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Surface Modifications of Polyaniline Films by Graft Copolymerization

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ABSTRACT: Both pristine and argon plasma pretreated emeraldine (EM) base films have been subjected to near-UV-light-induced graft copolymerization with acrylamide (AAm), the sodium salt of 4-styrenesulfonic acid (NaSS), and acrylic acid (AAc). The structure and chemical composition at each copolymer surface and interface are studied by angle-resolved X-ray photoelectron spectroscopy (XPS). In each case, the density of surface grafting is enhanced by plasma pretreatment. Surface grafting with the three polymers also leads to a more hydrophilic EM film. Furthermore, grafting with the NaSS and AAc polymers readily gives rise to a self-doped or self-protonated EM surface structure. However, a substantial proportion of the grafted protonic acid groups at the surface remains free for further surface modification and functionalization.

Introduction

The synthesis and characterization of electroactive polymers has become one of the most important research areas in polymer science in recent years.[1] Among the electroactive polymers, polyaniline (PAN) has been of particular interest because of its high electrical conductivity, environmental stability, and interesting redox properties associated with the chain nitrogens.[2,3] Most important of all, PAN also exhibits solution processibility[4,5] and partial crystallinity.[6,7] The aniline polymers have the general formula $[(\text{-BNHBNH-})_y(\text{-BN=Q=N-})_{1-y}]_x$, in which B and Q denote the C_6H_4 rings in the benzenoid and quinonoid forms, respectively.[2,3] Thus, the aniline polymers are basically poly(*p*-phenylene imine amines), in which the intrinsic oxidation states can range from that of the fully oxidized pernigraniline (NA, $y = 0$) to the fully reduced leucoemeraldine (LM, $y = 1$). The 50% oxidized polymer has been termed emeraldine (EM, $y = 0.5$). The polymer can achieve its highly conductive state either through the protonation of the imine nitrogens (=N– structure) in its EM oxidation state or through the oxidation of the amine nitrogens (–NH– structure) in the fully reduced LM.[2,3] Recently, it has been demonstrated that similar intrinsic redox states and protonation/deprotonation behavior are also observed in polypyrrole.[8]

The fact that the electrical properties of PAN can be drastically modified by oxidation/reduction, protonation/deprotonation, and the type of anions incorporated suggests that PAN and its complexes can be used as active materials for electrodes and sensors. In view of these applications, materials modifications, in particular surface modifications, may be required. Surface modifications with biocompatible polymeric materials for biochemical and biomedical applications have been well reported.[9,10] It has also been demonstrated that surface modifications can be performed through graft copolymerization under mild conditions for a number of polymers, such as polyethylene, poly(ethylene terephthalate), poly(vinyl chloride), nylons, polypropylene, etc., when their surfaces are pretreated with high-energy radiation, glow discharge, corona discharge, ozone exposure, or UV irradiation.[11–14] Furthermore, protein and enzyme immobilizations on the surface-modified polymer substrates have also been of great interest.[15]

Accordingly, it should be interesting to study the surface modifications of electroactive polymers, as the electroactive polymer substrates may provide an added advantage. This study involves a preliminary investigation of the surface modifications of PAN films by graft copolymerization with acrylamide (AAm), acrylic acid (AAc), and the sodium salt of 4-styrenesulfonic acid (NaSS). Grafting of these water-soluble polymers will hopefully improve the hydrophilicity of the PAN film surface and provide appropriate functional groups[15] at the surface for the subsequent immobilization of proteins and enzymes. The grafted PAN film surfaces were characterized using X-ray photoelectron spectroscopy (XPS) as a primary tool. It has been demonstrated earlier that XPS provides a unique analytical tool for the quantitative differentiation of the imine, amine, and positively charged nitrogens in PAN corresponding to a particular intrinsic redox state and protonation level.[16,17]

Experimental Section

Polyaniline Films. The emeraldine (EM)/perchlorate salt was prepared via the oxidative polymerization of aniline by $Fe(ClO_4)_3{\cdot}6H_2O$ in water and with an oxidant/monomer mole ratio of about 2.5, similar to the procedures reported earlier.[18] The EM base was obtained by treating the salt with excess 0.5 M NaOH. Similar EM base was also obtained from base-treated EM/sulfate salt prepared via the oxidative polymerization of aniline by ammonium persulfate in aqueous 1 M H_2SO_4.[2,19] The EM base powder was then cast into thin films of about 5–10 μm in thickness from *N*-methylpyrrolidinone (NMP) solutions. The trapped NMP in the polymer films was removed by exhaustive pumping and then by soaking and washing the film in doubly distilled water for at least 72 h.

Pretreatment of Polyaniline Films. Both pristine (untreated) and argon plasma treated EM films were used in the grafting experiment. A bell-jar-type glow discharge cell, Model LCVD12, manufactured by Shimadzu Corp. (Kyoto, Japan), was

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used for plasma pretreatment. The frequency applied was 5 kHz at a plasma power of 28 W (280 V and 100 mA). The EM films were fixed on a stainless steel sample holder rotating between the two electrodes. The electrode separation was about 6.5 cm. The pressure in the bell jar was reduced to 10^{-3} Torr or lower before argon gas at a flow rate of about 20 mL/min was introduced. When the pressure in the bell jar was maintained at about 0.03 Torr of Ar, the EM films were subjected to glow discharge for 5–30 s. These Ar plasma pretreated films were then exposed to the air before the grafting experiments.

Graft Copolymerization. All the pretreated EM films were subjected to grafting experiments within 1 day after plasma treatment. The monomers used were acrylamide (AAm), acrylic acid (AAc), and the Na salt of 4-styrenesulfonic acid (NaSS). EM film strips of about 1.5 cm × 3.5 cm were used for all grafting experiments. In the case of graft copolymerization with AAm, the EM film was placed in a Pyrex tube containing an aqueous solution of 20 mL of 10 wt % AAm and 5 mL of 0.053 mM riboflavin. The test tube was sealed with a silicone rubber stopper. The reaction mixture was then exposed to near-UV light (wavelength > 290 nm) at 25–30 °C in a rotary photochemical reactor equipped with a 400-W high-pressure Hg lamp (Riko Rotary Model RH400-10W). The exposure time for all AAm grafting experiments was kept at about 30 min. For AAm solution below 5 wt %, no appreciable homopolymerization of AAm was observed. Similar procedures were used for grafting with NaSS, except a 0.5 M aqueous NaSS solution was used in each experiment.

In the case of grafting with AAc, each EM film was immersed in 20 mL of aqueous AAc solution in a Pyrex tube. The concentrations of the AAc solutions were varied from 2 to 10 wt %. Each reaction mixture was thoroughly degassed and sealed off under a nitrogen atmosphere. It was then subjected to UV irradiation for about 30 min as in the case of AAm grafting. After each of the grafting experiments described above, the EM film was removed from the viscous homopolymer solution and washed with a jet of doubly distilled water. It was then either immersed in a 55 °C bath with continuous stirring for 8–10 h or subjected to repeated rinsing, soaking, and short-term ultrasonic cleaning in an ultrasonic bath for at least 24 h to remove the residual homopolymer. Both cleaning processes resulted in grafted film surfaces of similar quality, as suggested by X-ray photoelectron spectroscopic results.

Materials Characterization after Grafting. The polymer films after grafting were characterized by transmission and multiple internal reflection (MIR) infrared (IR) spectroscopy, contact angle measurements, and X-ray photoelectron spectroscopy (XPS). The transmission IR was measured on a Perkin-Elmer Model 620 spectrophotometer while the multiple internal reflection (MIR) IR was measured on a Shimadzu Model 8101 FT-IR. Static water contact angles were measured by the sessile drop method, using a 3-μL water droplet in a telescopic goniometer (Type M2010A-6GII, Elma Inc., Tokyo). The telescope with a magnification power of 40× was equipped with a protractor of 1° graduation. In each case, at least three measurements on different surface locations were averaged. The XPS 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 core-level signals were obtained at a number of take-off angles, ranging from 15° to 75°. The X-ray source was run at a reduced power of 120 W (12 kV and 10 mA). The pressure in the analysis chamber was maintained at 10^{-8} mbar or lower during each measurement. All binding energies were referenced to the C 1s neutral carbon peak at 284.6 eV. In peak synthesis, the line width (full width at half-maximum) 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 is liable to ±5% error.

Results and Discussion

Recent studies[16,17,20] have demonstrated that the quinonoid imine (=N– structure), benzenoid amine (–NH– structure), and positively charged nitrogens in a polyaniline (PAN) complex correspond respectively to peak components with binding energies (BEs) at about 398.2, 399.4, and >400 eV in the properly curve-fitted N 1s core-level spectrum. Parts a and b of Figure 1 show respectively the C 1s and N 1s core-level spectra of a thoroughly washed emeraldine (EM) base film cast from *N*-methylpyrrolidinone (NMP) solution. The film consists of about equal amounts of imine and amine nitrogens, consistent with the intrinsic redox state of the EM base. The residual high BE components above 400 eV in the N 1s core-level spectrum may have resulted at least in part from surface oxidation products or weakly charge-transfer complexed oxygen.[16] This is supported by the presence of a fairly strong O 1s signal and a small high BE tail in the C 1s core-level spectrum in all pristine EM films. This is also consistent with the more reactive nature of the conjugated polymer surfaces.[21]

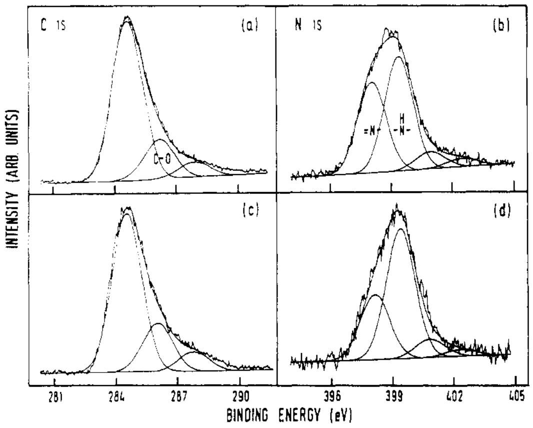

Figure 1. C 1s and N 1s core-level spectra of (a and b) a pristine EM film and (c and d) an EM film after 30 s of Ar plasma treatment. (XPS take-off angle = 75°.)

Plasma treatment followed by atmospheric exposure readily enhances the high BE tail in the C 1s and N 1s core-level spectra of the EM base. Parts c and d of Figure 1 show the EM base film after 30 s of plasma treatment, which is the maximum treatment time used in this study. The enhancement of the C 1s peak component at about 286.1 eV, attributable to the CO species,[22] and its subsequent oxidation to carbonyl species with BE at about 287.8 eV are consistent with the formation of the peroxide species on the surface upon plasma treatment. Plasma treatment also causes a small decrease in the water contact angle from about 65°, for the pristine film, to about 55° for a film with 30 s of plasma exposure. Furthermore, plasma treatment can also result in a noticeable decrease in the imine/amine nitrogen ratio of the polymer surface for a treatment time greater than 20 s. A similar change in the imine/amine ratio is also observed when the EM film is subjected to prolonged UV irradiation in air or in an aqueous medium. For example, the imine/amine nitrogen ratio can decrease by as much as 10–20% for the EM film in water when subjected to near-UV irradiation for 30 min.

Surface Grafting with Acrylamide (AAm) Polymer. Parts a and b of Figure 2 show the respective C 1s and N 1s core-level spectra for a pristine EM base film after being irradiated by near-UV light in an 8% AAm solution in the presence of riboflavin. Parts c and d of Figure 2 show the corresponding C 1s and N 1s core-level spectra for a similarly grafted EM base film, except the film has been pretreated with Ar plasma for 20 s. The presence of a surface-grafted AAm polymer in each case is readily suggested by the substantially enhanced C 1s high BE

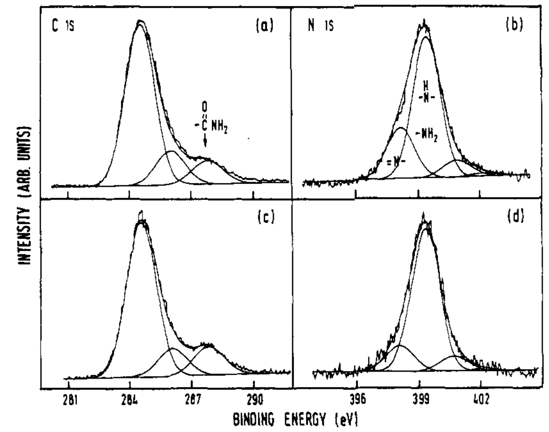

Figure 2. C 1s and N 1s core-level spectra for (a and b) a pristine (untreated) EM base film and (c and d) a 20-s plasma pretreated EM base film after both films have been subjected to graft polymerization in an 8% AAm solution. (XPS take-off angle = 75°.)

component at about 287.8 eV, attributable to the carbonyl group of an AAm polymer.[13] It is also indicated by a substantial increase in the N 1s core-level component at 399.4 eV, due to the contribution from the nitrogens ($-NH_2$ structure) of a grafted AAm polymer. An AAm homopolymer shows only a single N 1s component at about 399.4 eV. This BE coincides with that of the amine nitrogens of the EM base. Thus, Figure 2 readily suggests that a significant extent of AAm grafting is achieved, even for the EM film without any prior plasma treatment. However, plasma treatment does enhance the extent of grafting substantially.

In each sample, the amount of surface-grafted AAm polymer can be estimated either from the curve-fitted N 1s or C 1s core-level spectrum. In the case of a N 1s spectrum, the $-NH_2$ groups of the grafted AAm polymer result in an increase in the proportion of the high BE component at 399.4 eV and the mole ratio of a surface-grafted AAm polymer to EM repeating units or [AAm]/[Aniline] is given by

$$\frac{[\mathrm{AAm}]}{[\mathrm{Aniline}]} = [(\text{N 1s area of a 399.4-eV component}) - R^{*}(\text{N 1s area of a 398.2-eV component})]/(1 + R)^{*}(\text{N 1s area of a 398.2-eV component})$$

where R is the amine/imine nitrogen ratio of the EM film before grafting. R increases somewhat with increased plasma pretreatment time (Figure 1). The effect of near-UV irradiation on the amine/imine nitrogen ratio of the EM film in an AAm solution, if present, cannot be determined independently without the accompanying surface grafting and is not considered.

Alternatively, since 1 mol of AAm has 1 mol of carbon from the $NH_2C{=}O$ group and 2 moles of carbon from the vinyl chain, while 1 mol of aniline has 6 mol of carbon, the [AAm]/[Aniline] mole ratio can be estimated from the C 1s core-level spectrum as follows:

$$\frac{[\mathrm{AAm}]}{[\mathrm{Aniline}]} = (\text{C 1s area of } NH_2C{=}O)/[[\text{total C 1s area} - (\text{C 1s area of } NH_2C{=}O) \times 3]/6]$$

The mole ratios of the repeating AAm units estimated from the C 1s and N 1s spectra with the use of the above equations are shown in Table I. Thus, the densities of surface grafting estimated from the carbon and nitrogen balances are in fairly good agreement. Comparable extents of surface grafting have also been observed earlier for a poly(ethylene terephthalate) film grafted with PAAm.[13] The somewhat higher AAm mole ratio obtained from the C 1s spectrum of the sample without plasma pretreatment (sample 1) is probably attributable to the enhanced effect of the residual carbonyl component, present in all EM films, at a low level of grafting. Grafting of the EM films with PAAm also gives rise to a more hydrophilic surface. This is readily indicated by the decrease in water contact angles from about 65° for the pristine, ungrafted EM film to as low as about 20° for the "heavily" grafted surface. Table I also summarizes the changes in the water contact angle of the EM film surfaces upon surface grafting with an AAm polymer.

Table I
Mole Ratio of AAm Units to EM Units in the Grafted Surface Region[a] Estimated from the XPS Analysis[b]

sample no.	plasma pretreatment time, s	[AAm]/[Aniline] mole ratio estimated from C 1s spectrum	[AAm]/[Aniline] mole ratio estimated from N 1s spectrum	water contact angle after grafting,[c] deg
1	0	0.98	0.70	41
2	5	1.20	1.10	37
3	10	1.57	1.54	33
4	20	1.48	1.70	26
5	30	1.63	1.61	21

[a] Near-UV-light-induced graft copolymerization in an 8% AAm solution in the presence of riboflavin. [b] XPS take-off angle = 75°. [c] The water contact angle for the pristine, ungrafted EM film is about 65°.

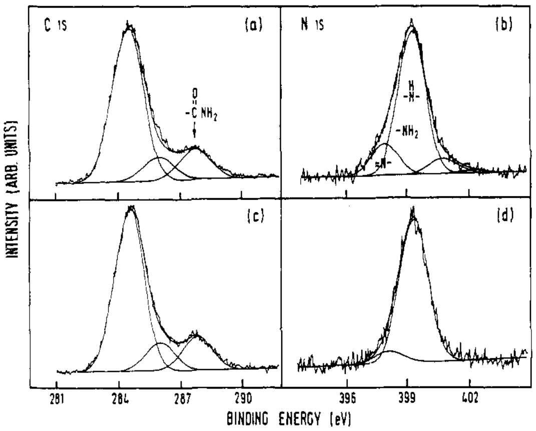

Figure 3. C 1s and N 1s core-level spectra acquired at take-off angles of (a and b) 75° and (c and d) 15° for a PAAm grafted EM film with 10 s of plasma pretreatment.

The fact that grafting with an AAm polymer occurs mainly at the surface region of the EM film is readily revealed by core-level signals acquired at different take-off angles. Parts a–d of Figure 3 compare the C 1s and N 1s core-level spectra acquired at take-off angles of 75° and 15°, respectively, for an AAm grafted EM film with 10 s of plasma pretreatment. Thus, as the core-level signal becomes even more surface oriented, the intensity of the high BE C 1s component attributable to the C=O groups of AAm is enhanced (Figure 3c). Furthermore, the N 1s spectrum in Figure 3d is also dominated by the nitrogens of a surface-grafted AAm polymer, and the imine nitrogen signal of the EM film has decreased considerably. This angular-dependent phenomenon is also observed for the other AAm grafted samples studied in this work.

Surface Grafting with the Na Salt of a 4-Styrenesulfonic Acid (NaSS) Polymer. Parts a–f of Figure 4 show the respective C 1s, N 1s, and S 2p core-level spectra for a pristine EM base film and a 20-s plasma pretreated

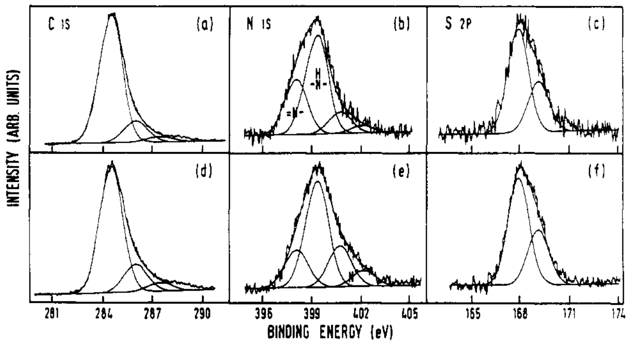

Figure 4. C 1s, N 1s, and S 2p core-level spectra for (a-c) a pristine EM film, and (d-f) a 20-s plasma pretreated EM base film after both films have been subjected to surface grafting with a NaSS polymer. (XPS take-off angle = 75°.)

Table II
Surface Structures and Compositions of the Various EM Films with a Surface-Grafted NaSS Polymer[a]

sample no.	plasma pretreatment time, s	XPS take-off angle, deg	S/N ratio[b]	proportion[c] of =N-	-NH-	N+
1 (pristine)	0	75	0.0	0.42	0.49	0.09
2	0	75	0.15	0.30	0.54	0.16
3	5	75	0.20	0.25	0.55	0.20
4a	10	75	0.26	0.23	0.54	0.23
4b	10	50	0.29	0.21	0.52	0.27
4c	10	30	0.36	0.18	0.51	0.30
4d	10	15	0.44	0.11	0.62	0.27
5	20	75	0.27	0.18	0.54	0.28
6	30	75	0.24	0.22	0.56	0.22

[a] Graft copolymerization in 0.5 M NaSS monomer solutions. [b] Determined from the corrected S 2p and N 1s core-level spectral area ratios. [c] Determined from the curve-fitted N 1s core-level spectra.

EM film after they have been surface grafted with the NaSS polymer. The presence of a surface-grafted NaSS component is readily suggested by the appearance of the S 2p core-level signal at about 168 eV, characteristic of the covalently bonded sulfonic acid group ($-SO_3^-$) of the NaSS polymer.[23] In this case, the surface compositions or the densities of surface grafting can be conveniently determined from the sensitivity factor corrected S/N spectral area ratios. An interesting and important phenomenon is also observed as a result of grafting the EM base with an anionic polymer. The N 1s spectra of the grafted samples all show the presence of a high BE tail above 400 eV, characteristic of the positively charged nitrogens.[16,17] Thus, the sulfonic acid groups of the grafted NaSS polymer must have also participated in the protonation of the imine nitrogens of the EM base to give rise to a self-protonated or self-doped EM surface. The presence of self-protonation is further supported by the lack of the Na 1s core-level signal in the copolymer complex and the transformation of the corresponding amount of the imine nitrogens into the protonated and positively charged form. The latter is consistent with the fact that protonation occurs preferentially at the imine units of the EM base.[2,3] The synthesis of sulfonic acid ring-substituted EM base and the resulting protonic acid self-doped conductive polymer have also been reported recently.[24]

Table II summarizes the surface structures and compositions of the various EM films with a surface-grafted NaSS polymer. Thus, the density of a surface-grafted NaSS polymer is enhanced in EM films with plasma pretreatment. The data in Table II also indicate that, for all samples measured at a take-off angle of 75° and thus more representative of the EM–NaSS polymer interface, a close balance between the proportion of positively charged nitrogens and the S/N ratio is observed in each sample. Charge neutrality consideration suggests that most of the grafted sulfonic acid groups at the copolymer interface must have been involved in the self-protonation process. The fact that grafting with the NaSS polymer occurs predominantly at the EM film surface is readily suggested by the signals obtained from angle-resolved XPS. Sample 4 in Table II indicates that the S/N ratio, and thus the NaSS/EM ratio, increases substantially as the take-off angle is reduced. The fact that the observed S/N ratio is substantially higher than the proportion of positively charged nitrogens, for example, for data obtained at a take-off angle of a mere 15° (sample 4d), readily indicates that the "excess" sulfonic acids at the very top surface of the grafted structure do not participate in the protonation of the EM base below.

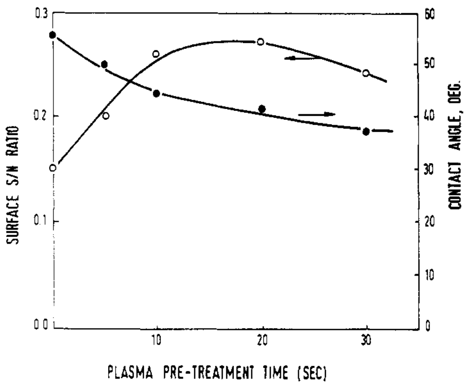

Figure 5. Densities of a surface-grafted NaSS polymer and the corresponding water contact angle of the EM film as a function of plasma pretreatment time.

It is appropriate to point out that since only a very thin layer of the EM film surface is protonated in each case, the EM film after grafting remains insulating in nature. Attempts to measure the surface conductance of the NaSS grafted EM films failed to produce consistent results. Nevertheless, grafting with a NaSS polymer results in a more hydrophilic EM film surface. This is consistent with the fact that the protonated EM salts are hygroscopic in nature.[19] Figure 5 summarizes the density of a surface-grafted NaSS polymer and the corresponding decrease in the water contact angle of the EM film as a function of plasma pretreatment time. In comparison with the AAm grafted EM films, the decrease in the water contact angle for the NaSS grafted surface is generally much smaller. This is attributable at least partially to the fact that the density of surface-grafted NaSS units is substantially lower than that of AAm units at the same degree of plasma pretreatment.

Finally, a control experiment has been performed to ensure that the NaSS units are actually grafted. For an EM film soaked either in a 0.5 M NaSS solution or in a NaSS homopolymer soution in the absence of UV irradiation for the same period of time as that required for the grafting experiment, followed by the same washing procedures, no appreciable S 2p core-level signal or positively charged nitrogens were observed.

Surface Grafting with an Acrylic Acid (AAc) Polymer. It can be expected that graft copolymerization of an EM base with an AAc polymer will also result in a self-doped or self-protonated structure. Furthermore, the imine units of an EM base are readily protonated by AAc even prior to grafting copolymerization. This is readily suggested by a change in the color of the EM film from dark blue to dark green, characteristic of protonated EM. For an EM film soaked in a 10% AAc solution, followed

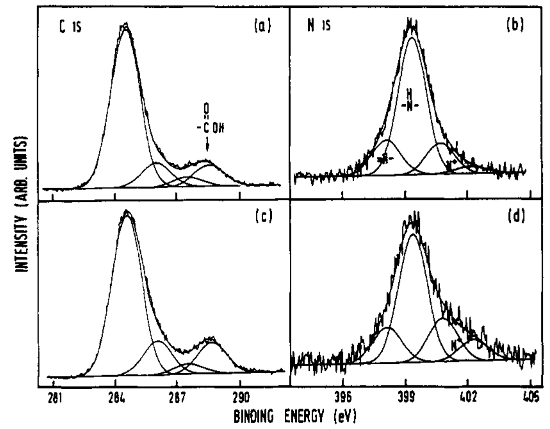

Figure 6. C 1s and N 1s core-level spectra for (a and b) a pristine EM base film and (c and d) a 20-s plasma pretreated EM base film after both films have been subjected to graft polymerization in a 5% AAc solution. (XPS take-off angle = 75°.)

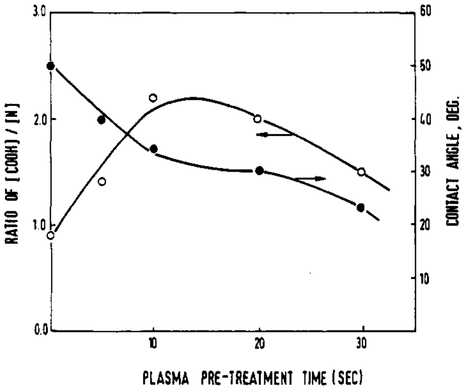

Figure 7. Densities of a surface-grafted AAc polymer and the corresponding water contact angle of the EM film as a function of plasma pretreatment time.

by drying in air without prior rinsing, the electrical conductivity increases from about 10^{-14} S/cm for the original EM base to about 10^{-3} S/cm. This initially protonated AAc monomer, when failing to become part of the grafted AAc polymer, will be readily removed during the subsequent exhaustic washing cycles after grafting, as protonation/deprotonation of EM is an equilibrium process.[2,3]

Parts a–d of Figure 6 show the respective C 1s and N 1s core-level spectra for the pristine EM film and a 20-s plasma pretreated EM film after being subjected to UV-induced grafting copolymerization in a 5% degassed AAc solution. The small but distinct high BE C 1s component at about 288.7 eV is characteristic of the carboxylic acid group of a grafted AAc polymer.[22] The presence of self-protonation is again indicated by the appearance of the high BE tail in the N 1s core-level spectrum. The extent of surface grafting in each case can be readily determined from the corrected area ratio of the C 1s peak component at 288.7 eV and the total N 1s area. The density of surface grafting, expressed as the ratio of the carboxylic acid groups per EM repeating unit of [COOH]/[N], and the corresponding water contact angle as a function of plasma pretreatment time are summarized in Figure 7.

The densities of a surface-grafted PAAc are comparable to those of a surface-grafted AAm polymer under the present experimental conditions. The surface structures and compositions of the various AAc grafted EM films are summarized in Table III. Although [COOH]/[N] ratios higher than 2 have been obtained at the EM–AAc polymer interface for a number of grafted samples, a significant proportion of the imine nitrogens in these samples remains unprotonated. Thus, steric hindrance and the grafted AAc polymer chain conformation must play an important role in the protonation of the EM surfaces. The presence of a large proportion of unreacted carboxylic acid groups on the AAc grafted EM surfaces, however, is highly desirable for further surface modification and functionalization. For instance, the carboxylic acid groups can be activated for the immobilization, via chemical bonding, of enzymes and proteins at the EM surface. This immobilization via a chemical linkage technique is probably more advantageous than the conventional entrapping method.[25] Work in this area is currently in progress.

Table III
Surface Structures and Compositions of the Various EM Films with a Surface-Grafted AAc Polymer[a]

sample no.	plasma pretreatment time, s	XPS take-off angle, deg	grafted density [COOH]/[N][b]	proportion[c] of =N–	proportion[c] of –NH–	proportion[c] of N+
1 (pristine)	0	75	0.0	0.42	0.49	0.09
2	0	75	0.9	0.17	0.65	0.18
3	5	75	1.4	0.21	0.56	0.24
4a	10	75	2.2	0.18	0.59	0.23
4b	10	15	3.0	0.12	0.61	0.27
5	20	75	2.0	0.16	0.56	0.28
6a	30	75	1.5	0.19	0.56	0.25
6b	30	15	2.5	0.07	0.66	0.27

[a] Graft copolymerization in 5% AAc monomer solutions. [b] Based on the corrected area ratios of a C 1s component at 288.6 eV and the total N 1s spectrum. [c] Determined from the curve-fitted N 1s core-level spectra.

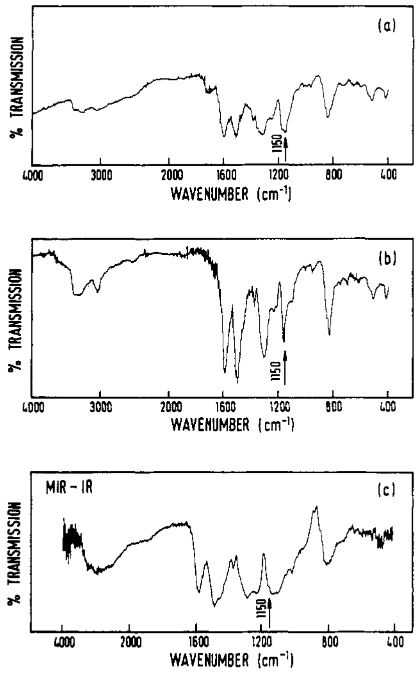

Figure 8. (a) Transmission IR spectrum of EM equilibrated in a 10% AAc solution without grafting, and (b) transmission and (c) MIR IR spectra of an AAc grafted EM film.

Again the fact that graft copolymerization occurs mainly at the EM surface is readily revealed by the XPS signals obtained at small take-off angles. For example, for samples 4 and 6 in Table III, a significantly higher [COOH]/[N] ratio is observed at the take-off angle of 15°. The presence of a surface-grafted and surface-self-protonated structure is further revealed by the difference in the transmission IR and multiple internal reflection (MIR) IR spectra of the AAc grafted EM film. Figure 8a shows the transmission IR spectrum of an EM film equilibrated in a 10% AAc solution without grafting. Parts b and c of Figure 8 show respectively the transmission and MIR IR absorption

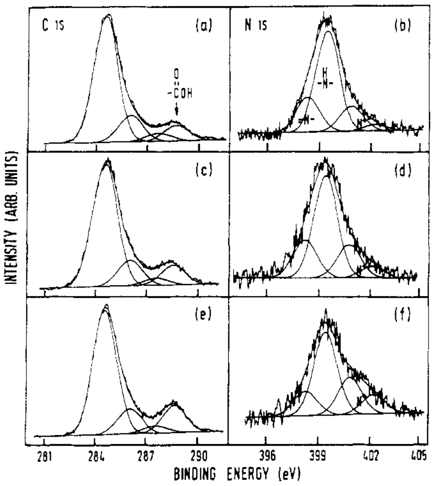

Figure 9. C 1s and N 1s core-level spectra of 5-s plasma pretreated EM films after graft copolymerization in (a and b) 2%, (c and d) 5%, and (e and f) 10% AAc solutions. (XPS take-off angle = 75°.)

spectra of a 10-s plasma pretreated EM film after graft copolymerization in a 10% AAc solution. For the EM film equilibrated in a 10% AAc solution without grafting, the transmission IR spectrum is characteristic of that of the acid protonated EM base. This is indicated by the presence of a strong and broadened absorption band at about 1150 cm^{-1}, which has been associated with a high electrical conductivity and a high degree of electron delocalization in PAN.[26] On the other hand, however, the transmission IR spectrum of the AAc grafted EM film (Figure 8b) is characteristic of that of the insulating EM base, as suggested by the narrow 1150-cm^{-1} band. When the same grafted film is measured in the MIR mode (Figure 8c), the IR spectrum again suggests a protonated sample, similar to that shown in Figure 8a. Thus, the IR results readily give a qualitative indication of a surface-grafted and surface-self-protonated EM structure.

Finally, Figure 9 shows the effect of the AAc monomer concentration on the density of surface grafting and the degree of surface protonation for the 5-s plasma pretreated EM films. Thus, increasing the AAc monomer concentration from 2 to 10 wt % readily results in an increase in the density of a surface-grafted AAc polymer and an increase in the proportion of positively charged nitrogens. Thus, the densities of a surface-grafted AAc polymer, expressed as the [COOH]/[N] ratios, for grafting carried out in 2%, 5%, and 10% AAc solutions are 0.7, 1.4, and 2.2, respectively. The use of an AAc concentration greater than 10 wt % under the present experimental conditions gives rise to a viscous homopolymer solution which makes the removal of the homopolymer and the subsequent cleaning of the grafted EM film difficult.

Mechanisms of Surface Grafting onto EM Films. A peroxide-initiated polymerization mechanism has generally been suggested for the near-UV-induced graft copolymerization for polymer surfaces pretreated with glow discharge.[11] The fact that grafting occurs to some extent even in the pristine or untreated EM films is consistent with the reactive nature of the conjugated polymer surfaces. This is readily supported by the constant presence of adsorbed or weakly charge-transfer complexed oxygen species on most of the conjugated polymer surfaces, as suggested by the presence of a fairly broad and intense O 1s spectrum from each sample. Our recent static secondary ion mass spectroscopic (SSIMS) study of the EM films also reveals the presence of substantial O^- (16 amu) and OH^- (17 amu) fragments in the negative spectra. The most obvious findings supporting the peroxide mechanism in the present study are the dependence of both the density of grafting and the density of CO species on the plasma pretreatment time. Furthermore, the decrease in the imine/amine ratio and the presence of a high BE tail in the N 1s spectrum of the plasma treated EM film are probably associated with the oxidation of some C=N units to N oxides in the presence of peroxides.[27] When UV light is applied to an EM film immersed in the monomer solution, radicals are generated on the polymer surface as a result of photo-induced decomposition of the peroxides and partly by direct attack of the light on the conjugated polymer surface. For grafting without prior degassing, the dissolved oxygen, which could inhibit the radical polymerization, is consumed by photoreaction with riboflavin.[28]

Conclusion

EM base films cast from NMP solutions are susceptible to near-UV-light-induced graft copolymerization with AAm, NaSS, and AAc. In all cases, grafting is limited to the surface region of the EM film. Thus, XPS has been found to provide a convenient tool for the investigation of the structure and chemical composition at the copolymer interface. The density of a surface-grafted polymer is enhanced if the EM film is pretreated with Ar plasma. Graft copolymerization with the three hydrophilic monomers readily results in a decrease in the water contact angle of the EM film surface. Furthermore, grafting with the NaSS and AAc polymers also gives rise to self-protonated EM surface structure.

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Registry No. (AAm)($PhNH_2$) (graft copolymer), 138956-28-2; (AAc)($PhNH_2$) (graft copolymer), 138956-29-3; (NaSS)-($PhNH_2$) (graft copolymer), 138956-30-6; Ar, 7440-37-1.