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Surface modification and functionalization of electroactive polymer films via grafting of polyelectrolyte, polyampholyte and polymeric acids

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Films of electroactive polymers, such as polyaniline (PAN) in its emeraldine base form, and poly(3-alkylthiophene), poly(3-hexylthiophene) (P6TH), poly(3-octylthiophene) (P8TH), and poly(3-dodecylthiophene) (P12TH) can be readily functionalized via thermal or near ultraviolet-light-induced surface graft copolymerization with monomers of polyelectrolyte, polyampholyte and polymeric acids. The monomers used in the present work include dimethyl sulphate quaternized dimethylamino-ethylmethacrylate (DMAEM·$C_2H_6SO_4$), 3-dimethyl(methacryloyloxyethyl)ammonium propane sulphonate (DMAPS), acrylic acid (AAc) and a sodium salt of styrene sulphonic acid (NaSS). The surface structures and compositions of the electroactive polymer films after functionalization via graft copolymerization were characterized by angle-resolved X-ray photoelectron spectroscopy. Graft copolymerization of poly(3-alkylthiophene) films, but not PAN films, with the hydrophilic monomers readily results in a stratified surface microstructure arising from the migration of the hydrophilic graft chains beneath a thin surface layer which is much richer in the substrate chains. On the other hand, graft copolymerization of PAN films with AAc and NaSS readily gives rise to a self-protonated (and thus conductive) surface structure.

1. Introduction

Surface modification of polymers is a convenient and effective means of producing polymers with improved physicochemical properties, such as wettability, adhesion, lubrication and biocompatibility [1–3]. A variety of techniques is useful for chemical modification of polymer surfaces. These techniques include acid etching [4], X-ray irradiation [5], ultraviolet irradiation [6], electron-beam bombardment [7], ozone treatment [8], corona discharge [9], and plasma treatments [10]. Among the various techniques used, surface modification by graft copolymerization appears to be one of the most versatile in the preparation of speciality polymers having tailored surface structure and composition. These "molecular-designed" surfaces are suitable for specific applications, such as protein/enzyme immobilization in biomedical application [11]. In a parallel development, the surfaces of electroactive polymer films, such as polyaniline (PAN) films, functionalized via graft copolymerization with a polymeric acid [12]. Recent studies have also revealed interesting morphologies and microstructures at most of the copolymer interfaces [13]. In the present work, the surfaces of some electroactive polymers, such as PAN and poly(3-alkylthiophene) films, are functionalized via graft copolymerization with quaternary polyelectrolytes, polyampholytes and polymeric acids. These functional polymers include poly(dimethyl sulphate quaternized dimethylaminoethyl methacrylate) (poly(DMAEM·$C_2H_6SO_4$)) [14], the internal salts of poly[3-dimethyl(methacryloyloxyethyl) ammonium propane sulphonate] (poly (DMAPS)) [15], polyacrylic acid and polystyrene sulphonic acid. Using angle-resolved X-ray photoelectron spectroscopy (XPS) and surface–water contact angle measurements as the main analytical tools, the physical and chemical structures of the copolymer surfaces and interfaces, as well as the effect of surface pretreatments on the extent of grafting were investigated.

2. Experimental procedure

2.1. Polymer synthesis

The chemical polymerization of aniline was carried out at 0–5 °C with $(NH_4)_2S_2O_8$ as oxidant, similar to the method described in the literature [16], except that 1 M H_2SO_4 was used instead of 1 M HCl. The

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oxidant to monomer ratio was 1:1. The emeraldine (EM) base was obtained by treating the PAN salt with excess 0.5 M NaOH. The base polymer was then cast into thin films about 5–10 μm thick from *N*-methylpyrrolidinone (*N*MP) solution. The residual solvent trapped in the polymer films was removed by exhaustive pumping.

The 3-alkylthiophene monomers used in the present study, namely 3-hexylthiophene, 3-octylthiophene, and 3-dodecylthiophene, were obtained from Tokyo Kasei Co. and were used without further purification. The thiophene polymers were synthesized by the oxidative polymerization of the respective monomers in the presence of anhydrous $FeCl_3$ in dry $CHCl_3$, according to the method of Hotta *et al.* [17]. An oxidant to monomer ratio of 3:1 was used in all cases. Thus, 0.06 mol pulverized $FeCl_3$ was thoroughly dried at about 100 °C in the reaction flask under reduced pressure. Dry nitrogen was then introduced into the reaction vessel, followed by about 200 ml dry chloroform. About 0.02 mol thiophene monomer was subsequently added dropwise into the oxidant solution with stirring. The reaction mixture was stirred for about 48 h at room temperature and under a continuous flow of nitrogen. The hydrogen chloride evolved during polymerization was purged by the nitrogen stream and scrubbed with 2 M NaOH in a U-tube. The reaction mixture was then poured into a large excess of methanol to precipitate the thiophene polymer. Because the thiophene polymers so prepared were partially "doped" by $FeCl_3$, they were further purified by Soxhlet extraction and reprecipitation to remove the dopant. The so-prepared alkylthiophene polymer can be cast into free-standing, dark-red films from, for example, a 10^{-2} M chloroform solution.

2.2. Monomers for graft copolymerization

The functional monomer, dimethyl sulphate quaternized dimethylaminoethyl methacrylate ($DMAEM \cdot C_2H_6SO_4$), used in the grafting experiment was prepared according to the procedures reported earlier [14]. Similarly, the ampholyte monomer, 3-dimethyl(methacryloyloxyethyl)ammonium propane sulphonate (DMAPS) was prepared according to the method reported in the literature [15]. Other hydrophilic and functional monomers, such as acrylic acid (AAc) and a sodium salt of 4-styrenesulphonic acid (NaSS) were used as-received from Aldrich Chemical Co.

2.3. Graft copolymerization

Polyaniline and poly(3-alkylthiophene) film strips of about 1.5 cm × 3.5 cm were used for all grafting experiments. Graft copolymerizations were carried out in the 2% aqueous solutions of $DMAEM \cdot C_2H_6SO_4$ or DMAPS at various temperatures, ranging from 20–70 °C, in the case of near-ultraviolet-light-induced reaction. The photopolymerization time was maintained at 60 min. A Rayonet photochemical chamber reactor (Model RPR-100), equipped with a RPR-300 nm light source ($\lambda_{max} \sim 300$ nm), was used for photopolymerization. In the case of thermal polymerization, BPO was used as the initiator and the temperatures were varied between 40 and 70 °C, while the polymerization time was kept at 120 min. In all cases, the monomer solution was thoroughly degassed and sealed off under a nitrogen atmosphere prior to the initiation of polymerization reaction. Similar experimental procedures were employed for the graft copolymerization of AAc and NaSS polymers. After each grafting experiment, the electroactive polymer film was removed from the viscous homopolymer solution and washed with a jet of deionized water. It was then immersed in a gently stirred, room-temperature water bath for at least 48 h to remove the residual homopolymer.

2.4. Materials characterization after grafting

The polymer films after graft copolymerization were characterized by contact angle measurements and angle-resolved X-ray photoelectron spectroscopy (XPS). Static water contact angles were measured in a telescopic goniometer (Ramé-hart, Model 100-00-(230)). The telescope, with a magnification power of × 23, was equipped with a protractor of 1° graduation. XPS measurements were made on a VG ESCALAB MKII spectrometer with a MgK_α X-ray source (1253.6 eV photons) at a constant retard ratio of 40. 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 (BEs) were referenced to the C_{1s} neutral carbon peak at 284.6 eV. In peak synthesis, the linewidth (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 are accurate to within ± 10%. The core-level spectra were obtained at photoelectron take-off angles (α, measured with respect to the film surface) of 20° and 75°.

3. Results and discussion

XPS has been shown to be an ideal tool for the study of the intrinsic structure and charge-transfer interactions in electroactive polymers [12]. In the case of polyaniline (PAN), the quinonoid imine (=N–), benzenoid amine (–NH–) and positively charged nitrogens corresponding to any particular intrinsic redox state and protonation level 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. Fig. 1a–d show the N_{1s} core-level spectra, obtained at a take-off angle, α, of 75°, for the nigraniline (NA), emeraldine (EM), leucoemeraldine (LM), and H_2SO_4-protonated EM films respectively. Fig. 2a and b show the respective C_{1s} and S_{2p} core-level spectra, obtained at $\alpha = 75°$, for a pristine poly(3-dodecylthiophene)(P12TH) film. The C_{1s} core-level spectrum is dominated by a peak component with a BE at about 284.6 eV, arising from the

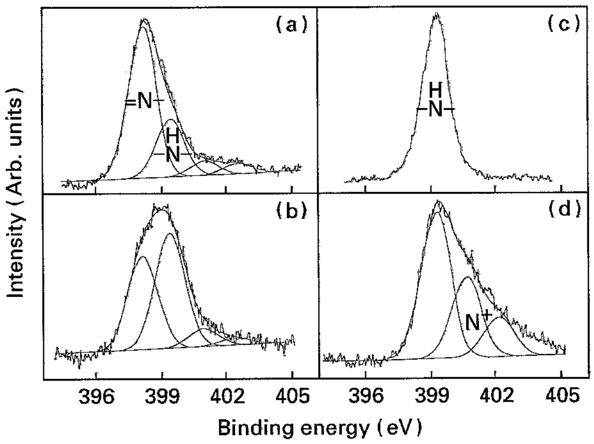

Figure 1 N_{1s} core-level spectra of (a) nigraniline, (b) emeraldine, (c) leucoemeraldine and (d) 1 M H_2SO_4 protonated EM films ($\alpha = 75°$).

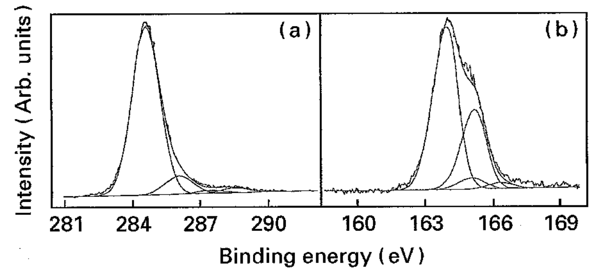

Figure 2 (a) C_{1s} and (b) S_{2p} core-level spectra of a pristine P12TH film ($\alpha = 75°$).

carbon in the thiophene ring and the alkyl substituent. The presence of a small, high-BE component at about 286.2 eV may have resulted from surface oxidation products or weakly charge-transfer complexed oxygen. This is consistent with the presence of a weak O_{1s} core-level signal. The S_{2p} core-level spectrum is resolved into a major and a minor spin-orbit-split doublet ($S_2p_{3/2}$ and $S_2p_{1/2}$), with the BE for the respective $S_2p_{3/2}$ peaks lying at about 163.9 eV and 165.2 eV. The former is attributable to the neutral thiophene units [18]. The latter is probably associated with a trace amount of surface oxidized thiophene units [19]. C_{1s} and S_{2p} core-level spectra of similar line shape and BEs were observed for the poly(3-hexylthiophene)(P6TH) and poly(3-octylthiophene) (P8TH) films.

The N_{1s} core-level spectra for PAN film surfaces after graft copolymerization with DMAPS can be resolved into three main components with BEs at about 398.2, 399.4 and 401.5 eV, attributable to the imine, amine and positively charged nitrogens, respectively. The positively charged nitrogens must have arisen from the grafted DMAPS polymer. Thus, the graft density, defined as the molar ratio of the DMAPS units to the substrate PAN monomer units can be readily determined from the area ratio of the spectral component at 401.5 eV and the sum of components at 398.2 and 399.4 eV. Alternatively, the grafted DMAPS polymer has a characteristic S_{2p} peak component at a BE of about 168.5 eV associated with the sulphate anion group [18]. Thus, the density of grafting is given directly from the sensitivity factors corrected spectral area ratio of the S_{2p} peak component and the sum of the N_{1s} components at BEs of 398.2 and 399.4 eV. Fig. 3a and b show the respective N_{1s} and S_{2p} core-level spectra, obtained at the photoelectron take-off angle of 75° for a PAN film after thermally induced graft copolymerization with DMAPS at 50 °C for 120 min. The corresponding spectra obtained at an α of 20° are shown in Fig. 3c and d.

Table I summarizes the graft densities, as revealed by the XPS analyses at two photoelectron take-off angles of 20° and 75°, for PAN films after thermally induced graft copolymerization with DMAPS at various temperatures. Thus, the densities of surface grafting are substantially enhanced upon increasing the copolymerization temperatures. Furthermore, a substantially higher extent of grafting is also observed at the more surface-glancing angle of 20°.

In the case of polythiophene films, graft copolymerization with DMAPS results in the appearance of a prominent new S_{2p} component at about 168.5 eV, attributable to the sulphate group of DMAPS. Thus, the density of grafting in each case can be readily determined from the spectral area ratio of the S_{2p} components at 163.9 and 168.5 eV. Fig. 4a–d show the respective S_{2p} and N_{1s} core-level spectra obtained at $\alpha = 75°$ and 20° of a P12TH film surface after thermal graft copolymerization with DMAPS at 70 °C for 120 min. Table II summarizes the graft densities, as revealed by the XPS analyses at two photoelectron

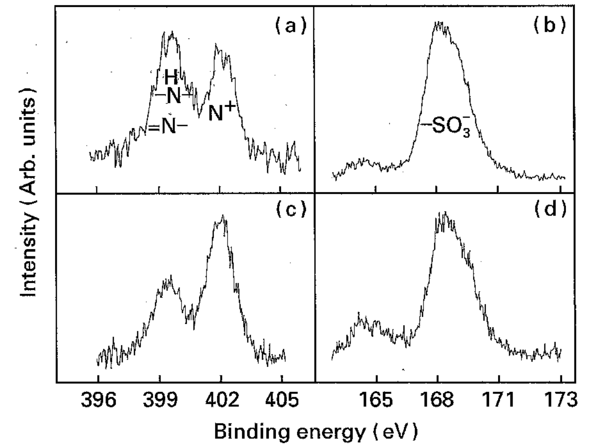

Figure 3 (a, c) N_{1s} and (b, d) S_{2p} core-level spectra obtained at (a, b) $\alpha = 75°$, and (c, d) $\alpha = 20°$ for a PAN film after graft copolymerization with DMAPS at 50 °C.

TABLE I XPS results for EM base films after thermal graft copolymerization with DMAPS

Sample	Copolymerization temperature (°C)	Graft densities, S/N[a]	
		$\alpha = 75°$	$\alpha = 20°$
1	40	0.05	0.10
2	50	0.90	1.9
3	60	3.2	3.3
4	70	7.0	10.0

[a] N_{1s} components associated with the PAN only.

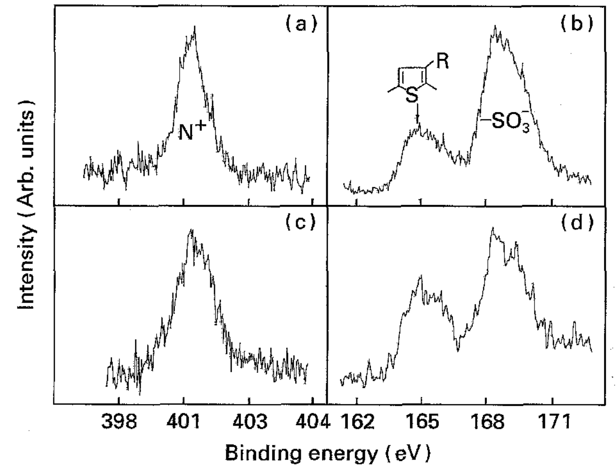

Figure 4 (a, c) N_{1s} and (b, d) S_{2p} core-level spectra obtained at (a, b) $\alpha = 75°$, and (c, d) $\alpha = 20°$ for a P12TH film after graft copolymerization with DMAPS at 70 °C.

TABLE II XPS results for P12TH films after thermal graft copolymerization with DMAPS

Sample	Copolymerization temperature (°C)	Graft densities, SO_3^-/S	
		$\alpha = 75°$	$\alpha = 20°$
1	40	0.25	0.18
2	50	0.80	0.61
3	55	1.42	1.33
4	60	1.80	1.43
5	70	4.0	1.50

TABLE III XPS results for P8TH films after thermal graft copolymerization with DMAPS

Sample	Copolymerization temperature (°C)	Graft densities, SO_3^-/S	
		$\alpha = 75°$	$\alpha = 20°$
1	40	0.17	0.18
2	50	0.68	0.50
3	55	0.94	0.77
4	60	1.42	1.10
5	70	2.02	1.51

TABLE IV XPS results for P6TH films after thermal graft copolymerization with DMAPS

Sample	Copolymerization temperature (°C)	Graft densities, SO_3^-/S	
		$\alpha = 75°$	$\alpha = 20°$
1	40	0.05	0.05
2	50	0.18	0.15
3	55	0.25	0.20
4	60	0.51	0.44
5	70	0.77	0.65

take-off angles of 20° and 75°, for P12TH films after thermally induced graft copolymerization with DMAPS at various temperatures. Again, the densities of surface grafting are substantially enhanced for graft copolymerization carried out at elevated temperatures. In the case of polythiophene substrates, however, a significantly larger amount of the hydrophilic graft was observed below the film surface at the take-off angle of 75°. Similar distributions of the hydrophilic graft in the surface regions were also observed for the surface graft copolymerized P8TH and P6TH films. Tables III and IV show, respectively, the graft densities, as revealed by the XPS analyses at $\alpha = 20°$ and 75°, for the P8TH and P6TH surfaces after thermal graft copolymerization with DMAPS.

The presence of significantly higher graft densities below all the polythiophene films surfaces suggests that, in each case, the hydrophilic graft must have migrated beneath a thin surface layer which is much richer in the substrate polymer chains. This chain migration and counter migrations in the surface region to form a stratified microstructure must have been facilitated by the fact that the present alkyl-substituted thiophene polymers have glass transition temperatures, T_g, around room temperature [20], as is also evident from the elastic nature of the films at room temperature. Earlier studies [19] have also shown that polymer molecules could migrate together with the graft layer at temperatures higher than the T_g of the substrate polymer. The effect of polar group orientation, polymer chain mobility and substrate permeability on the stability of the graft layer has been discussed by Ratner *et al.* [21] for poly(dimethylsiloxane), poly(ester urethane), and polystyrene grafted with 2-hydroxyethyl methacrylate, acrylamide, and ethyl methacrylate polymers. For silicone polymer grafted with polyacrylamide, the penetration of the hydrophilic graft occurred to such an extent that the graft was found only at a depth of ~50 nm below the silicone polymer surface, as suggested by the sputtering experiment. The reorientation of polar groups into the hydrophobic bulk phase has also been known to reduce the overall free energy of the system [22].

The stratified microstructure, however, is not observed for the PAN films after graft copolymerization. This result is indicated by the fact that a substantially higher graft density is always observed at the outermost surface of the film. The lack of migration or reorientation of the substrate and the graft chains is probably associated with the dense morphology of PAN films cast from NMP solutions [23]. Recent studies [24] have also shown that for emeraldine-base film cast from concentrated NMP solutions, extensive cross-linking reactions may also be involved. As a result, the migration of the substrate chains is severely limited.

Similar surface compositions and structures were observed for PAN and polythiophene films graft copolymerized with the polyelectrolyte, DMAEM·$C_2H_6SO_4$. In general, the densities of surface grafting increase with increasing temperature, as in the case of graft copolymerization with DMAPS. The structure of the grafted surfaces again is controlled by the microstructures of the polymer substrates. The hydrophilic graft remains on the outermost surface of the PAN films, but submerged below a thin surface layer of polythiophene chains to form a stratified surface structure. Table V summarizes the surface compositions, as revealed by XPS, for PAN films after thermal

TABLE V XPS results for PAN films after thermal graft copolymerization with DMAEM·$C_2H_6SO_4$

Sample	Copolymerization temperature (°C)	Graft densities, S/N[a]	
		α = 75°	α = 20°
1	30	0.20	0.22
2	45	0.25	0.39
3	60	0.42	0.66
4	75	0.46	0.84
5	90	0.73	0.81

[a] N_{1s} components associated with the PAN only.

graft copolymerization with DMAEM·$C_2H_6SO_4$. As in the case of graft copolymerization with DMAPS, the graft densities can be determined from the spectral area of the N^+ component in the N_{1s} core-level spectrum or the area of the S_{2p} core-level spectrum.

Polyaniline and poly(3-alkylthiophene) films are also susceptible to near-ultraviolet-light-induced graft copolymerization with monomer of polymeric acids, such as polyacrylic acid and polystyrene sulphonic acid. In the case of PAN films, it is expected that a functionalized surface, such as a self-protonated surface structure, can be readily achieved by graft copolymerization with these acids. The density of grafting in this case can be substantially enhanced by plasma or ozone pretreatment of the substrate films.

Fig. 5 shows the surface–water contact angles of PAN films as a function of ozone treatment time. The contact angle of the pristine film is about 67°. The decrease in water contact angle (or an increase in surface hydrophilicity) is consistent with the formation of a polar functional group, such as the oxidized carbon species. Fig. 6a–d show the respective N_{1s} and C_{1s} core-level spectra, obtained at a take-off angle of 75°, for the 25s and 55s ozone-pretreated PAN films after near-ultraviolet-light-induced graft copolymerization in a 10% AAc monomer solution. The distinct high BE C_{1s} component at about 288.7 eV is characteristic of the COOH [25] group of the grafted AAc polymer. The component at about 287.2 eV is attributable to the C–O species. The presence of a self-protonated surface structure is indicated by the appearance of the high BE components with BE > 400.5 eV in the N_{1s} core-level spectrum associated with the positively charged nitrogens. 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.

Table VI summarizes the surface structures, compositions and electrical conductivities of the AAc graft copolymerized PAN films. The composition data obtained at the reduced α readily suggest that the grafted AAc polymer remains mainly at the outermost surface. Furthermore, as the [COOH]/[N^+] ratios are substantially larger than 1, a large proportion of the grafted COOH groups remain free for further surface modifications and functionalizations. 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 chemical bonding is probably more advantageous over the conventional entrapping method [26].

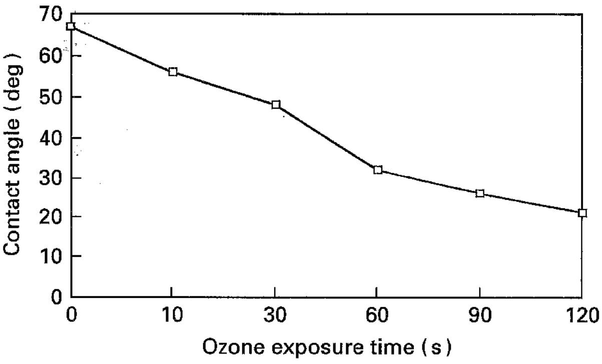

Figure 5 The surface–water contact angles of a PAN film as a function of ozone exposure time.

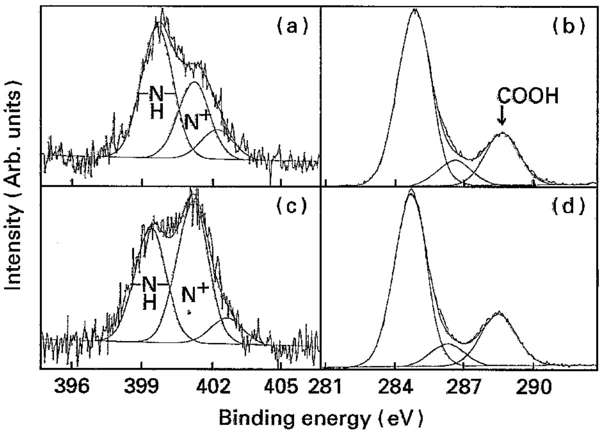

Figure 6 (a, c) N_{1s} and (b, d) C_{1s} core-level spectra obtained at α = 75° (a, b) 25 s, and (c, d) 55 s ozone pretreated PAN film after graft copolymerization in 10% AAc monomer solution.

Fig. 7a–d show the respective N_{1s} and S_{2p} core-level spectra, obtained at α = 20°, for the 15s and 60s ozone pretreated PAN film after near-ultraviolet-light-induced graft copolymerization in 0.5 M NaSS monomer solution. The appearance of the S_{2p} core-level signal at about 168.5 eV is consistent with the presence of the covalently bonded sulphonic acid ($-SO_3^-$) group arising from the NaSS polymer. The N_{1s} core-level spectra of the grafted PAN film again show the presence of a high BE tail above 400 eV, characteristic of the positively charged nitrogens. Thus, the sulphonic acid groups of the grafted NaSS polymer must have participated in the protonation of the PAN substrate to give rise to a self-doped and conductive surface structure.

The surface compositions or the graft densities can be readily determined from the sensitivity factor-corrected S_{2p} and N_{1s} core-level spectral area ratios. Table VII summarizes the surface structures and compositions, as revealed by the XPS technique, of the various ozone pretreated PAN films after graft copolymerization with NaSS. As in the case of graft copolymerization with the AAc polymer, the density of grafting is substantially enhanced by ozone pretreatment. Furthermore, the higher graft density obtained at the reduced XPS take-off angle of 20° readily

TABLE VI Surface structures, compositions and water contact angles for various PAN films after graft copolymerization with AAc

O_3 pretreatment time (s)	α (deg)	Graft density[a]	Proportion of			Water contact angle (deg)	Surface resistance (Ω/□)
			=N–	–NH–	N^+		
0	75	0.90	0.17	0.65	0.18	51	> 10^7
25	75	4.20	0.0	0.55	0.45	32	10^5
	20	4.65	0.0	0.50	0.50		
55	75	4.84	0.0	0.40	0.60	14	10^4
	20	6.26	0.0	0.39	0.61		
130	75	2.72	0.08	0.62	0.30	12	10^6
	20	3.46	0.05	0.65	0.30		

[a] Graft density is expressed as the [COOH]/[N] mole ratio.

TABLE VII Surface structures, compositions and water contact angles for various PAN films after graft copolymerization with NaSS

O_3 pretreatment time (s)	α (deg)	Graft density[a]	Proportion of			Water contact angle (deg)	Surface resistance (Ω/□)
			=N–	–NH–	N^+		
0	75	0.15	0.30	0.54	0.16	58	> 10^7
15	75	0.16	0.27	0.46	0.27	47	10^7
	20	0.36	0.11	0.53	0.36		
30	75	0.22	0.25	0.45	0.30	31	10^6
	20	0.40	0.11	0.50	0.39		
45	75	0.36	0.22	0.43	0.35	29	10^5
	20	0.67	0.10	0.48	0.42		
60	75	0.42	0.17	0.40	0.43	24	10^4
	20	0.91	0.00	0.43	0.57		

[a] Defined as the [S]/[N] mole ratio and determined from the S_{2p} and N_{1s} core-level spectral area ratio.

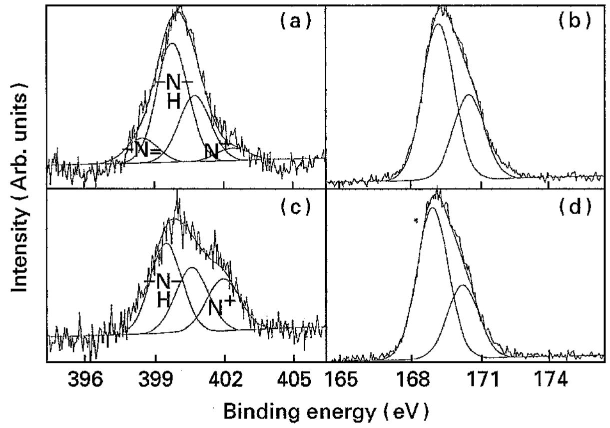

Figure 7 (a, c) N_{1s} and (b, d) S_{2p} core-level spectra obtained at $\alpha = 20°$ for (a, b) 15 s, and (c, d) 60 s ozone pretreated PAN film after graft copolymerization in 0.5 M NaSS solution.

suggests that the NaSS polymer graft remains predominantly at the outermost surface of the PAN film. This non-stratified surface microstructure for the self-protonated PAN surfaces is also consistent with that observed in PAN films grafted with polyelectrolyte and polyampholyte.

4. Conclusion

The surfaces of polyaniline and poly(3-alkylthiophene) films were functionalized by graft copolymerization with monomers of polyelectrolyte, polyampholyte and polymeric acid. The interfacial structure and composition of the modified electroactive polymers were characterized by angle-resolved XPS technique. Graft copolymerization with the hydrophilic monomers gives rise to a stratified surface microstructure in the alkylthiophene polymers. Graft copolymerization with monomers of polymeric acids, on the other hand, results in a self-protonated and conductive polyaniline surface.

References

1. Y. IKADA and Y. UYAMA, "Lubricating Polymer Surfaces" (Technomic, Lancaster, PA, 1993).
2. J. P. FISCHER, U. BECKER, S. P. HALASZ, K. F. MUCK, H. PUSCHNER, S. ROSINGER, A. SCHMIDT and H. H. SUHR, *J. Polym. Sci. Polym. Symp.* **63** (1979) 443.
3. Y. IKADA, *Adv. Polym. Sci.* **57** (1984) 104.
4. D. BRIGGS, D. M. BREWIS and M. B. KONIECZO, *J. Mater. Sci.* **11** (1976) 1270.
5. K. GARGAN, E. KRONFLI and K. V. LOVELL, *Radiat. Phys. Chem.* **36** (1990) 757.
6. Y. UYAMA and Y. IKADA, *J. Appl. Polym. Sci.* **36** (1988) 1087.
7. G. ELLINGHORST, J. FUEHRER and D. O. HUMMEL, *Radiat. Phys. Chem.* **18** (1981) 889.
8. K. FUJIMOTO, Y. TAKEBAYASHI, H. INOUE and Y. IKADA, *J. Polym. Sci. A Polym. Chem.* **31** (1993) 1035.
9. B. LECLERCQ, M. SOTTON, A, BASZKIN and L. TER-MINASSIAN-SARAGA, *Polymer* **18** (1977) 675.
10. Y. DAO, H. J. GRIESSER, A. W. H. MAU, R. SCHMIDT and J. LIESEGANG, *ibid.* **32** (1991) 1126.
11. S. EMI, Y. MURASE, T. HAYASHI and A. NAKAJIMA, *J. Appl. Polym. Sci.* **41** (1990) 2753.
12. E. T. KANG, K. G. NEOH and K. L. TAN, *Synth. Met.* **55–57** (1993) 1232.
13. E. T. KANG, K. G. NEOH, K. L. TAN, F. C. LOH and D. J. LIAW, *Polym. Adv. Technol.* **5** (1994) 837

14. D. J. LIAW, W. F. LEE, Y. C. WHUNG and M. C. LIN, *J. Appl. Polym. Sci.* **30** (1985) 4697.
15. D. J. LIAW, S. J. SHIAU and K. R. LEE, *ibid.* **45** (1992) 61.
16. A. RAY, G. E. ASTURIES, G. E. KERSHNER, A. F. RICHTER, A. G. MACDIARMID and A. J. EPSTEIN, *Synth. Met.* **29** (1989) E141.
17. S. HOTTA, S. D. RUGHOOPRTH and A. J. HEEGER, *ibid.* **22** (1987) 79.
18. G. E. MUILENBERG, "Handbook of X-ray Photoelectron Spectroscopy" (Perkin–Elmer, Eden Prairie, MN, 1977) p. 56.
19. E. T. KANG, K. G. NEOH and K. L. TAN, *Macromolecules* **25** (1992) 6842.
20. S. HOTTA, M. SOGA and N. SONODA, *Synth. Met.* **26** (1988) 267.
21. B. RATNER, P. K. WEATHERSBY, A. S. HOFFMAN, M. A. KELLEY and L. H. SCHARPEN, *J. Appl. Polym. Sci.* **22** (1978) 643.
22. Y. IKADA, T. MATSUNAGA and M. SUZUKI, *Nippon Kagaku Gakkaishi* **6** (1985) 1079.
23. T. L. PORTER, K. CAPLE and G. CAPLE, *Synth. Met.* **60** (1993) 211.
24. S. K. JEONG, J. S. SUH, E. J. OH, Y. W. PARK, C. Y. KIM and A. G. MacDIARMID, in "Proceedings of ICSM '94", Y. W. PARK (ed.), Seoul, Korea, July 24–29, 1994, p. 81.
25. G. E. MUILENBERG (ed.), "Handbook of X-ray Photoelectron Spectroscopy" (Perkin–Elmer, Eden Prairie, MN, 1977), p. 38.
26. M. UMANA and J. WALLER, *J. Anal. Chem.* **58** (1986) 2979.

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