Macromolecules **1999,** *32,* 8183−8188

Surface Modification of Poly(tetrafluoroethylene) Film by Consecutive Graft Copolymerization with 4-Vinylaniline and Aniline

L. Y. Ji, E. T. Kang,* and K. G. Neoh

Department of Chemical Engineering, National University of Singapore, Kent Ridge, Singapore 119260

K. L. Tan

Department of Physics, National University of Singapore, Kent Ridge, Singapore 119260

Received April 26, 1999; Revised Manuscript Received August 27, 1999

ABSTRACT: Surface modification of argon plasma-pretreated poly(tetrafluoroethylene) (PTFE) film by UV-induced graft copolymerization with 4-vinylaniline (4-VAn), followed by oxidative copolymerization of the aniline moiety of the grafted 4-VAn polymer with aniline, was carried out to render the PTFE surface conductive. The surface compositions of the graft-modified PTFE films were studied by X-ray photoelectron spectroscopy (XPS). The yield of the initially grafted 4-VAn polymer increased with increasing monomer concentration and UV graft copolymerization time. The efficiency of the subsequent surface oxidative copolymerization with aniline (and thus the resulting surface conductivity) was enhanced by the high concentration of the 4-VAn polymer from the initial graft copolymerization. The surface resistivity of the PTFE films was reduced to the order of 10^6 Ω/□ by the two consecutive surface graft copolymerization processes. The doping−undoping (protonation−deprotonation) behavior of the surface graft copolymerized aniline polymers was similar to that of the aniline homopolymer or polyaniline (PAn).

Introduction

Surface modification of polymers is a convenient and effective means to render the existing polymers with improved physicochemical properties, such as wettability, adhesive and lubricative properties, and biocompatibility.[1,2] Among the many techniques available, surface modification via graft copolymerization appears to be one of the most versatile techniques, as it allows the molecular redesign of most polymer surfaces to impart new and specific functionalities.[3−6]

Polyaniline (PAn) is one of the most widely studied conducting polymers.[7−16] The unique properties and characteristics associated with its intrinsically redox states made it a potential material for various applications, such as electrode or active materials in energy storage devices,[17] optoelectronic devices,[18] and display devices.[19] Other envisaged applications are in the areas of the control of electromagnetic radiation (EMR) and the dissipation of electrostatic charges.[20,21] In recent years, a great deal of effort has been made to overcome the lack of processability of conducting polymers. Thin film coatings of polyaniline or polypyrrole have been prepared chemically[22] and electrochemically.[23] The use of textile materials as substrates and reinforcing materials in conducting polymer composites to impart conductivity into these structures has been known for some time.[24,25] The conductivity of the composite and the coating on the fibers depend on the proper deposition of the powdery conductive polymer in the interstices of the fabric, much like the impregnation of a textile materials with a dispersion of carbon black. Their potential applications as new materials for the shielding of electromagnetic interference (EMI) and the control of electrostatic charge dissipation (ESD) have been assessed by various investigators.[26,27] Other fine works in this area include the modification of fluoropolymer surfaces by wet chemical treatment, by hydrogen plasma, by UV laser, and by electron beams to promote the strong adhesion of PAn and other conductive polymers.[28] Coating of the emeraldine (EM) base of PAn on a surface-functionalized conventional polymer substrate (from, for example, graft copolymerization with a protonic acid-containing monomer) can result in strong interfacial charge transfer interactions between the coating and the substrate surface. The interfacial charge transfer interaction not only has given rise to a conductive substrate surface but also has resulted in strong adhesion of the aniline polymer on conventional polymer substrates.[29]

In the present work, we report on a novel method for covalently tethering the aniline polymer chains onto the surface of poly(tetrafluoroethylene) (PTFE) film. The PTFE substrate is ideal for a wide range of industrial applications because of its excellent dielectric property, thermal stability, and chemically inertness. The present method involves first the UV-induced graft copolymerization of an aniline group-containing vinyl monomer, 4-vinylaniline (4-VAn), on the plasma-pretreated PTFE substrate. The aniline groups of the grafted 4-VAn chains on the PTFE surface are subsequently copolymerized with aniline via oxidative polymerization. The covalently tethered aniline copolymers readily impart electrical conductivity onto the surface of the highly insulating PTFE substrate. The introduced amine groups on the so-modified PTFE surface may also be utilized for further chemical modification and functionalization.

Experimental Section

Materials. The substrate polymer used for graft copolymerization was a poly(tetrafluoroethylene) (PTFE) film of 0.1 mm in thickness. It was purchased from Goodfellow Inc., Cambridge, U.K. The PTFE films were washed overnight in acetone before use. The 4-vinylaniline (4-VAn) (90% purity) and aniline (99.5% purity) monomers were obtained from

---

* To whom correspondence should be addressed. Fax (65) 779-1936; E-mail cheket@nus.edu.sg; telephone (65) 874-2189.

10.1021/ma990646f CCC: $18.00

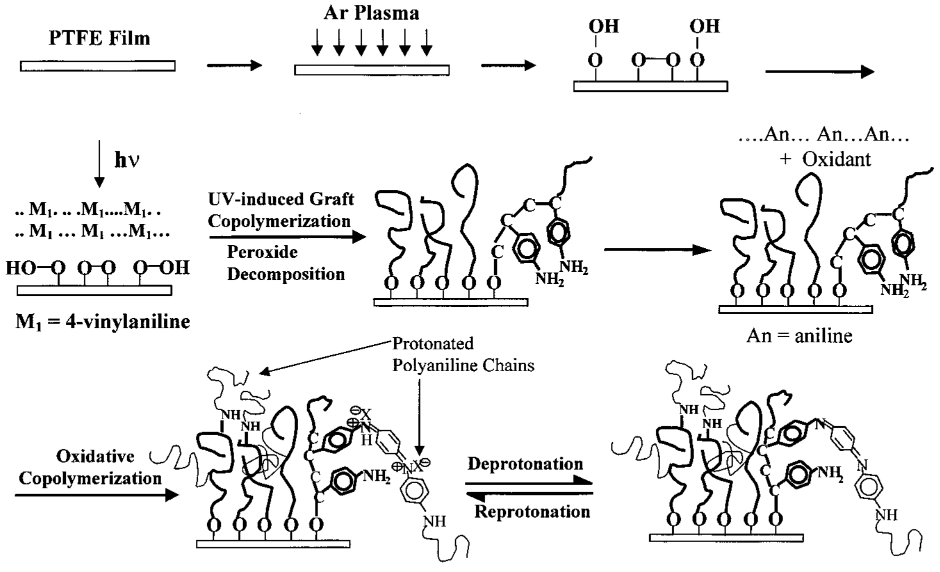

Figure 1. Schematic representations of the graft modification processes and the surface structures of the aniline-4-VAn copolymer-modified PTFE substrate film.

Aldrich Chemical Co., Milwaukee, WI, and were used as received. The solvents, such as *N*-methylpyrrolidinone (NMP) and acetone, and other chemicals were of reagent grade. They were also obtained from Aldrich Chemical Co. and were used without further purification.

Plasma Pretreatment. A cylindrical quartz glow discharge cell, model SP-100, manufactured by Anatech Ltd. USA, was used for the plasma pretreatment of the PTFE substrate. The glow discharge was generated at a frequency of 40 kHz and a plasma power of 35 W. The pressure in the quartz cell was maintained at ~0.58 Torr of argon while the polymer films were subjected to the glow discharge for a period of time, ranging from 0 to 120 s. The Ar plasma-pretreated PTFE films were exposed to air for about 10 min to facilitate the formation of surface peroxides and hydroxyl peroxides species for the subsequent UV-induced surface graft copolymerization process.[30]

Surface Graft Copolymerization. The surface modification of PTFE substrate film by graft copolymerization with 4-VAn and aniline was carried out in two steps. The first step involved the UV-induced graft copolymerization of 4-VAn on the Ar plasma-pretreated PTFE substrate. The second step involved the surface oxidative copolymerization of aniline with the aniline functional groups of the 4-VAn polymer covalently tethered on the PTFE substrate.

The UV-induced surface graft copolymerization with 4-VAn was carried out in a Riko rotary model RH 400-10W photochemical reactor, manufactured by Riko Denki Kogyo, Chiba, Japan. The reactor was equipped with a 1000 W high-pressure Hg lamp and a constant temperature water bath. All UV-induced graft copolymerization was carried out at a constant temperature of 28 °C. Several drops of NMP solution of 4-VAn monomer of concentrations ranging from 20 to 80 wt % were introduced onto the Ar plasma-pretreated PTFE film surface and spread to form a uniform thin liquid film. The wetted PTFE film was sandwiched between two quartz plates. The assembly was then subjected to UV irradiation in a Pyrex tube for a predetermined period of time. After the UV-induced surface graft copolymerization, the polymer substrate was washed thoroughly with copious amounts of NMP to remove the unreacted monomer and homopolymer. The graft-modified PTFE substrate was then dried under reduced pressure before the second surface graft copolymerization experiment with the aniline monomer.

The oxidative copolymerization of aniline with the aniline functional groups of the grafted 4-VAn polymer on the PTFE film was carried out in 1 M aqueous solution of HCl, containing the graft-modified PTFE film, 0.1–0.5 M aniline, and the corresponding amount of $(NH_4)_2S_2O_8$ oxidant to achieve a monomer-to-oxidant molar ratio of 1. The reaction was allowed to proceed for about 5 h. The method was thus similar to that reported earlier for the homopolymerization of aniline to produce the emeraldine (EM) salt.[31,32] The graft-copolymerized EM salt on the PTFE surface was converted to the neutral EM base form by treatment with a large excess of 0.5 M NaOH solution. The surface-modified film was subsequently immersed in a large volume of NMP for at least 10 h with continuous stirring to remove the adhered and physically adsorbed aniline homopolymer before been dried under reduced pressure. The processes of UV-induced graft copolymerization of 4-VAn on the Ar plasma-pretreated PTFE film, and the subsequent oxidation copolymerization with aniline, are shown schematically in Figure 1. It is conceivable that polymerization among the aniline functional groups of the grafted 4-VAn chains, as well as among aniline and the aniline groups of the 4-VAn chains, by processes other than the 1,4-addition might have also occurred to some extent during the oxidative copolymerization experiment.

Characterization of the Modified PTFE Surfaces. Earlier X-ray photoelectron spectroscopy (XPS) studies have shown that the quinonoid imine (=N–), benzenoid amine (–NH–), and positively charged nitrogen atoms corresponding to any particular intrinsic redox state and protonation level of polyaniline (PAn) can be quantitatively differentiated in the properly curve-fitted N 1s core-level spectrum.[31-33] In the present work, 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 the photoelectron takeoff angle of 75° (α, with respect to the sample surface). The X-ray source was run at a reduced power of 120 W. The pressure in the analysis chamber was maintained at 7.5×10^{-9} Torr or lower during each measurement. All binding energies (BEs) were referenced to the C 1s neutral carbon peak at 284.6 eV. In peak synthesis, the line width (full width at half-maximum or fwhm) for 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 reliable to ±10%. The elemental sensitivity factors were determined using stable binary compounds of well-established stoichiometries. The surface resistances of the surface-modified PTFE films were measured by the two-probe method, using a Hioki model 3265 digital electrometer. For each resistance value reported, at least three sample measurements were averaged.

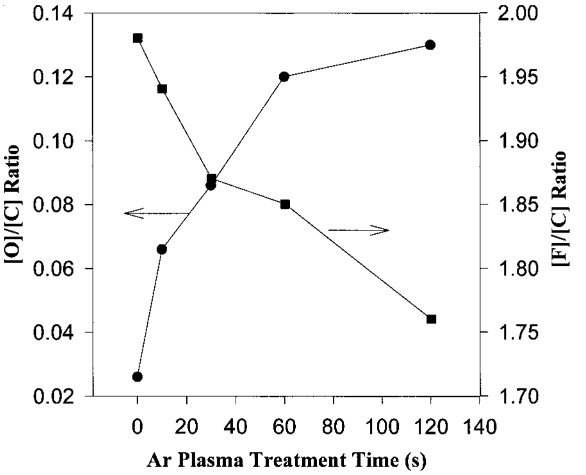

Figure 2. Effect of argon plasma treatment time on the surface [O]/[C] and [F]/[C] ratio of the PTFE substrate film.

Results and Discussion

Argon Plasma Pretreatment of the PTFE Substrate. The C 1s core-level spectrum of the pristine PTFE film surface consists of a main component at the binding energy (BE) of 291.4 eV, attributable to the CF_2 species, and a broad minor component at about 8.4 eV below the main peak. The minor component can be attributed mainly to the contribution of the CF_2 X-ray satellite peaks arising from the Mg $K\alpha_{3,4}$ radiation. Ar plasma treatment, followed by atmospheric exposure, readily results in the formation of oxidized carbon species at the surface. The formation of the latter is also indicated by the appearance of a broad low BE peak at about 286 eV, as well as by the substantial increase in the surface [O]/[C] ratio of the PTFE film. The effect of Ar plasma treatment on the surface composition of the PTFE film has been reported earlier.[34]

Figure 2 shows the changes in the surface [F]/[C] and [O]/[C] atomic ratios, as determined from the C 1s, O 1s, and F 1s core-level spectral peak-area ratios at the photoelectron takeoff angle (α) of 75°, as a function of the Ar plasma treatment time. An increase in the [O]/[C] ratio and a decrease in the [F]/[C] ratio are observed upon increasing the Ar plasma treatment time, in agreement with the results generally reported in the literature.[35,36] The glow discharge causes the breakage of C−F bonds, resulting in the abstraction of fluorine atoms from the surface. The subsequent exposure of the activated surface to air causes oxygen to be incorporated on the PTFE surfaces, leading to surface oxidation and the formation of peroxide and hydroxyl peroxide species. The peroxide species can readily initiate the surface free radical polymerization in a mechanism generally proposed for the UV-induced surface graft copolymerization.[30,37]

Surface Graft Copolymerization with 4-Vinylaniline. Since 4-vinylaniline (4-VAn) contains the unsaturated vinyl group, it is susceptible to graft copolymerization on the plasma-pretreated PTFE surface after the UV-initiated decomposition of the peroxide and hydroxyl peroxide species, as depicted in Figure 1. Figure 3a−d shows the respective C 1s and N 1s core-level spectra, obtained at α of 75°, for the 60 s Ar plasma-pretreated PTFE films after having been subjected to UV-induced graft copolymerization in 40 wt % (parts a and b) and 70 wt % (parts c and d) NMP solutions of 4-VAn for 1 h. The presence of surface-grafted 4-VAn polymer can be deduced from the appearance of a low-BE component centered at about 284.6 eV in the C 1s core-level spectrum, in addition to the CF_2 component of reduced intensity at about 293 eV, as well as the appearance of a N 1s core-level signal. The BE of the CF_2 peak shifts from 291.4 eV for the pristine PTFE surface to about 293 eV after the surface modification, probably due to the differential charging effect of the surface-grafted 4-VAn chain and the highly insulating substrate PTFE chain. The N 1s core-level spectra are comprised of a single peak component at the BE of about 399.4 eV, attributable to the $-NH_2$ species[38,39] of the 4-VAn polymer. The graft concentration, defined in the present work as the number of repeat units of the grafted 4-VAn polymer per repeat CF_2 unit of the PTFE substrate or the $[N]/[CF_2]$ ratio, can be determined simply from the N 1s and F 1s spectral area ratio, taking into account of the fluorine stoichiometry in the CF_2 units.

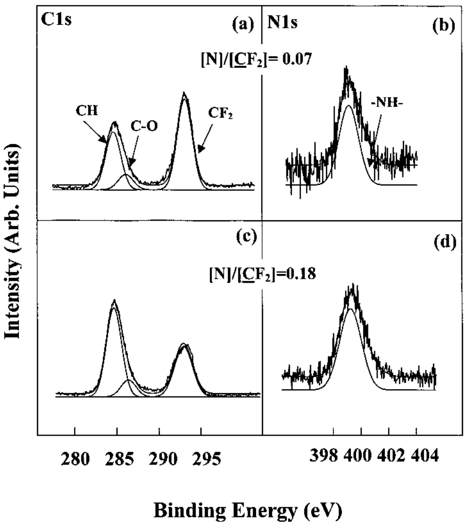

Figure 3. C 1s and N 1s core-level spectra, obtained at α = 75°, after 1 h of UV-induced graft copolymerization of the 60 s Ar plasma-pretreated PTFE film in (a, b) 40 wt %, and (c, d) 70 wt % NMP solutions of the 4-VAn monomer.

The graft concentration on a 60 s Ar plasma-pretreated PTFE film as a function of the 4-VAn monomer concentration used for the UV-induced graft copolymerization is shown in Figure 4. The concentration of the grafted 4-VAn polymer increases with increasing monomer concentration in the monomer concentration range of 20−80 wt %. The UV graft copolymerization time was fixed at 1 h, which had been found to be sufficient for the graft copolymerization. Figure 5 shows the effect of UV graft copolymerization time on the concentration of 4-VAn polymer grafted on the 60 s Ar plasma-pretreated PTFE substrate. The graft copolymerization was carried out at two monomer concentrations, 40 and 70 wt % in NMP. In both cases, the graft concentration increase with increasing UV irradiation time up to about 1 h, after which the graft concentration tends to remain relatively constant, indicative of the completion of the surface graft copolymerization process.

Oxidative Graft Copolymerization of Aniline onto the 4-VAn Graft Copolymerized PTFE Surface. Oxidative graft copolymerization of aniline onto the surface of PTFE film, which has been previously modified by graft copolymerization with 4-VAn, is then carried out. For convenience, the resulting graft concentration is also reported as the $[N]/[CF_2]$ ratio, in

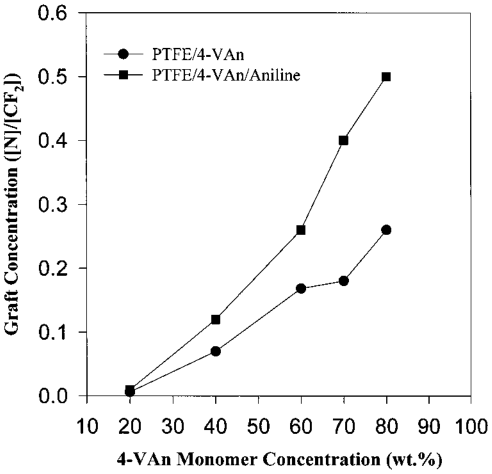

Figure 4. Effect of the 4-VAn monomer concentration on the graft concentration ([N]/[CF_2] ratio) of the 60 s Ar plasma-pretreated PTFE substrates after (●) 1 h of UV-induced graft copolymerization with the 4-VAn monomer and (■) subsequent oxidative copolymerization with the aniline monomer.

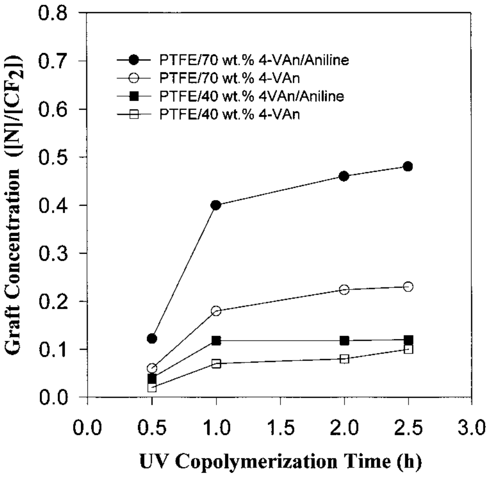

Figure 5. Effect of UV graft copolymerization time on the graft concentration ([N]/[CF_2] ratio) of a 60 s Ar plasma-pretreated PTFE substrate after having been modified by (□, ○) UV-induced graft copolymerization in 40 and 70 wt % NMP solution of 4-VAn and (■, ●) the subsequent oxidative graft copolymerization with aniline in 1 M HCl.

which [N] represents the total nitrogen atoms coming from both the grafted 4-VAn polymer and the aniline polymer.

Figure 6a–d shows the respective C 1s and N 1s core-level spectra of the PTFE films from initial graft copolymerization in 40 and 70 wt % 4-VAn solution, after the subsequent oxidative copolymerization in 1 M HCl solution containing 0.2 M aniline and 0.2 M $(NH_2)_4S_2O_8$. The grafted aniline polymer salt has been compensated by treatment with 0.5 M NaOH. The corresponding C 1s and N 1s core-level spectra of the PTFE surface from graft copolymerization with 4-VAn only have been shown earlier in Figure 3. In comparison with the C 1s core-level spectra in Figure 3, it is obvious that the intensity of the corresponding CF_2 peak component in either Figure 6a or Figure 6c has decreased substantially after the surface oxidative copolymerization with aniline. Also, the peak component at the BE of 287.0 eV, attributable to the C=O group,[6] becomes discernible after the oxidative copolymerization with aniline. This is in agreement with the reactive nature of the conjugated polymer surface. For the N 1s core-level spectra in Figure 6, the appearance of the new peak component at the BE of 398.2 eV suggests the presence of the imine group (=N–)[39] after the surface oxidative copolymerization with aniline. The area ratio of imine group to amine group ([=N–]/[NH] ratio) is somewhat less than the theoretical value of unity for a completely copolymerized emeraldine (EM) base network. The result thus suggests the persistence of the amine groups from the initially grafted 4-VAn polymer in the graft copolymerized aniline polymer network. This fact is also shown in the schematic diagram of Figure 1.

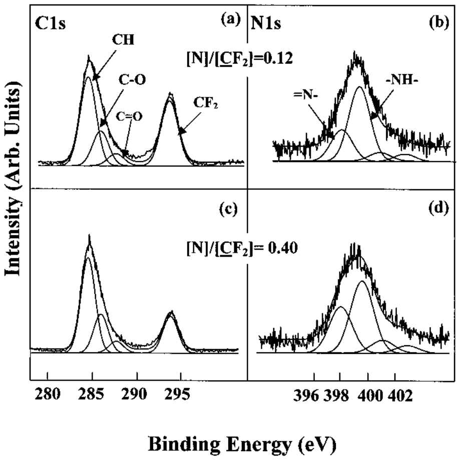

Figure 6. C 1s and N 1s core-level spectra of the base-treated aniline-4-VAn copolymer-modified PTFE films, prepared from the UV-induced graft copolymerization in (a, b) 40 wt % and (c, d) 70 wt % NMP solutions of 4-VAn monomer, followed by oxidative graft copolymerization with aniline in 1 M HCl for 5 h.

The copolymerization of aniline with the grafted 4-VAn polymer on the PTFE substrate surface occurs via the oxidative copolymerization between the “free” aniline monomer and the aniline moiety of the grafted 4-VAn polymer. The effects of the 4-VAn polymer concentration from initial UV-induced graft copolymerization on the efficiency of subsequent oxidative copolymerization with aniline are shown in Figures 4 and 5. From the data in Figures 4 and 5, the overall graft concentrations, as determined from the [N]/[CF_2] ratios, and with [N] coming from both the grafted 4-VAn and aniline polymers, are calculated to be about 1.5–2.2 times those of the corresponding PTFE surfaces with the 4-VAn polymer graft only. The higher the 4-VAn polymer concentration from the first graft copolymerization, the higher the resulting overall graft concentration after the oxidative copolymerization with aniline. On the other hand, parallel experiments have shown that the concentration of aniline used during oxidative copolymerization has little effect on the copolymerization yield for the aniline concentration range of 0.1–0.5 M examined.

To investigate the surface conductivity of the aniline-4-VAn polymer-modified PTFE substrate, acid redoping has been carried out to convert the insulating EM base form to the conducting EM salt form of PAn. Three types of inorganic acid, H_2SO_4, HCl, and $HClO_4$, were used to examine the protonation behavior of the modified PTFE surface. The respective C 1s and N 1s core-level spectra of the aniline-4-VAn polymer-modified PTFE films after redoping for 2 h in the 1 M $HClO_4$ and 1 M H_2SO_4 acid solutions are shown in Figure 7. The N 1s core-level spectra of the corresponding EM base form

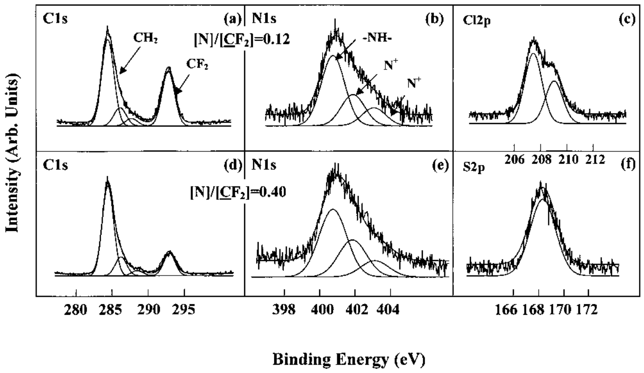

Figure 7. C 1s, N 1s, Cl 2p, and S 2p core-level spectra of aniline-4-VAn copolymer-modified PTFE films after reprotonation in (a–c) 1 M $HClO_4$ and (d–f) 1 M H_2SO_4 for 2 h.

Table 1. Effect of Protonation on the Chemical Composition of the Aniline-4-V-An Copolymer-Modified PFTE Surface

graft conc [N]/[CF$_2$]	doping acid	[−NH−]/[N]	[N$^+$]/[N]	[Cl]/[N] or [S]/[N]
0.12[a]	$HClO_4$	0.59	0.41	0.43
0.40[b]	H_2SO_4	0.53	0.47	0.24

[a] From the oxidative copolymerization of aniline on the surface-modified PTFE film from 1 h of UV-induced graft copolymerization in 40 wt % 4-VAn. [b] From the oxidative copolymerization of aniline on the surface-modified PTFE film from 1 h of UV-induced graft copolymerization in 70 wt % 4-VAn.

on the PTFE films have been shown earlier in Figure 6. The counterions in the polymer salts are reported as sulfate and perchlorate anions.[40] The perchlorate anion has a characteristic Cl $2p_{3/2}$ BE at about 207 eV in the Cl 2p core-level spectrum, while the sulfate anion has a characteristic BE at about 168 eV in the S 2p core-level spectrum.[40] The Cl 2p and S 2p core-level spectra of the reprotonated surfaces are also shown in Figure 7 for comparison purposes.

When the line shapes of the N 1s spectra in Figures 6 and 7 are compared, it is obvious that protonation has resulted in the transformation of all the imine (=N−) units into the positively charged nitrogen species (N^+) at BE's above 400 eV. The proportion of the amine (−NH−) groups remains relatively constant, indicating that protonation has occurred preferably at the imine site in each case. Thus, the protonation−deprotonation behavior of the aniline-4-VAn copolymer on the PTFE surface is not unlike that of the EM base form of PAn.[39] The amounts of dopant counterions introduced onto the surface-modified PTFE films can be determined from the corrected Cl 2p, S 2p, and N 1s core-level spectral area ratios and expressed as the [Cl]/[N] and [S]/[N] ratios. The results are tabulated in Table 1. Thus, the [Cl]/[N] ratio of the $HClO_4$ protonated surface is very close to the [N^+]/[N] ratio, indicating that the counterion introduced onto the surface-modified PTFE films is monovalent ClO_4^- species. This is in agreement with that reported earlier for the $HClO_4$ protonated PAn homopolymer.[40] In the case of the H_2SO_4 protonated surface, the [S]/[N] ratio is only about half the [N^+]/[N] ratio, suggesting that the dopant anion is the SO_4^{2-} divalent species. Both HSO_4^- and SO_4^{2-} anions have been observed in the H_2SO_4 protonated PAn samples.[39] The presence of the sulfate anion predominantly in the divalent SO_4^{2-} state in the present case is attributable, at least in part, to the steric effect associated with the spatial orientation and distribution of the grafted copolymer chains. The steric effect and the covalent tethering of the aniline polymer chains on the PTFE surface have forced a more intimate interaction between the polymer and the protonic acid dopant.

Table 2. Effect of UV Graft Copolymerization Time of 4-VAn and the Type of Protonic Acid on the Surface Resistance of the Aniline-4-VAn Copolymer-Modified PTFE Surface[a]

UV time, h	graft conc [N]/[CF$_2$]	surface resistance ($\Omega/\square$) after protonation by		
		H_2SO_4	HCl	$HClO_4$
0.5	0.12	3×10^7	5×10^8	6×10^7
1.0	0.40	7×10^6	1×10^7	1×10^6
1.5	0.43	6×10^6	3×10^6	2×10^6
2.0	0.46	5×10^6	3×10^6	1×10^6

[a] Conditions: monomer concentration of 4-VAn: 70 wt %. The 4-VAn polymer-modified surfaces were oxidatively copolymerized in 0.2 M aqueous solution of aniline. Doping time: 2 h.

PTFE is a very useful dielectric material with a surface resistance of about 10^{15} $\Omega/\square$.[41] After having been modified by UV-induced graft copolymerization with 4-VAn and then oxidative copolymerization with aniline, its electrical resistance decreases sharply to the order of 10^6 $\Omega/\square$, making it potentially valuable for antistatic applications.[26] Table 2 summarizes the effect of UV graft copolymerization time (and thus the graft concentration) on the observed surface resistance of the aniline polymer-modified PTFE surfaces after protonation by H_2SO_4, HCl, and $HClO_4$. For UV irradiation time longer than 1 h, the decrease in resistance becomes less significant. In general, the surface resistance decreases with increasing the UV graft copolymerization time. This phenomenon is consistent with the earlier result that higher graft concentration of the 4-VAn polymer often leads to higher copolymerization efficiency with aniline and thus lower resistance of the resulting aniline-4-VAn polymer-modified substrate surface. For graft concentration ([N]/[CF$_2$] ratio) below 0.1, the surface resistance increases rapidly to above 10^8 $\Omega/\square$.

In the present work, the graft concentration of aniline-4-VAn copolymer-modified substrate varies from 0.01 to 0.5, or about 50 times in magnitude. For a graft concentration, or [N]/[CF$_2$] ratio, of about 0.10, the surface resistance is greater than 5×10^8 $\Omega/\square$. When graft concentration is increased to between 0.10 and 0.50, the resistance decreases on the order of 10^6–10^7 $\Omega/\square$. The surface resistance (R_s) value of the present aniline-4-VAn copolymer-modified PTFE film is characteristic of the thickness of the grafted aniline polymers. The grafted aniline polymers layer has a thickness comparable to the probing depth of the XPS technique, as the underlying PTFE substrate is still discernible in most cases. Earlier work[42] on the surface-modified PTFE films has suggested the probing depth of the XPS technique in the organic matrix to be in the order of about 7.5 nm at the photoelectron takeoff angle of 75°. The relation between surface resistance and bulk resistivity (ρ) is $R_s = \rho/t$, where t is the thickness of the film. Thus, using 7.5 nm as the thickness of the aniline polymers layer, the bulk resistivity is about 0.75 ohm·cm, which is equivalent to a bulk conductivity value (σ) on the order of 1 S/cm, as $\sigma = 1/\rho$. This conductivity value is typical of that of the protonated aniline homopolymer.[43]

Finally, it is appropriate to emphasize that the grafted 4-VAn chains and the copolymerized aniline chains are covalently tethered on the PTFE film to form a covalent network structure. Despite its small thickness, the semiconductive graft layer cannot be easily removed. The present approach also differs from those of the earlier works that involve coating or physically adsorption of the conductive PAn on the surface-modified PTFE substrates.[28,29,44]

Conclusion

Argon plasma-pretreated PTFE films were subjected to further surface modification by UV-induced graft copolymerization with 4-vinylaniline, followed by oxidative copolymerization of the aniline moiety of the grafted 4-VAn polymer with aniline. The chemical compositions of the singly and doubly graft copolymerized surfaces were characterized by XPS. The yield of the 4-VAn polymer from the initial graft copolymerization increased with increasing monomer concentration and UV graft copolymerization time. When the 4-VAn polymer-modified PTFE films were further functionalized via surface oxidative copolymerization with aniline, the copolymerization efficiency was enhanced by the high concentration of the 4-VAn polymer from the initial graft copolymerization. The aniline-4-VAn copolymer-modified PTFE films were subjected to deprotonation to reveal the emeraldine base structure on the PTFE surface. The deprotonated surfaces, however, were readily susceptible to reprotonation by acids to become semiconductive. The surface resistance was reduced from 10^{15} Ω/□ for the pristine PTFE film to the order of 10^{6} Ω/□ for the modified PTFE film with an overall graft concentration, or $[N]/[CF_2]$ ratio, of about 0.5. For a graft concentration of about 0.1, the surface resistance was greater than 5×10^{8} Ω/□.

References and Notes

(1) Clark, D. T.; Dilks, A.; Shuttleworth, D. In *Polymer Surfaces;* Clark, D. T., Feast, W. J., Eds; Wiley: New York, 1978; Chapter 9, p 185.

(2) Penn, L. S.; Wang, H. *Polym. Adv. Technol.* **1994**, *5*, 809.

(3) Uyama, Y.; Kato, K.; Ikada, Y. *Adv. Polym. Sci.* **1998**, *137*, 1.

(4) ACS Symposium Series 364; American Chemical Society: Washington, DC, 1988; p 168.

(5) Kang, E. T.; Neoh, K. G.; Tan, K. L.; Senn, B. C.; Pigram, P. J.; Liesegang, J. *Polym. Adv. Technol*. **1997**, *8*, 683.

(6) Kang, E. T.; Neoh, K. G.; Tan, K. L.; Uyama, Y.; Morikawa, N.; Ikada, Y. *Macromolecules* **1992**, *25*, 1959.

(7) Green, A. G.; Woodhead, A. E. *J. Chem. Soc. Trans.* **1910**, *97*, 2388.

(8) Green, A. G.; Woodhead, A. E. *J. Chem. Soc. Trans.* **1912**, *101*, 1117.

(9) Honzl, J.; Tlustakova, M. *J. Polym. Sci.* **1968**, *C22*, 451.

(10) Mohilner, D. M.; Adams, R. N.; Argersinger, W. J., Jr. *J. Am. Chem. Soc.* **1962,** *84*, 3618.

(11) Diaz, A. F.; Logan, J. A. *J. Electroanal. Chem.* **1980**, *111*, 111.

(12) Yang, C. Y.; Cao, Y.; Smith, P.; Heeger, A. J. *Synth. Met.* **1993**, *53*, 293.

(13) Joo, J.; Epstein, A. J. *Appl. Phys. Lett.* **1994**, *65*, 2278.

(14) Avlyanov, J. K.; Min, Y.; MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1995**, *72*, 65.

(15) MacDiarmid, A. G. *Synth. Met.* **1997**, *84*, 27.

(16) Barthet, C.; Armes, S. P.; Chehimi, M. M.; Bilem, C.; Omastova, M. *Langmuir* **1998**, *14*, 5032.

(17) Nakajima, T.; Kawogoe, T. *Synth. Met.* **1989**, *28*, c-629.

(18) Chao, S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 6627.

(19) Dhawan, S. K.; Trivedi, D. C. *Polym. Int. (*formerly *Br. Polym. J.)* **1992**, *25*, 55.

(20) Trivedi, D. C.; Dhawan, S. K. In *Polymer Science Contemporary Themes;* Sivaram, S., Ed.; Tata McGraw-Hill: New Delhi, 1991; Vol. II, p 746.

(21) Joo, J.; Wu, C. Y.; Benatar, A.; Faisst, C. F., Jr.; Zegarski, J.; MacDiarmid, A. G. In *Intrinsically Conducting Polymers: An Emerging Technology;* Aldissi, M., Ed.; Kluwer Press: Dordrecht, 1993; p 165.

(22) Schoch, K. F., Jr.; Byers, W. A.; Buckley, L. J. *Synth. Met.* **1995**, *72*, 13.

(23) Dogan, S.; Akbulut, U.; Yalcin, T.; Toppare, L. *Synth. Met.* **1992**, *53*, 29.

(24) Gregory, R. V.; Rimbrell, W. C.; Ruhn, H. H. *Synth. Met.* **1989**, *28*, C823.

(25) Trivedi, D. C.; Dhawan, S. K. *J. Mater. Chem*. **1992**, *2*, 1091.

(26) Colaneri, N. F.; Shacklette, L. W. *IEEE Trans. Instrum. Meas.* **1992**, *41*, 291.

(27) Joo, J.; Epstein, A. J. *Appl. Phys. Lett.* **1994**, *65*, 2278.

(28) Van Dyke, L. S.; Brumlik, C. J.; Liang, W.; Lei, J.; Martin, C. R.; Yu, Z.; Li, L.; Collins, G. J. *Synth. Met.* **1994**, *62*, 75.

(29) Pun, M. Y.; Neoh, K. G.; Kang, E. T.; Loh, F. C.; Tan, K. L. *J. Appl. Polym. Sci*. **1995**, *56*, 355.

(30) Suzuki, M.; Kishida, A.; Iwata, H.; Ikada, Y. *Macromolecules* **1986**, *19*, 1804.

(31) Kang, E. T.; Neoh, K. G.; Tan, K. L. *Surf. Interface Anal.* **1993**, *20*, 833.

(32) Kang, E. T.; Neoh, K. G.; Tan, K. L. *Adv. Polym. Sci*. **1993**, *106*, 135.

(33) Kang, E. T.; Neoh, K. G.; Woo, Y. L.; Tan, K. L.; Huan, C. H. A.; Wee, A. T. S. *Synth. Met*. **1993**, *53*, 333.

(34) Wu, S. Y.; Kang, E. T.; Neoh. K. G.; Tan, K. L. *Macromolecules* **1999**, *32*, 186.

(35) Badey, J. P.; Espuche, E. U.; Jaghet, Y.; Sage, D.; Duc, T. M.; Chabert, B. *Polymer* **1994**, *35*, 2472.

(36) Da, Y. X.; Griesser, H. J.; Mau, A. W. H.; Schmidt, R.; Liesegang, J. *Polymer* **1991**, *32*, 1126.

(37) Momose, Y.; Tamura, Y.; Tamura, M.; Okazaki, S. Hirayama, M. *J. Vac. Sci. Technol*. **1992**, *A10*, 229.

(38) Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. D. *Handbook of X-ray Photoelectron Spectroscopy;* Chastain, J., Ed.; Perkin-Elmer Corporation: Eden Prairie, MN, 1992; p 43.

(39) Kang, E. T.; Neoh, K. G.; Tan, K. L. *Prog. Polym. Sci.* **1997**, *23*, 277.

(40) Neoh, K. G.; Kang, E. T.; Tan, K. L. *J. Polym. Sci., Part B: Polym. Phys.* **1995**, *33*, 833.

(41) *Goodfellow Catalogue* (Metals, Alloys, Compounds, Ceramics, Polymers, Composites); Goodfellow, Ltd.: Cambridge, U.K., 1996/97; p 447.

(42) Tan, K. L.; Woon, L. L.; Wong, H. K.; Kang, E. T.; Neoh, K. G. *Macromolecules* **1993**, *29*, 2832.

(43) Gospodinova, N.; Terlemezyan, L. *Prog. Polym. Sci.* **1998**, *23*, 1443.

(44) Kang, E. T.; Tan, K. L.; Kato, K.; Uyama, Y.; Ikada, Y. *Macromolecules* **1996**, *29*, 6872,

MA990646F