persulfate in aqueous 1 M H_2SO_4, similar to the method[3] reported for the synthesis carried out in HCl. The EM salt was converted to the neutral EM base by treatment with excess 0.5 M NaOH. The EM base was then cast into thin films of about 5–10 μm in thickness from *N*-methylpyrrolidinone (NMP) solution. The solvent trapped in the polymer films was removed by exhaustive pumping, followed by washing with deionized water for at least 8 h.

Poly(styrenesulfonic acid) (PSSAc) with an average molecular weight (*MW*) of about 70000 was obtained

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* To whom correspondence should be addressed.

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from Polyscience Inc. in 30% solution. Poly(acrylic acid) (PAAc) powders with *MWs* of about 2000 and 750000 were obtained from Aldrich Chemical Co. Blending of PAAc and EM was carried out by mixing the NMP solutions of both components, followed by casting the blend into thin films of 10 μm or less. Near-u.v. light-induced graft copolymerizations of the EM base films with acrylic acid (AAc) and sodium salt of styrene sulfonic acid (NaSS) were carried out in 8 wt% aqueous solutions of the respective monomers according to the method reported earlier[15]. Ozone pretreatments of EM films before grafting were carried out using a Fischer model 500 ozonizer at an oxygen flow rate of 100 l h^{-1} and an applied voltage of 100 V.

Materials characterization

The intrinsic structures, in particular the intrinsic oxidation states (imine/amine ratios), and the protonation levels of the polymer films were determined by X-ray photoelectron spectroscopy (X.p.s.). The X.p.s. measurements were made on a VG Escalab MkII spectrometer with a Mg Kα X-ray source (1253.6 eV photons) at a constant retard ratio of 40. The polymer films were mounted on the standard sample studs by means of double-sided adhesive tape. The X-ray source was run at a reduced power of 120 W (12 kV and 10 mA). To compensate for surface charging effects, all binding energies were referenced to the C 1s neutral carbon peak at 284.6 eV. In peak synthesis, the linewidth (full width at half-maximum or f.w.h.m.) of the Gaussian peaks was maintained constant for all components in a particular spectrum. Surface elemental stoichiometries were determined from peak area ratios, after correcting with the experimentally determined sensitivity factors, and were accurate to within ±10%. The core-level spectra for some film samples were obtained at a number of take-off angles (with respect to the film surface), ranging from 20° to 75°.

RESULTS AND DISCUSSION

A number of recent X-ray photoelectron spectroscopic (X.p.s.) studies on chemically[8,16] and electrochemically[17,18] synthesized PAN have demonstrated that the quinoid imine (=N–), benzenoid amine (–NH–) and positively charged nitrogens corresponding to any particular intrinsic redox state and protonation level of PAN can be quantitatively differentiated in the properly curve-fitted N 1s core-level spectrum. They correspond to peak components with binding energies (*BEs*) at about 398.2, 399.4 and >400 eV, respectively. The applications of X.p.s. technique in studying electroactive polymers have recently been reviewed[19].

Direct protonation by poly(acrylic acid)

The protonations of EM base films by poly(acrylic acid)s (PAAc) of vastly different molecular weights (*MW*) are compared first. *Figures 1a* and *1b* show, respectively, the C 1s and N 1s core-level spectra of an EM base film after equilibrating in 0.1 M aqueous PAAc of low *MW* (~2000). The corresponding core-level spectra for a 0.1 M high-*MW* (750000) PAAc protonated EM film are shown in *Figures 1d* and *1e*. In each sample, the presence of PAAc on the film surface is readily indicated by the appearance of a high-*BE* C 1s component at about 288.6 eV, attributable to the COOH functional groups of the acrylic polymer[20]. The surface stoichiometry can thus be readily determined from the [COOH]/[N] mole ratios, based on the corrected area ratio of the C 1s spectral component at 288.6 eV and the N 1s spectrum. The extent of protonation, on the other hand, is

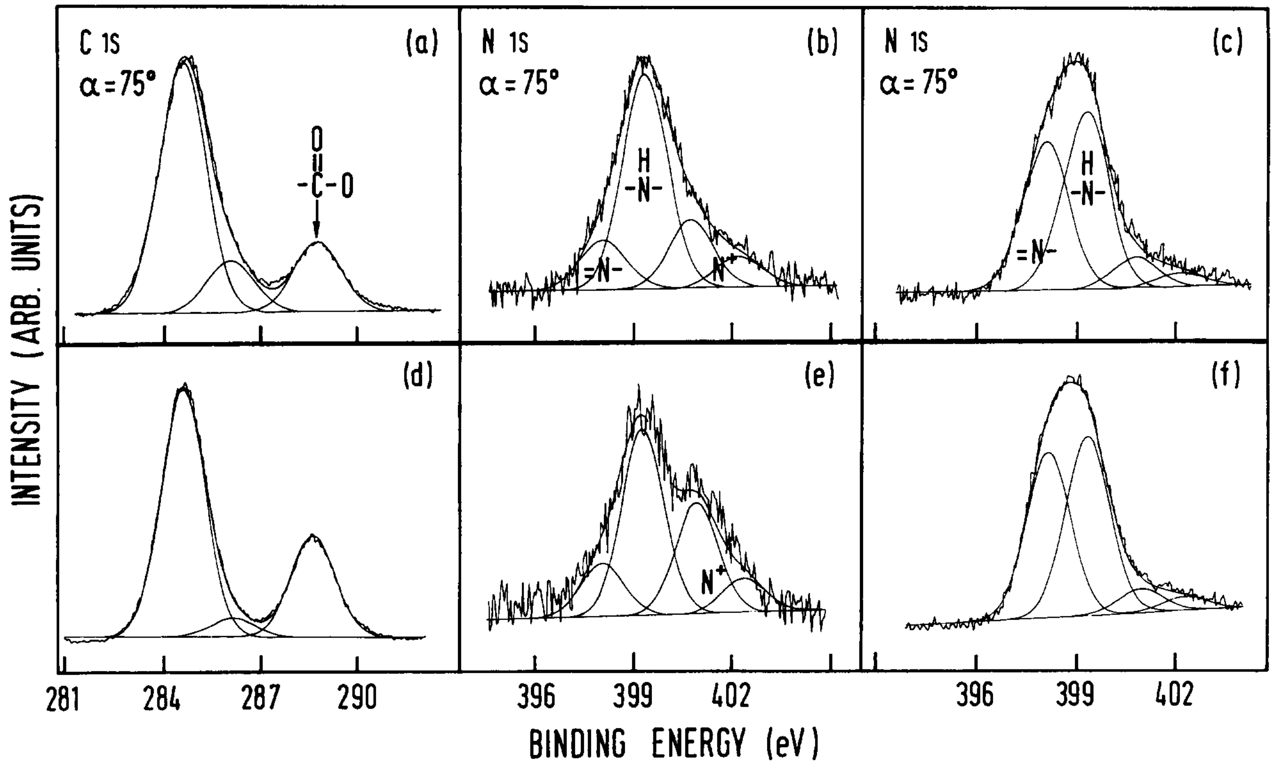

Figure 1 (a) C 1s and (b) N 1s core-level spectra of an EM base film after protonation by 0.1 M PAAc of *MW* ~2000, and (c) the N 1s core-level spectrum after deprotonation by NaOH. The corresponding C 1s and N 1s spectra for a similar EM film after protonation by 0.1 M PAAc of *MW* ~750000 are shown in (d), (e) and (f)

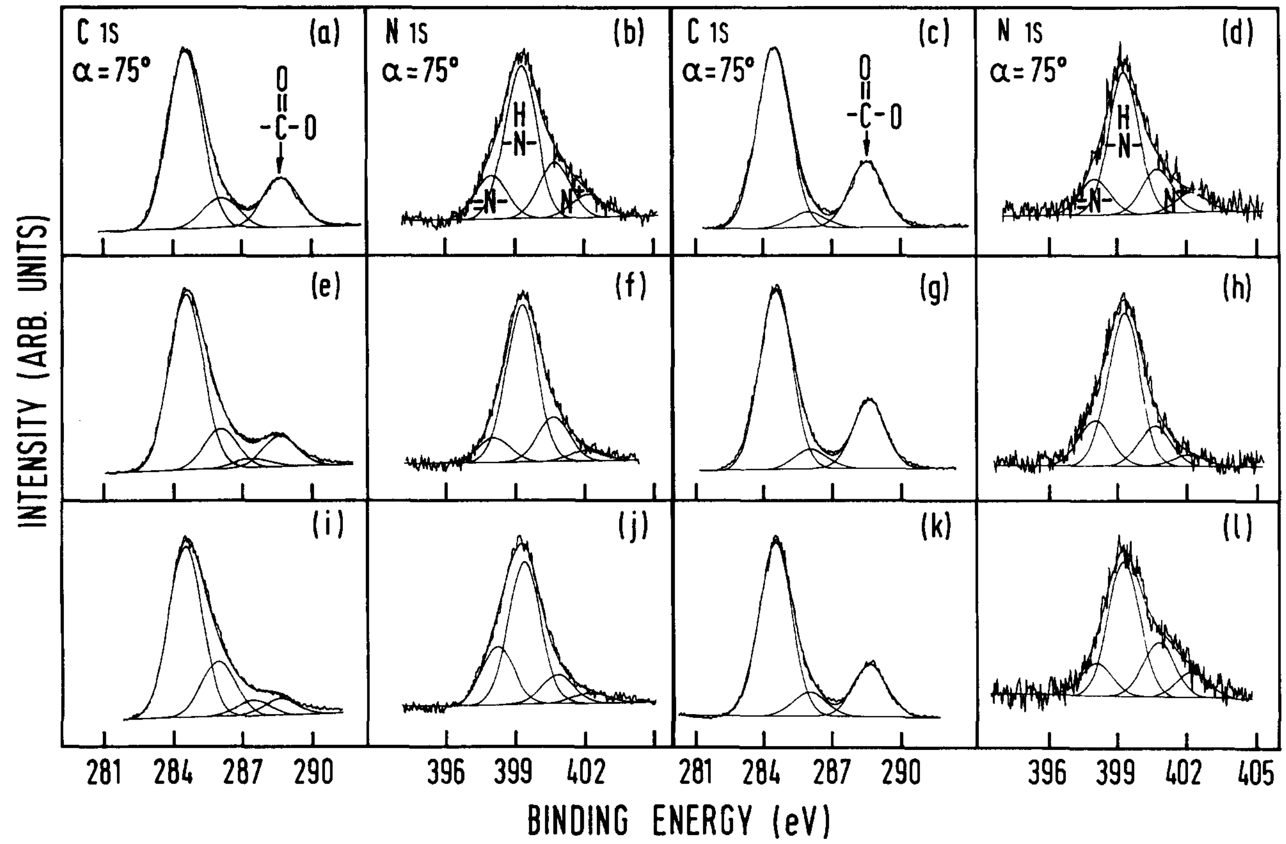

Figure 2 C 1s and N 1s core-level spectra of EM films blended with equal moles of (a) and (b) low-*MW* (~2000) PAAc, and (c) and (d) high-*MW* (~750000) PAAc. The corresponding C 1s and N 1s core-level spectra for the two films after soaking in water for more than two weeks are shown in (e)–(h), and after one external protonation/deprotonation cycle in (i)–(l)

determined from the proportion of the high-*BE* tail in the N 1s core-level spectrum, attributable to the positively charged nitrogens. Based on the fixed f.w.h.m. approach in the peak synthesis used in the present work, the high-*BE* tail in the N 1s spectrum has been resolved into two peaks separated by about 1.5 and 3.0 eV from the amine peak, respectively.

The surface [COOH]/[N] ratios for the low-*MW* and high-*MW* PAAc protonated EM films are about 5.0 and 13.0, respectively. However, the proportions of positively charged nitrogens are substantially below 0.5. Thus, a substantial proportion of the imine nitrogens remains unprotonated in both samples, even in the presence of a large excess of the COOH functional groups. Nevertheless, a somewhat higher extent of protonation is observed for the high-*MW* PAAc protonated film. The low protonation levels observed are probably consistent with the fact that PAAc is a relatively weak organic acid[13], although other factors, such as stereospecificity and steric effects of the COOH groups on PAAc chains, must also be considered. This protonation behaviour appears to differ significantly from the earlier observation[9] that for EM film protonated by a strong, non-volatile inorganic acid, such as $HClO_4$, almost all the amine nitrogens, in addition to the imine nitrogens, are susceptible to protonation. *Figures 1c* and *1f* show the respective N 1s core-level spectra of the two PAAc protonated EM films after treatment with 0.5 M NaOH. Thus, base treatment returns the two PAAc protonated films to their EM form, as indicated by the appearance of about equal amounts of the imine and amine nitrogens in the N 1s core-level spectra. This deprotonation behaviour again is somewhat different from the earlier finding that deprotonation of the $HClO_4$ protonated EM film readily results in an increase in the intrinsic oxidation state of the EM base to give rise to a 75% intrinsically oxidized nigraniline base[9].

Blending with poly(acrylic acid)

The C 1s and N 1s core-level spectra of two EM films blended with equal moles of either low-*MW* (~2000) PAAc or high-*MW* (~750000) PAAc are compared in *Figures 2a* to *2d*. The surface [COOH]/[N] ratios for the low-*MW* PAAc and high-*MW* PAAc blends are about 2.9 and 6.6, respectively. These ratios readily indicate that, in both cases, the film surfaces are much richer in the acrylic polymer. The surface [COOH]/[N] ratio is always higher than that of the bulk, even when the proportion of PAAc used for blending is substantially reduced. In spite of the presence of a large excess of the COOH functional groups at the surface, the protonation level in each sample is substantially below 50% and a large proportion of the imine nitrogens remains unprotonated. The interference[13] of any trapped NMP solvent on the PAN–acid dopant interaction can be ruled out, at least in the surface region, as the samples were measured in the ultra-high-vacuum environment of X.p.s. Furthermore, subsequent exhaustive washings (see below) did not appear to improve the extent of protonation. This low protonation level is also consistent with that observed above during the direct protonation of EM film by a large excess of PAAc. This phenomenon is also of particular importance, as the 'free' COOH groups may serve as sites for subsequent functionalization of the polymer system, such as enzyme/protein immobilization via covalent bonding[21]. Thus, it would be of great importance to assess the stability of the present EM–PAAc blends in aqueous solutions.

Figures 2e to *2h* show the corresponding C 1s and N 1s core-level spectra of the two polymer films after they have been soaked in water for more than two weeks. A substantial decrease in the intensity of the COOH component in the C 1s core-level spectrum is observed in the case of low-*MW* PAAc blend. On the other hand, however, no apparent loss of the water-soluble acrylic polymer is discernible from the C 1s core level of the high-*MW* PAAc blend. This observation is further supported by the fact that the actual [COOH]/[N] ratio does not decrease by more than 10%. The leaching out of the low-*MW* PAAc is aggravated if the polymer film was equilibrated in a strong mineral acid, such as 1 M $HClO_4$, followed with exhaustive soaking and washing to remove the latter. Incorporation and removal of the anions during a protonation/deprotonation cycle have been known to increase the porosity (at the molecular level) of EM film[22]. The effect of this external protonation/deprotonation, however, is not observed in the case of EM film blended with high-*MW* PAAc, as indicated by the persistence of an intense COOH component in the C 1s core-level spectrum. *Figures 2i* to *2l* show the corresponding C 1s and N 1s core-level spectra of the two polymer blends after the external protonation/deprotonation cycle.

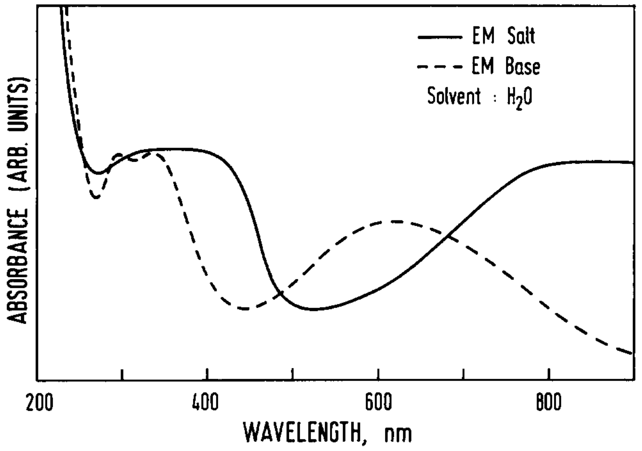

Figure 3 U.v.-visible absorption spectra of EM salt and base in aqueous media for the sample prepared from polymerization of aniline in PAAc solution

Polymerization of aniline in poly(acrylic acid) medium

Oxidative polymerizations of aniline in 1 to 5 wt% aqueous PAAc (*MW* ~750 000) solutions, with initial [COOH]/[aniline] mole ratios ranging from 2 to 10, and an [aniline]/[oxidant] mole ratio of 1, always give rise to a dark-green gel. For [COOH]/[aniline] mole ratio less than 2, black precipitates of aniline polymer are also formed. The dark-green gel readily disperses in an aqueous medium to give rise to a green solution with a broad u.v.-visible absorption maximum at about 860 nm, characteristic of the EM salt absorption spectrum[23] (*Figure 3*). Addition of a base, such as NaOH, gives rise to a blue aqueous solution with an absorption maximum at about 610 nm, as is also shown in *Figure 3*. This aqueous EM base absorption spectrum is not unlike the EM base absorption spectrum obtained in a good organic solvent, such as *N*-methylpyrrolidinone (NMP).

The green EM–PAAc salt gel was purified by dehydration under reduced pressure, followed by repeated rinsing, rehydration, centrifugation and dehydration to remove the oxidant and unreacted monomer. *Figures 4a* and *4b* show the respective C 1s and N 1s core-level

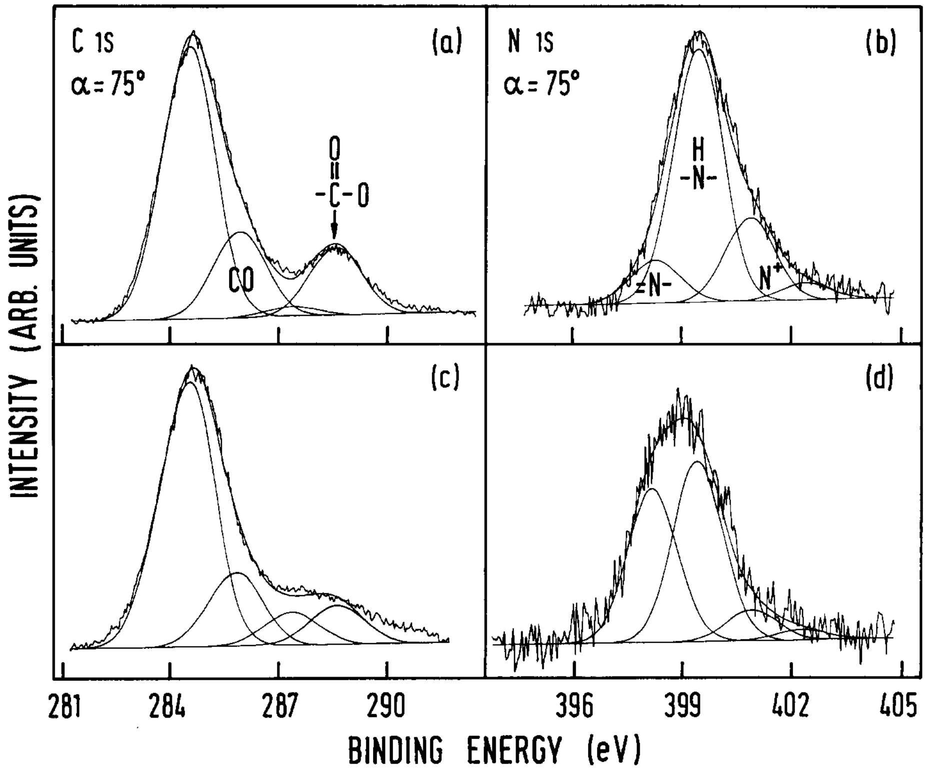

Figure 4 (a) C 1s and (b) N 1s core-level spectra of an EM–PAAc complex obtained from oxidative polymerization in 2% aqueous PAAc solution. The corresponding spectra for the base polymer after NaOH treatment are shown in (c) and (d)

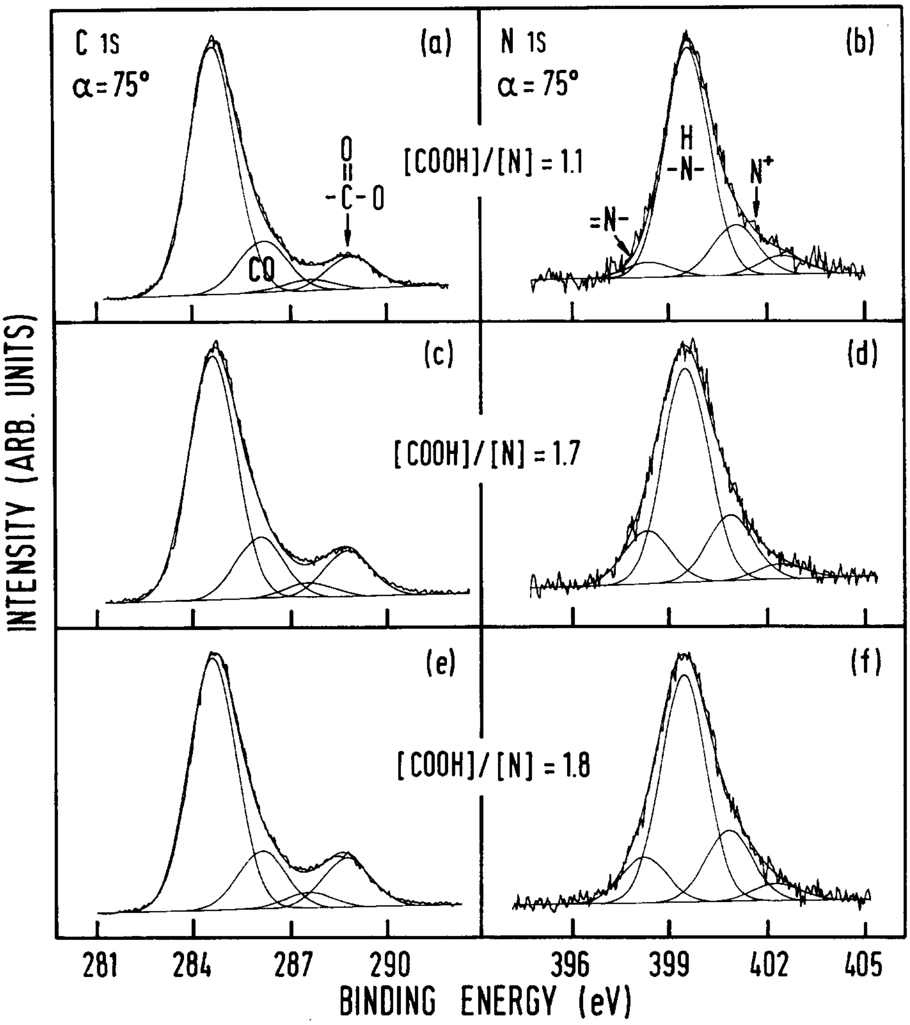

Figure 5 C 1s and N 1s core-level spectra of (a) and (b) a pristine EM film, (c) and (d) a 1 min O_3-pretreated EM film, and (e) and (f) a 5 min O_3-pretreated EM film after each film has been subjected to near-u.v.-induced graft copolymerization with AAc polymer

spectra of an EM–PAAc salt complex obtained from oxidative polymerization in 2% aqueous PAAc solution with an initial [COOH]/[aniline] mole ratio of about 4. The resulting complex has a [COOH]/[aniline] mole ratio of about 2.4, as determined from the corrected area ratio of the COOH component in the C 1s core-level spectrum and the N 1s core-level spectrum. Again, the protonation level for this complex is substantially below 50%, even in the presence of excess COOH groups. Treatment of the EM–PAAc complex with a base readily returns the aniline polymer to its neutral EM base form, with about equal amounts of the imine and amine nitrogens. The resulting C 1s and N 1s core-level spectra for the base polymer are presented in *Figures 4c* and *4d*, respectively.

Surface graft copolymerization with acrylic acid

Figures 5a and *5b* show, respectively, the C 1s and N 1s core-level spectra of a pristine (as-cast) EM film after near-u.v. light-induced graft copolymerization in 8 wt% aqueous acrylic acid (AAc) solution. The presence of the surface PAAc graft is indicated by the appearance of the COOH component in the C 1s core-level spectrum and the enhanced N 1s high-*BE* tail above 400 eV. Thus, graft copolymerization with AAc polymer readily results in a self-protonated EM surface. The density of the surface graft, determined directly from the [COOH]/[N] ratio, is enhanced if the EM film surface is pretreated with ozone. *Figures 5c* and *5d* show the corresponding C 1s and N 1s core-level spectra for a 1 min O_3-pretreated EM film after graft copolymerization with the AAc polymer. The increase in density of the surface graft is readily indicated by the enhanced COOH component in the C 1s core-level spectrum. The increase in graft efficiency for EM film pretreated with O_3 is consistent with a peroxide-initiated polymerization mechanism generally proposed for the near-u.v. light-induced graft copolymerization[24]. The fact that grafting occurs to some extent even in the pristine or untreated EM film is consistent with the reactive nature of the conjugated polymer surface.

No significant increase in graft density, however, was observed for O_3 pretreatment time above 1 min. *Figures 5e* and *5f* show, respectively, the C 1s and N 1s core-level spectra for a 5 min O_3-pretreated EM film after graft copolymerization with AAc polymer under similar condition. An earlier study[9] has shown that O_3 pretreatment results in the formation of blisters of micrometre size on the EM film surface, with the blisters comprising the oxidized materials and serving as active sites for further surface reactions. Thus, prolonged exposure to O_3 may result in over-oxidation and reduction in the structural integrity of the surface grafts, leading to their loss during the subsequent vigorous washing process. This effect can then account, at least in part, for the lack of a significant increase in the amount

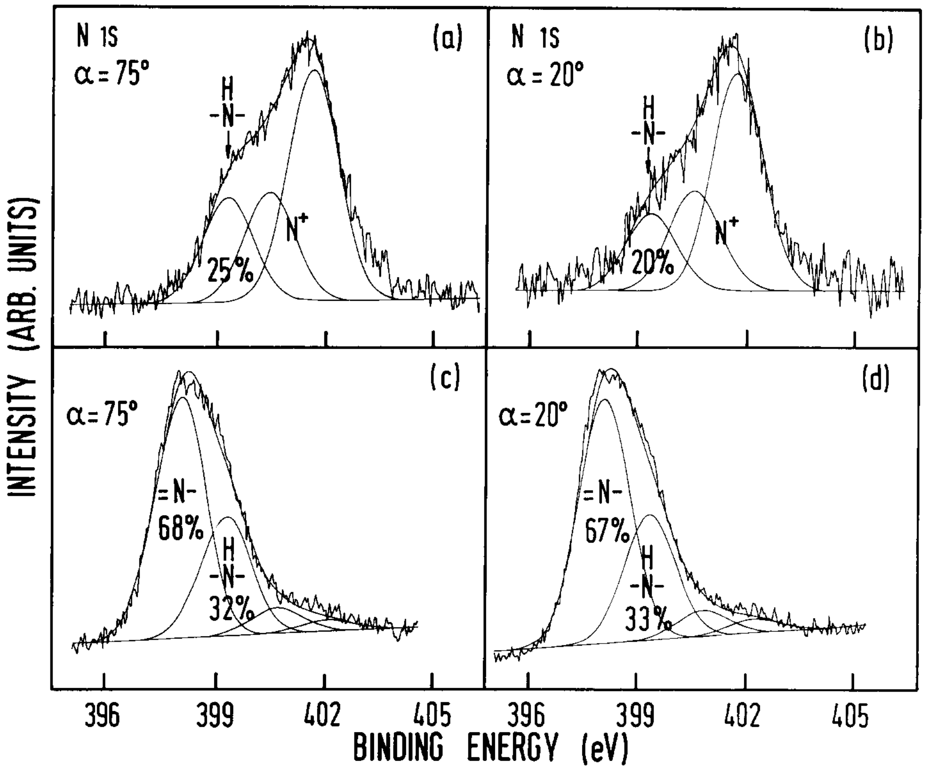

Figure 6 N 1s core-level spectra obtained at take-off angles of 75° and 20° for (a) and (b) an EM film protonated by 0.1 M PSSAc, and (c) and (d) the protonated film after treatment by 0.5 M NaOH

of surface graft upon prolonged O_3 pretreatment of the EM film. *Figure 5* further suggests that, in all cases, the [COOH]/[N] ratio is always much higher than the proportion of positively charged nitrogens. Thus, a substantial amount of the surface grafted COOH groups remains free for further functionalization. This phenomenon is consistent with the weak protonation behaviour of the organic acid.

Direct protonation by poly(styrenesulfonic acid)

Substantially different protonation behaviour is observed for EM base film exposed to a strong polymeric acid. *Figures 6a* and *6b* show the N 1s core-level spectra, obtained at photoelectron take-off angles α of 75° and 20°, respectively, for an EM base film after exposure to 0.1 M poly(styrenesulfonic acid) (PSSAc). The S 2p core-level spectrum of the sample shows a major component with a S $2p_{3/2}$ *BE* at about 168.0 eV, characteristic of covalently bonded $-SO_3^-$ species[25]. The [S]/[N] ratios, as determined from the corrected S 2p and N 1s spectral area ratios, at the two α values are about 1.0 and 1.3, respectively. The N 1s core-level spectra readily indicate that protonation levels much higher than 50% have been achieved. The proportions of the positive nitrogens (N^+/N ratios) at the two α are 0.75 and 0.80, respectively. Thus, in addition to the imine nitrogens, almost all the amine nitrogens are susceptible to protonation by PSSAc. Furthermore, a significantly higher polymeric acid concentration and protonation level are observed towards the top surface of the film. This protonation behaviour is similar to that observed during the protonation of EM film by a simple, non-volatile acid, such as $HClO_4$ or H_2SO_4 (ref. 9).

Deprotonation of the present PSSAc protonated EM film by NaOH readily returns the polymer to its neutral base form, but with a significant increase in the intrinsic oxidation state. In fact, oxidation state characteristic of that of nigraniline ([=N–]/[N] ratio ~0.75) is readily achieved. *Figures 6c* and *6d* show the corresponding N 1s core-level spectra at the two α, after the EM–PSSAc film has been deprotonated by 0.5 M NaOH. The relatively constant imine/amine ratios obtained at the two α values readily indicate that the outermost surface of the deprotonated film still maintains a high intrinsic oxidation state. Thus, unlike protonation by 1 M H_2SO_4 or $HClO_4$ (ref. 9), the surface hydrolysis reaction, which can reduce the imine units to the amine units, must have been minimized in the present case of protonation by polymeric acid of relatively low concentration (0.1 M).

Blending with poly(styrenesulfonic acid)

Unlike the EM–PAAc blends, blends of PSSAc with EM base fail to produce a uniform and tractable film when cast from NMP solutions. Nevertheless, EM base powders are readily protonated by PSSAc in aqueous solution. Protonation level in the order of 50% (N^+/N ~0.5) is readily achieved, as in the case of protonation of EM powders by simple acids.

Surface graft copolymerization with styrenesulfonic acid

Graft copolymerizations of pristine and O_3-pretreated EM films with the sodium salt of styrenesulfonic acid (NaSS) also readily result in self-protonated film surfaces. *Figures 7a* and *7b* shows the N 1s and S 2p core-level spectra for a pristine EM film after near-u.v. light-induced graft copolymerization in 8 wt% NaSS solution. The corresponding N 1s and S 2p core-level spectra for a 5-min O_3-pretreated EM film after graft copolymerization are shown in *Figures 7c* and *7d*. The presence of the surface graft in each case is indicated by the appearance of a S 2p core-level signal, with a S $2p_{3/2}$ core-level *BE* at about 168.0 eV and an enhanced N 1s high-*BE* tail above 400 eV. The density of surface grafting is determined from the [S]/[N] ratio and is enhanced by

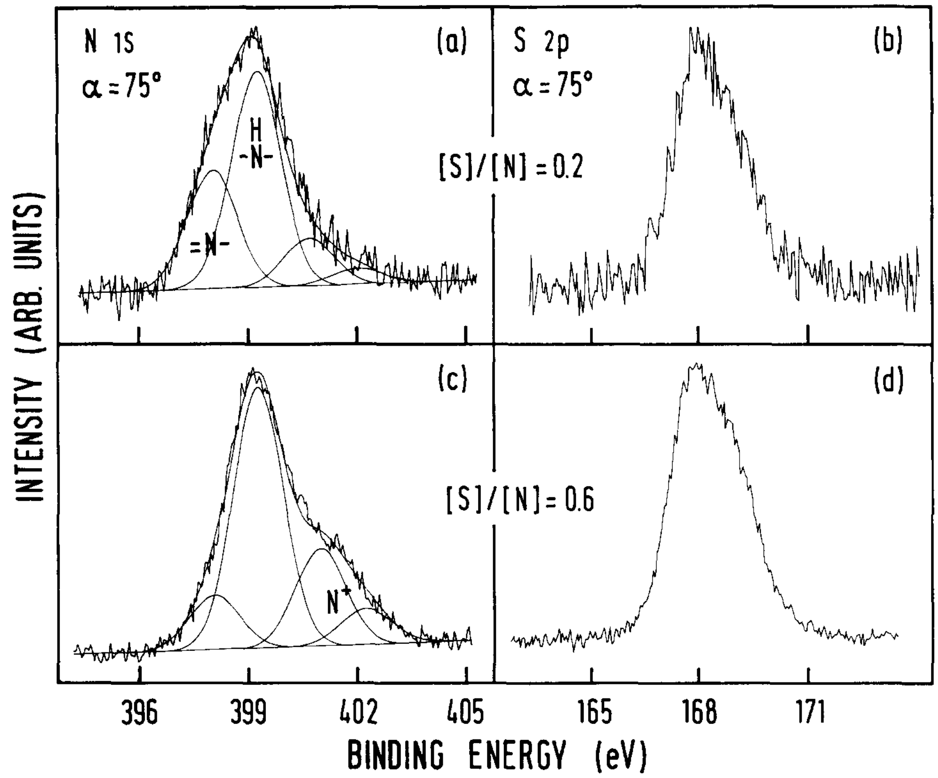

Figure 7 N 1s and S 2p core-level spectra of (a) and (b) a pristine EM film, and (c) and (d) a 5 min O_3-pretreated EM film after each film has been subjected to near-u.v.-induced graft copolymerization with NaSS polymer

O_3 pretreatment, but shows approximately the same dependence on O_3 pretreatment time as in the case of graft copolymerization with the AAc polymer.

A significantly higher degree of self-protonation by the grafted sulfonic acid groups than by the grafted carboxylic acid groups, even at a much lower graft density of the former, is again observed. This protonation behaviour is consistent with that observed during the direct protonation of the EM films by PSSAc and PAAc. Nevertheless, the [S]/[N] ratios for the NaSS polymer grafted EM films are still considerably higher than the corresponding [N^+]/[N] ratios, especially towards the outermost surface of the film corresponding to a reduced α of 20°.

CONCLUSION

The protonation of EM base films by two polymeric acids, poly(acrylic acid) (PAAc) and poly(styrenesulfonic acid) (PSSAc), was compared, using X.p.s. as a primary tool. Regardless of the method of preparation of the EM–PAAc salts, the degree of protonation is generally much below 50%, even in the presence of a large excess of the PAAc units. Nevertheless, relatively stable films of polymer blends of EM base and high-molecular-weight PAAc can be prepared. Almost all the amine nitrogens, in addition to the imine nitrogens, of EM films are susceptible to protonation by PSSAc. Deprotonation of the EM–PSSAc salt film by a base always results in a substantial increase in the intrinsic oxidation state of the aniline polymer to give rise to a nigraniline film.

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