Surface Modifications of Poly(3-alkylthiophene) Films by Graft Copolymerization

E. T. Kang* and K. G. Neoh

Department of Chemical Engineering, National University of Singapore, Kent Ridge, Singapore 0511

K. L. Tan

Department of Physics, National University of Singapore, Kent Ridge, Singapore 0511

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ABSTRACT: Films of alkyl-substituted polythiophenes (PTH), such as poly(3-hexylthiophene) (P6TH), poly(3-octylthiophene) (P8TH) and poly(3-dodecylthiophene) (P12TH) are susceptible to near-UV light induced graft copolymerization with acrylamide (AAm), acrylic acid (AAc), and the Na salt of styrenesulfonic acid (NaSS). In each case, the graft density is substantially enhanced if the PTH film has been pretreated with O_3. Angle-dependent X-ray photoelectron spectroscopy (XPS) core-level spectra and surface water contact angle measurements reveal that for P8TH and P12TH films, but not the P6TH film, the grafted AAm and AAc polymers become submerged completely below the film surface to give rise to a hydrophobic surface and a hydrophilic interface. For aliphatic graft with a bulky substituent, such as NaSS, only partial penetration of the graft below the PTH surface was observed. The phenomena have been explained in terms of polymer chain mobility, substrate permeability and steric effect of the graft. Comparison is made with the similarly grafted polyaniline film, in which an abundance of graft has been found only at the film surface.

Introduction

During the past one and a half decades, the synthesis and characterization of electroactive polymers have quickly become one of the most important research areas in polymer science.[1] The thiophene polymers, in particular, the alkyl-substituted polythiophenes (PTH), are among some of the most studied conducting polymers today.[2-8] PTH and its alkyl-substituted derivatives are unique in their stability in the reduced and oxidized states.[9,10] Furthermore, the alkyl-substituted PTH also exhibits a high degree of processibility,[2,3] and in some cases, interesting reversible thermochromism[11] and electrochromism.[12] The fact that the electrical properties of the thiophene polymers can be critically controlled by oxidation and reduction, as well as by the type of anions incorporated, suggests that they can be used as active materials for electrodes and sensors. In view of these applications, material modifications, in particular surface modifications and functionalization, will be necessary. For conventional polymers, surface modifications with biocompatible materials for biochemical and biomedical applications have been well reported.[13,14] It has also been demonstrated that surface modifications can be performed through, for example, graft copolymerization under mild conditions for a number of conventional polymers, such as polyethylene, poly(ethylene terephthalate), silicone polymers, Nylons, polypropylene, etc., when their surfaces are pretreated with high-energy radiation, plasma, corona discharge, ozone exposure, or ultraviolet (UV) irradiation.[15-18] Furthermore, protein and enzyme immobilizations on the surface-modified polymer substrates have also been of recent interest.[19,20]

As electroactive polymer substrates may provide an added advantage over conventional polymer substrates, it should be interesting to study the surface-modified and functionalized electroactive polymers. We reported recently on the surface modifications of polyaniline film by graft copolymerization.[21] This study is devoted to the investigation of the surface modifications of films of some chemically synthesized poly(3-alkylthiophene)s, such as poly(3-hexylthiophene) (P6TH), poly(3-octylthiophene) (P8TH), and poly(3-dodecylthiophene) (P12TH), by graft copolymerization with acrylamide (AAm), acrylic acid (AAc), and the sodium salt of 4-styrenesulfonic acid (NaSS). Grafting of these water-soluble polymers is expected to improve the hydrophilicity of the thiophene polymers and to provide appropriate functional groups for the subsequent immobilization of proteins and enzymes via covalent bonding. The grafted thiophene polymer surfaces and interfaces were characterized using X-ray photoelectron spectroscopy (XPS) as a primary tool.

Experimental Section

Synthesis of Poly(3-alkylthiophene)s. The 3-alkylthiophene monomers used in the present study, viz. 3-hexylthiophene, 3-octylthiophene, and 3-dodecylthiophene, were obtained from Aldrich Chemical Co. and were used without further purification. The 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.[22] An oxidant to monomer ratio of 3:1 was used in all cases. Thus, 0.06 mol of 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 of dry chloroform. About 0.02 mol of the thiophene monomer was then added dropwise into the oxidant solution with stirring. The reaction mixture was subsequently 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. Since the thiophene polymers so prepared were partially "doped" by $FeCl_3$, they were further purified by Soxhlet extraction and reprecipitation to remove the dopant. Typical bulk compositions, obtained from the chemical microanalysis, for the three alkylthiophene polymers were $C_{10.2}H_{14.2}S_{1.0}$ for P6TH, $C_{12.5}H_{19.0}S_{1.0}$ for P8TH, and $C_{16.4}H_{27.0}S_{1.0}$ for P12TH. For all the samples prepared, a trace amount (<1 mol %) of Fe was also detected. The presence of the latter was also reported by Hotta et al.[22] All three alkyl-substituted thiophene polymers are readily soluble in chloroform and can be cast into free-standing, dark-red films from, for example, a 10^{-2} M chloroform solution.

Pretreatment of Substituted Polythiophene Films. Both pristine and O_3-pretreated poly(3-alkylthiophene) films were used

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in the grafting experiment. Ozone was generated with an ozonizer (Fischer, Model 500) at 100 V by allowing oxygen to enter the ozoniser at a flow rate of 100 L·h^{-1}. The mixture of the ozone generated and the oxygen was introduced into a U-shaped glass cell containing the polymer film. The exposure time was varied from 5 to 90 s.

Graft Copolymerization. All the O$_3$-pretreated polythiophene films were subjected to graft copolymerization immediately. The monomers used for grafting were acrylamide (AAm), acrylic acid (AAc), and the Na salt of 4-styrenesulfonic acid (NaSS). Poly(3-alkylthiophene) 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 polymer film was immersed in an aqueous solution of 20 mL of 10 wt % AAm and 5 mL of 0.05 mM riboflavin in a Pyrex tube. The latter is transparent to near-UV light of wavelength greater than 300 nm. The dissolved oxygen, which could inhibit the radical polymerization, is consumed by the photoreaction with riboflavin.[16,23] The test tube was purged with N$_2$ and sealed with a silicone rubber stopper. The reaction mixture was then exposed to near-UV light at room temperature (~25–28 °C) for 30 min. The light source was provided by a 150-W Xe arc lamp (Kratos Model LH151). The NaSS polymer was similarly grafted, except a 0.5 M aqueous NaSS solution was used instead. The AAc monomer was purified by vacuum distillation. In this case, the polythiophene film was immersed in 20 mL of 5% aqueous AAc solution in a Pyrex tube. The reaction mixture was thoroughly degassed on a vacuum line and sealed off under a nitrogen atmosphere. It was then subjected to near-UV irradiation for about 30 min, as in the case of AAm and NaSS grafting. After each grafting experiment, the poly(3-alkylthiophene) 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.

Material Characterization after Grafting. The polymer films after graft copolymerization were characterized by contact angle measurements, scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS). Static water contact angles were measured by the sessile drop method, using a 3-μL water droplet 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. For each film, at least three measurements on different surface locations were averaged. SEM images were obtained from a JEOL JSM-T330A scanning electron microscope. XPS measurements were made on a VG ESCALAB MkII spectrometer with a Mg Kα X-ray source (1253.6-eV photons). The X-ray source was run at a reduced power of 120 W (12 kV and 10 mA). The polymer films were mounted on the standard VG sample studs by means of double-sided adhesive tape. The core-level spectra were obtained at a number of takeoff angles (with respect to the film surface), ranging from 20 to 75°. The pressure in the analysis chamber was maintained at 10^{-8} mbar or lower during the measurements. To compensate for surface charging effects, all binding energies were referenced to the C1s neutral carbon peak at 284.6 eV. In spectral deconvolution, the line width (full width at half maximum) of Gaussian peaks was maintained constant for all components in a particular spectrum. Surface elemental stoichiometries were obtained from peak area ratios, corrected with the experimentally determined sensitivity factors, and is liable to not more than ±5% error. Bulk elemental analyses were carried out on a Perkin-Elmer 2400 elemental analyzer.

Results and Discussion

Parts a and b of Figure 1 show the respective C1s and S2p core-level spectra, obtained at a takeoff angle of 75°, for a pristine poly(3-dodecylthiophene) (P12TH) film. The C1s core-level spectrum is dominated by a peak component with a binding energy (BE) at about 284.6 eV, arising from the 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 O1s core-level signal.

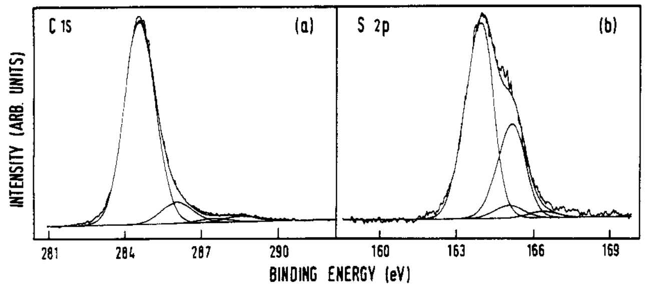

Figure 1. (a) C1s and (b) S2p core-level spectra of a pristine P12TH film (XPS takeoff angle = 75°).

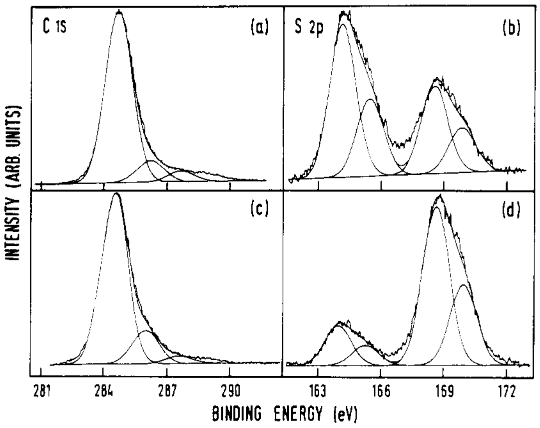

Figure 2. C1s and S2p core-level spectra of a (a,b) 10-s and a (c,d) 90-s O$_3$-treated P12TH film (XPS takeoff angle = 75°).

The S2p core-level spectrum is resolved into a major and minor spin–orbit-split doublet (S2p$_{3/2}$ and S2p$_{1/2}$), with the BE for the respective S2p$_{3/2}$ peaks lying at about 163.9 and 165.2 eV. The former is attributable to the neutral thiophene units.[24,25] The latter is probably associated with a trace amount of surface oxidized thiophene units.[26] C1s and S2p core-level spectra of similar line shape and BE's are also observed for the poly(3-hexylthiophene) (P6TH) and poly(3-octylthiophene) (P8TH) films.

Treatment of the alkyl-substituted polythiophene (PTH) with a mixture of oxygen and ozone causes only a minor enhancement of the C1s high-BE tail. However, a prominent new S2p component at about 168.5 eV, which is chemically shifted by about +4.6 eV from that of neutral thiophene unit, has appeared as a result of O$_3$ treatment. This high-BE component is associated with the formation of oxidized sulfur, such as the sulfone or peroxide species.[27] It is enhanced upon increasing the O$_3$ treatment time. Parts a–d of Figure 2 compare the respective C1s and S2p core-level spectra, obtained at a takeoff angle of 75°, for two P12TH films with different degrees of O$_3$ exposure (10 s vs 90 s). Similar changes in the C1s and S2p core-level spectra are also observed for the P6TH and P8TH films upon treatment with O$_3$. In all cases, the proportion of the high-BE S2p component does not vary appreciably with the electron takeoff angles between 75 and 20°, indicating that O$_3$ has penetrated substantially and uniformly into the polymer film. The oxidized sulfur species in each case is consumed or reduced in the subsequent near-UV light induced graft copolymerization in aqueous medium (see below). The ease in the reduction of sulfone and sulfoxide species in the thiophene polymers has been reported.[28] In fact, for the present O$_3$-treated PTH films, illumination of the films in an aqueous medium with near-UV light readily results in the loss of the oxidized sulfur species.

Ozone treatment also results in an increase in the surface hydrophilicity of three alkyl-substituted PTH. Figure 3

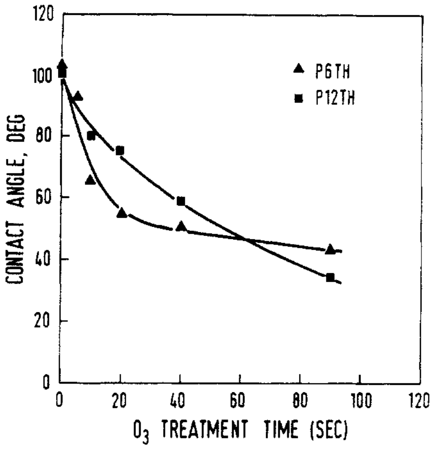

Figure 3. Changes in water contact angles for the alkyl-substitued PTH films as a function of O_3 treatment time.

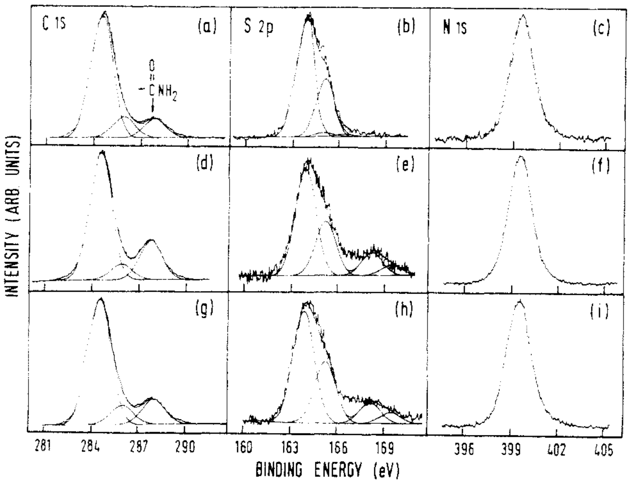

Figure 4. C1s, S2p, and N1s core-level spectra for (a–c) a pristine P12TH film, (d–f) a 5-s O_3-pretreated P12TH film, and (g–i) a 40-s O_3-pretreated film after having been subjected to graft copolymerization in 8% AAm solution (XPS takeoff angle = 75°).

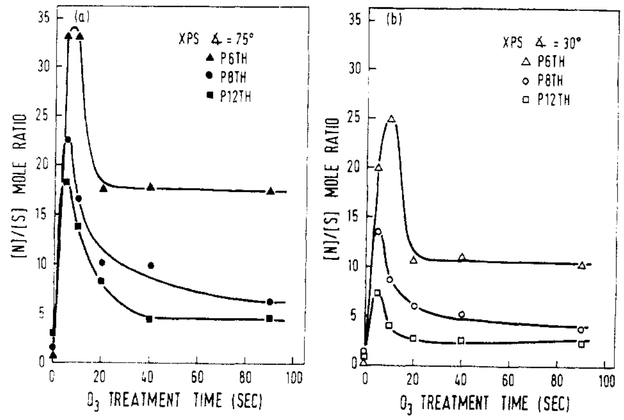

Figure 5. Densities of grafted AAm polymer derived from XPS core-level signal intensities obtained at takeoff angles of (a) 75° and (b) 30° as a function of O_3 treatment time.

shows the decrease in the water contact angles for P6TH and P12TH films upon increasing O_3 exposure. The behavior of P8TH film upon increasing O_3 exposure is intermediate between those of P6TH and P12TH. This increase in surface hydrophilicity is consistent with the formation of polar functional groups upon oxidation by O_3.

Parts a–c of Figure 4 show the respective C1s, S2p, and N1s core-level spectra, obtained at a takeoff angle of 75°, for a pristine P12TH film after having been subjected to near-UV light induced graft copolymerization in 8% acrylamide (AAm) solution. Parts d–i of Figure 4 show the corresponding C1s, S2p, and N1s core-level spectra for two similarly grafted P12TH films, except the films have been pretreated with O_3 for 5 and 40 s, respectively. The presence of surface-grafted AAm polymer in each case is readily suggested by the appearance of a C1s high-BE component at about 287.9 eV, attributable to the carbonyl group of the AAm polymer.[29] It is also indicated by the appearance of the N1s core-level signal at about 399.4 eV due to contribution from the nitrogen of the $-NH_2$ group in the AAm polymer. In the case of O_3-pretreated films, the S2p core-level spectrum suggests that the high-BE component at about 168.5 eV, attributable to the oxidized sulfur species arising from O_3 treatment, has been reduced almost completely during the near-UV light induced graft copolymerization. Similar C1s, S2p, and N1s core-level spectra are also obtained for the pristine and O_3-pretreated P6TH and P8TH films when subjected to graft copolymerization with AAm polymer under similar conditions.

The density of grafting at the surface, represented as the [N]/[S] mole ratio in each case, can be estimated from the sensitivity factors corrected N1s and S2p core-level spectral area ratios. These ratios in the surface region for the three alkyl-substituted thiophene polymers as a function of O_3 pretreatment time are summarized in Figure 5a, based on the core-level signals obtained at a takeoff angle of 75°. Thus, the density of grafting in each polymer is substantially enhanced by the O_3 pretreatment. The increase in the density of grafting upon exposure to O_3 is consistent with a peroxide-initiated polymerization mechanism generally proposed for the near-UV light induced graft copolymerization.[15] The fact that grafting occurs to some extent even in the pristine or untreated PTH films is consistent with the reactive nature of the conjugated polymer surfaces. This reactive nature is apparent from the constant presence of adsorbed or weakly charge-transfer complexed oxygen species on most of the conjugated polymer surfaces. If the core-level signals were obtained closer to the outermost surface, for example at a takeoff angle of 30°, the density of grafting or the [N]/[S] mole ratio for each sample falls substantially below the corresponding ratio obtained at a takeoff angle of 75°. Figure 5b shows the corresponding density of grafting, as determined from the N1s and S2p core-level signals obtained at a reduced takeoff angle of 30°. These results readily indicate that the grafted AAm polymer has submerged below the film surface. Alternatively, the PTH chains have migrated to the outermost surface after grafting of the AAm polymer.

A similar XPS angle-dependent phenomenon is also observed when the three alkyl-substituted thiophene polymers with varying degrees of O_3 pretreatment are subjected to near-UV light induced graft copolymerization with acrylic acid (AAc) and the Na salt of styrenesulfonic acid (NaSS) polymers. The results are summarized in Figures 6 and Figure 7, respectively. As in the case of grafting with the AAm polymer, the copolymer compositions in the surface region suggest that the grafted AAc and NaSS polymers have submerged or partially submerged below the film surface. In the case of grafting with the AAc polymer, the presence of the grafted AAc units is readily indicated by the appearance of a high-BE C1s component at about 288.7 eV, which is associated with the $-COOH$ group of the grafted AAc polymer.[29] Thus, the densities of grafting in the surface region are determined directly from the [COOH/[S] mole ratios. In the case of grafting with the NaSS polymer, the presence of

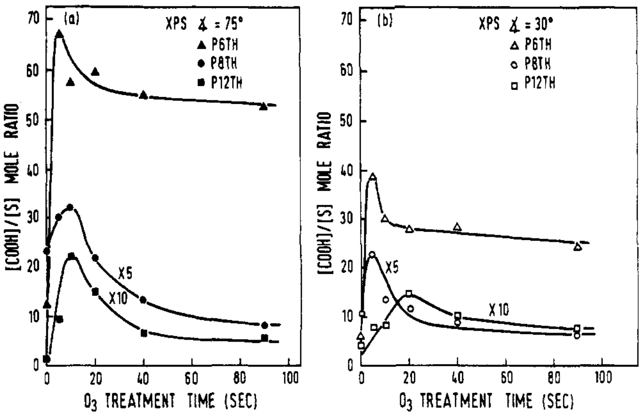

Figure 6. Densities of grafted AAc polymer derived from XPS core-level signal intensities obtained at takeoff angles of (a) 75° and (b) 30° as a function of O_3 treatment time.

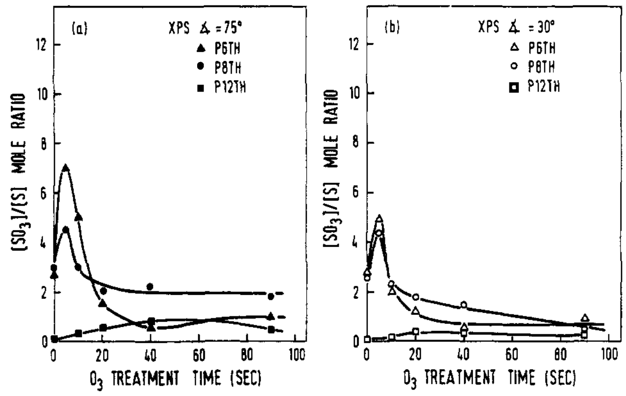

Figure 7. Densities of grafted NaSS polymer derived from XPS core-level signal intensities obtained at take-off angles of (a) 75° and (b) 30° as a function of O_3 treatment time.

grafted NaSS units is indicated by the presence of a distinct high-BE component in the S2p core-level spectrum at about 167.8 eV, characteristic of the covalently bonded sulfonic acid group ($-SO_3^-$) of the NaSS polymer.[25] The density of grafting is thus determined from the S2p spectral component ratio of each copolymer at about 167.8 and 163.9 eV, or the $[SO_3^-]/[S]$ ratio. Parts a–f of Figure 8 show the respective C1s and S2p core-level spectra, obtained at a takeoff angle of 30°, for a pristine, a 5- and 40-s O_3-pretreated P6TH film after having been subjected to near-UV light induced graft copolymerization with the NaSS polymer.

Figures 5–7 indicate that for the graft copolymerization with the three hydrophilic polymers, the density of grafting at the surface region of the PTH film decreases with increasing length of the alkyl substituent. Taking into account also of the fact that in the surface region of each PTH film, significantly higher density of grafting is observed below the film surface (compare core-level signal intensities at the takeoff angles 75 and 30°), the migration of the hydrophilic polymer below the film surface must have been facilitated by the increasing size of the alkyl substituent, which would result in a less efficient packing of the PTH chains. Furthermore, polymer molecules could migrate together with the graft layer at temperatures higher than the glass transition temperature (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.[30] for poly(dimethylsiloxane), poly(ester urethane), and polystyrene grafted with 2-hydroxyethyl methacrylate, AAm, and ethyl methacrylate polymers. For AAm-grafted silicone polymer, the penetration of the hydrophilic graft occurred to such an extent that the graft was found only at a depth of ~500 Å 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.[31] The fact that the present alkyl-substituted thiophene polymers have T_g's around or below room temperature,[22] as is also evidenced from the elastic nature of the films at room temperature, will greatly reduce the stability of the graft–substrate interface due to PTH chain mobility. The permeation of O_3 into the polymer film and the oxidation of thiophene units will result in the further increase in PTH chain mobility, as well as an increase in the permeability of the polymer film. As a result, the proportion of thiophene units in the surface region after grafting increases with increasing O_3 exposure, although the actual amount of graft, based on the approximate sample weight gain after grafting, at long O_3 exposure time is comparable to that at short O_3 exposure time which gives rise to maximum surface graft concentration.

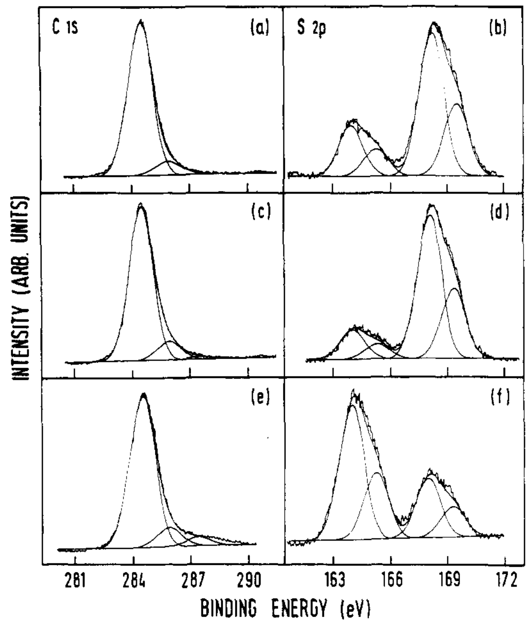

Figure 8. C1s and S2p core-level spectra for (a,b) a pristine P6TH film, (c,d) a 5-s O_3-pretreated P6TH film, and (e,f) a 40-s O_3-pretreated P6TH film after having been subjected to graft copolymerization in 0.5 M NaSS solution (XPS takeoff angle = 30°).

The estimated escape distance of only 40–50 Å for photoelectrons in an organic matrix at the maximum takeoff angle suggests that the overall density of grafting for the present PTH polymers cannot be determined solely from the XPS technique. Nevertheless, a knowledge of the copolymer compositions at the surface and interface is essential in elucidating the physicochemical properties of the PTH film surface. On the basis of the angle-dependent XPS results, the graft structure or morphology at the film surface could be equally well described by the two models shown in Figure 9. Both the complete penetration of the graft below the thiophene polymer surface (model a) and the partial penetration with clustering together of some of the graft on the surface after the sample has been dehydrated (model b) can account for the decreasing graft signal toward the outermost surface. To distinguish between these two models, the water contact angle of each graft surface was determined, as water contact angle depends only on the nature of the outermost polymer surface. Pristine P6TH, P8TH, and P12TH films are hydrophobic, with the surface water

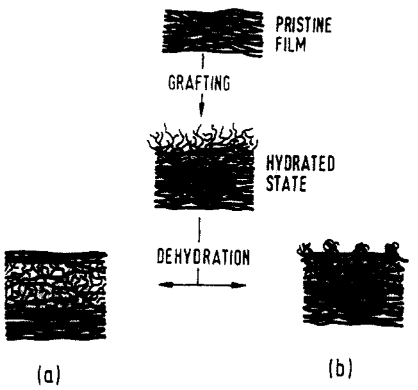

Figure 9. Schematic representation of plausible graft structures: (a) complete penetration model; (b) partial penetration model.

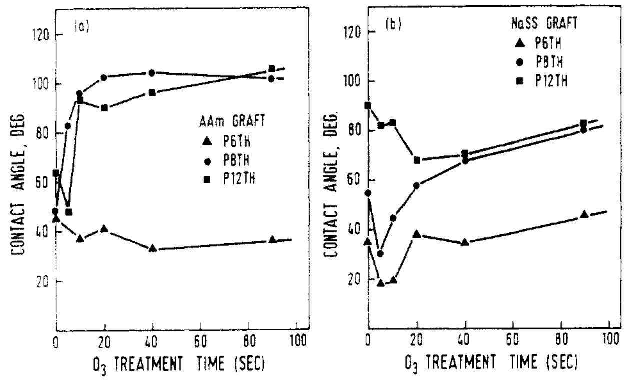

Figure 10. Surface water contact angles of the O_3-pretreated P6TH, P8TH, and P12TH films after graft copolymerization with (a) AAm polymer and (b) NaSS polymer as a function of O_3 treatment time.

contact angles falling in the range of 95–105°. Figure 10a summarizes the surface water contact angles of various O_3-pretreated PTH films after graft copolymerization with the AAm polymer. Thus, for films without prior O_3 treatment, the substantially reduced water contact angle after grafting for all three thiophene polymers readily suggests that a significant amount of the AAm graft must have remained on the top surface. On the other hand, in spite of the presence of large amounts of AAm graft, the water contact angles for the O_3-pretreated P8TH and P12TH films after grafting are comparable to those of the pristine (ungrafted) PTH films, while the grafted P6TH surfaces are fairly hydrophilic. Thus, complete penetration of the AAm graft (model a) must have occurred in the case of O_3-pretreated P8TH and P12TH films, while model b seems to be more appropriate for the O_3-pretreated P6TH films. This is consistent with the argument that the shorter alkyl substituent must have given rise to less interruption of the thiophene polymer matrix. As a consequence, the intermigration of the thiophene and AAm polymer chains is somewhat reduced.

Similar changes in the surface water contact angle as those shown in Figure 10a were observed for the three thiophene polymers upon graft copolymerization with the AAc polymer. However, for the aliphatic graft with bulky substituent, such as the NaSS polymer, the migration or penetration of the graft must be somewhat sterically hindered. As a result, the water contact angles for the NaSS graft copolymerized films, either with or without O_3 pretreatment, all fall substantially below those of the pristine films. The results are summarized in Figure 10b. Thus, the NaSS polymer must have only partially withdrawn below the thiophene polymer surface and model b seems to be more appropriate for describing the graft structure in this case.

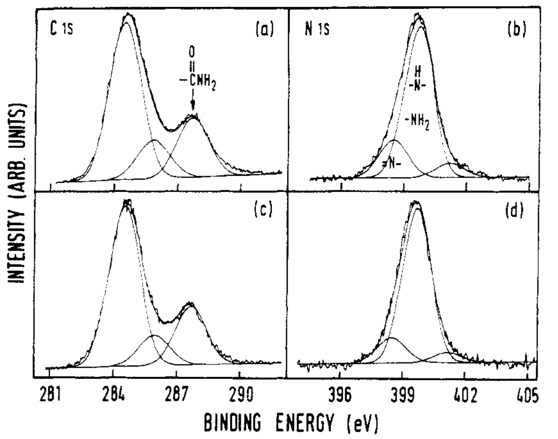

Figure 11. C1s and N1s core-level spectra acquired at takeoff angles of (a,b) 75° and (c,d) 20° for an AAm polymer grafted polyaniline film with 40 s of O_3 pretreatment.

Finally, it may be appropriate to point out that although the polymer graft can become buried or partially buried below the thiophene polymer surface in the dehydrated state, the grafted film can be readily rehydrated, with the hydrophilic nature of the surface restored, after prolonged soaking in an aqueous medium.

The tendency for the hydrophilic graft to become submerged below the PTH film surface differs from that observed in other electroactive polymers containing aromatic rings and heteroatoms in the backbone. Parts a–d of Figure 11 show the respective C1s and N1s core-level spectra, obtained at takeoff angles of 75 and 20°, for a 40-s O_3-pretreated polyaniline film (in its emeraldine oxidation state) after near-UV light induced graft copolymerization with the AAm polymer. Earlier studies[32-34] have demonstrated that the quinonoid imine (=N–structure), benzenoid amine (-NH- structure), and positively charged nitrogens of polyaniline of any intrinsic oxidation state and protonation level are discernible in the properly curve-fitted N1s core-level spectrum. They correspond to N1s peaks components with BE's at about 398.2, 399.4, and >400 eV. In the case of the present sample, the presence of grafting is readily indicated either by the appearance of a substantially enhanced C1s high-BE component at about 287.8 eV or by a substantial increase in the intensity of the N1s core-level component at about 399.4 eV. The former is attributable to the C=O group, and the latter to the $-NH_2$ group of the AAm graft. AAm homopolymer shows only a single N1s component at about 399.4 eV. This BE coincides with that of the amine nitrogens of polyaniline. Nevertheless, the angle-dependent C1s core-level signals indicate that a slightly larger amount of AAm graft is obtained at the top surface of the polyaniline film. This result is in sharp contrast to that observed in the grafted thiophene polymers.

The conclusion that graft copolymerization with the AAm polymer occurs mainly at the surface region in the case of polyaniline film and below the surface in the case of the alkyl-substituted PTH films is further supported by the morphology of the grafted film surface. Parts a and b of Figure 12 compare the scanning electron microscopic (SEM) images of a 40-s O_3-pretreated polyaniline film and a similarly treated P6TH film after grafting with the AAm polymer. The densities of grafting, as determined from the XPS results at a takeoff angle of 75° and expressed as the [AAm]/[monomer] mole ratios,[35] for the two films are about 4.0 and 17.5, respectively. The fact that grafting occurs predominantly at the top surface

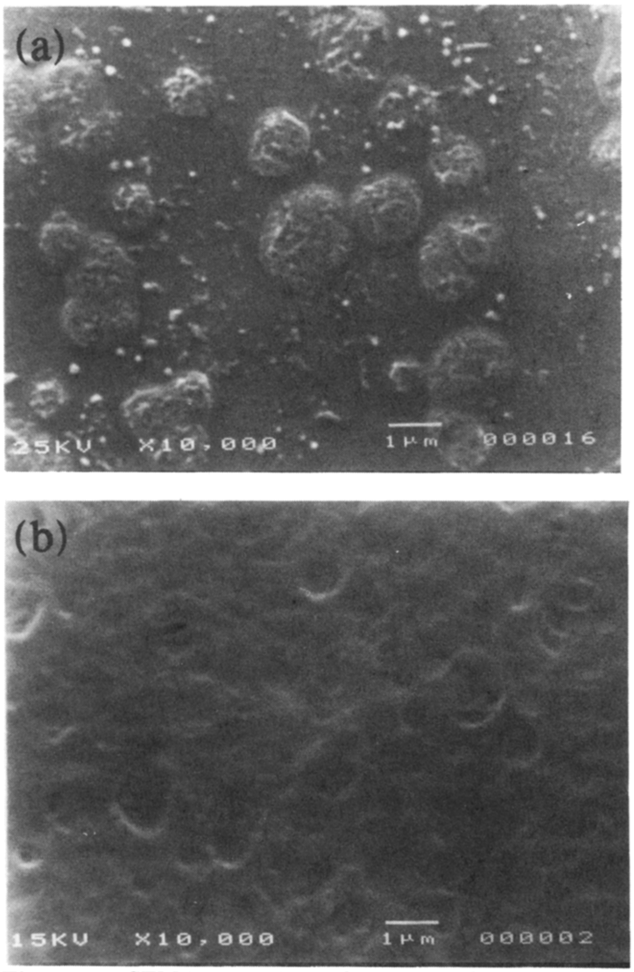

Figure 12. SEM images of 40-s O_3-pretreated (a) polyaniline and (b) P6TH films after graft copolymerization with the AAm polymer.

of the polyaniline film has also resulted in the formation of AAm polymer clusters of submicron size on the film to give rise to a very hydrophilic surface (contact angle as low as 12°). This phenomenon, however, is not observed in the case of grafted PTH film. The outermost surface of the grafted thiophene polymer film remains rather featureless, in spite of the presence of a substantially higher density of grafting in this film. Similar SEM images were observed for other grafted PTH films shown in Figures 5–7.

Finally, Figure 12 also reveals that O_3 pretreatment has resulted in the blister formation on the polyaniline film surface, but not on the PTH film surface. This phenomenon is attributable, at least in part, to the relatively low T_g's for the alkyl-substituted thiophene polymers and to the relative ease with which the polar groups can migrate below the PTH film surface. In our previous study[21] on the argon plasma pretreated polyaniline film, we did not observe any blister formation. The role of the blisters in the O_3-pretreated polyaniline surface during graft copolymerization is readily revealed in the SEM images of samples subjected to less vigorous washing conditions. The O_3-activated materials comprising the blisters serve as sites for a concentrated surface graft, which, however, is easily stripped off during the subsequent washing process due to the lack of structural integrity. For O_3-treated polyaniline films, angular dependent C1s XPS spectra do not reveal a sharp increase in the intensity of the high-BE tail, attributable to the peroxide and oxidized carbon species, as the takeoff angle is decreased. This result gives further confirmation to a blistering morphology. Similar XPS studies have been used by Thomas and O'Malley[36] and Clark et al.[37] to resolve the morphology of different domains on copolymer surfaces.

Conclusion

The angle-dependent XPS technique has been used to study the surface composition and structure of pristine and O_3-pretreated films of some poly(3-alkylthiophene)s after graft copolymerization with hydrophilic polymers, such as the AAm, AAc, and NaSS polymers. With the help of water contact angle measurements, and by taking into account the polymer chain mobility, substrate permeability, and steric effect of the graft, graft copolymerization of P8TH and P12TH, but not P6TH, with AAm and AAc polymer is best described by a complete penetration model of the graft. On the other hand, a partial penetration model better describes the grafting of NaSS polymer on the three thiophene polymer substrates and the grafting of AAm and AAc polymer on P6TH film. The results are briefly compared with those of surface-grafted polyaniline film.

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References and Notes

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(35) Note: Since 1 mol of AAm has 1 mol of carbon from the NH_2—C=O group, and 2 mol 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 C1s core-level spectrum as follows:

$$\frac{[\mathrm{AAm}]}{[\mathrm{aniline}]} = \frac{\text{C1s area of } \mathrm{NH_2{-}C{=}O}}{[\text{total C1s area} - (\text{C1s area of } \mathrm{NH_2{-}C{=}O}) \times 3]/6}$$

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Registry No. P6TH, 104934-50-1; P12TH, 104934-53-4; (P6TH)(AAm) (graft copolymer), 143969-77-1; (P8TH)(AAm) (graft copolymer), 143969-78-2; (P12TH)(AAm) (graft copolymer), 143969-79-3; (P6TH)(AAc) (graft copolymer), 143969-80-6; (P8TH)(AAc) (graft copolymer), 143969-81-7; (P12TH)(AAc) (graft copolymer), 143969-82-8; (P6TH)(NaSS) (graft copolymer), 143969-83-9; (P8TH)(NaSS) (graft copolymer), 143969-84-0; (P12TH)(NaSS) (graft copolymer), 143969-85-1; O_3, 10028-15-6; water, 7732-18-5.