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Spectroscopic, Microscopic, and Surface Analysis of Alkanethiol- and Fluoroalkanethiol-Modified Conducting Polymer Thin Films

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ABSTRACT: Electrochemically grown films of polyaniline, polypyrrole, polythiophene, and poly(ethylenedioxythiophene) were treated with alkane- and fluoroalkanethiols for 1−24 h. The resulting films showed surface energies and polarities similar to glass slides coated with monolayers of the corresponding alkyl- and fluoroalkylsilanes. Treatment of the polyaniline, polypyrrole, and, to a lesser extent, poly(ethylenedioxythiophene) films resulted in covalent bonding of the thiol to the polymer backbone as evidenced by X-ray photoelectron, energy-dispersive X-ray, and electronic spectroscopies. Polypyrrole and poly(ethylenedioxythiophene) films showed reduced electroactivity upon treatment, while the derivatized polyaniline could be returned to a conducting state. Polythiophene primarily oxidized the thiols to soluble products, leaving the polymer backbone unaffected.

Introduction

Common electronically conducting polymers, such as polypyrrole, polythiophene, and polyaniline, have been investigated for use as sensors, electrocatalysts, and components for other molecular devices. The functionality of these materials, however, can be greatly extended by the incorporation of other moieties into the polymer matrix.[1] Additives that have been recently investigated include metal complexes, various organic species, enzymes, and antibodies. While efforts to produce conducting polymer/functional molecular hybrids have met with varying degrees of success, it is clear that this is a promising synthetic strategy.

There are several strategies for immobilizing molecular components into or onto conducting polymer films. Perhaps the simplest of these is to perform the polymerization from solutions containing both the monomer and the additive of interest. This approach has been realized for both neutral and ionic species. For example, glucose sensors have been prepared by the electropolymerization of pyrrole in solutions containing glucose oxidase.[2] The resulting composites are structurally sound but are not satisfactory sensors. To act catalytically, the encapsulated enzyme requires an electron mediator. The mediator may simply be dissolved in the solution to be analyzed, but there are advantages to incorporating it into the polymer matrix along with the enzyme. Since the growing polycationionic film requires counterions, an effective approach has been to use hydroquinonesulfonate ions to serve as both a counterion and an electron mediator. Similarly, functional counterions ions have been used in other systems to enhance polymer solubility,[3] to induce chirality,[4] or to act as sensing elements.[5]

The entrapment approach, while easy to implement, has limitations. The additive must be compatible with the polymerization reaction, neither interfering with the reaction nor being degraded by it. The same holds for any postpolymerization processing. Long-term stability in a composite is also an issue, since the molecular components may diffuse from the matrix or (in the case of ions) be expelled during an oxidation/reduction cycle.

Another strategy is to chemically modify the monomer itself. For example, the attachment of metal centers to the heterocycle, either directly[6] or by way of insulating tethers,[7] has been examined by several investigators. Likewise, some very clever chemistry has gone into attaching specific binding groups such as crown ethers or calixarenes to the polymer backbones.[1] In some cases, the added group directly affects the redox properties or the conjugation of the polymer backbone, while in others, the pendant group behaves as if it were an independent system. In these materials, diffusion of the additive from the bulk polymer is not an issue, but there remains the possibility that the substituent could interfere with the polymerization reaction or degrade the physical properties of the polymer. In addition, the synthetic routes required to create many of these elaborate materials greatly increase the cost of device fabrication.

Problems in the polymerization reaction or in polymer processing can be avoided if the polymer is derivatized after these steps are completed. For example, monomers have been prepared with reactive sites for postpolymerization derivatization.[8] This strategy permits the polymerization of relatively inexpensive, highly reactive monomers with substituents that are compatible with polymerization conditions. A related approach is to generate reactive sites on polymer surfaces by UV irradiation or glow discharges.[9] A potential limitation of these methods is that subsequent coupling of a functional moiety requires migration of that group to the reactive sites on the polymer. In some cases, this might limit loading levels, since diffusion deep into the bulk polymer may be slow. Accounting for this will be an important design consideration for practical applications of the technology.

There are indications, however, that neither monomer alteration nor high-energy processes are required to modify conjugated polyheterocycles, since they potentially contain “built-in” reactive sites. It has long been known that exposure of polypyrrole to ammonia and water vapor leads to a loss in electrical conductivity. While not completely understood, there appear to be both reversible and irreversible processes involved in this phenomenon. Importantly, the irreversible reaction displays characteristic changes in the electronic spectra that indicates a decrease in the conjugation of the

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polymer.[10] More recently, Tarcha has reported that antibodies “absorbed” to the surface of polypyrrole colloids adhere more strongly than can be explained by electrostatic arguments.[11] Finally, we have shown that treatment of polyaniline films with 4-alkyl- or 4-perfluoroanilines leads to irreversible changes in the surface energies.[12] These observations suggest that the polycationic backbone of the polymer itself offers a site for elaboration, presumably through a nucleophilic addition reaction.

Here we demonstrate a simple, yet highly efficient, method for derivatizing the surfaces (and, to a varying extent, the bulk) of polyaniline, polypyrrole, polythiophene, and poly(ethylenedioxythiophene) films with thiols. This strategy offers an important alternative for the synthesis of electroactive polymer-based devices.

Experimental Section

Materials. Aniline, pyrrole, bithiophene, dodecanethiol (DDT), 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyltrichlorosilane (TDFSi), dodecyltrichlorosilane (DDSi), thiourea, and tetrabutylammonium tetrafluoroborate were purchased from Aldrich and used as received. Ethylenedioxythiophene was purchase from Baeyer and distilled from calcium hydride before use. 3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctanethiol (TDFT) was prepared by a modification of the method of Rondestvedt.[13] Solvents were purchased from commercial houses and distilled under argon from appropriate drying agents immediately prior to use. Indium−tin oxide (ITO) glass slides were purchased from Delta Technologies, Inc.

General Instrumental Methods. Electronic spectra were recorded on all films using a double-beam Cary 100 Bio spectrometer (Varian) with a pristine ITO glass slide in the reference beam. Scanning electron (SEM) micrographs and energy-dispersive X-ray (EDS) data were collected on an R. J. Lee Personal SEM II microscope directly on the as-grown and treated films. The ITO glass slides were grounded to the aluminum support block with silver paint to ensure that charging of polymers would not prove problematic. Excitation voltages of 20 keV were used for the SEM studies, while both 20 and 5 keV voltages were used for EDS measurements. X-ray photoelectron (XPS) spectroscopic data were collected on a Physical Electronics Quantum 2000 scanning ESCA microprobe using Mg Kα radiation directly on the as-grown and treated films. Compensation for charging effects in the sample was found to be unnecessary.

Film Preparation. Polypyrrole (PPY), polythiophene (PTH), and poly(ethylenedioxythiophene) (PEDOT) films were prepared from solutions of corresponding monomers (pyrrole, 2,2′-bithiophene, and ethylenedioxythiophene) (500 mg) and tetrabutylammonium tetrafluoroborate (700 mg) in 10 mL of dry dichloromethane. The polyaniline (PANI) films were prepared from an aqueous solution of aniline (0.5 mL) in 10 mL of 1 M HCl. The syntheses were conducted in a three-electrode electrochemical cell using a computer-controlled BAS 100B electrochemical analyzer. Films were grown on ITO-coated glass slides (25 × 75 × 0.6 mm or 50 × 7 × 0.7 mm) that served as the working electrode. A platinum wire was used as an auxiliary electrode, and a $Ag/AgNO_3$ (in dichloromethane) glass tube fitted with a porous glass frit was used as a reference electrode in all preparations using that solvent. In the case of PANI, an aqueous Ag/AgCl reference electrode was used. All electrochemical potentials are reported as uncorrected values versus these electrodes. The working electrode was rapidly (500 mV/s) cycled between 1000 and 1500 mV, giving uniform films approximately 5 μm thick. Films were washed with water, ethanol, and acetone and stored over methylene chloride until used.

Surface Coating of Polymer Films. The polymer-coated glass slides were immersed in a solution of the appropriate thiol (12 mL) dissolved in 50 mL of THF and allowed to react at room temperature for 1−24 h (as indicated). The films were then removed, washed sequentially with THF, ethanol, and acetone, and then dried under a stream of nitrogen.

Electrochemical Analysis of Films. a. Polyaniline. All CV curves were obtained on a BAS 100B electrochemical analyzer scanning between −100 and 750 mV in a 1.0 M solution of aqueous HCl at a scan rate of 30 mV/s. An aqueous Ag/AgCl reference electrode was used with a Au wire auxiliary electrode. A Pt-disk working electrode was coated electrochemically with polyaniline using a 1.0 M aqueous HCl solution with 0.500 mL of aniline and cycled 50 times between 1000 and 1500 mV at a rate of 500 mV/s. This deposited a thick uniform film onto the electrode. The films were then rinsed sequentially with H_2O, ethanol, and acetone and then dried. The PANI-coated Au electrode was then chemically modified in the same manner as the films grown on ITO. The modified films were analyzed under the same conditions.

b. Other Polymers. All CV curves were obtained on a BAS 100B electrochemical analyzer scanning between −1000 and 2000 mV in CH_2Cl_2 at a scan rate of 100 mV/s. The reference electrode was a $Ag/AgNO_3$ electrode, and the auxiliary consisted of a Au wire. The Au working electrode was first coated electrochemically with polymer (using a CH_2Cl_2 solution with 0.500 mL of the monomer and 700 mg of tetrabutylammonium tetrafluoroborate) and then cycled 50 times between 1000 and 1500 mV at a rate of 500 mV/s, depositing a thick uniform film onto the electrode. The freshly prepared films were then rinsed with H_2O, ethanol, and acetone followed by drying under a nitrogen stream. The polymer was coated and analyzed as above.

Surface Coating of Glass or Mica Surfaces. Glass slides (or mica wafers) were cleaned in a 20 wt % solution of ethanolamine in water heated to 100 °C and sonicated for 15 min. A 0.20 mM solution of the DDSi or TDFSi in methylene chloride was prepared under dry nitrogen and added to the glass slide in a clean Petri dish. After 30 min, the slide was removed, rinsed thoroughly with methylene chloride, water, and acetone, and then dried under a stream of nitrogen.

Contact Angle Analysis. All contact angle data were collected on a VCA-2500 (Instruments S.A., (UK) Ltd). Films were placed on a level surface, and the film level was checked with a goniometer. A single drop of each test liquid (water or methylene iodide) was placed onto the film using a 1 mL glass syringe. The contact angles were measured directly after a 30 s equilibration time. The contact angle with each test liquid was measured a minimum of 20 times (two sides of 10 different drops) on each of at least three independently prepared films.

The solid surface energy was calculated according to the method suggested by Wu:[14]

$$(1 + \cos\phi)\gamma_L = 4\left(\frac{\gamma_s^d \gamma_L^d}{\gamma_s^d + \gamma_L^d} + \frac{\gamma_s^p \gamma_L^p}{\gamma_s^p + \gamma_L^p}\right) \tag{1}$$

where ϕ is the contact angle between solid and liquid, γ_L is the surface energy of the liquid in units of erg/cm^2, γ_s^d is the dispersion component of the surface energy of the solid, γ_L^d is the dispersion component of the surface energy of the liquid, γ_s^p is the polar component of the surface energy of the solid, and γ_L^p is the polar component of the surface energy of the liquid. This analysis considers the total surface energy of a material to be the sum of the dispersive (γ^d) and polar components (γ^p):

$$\gamma = \gamma^d + \gamma^p \tag{2}$$

On the basis of a theoretical description by Fowkes,[15] the polarity (X) of a material can then be defined as the ratio of the polar component of the surface energy to the total energy, a dimensionless value:

$$X = \gamma^p/\gamma \tag{3}$$

Thus, if two test liquids for which the polar and dispersive components are known are used for contact angle measurements, the total surface energy as well as the polar and dispersive contributions and the polarity of the solid surface can be defined by using eqs 1−3.

Atomic Force Microscopy. All data were collected on a Nanoscope III AFM/STM (Digital Instruments) using an "E" type scanner head. All samples were imaged using "Tapping Mode", simultaneously collecting topographical and phase data.[16] Images were scanned over a $10\ \text{mm}^2$ range ($x-y$ plane) and with a maximum z range of 250 nm for topographical images and 20° for phase images.

Force−distance curves were obtained using the "Force Mode" software on samples immersed in distilled, deionized water in an AFM fluid cell. Measurements were taken with modified Park Scientific triangular silicon nitride cantilever with a $5\ \mu$m silica sphere attached to the tip with epoxy (BioForce Laboratories). Values reported represent an average of measurements taken at four independent sites. At each site, four independent samplings were taken, each an average of 20 force−distance measurements. Between sample measurements a freshly cleaved mica standard was run to verify tip integrity. All data were collected with the same cantilever.

Force data are reported in units of nanonewtons, obtained by multiplying the deflection of the cantilever by its spring constant.[17] The value of the spring constant used was that given by the manufacturer, which may differ from the actual value by a large amount. Therefore, the values reported are strictly relative.

Results and Discussion

We have previously noted that treatment of polyaniline thin films with substituted anilines results in a reduction of the polymer from the EB oxidation state to the LEB oxidation state.[12] The resulting polymer could be reoxidized to a conducting form but showed dramatic reduction in the polarity of the surface. Similarly, Han has reported that a variety of nucleophiles attack EB polyaniline, giving rise to derivatized polyanilines.[18] Very recently, the reaction of nucleophiles and polypyrrole latex has also been examined.[19] Amines and especially thiols were found to irreversibly add to the polymer backbone. These results point to the development of a valuable methodology for creating surface (or "near surface") functionalized conducting polymers. Here, we contrast and compare the reaction of thiols with four different electronically conducting polymers. We find significant differences in behavior among the systems, due to not only their intrinsic reactivity toward the thiols but also the response of the polymer films to the conditions employed.

Surface Properties of Coated Films. Thin films of PANI, PPY, PTH, and PEDOT were electrochemically grown on ITO glass slides and treated with either an alkanethiol (dodecanethiol, DDT) or a fluoroalkanethiol (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanethiol, TDFT). The surface energies and polarities of the films were examined by contact angle analysis (Table 1). For these experiments, the contact angles of both distilled water and methylene iodide were measured, using the sessile drop method, for each coated sample as well as for the control. Using the method of Wu,[14] the dispersive and polar components of the film's surface energy were calculated as well as the polarity of the film. In addition to the polymer films, reference samples were prepared by coating glass slides with monolayer films of the corresponding alkyl- and fluoroalkylsilanes.

Table 1. Total Surface Energy (γ), the Dispersive (γ^d) and Polar (γ^p) Components of the Surface Energy (erg/cm^2), and the Polarity (X) of As-Grown and Modified Polymer Films

	surface energies			
compound	γ	γ^d	γ^p	polarity X
water	72.8	22.8	50.0	0.69
CH212	50.8	49.9	1.8	0.04
glass	75.3	33.7	41.6	0.55
glass−DDT	30.7	27.1	3.6	0.12
glass−TDFT	18.2	15.1	3.1	0.17
PANI	47.0	27.3	19.6	0.42
PANI−DDT	37.2	27.5	9.7	0.26
PANI−TDFT	25.1	19.2	5.8	0.23
PPY	52.2	30.0	22.2	0.43
PPY−DDT	34.7	33.8	0.9	0.03
PPY−TDFT	23.0	21.5	1.5	0.06
PTH	59.4	31.2	28.2	0.47
PTH−DDT	37.3	33.0	4.3	0.11
PTH−TDFT	29.5	25.0	4.5	0.15
PEDOT	70.9	27.6	43.4	0.61
PEDOT−DDT	39.4	36.8	1.6	0.04
PEDOT−TDFT	41.2	34.2	7.0	0.17

All films showed a marked decrease in the overall surface energy as compared to the native polymer. The decrease in the surface energy is due almost entirely to the decrease in the polar component. The dispersive component of the surface energy typically increases slightly with DDT coating and decreases slightly with TDFT coating. As expected, the coating process in all cases makes the surface substantially more hydrophobic, and the behavior of the polymers parallels that of the corresponding silane-treated glass slides.

The variations in contact angle for a given sample were small (generally $<\pm 2°$), suggesting homogeneous thiol coverage on the scale of the experiment. While the films showed similar trends upon treatment, differences among polymers and between the coated polymers and the coated glass standard were observed. These are probably due to multiple factors, including the extent of the derivatization reaction, the extent of alkyl chain organization on the surface, and the roughness of the polymer surface. The extent of reaction is discussed later in this work, while the issue of chain organization will be addressed in a future publication.

Contact angle measurements are known to be affected by surface morphology,[9a] and there were significant differences among these four polymers. SEM images of the films before and after thiol treatment help to explain some of the differences in the contact angle data (Figure 1). PPY films were very smooth and densely packed. They showed little change in surface morphology upon treatment but became very hydrophobic. PANI and, to a lesser extent, PTH showed a relatively porous, fibroid structure. Additionally, both displayed some evidence of fiber reorganization during the coating process. Not surprisingly, these rougher surfaces displayed smaller contact angles than observed either in the PPY or on glass.[9a] The PEDOT films proved to be the most problematic to study. As can be seen by the SEM micrographs in Figure 1c, the polymer grew as both a film and a fine precipitate. This behavior is likely due to the additional solubility imparted by the dioxyethylene moiety. Rather than rapidly condensing on the electrode surface, oligomeric radical cations generated at the electrode are able to diffuse away from the electrode surface.[20] When they finally precipitate from solution, it is partially as a flocculent powder. The greater compatibility of the polymer with organic solvents also causes problems during the coating process as the film swelled dramatically. Figure 1d shows the results of this extensive swelling and the resulting cracking caused by the subsequent drying of the film.

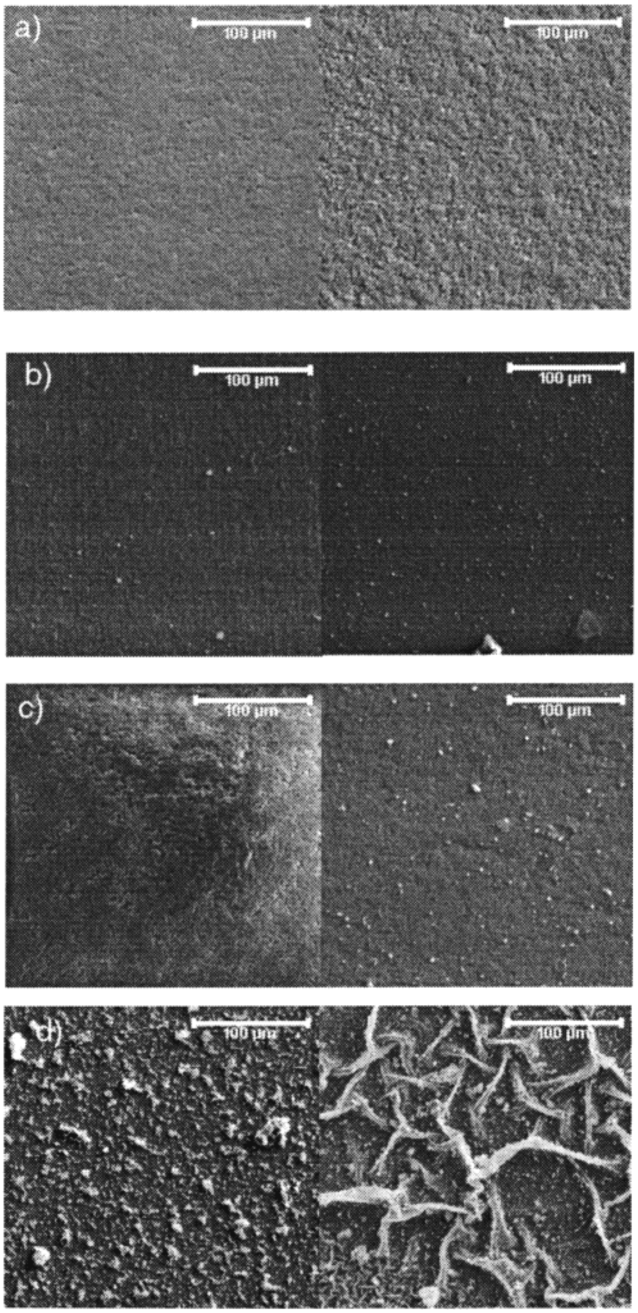


Figure 1. SEM micrographs of (a) PANI, (b) PPY, (c) PTH, and (d) PEDOT thin films before (left) and after (right) exposure to DDT for 1 h.

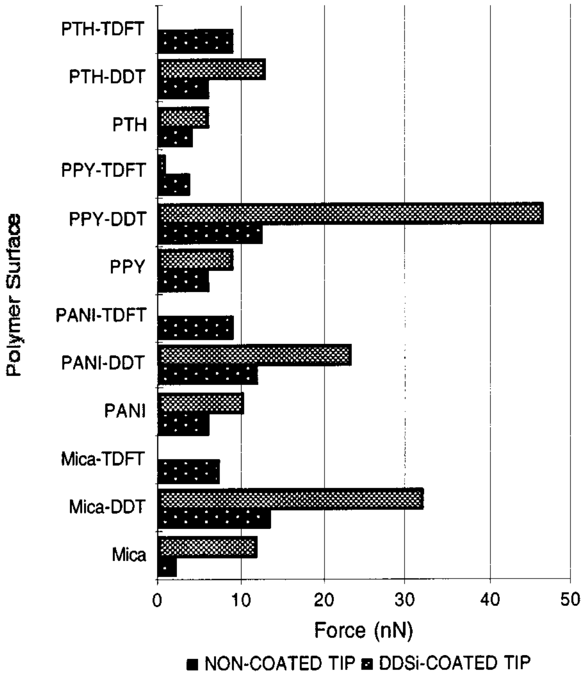


Figure 2. Relative energies (nN) of AFM probe/polymer surface interactions using either an uncoated or a dodecasilane-coated 5 μm silica sphere.

Atomic force microscopy has proven itself to be a useful technique for examining the morphology of conducting polymers, particularly during doping/dedoping processes. The topographical data on our films were consistent with previous work and will not be discussed here.[21] Phase data were also collected. In all cases, the images showed little phase contrast, indicating either highly homogeneous coverage or insensitivity of the technique to variations in the film surface energies. The latter interpretation could, in theory, be disproved by comparing coated and pristine samples of the same film. Unfortunately, it is difficult to compare phase measurements between different samples. There is way of using the AFM to quantify probe/surface interactions, however. “Force−distance” measurements involve bringing the AFM probe into contact with a surface, while monitoring the deflection of the AFM cantilever. The tip is pressed into the surface and then slowly withdrawn. The tip adheres to the surface until the stress on the cantilever (as measured by the deflection of a probing laser beam) becomes greater than the attraction between the tip and the surface. It is also possible to gain some chemical selectivity on the probe by modifying the surface of the AFM probe tip.[22]

In these systems, we have found that reproducibility is poor when force−distance measurements are made in air with a standard AFM probe. There are two major reasons for this. First, the polymer surface is very rough on the scale of the AFM tip. Thus, the tip can encounter various slopes on the surface and can interact with the surface with varying amounts of tip area. To address this problem, a 5 μm silica sphere was attached to the cantilever. The larger surface area of the tip averaged out some of the surface roughness, and since the modified tip is isotropic, the angle between the probe and the surface becomes less significant. A second problem is that the surface of the polymer is inevitably covered with a layer of adsorbed water. The thickness of this layer varies with the humidity above the sample while the probe/water interaction contributes to the total probe/surface interaction that is measured in the experiment. To avoid this complication, all force measurements were made in a fluid cell where both the polymer and the probe remained under water throughout the experiment. An additional benefit of this procedure is that interactions between hydrophobic surfaces are maximized in the aqueous environment, giving more contrast to the data.[21] PEDOT films could not be measured by this technique as the coating process resulted in a loss of adhesion between the film and the glass slide. This caused the film to partially detach from the slide and to give wildly varying results.

Figure 2 shows the force−distance data for both an unmodified and a DDSi-modified silica sphere interacting with as-grown and treated films from the other three polymers as well as a mica reference. Several trends

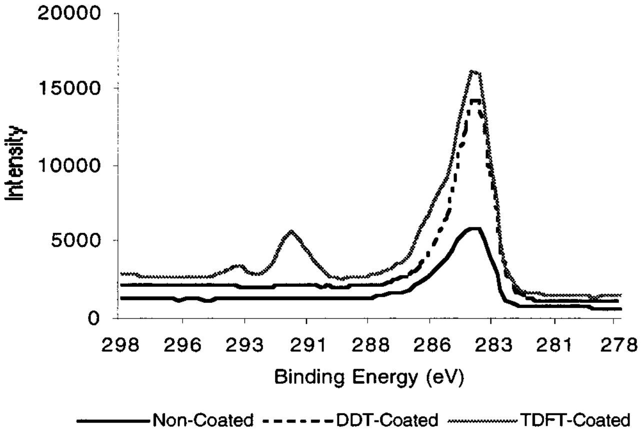


Figure 3. High-resolution XPS $C_{(1s)}$ data for uncoated, DDT-coated, and TDFT-coated PANI films.

are evident: (1) The unmodified probe adheres better to the soft polymer than to a hard mica surface. (2) Coating *either* the polymer or the film with a long-chain alkane results in an increase in adhesion. Adhesion between the unmodified probe and all alkane modified surfaces was approximately the same. Likewise, the coated probe adhered to all polymer surfaces with similar strength. (3) Coating *both* the probe and the polymer with a long-chain alkane results in a dramatic increase in adhesion. Interestingly, this effect is much less pronounced with the DDT-coated PTH. An explanation for this will be offered based upon other data presented below. (4) Coating the film with a fluoroalkane also results in an increase in adhesion to the unmodified probe but a dramatic decrease in adhesion to the alkane-modified probe. In most cases, this value is less than 1 nN and does not show up on the graph. A table of the raw deflection data as well as the calculated interaction energies can be found in the Supporting Information.

Chemical Composition of Treated Films. To confirm that the observed changes in surface properties were due to covalent attachment of the thiols, additional spectroscopic tools were employed to examine the film. XPS analysis of the films showed that there were distinct changes in the chemical composition of the surface of the film after the exposure to the thiols. Figure 3 shows the high-resolution spectra of the carbon 1s region for coated and uncoated PANI films. The data for the PPY, PTH, and PEDOT films are virtually superimposable. The TDFT-coated films all show clear signals for the $-CF_3$ carbons at 293.4 eV, the $-CF_2$ carbons at 291.2 eV, and a shoulder on the main peak (285.3 and 283.7 eV, respectively) that is due to the nonfluorinated methylene carbons.

The sulfur, nitrogen, and fluorine high-resolution spectra were also obtained, and they are fully consistent with a high-coverage, homogeneous coating. Particularly significant is the sulfur spectra. Each polymer contained sulfur with a $2p_{3/2}$ binding energy of 163.2(2) eV for the DDT-treated films and 163.8(2) eV for the TDFT-treated films. These are consistent with a sulfide linkage and, combined with the persistence of the sulfur-containing material despite repeated washing, strongly suggest a covalent sulfide linkage to the polymer surface in all cases.[23]

While the top few nanometers of the four polymers appeared to have been modified in a similar fashion, it was also of interest to probe further into the bulk polymer. An energy-dispersive X-ray (EDS) detector was used to examine the X-ray emissions resulting from excitation from the SEM electron beam. The detection depth by this technique is very sensitive to the excitation voltage.[24] The 20 keV excitation voltage used to obtain the data in Figure 1 resulted in X-ray generation at depths >1 μm. In our films, this interrogates the entire depth of the film and into the ITO coating underneath. In these spectra, only carbon and the heteroatom of the polymer (nitrogen or sulfur) could be detected. Thus, even after 24 h, only a small portion of the polymer bulk was derivatized.

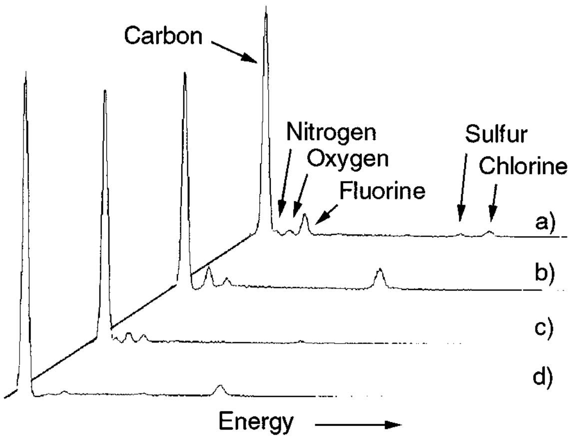
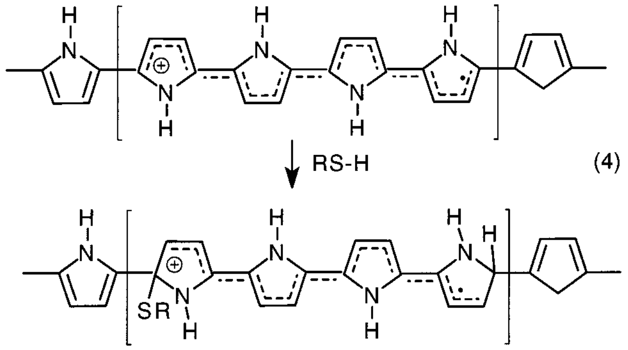


Figure 4. EDS spectra of TDFT-coated (a) PANI, (b) PEDOT, (c) PPY, and (d) PTH films using a 5 keV excitation voltage.

By reducing the acceleration voltage, the top few hundred nanometers of the film could be probed. Figure 4 shows the X-ray spectra of the four TDFT-modified polymer films with a 5 keV accelerating voltage. In each case, carbon, oxygen, fluorine, and sulfur could be observed. Nitrogen was found in the PANI and PPY spectra, while chlorine could be found in the PANI spectrum due to the counterion taken up during film preparation. Oxygen, probably from incipient water, is commonly found in EDS analysis of polycationic polymer films.[24a]

Since our materials are not homogeneous, it was not feasible to quantify the amount of thiol incorporation into a particular polymer. A comparison of the relative incorporation of TDFT onto the polymers, however, was possible by comparing the carbon to fluorine areas. The results show significant differences among the films. The fluorine-to-carbon ratios (based on the integration of the deconvoluted peak areas) were PANI-0.103, PEDOT-0.033, PPY-0.040, and PTH-0.012. These variations are not due strictly to differences in the permeability of the films, since PPY, the most densely organized of the group, and PEDOT, the polymer that swelled the most, have similar F/C ratios that are intermediate to the other two. Most interesting is the very low fluorine content in the PTH, which has an open fibrous morphology and swells substantially during the treatment. These data indicate either a substantially slower reaction rate between the thiol and PTH or the competition from an alternative reaction pathway in which the thiol does not covalently bond to the polymer.

Electronic Spectra and Cyclic Voltammetry of Polymer Films. It has previously been noted that exposure of PANI or PPY to nucleophiles results in a change in the color of the polymer. Han has suggested that the partially oxidized EB form of PANI adds neutral nucleophiles to give a substituted polymer in the fully reduced LEB form.[18] Upon reoxidation to the EB form, a conductive material would be recovered as shown in eq 4. Bieniarz and co-workers showed that the rate and extent of attack on polypyrrole latexes depended upon the nucleophilicity of the incoming group (thiol > amine > alcohol).[19] Polypyrrole is thought to consist primarily of α-coupled monomers oxidized to delocalized radical cations (polarons) or dications (bipolarons). Each of these charge carriers is delocalized over approximately four monomer units and has a greater deficit of electron density at the α-positions. Reaction with a nucleophile could result in an addition reaction to a polaron (eq 5) or to a bipolaron (eq 6). PTH and PEDOT have backbones that are isoelectronic with that of PPY, and they might be expected to react in a similar fashion.



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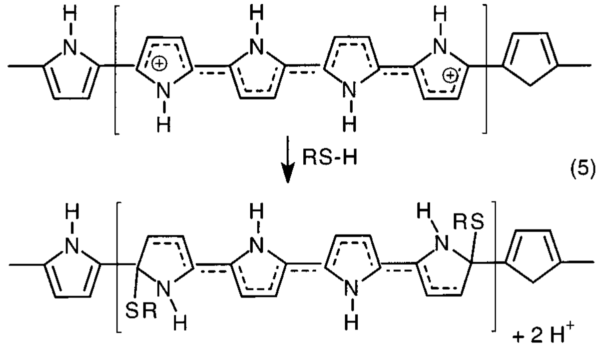

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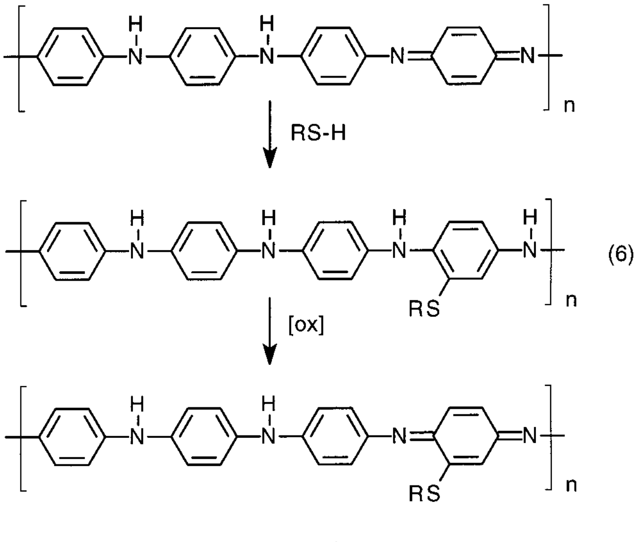

(6)

The electronic spectra of PANI, PPY, PTH, and PEDOT films before and after exposure to DDT are shown in Figure 5. Also shown are the spectra of the films after being placed in an electrochemical cell and being brought to a potential high enough to ensure that the polymer was fully oxidized. Figure 6 shows cyclic voltammagrams (CV) of the same films before and after exposure to DDT for 4 h (PANI) or 24 h (PPY, PEDOT, PPT).

The data for the PANI film are consistent with the mechanism proposed in eq 4. There is a steady decrease in the intensity of the polaron/bipolaron band in the infrared and an increase in the π to π^* band at 426 nm. Reoxidation of the film restores the polaron/bipolaron absorbance, with a small change in the λ_{max}. The CV of the treated film shows a reduction in the redox couple of the original polymer (245 mV) and the growth of a new couple (600 mV) due to the derivatized chain segments.

The PPY film behaves quite differently, as would be expected from eqs 4 and 5. Initially, there is a slow reduction of the polaron/bipolaron band and an increase in the π to π^* transition. At longer times, there is a blue shift in the latter absorption, consistent with a reduction in the conjugation length of the polymer backbone. Neither effect is reversed on reoxidation. Indeed, placing the film at a higher positive potential reduces the intensity of the polaron/bipolaron band even further. This may be due to reaction of entrapped thiol with reoxidized chain segments in the polymer or to reaction with oxygen. The CV of the treated polymer shows substantially less current flow, indicating a loss of electroactivity in a large portion of the film.

The PTH film reacted very rapidly with the thiol, becoming completely reduced in less than 1 h. Reoxidation restored the polaron/bipolaron band completely with a small blue shift (ca. 34 nm) in the λ_{max}. The CVs of the treated and untreated films were identical. Clearly, the observation of only very small amounts of fluorine in the EDS spectra of the PTH−TDFT film was not a result of a slow reaction rate caused by poor permeability of the film to the thiol, but rather to a competing reaction mechanism. Most likely, the PTH oxidizes the thiol to a disulfide that is removed from the polymer matrix during our film washing step. This reaction appears to be very facile and allows for only a fraction of the thiol to chemically react with the polymer.

Finally, the PEDOT appears to act in a fashion intermediate to PTH and PPY. The film reacts rapidly (as indicated by the electronic spectrum), though not as fast as PTH. Reoxidation restores much of the polaron/bipolaron band, but there are definite changes in the spectrum. Finally, there is a reduction in the total redox current, though it is smaller than that observed in PPY. This is consistent with the observation that, while the polymer is far more porous than PPY, the total fluorine content after treatment with TDFT is less.

In summary, nucleophilic attack of thiols results in substantial modification of the surface properties of all of these polymers as evidenced by the contact angle and force curve measurements. In the case of PTH, the process is very inefficient, since most of the thiol is reduced to the disulfide in a competing reaction and extracted. PPY and PANI films seem to undergo primarily nucleophilic addition, while both addition and reduction processes seem to be occurring in PEDOT films.

The nucleophilic substitution offers a potentially valuable route to mounting molecular devices on conducting polymer films, but at the price of reduced electroactivity in some cases. PEDOT and, to a lesser

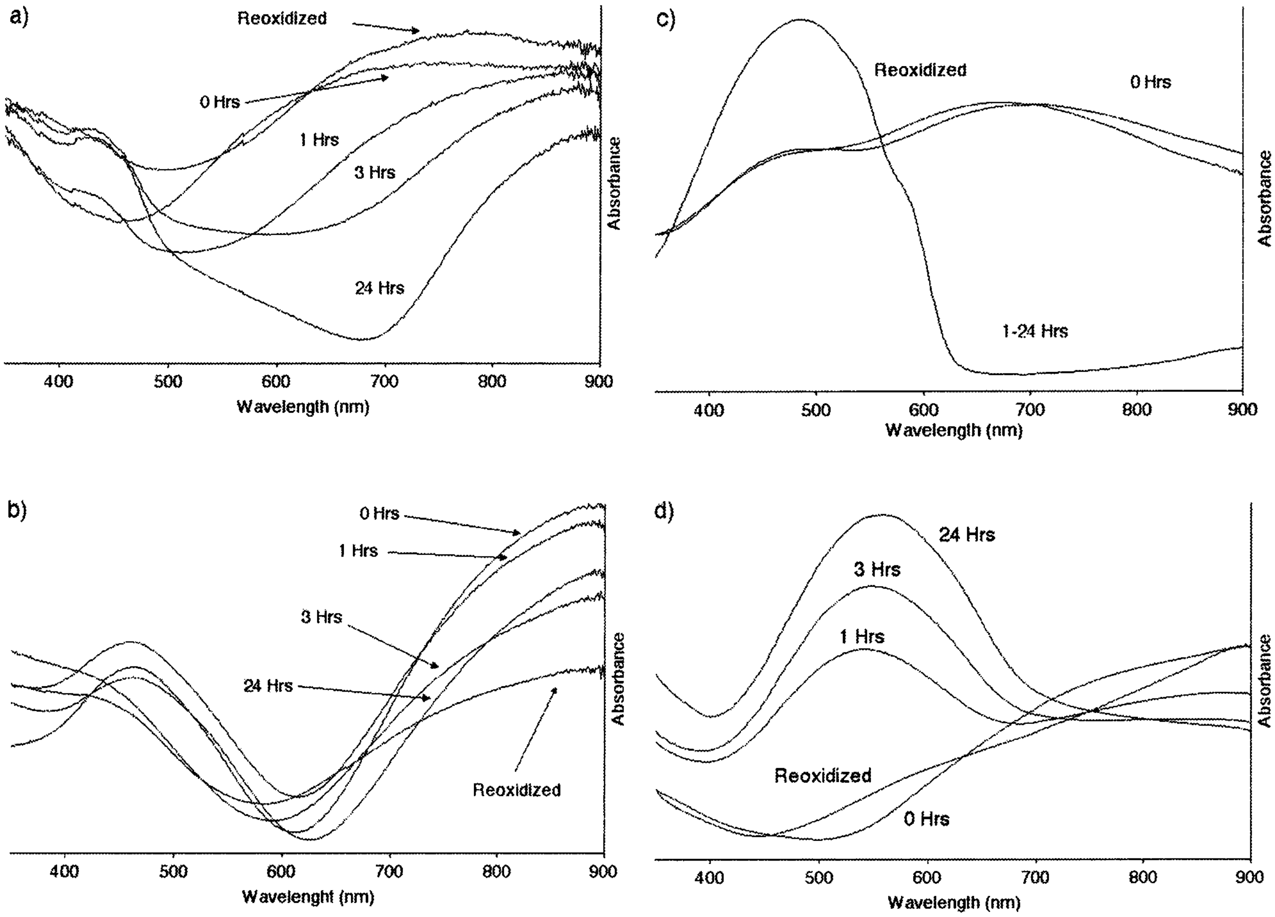

Figure 5. Electronic spectra of (a) PANI, (b) PPY, (c) PTH, and (d) PEDOT thin films after exposure to DDT for 0−24 h.

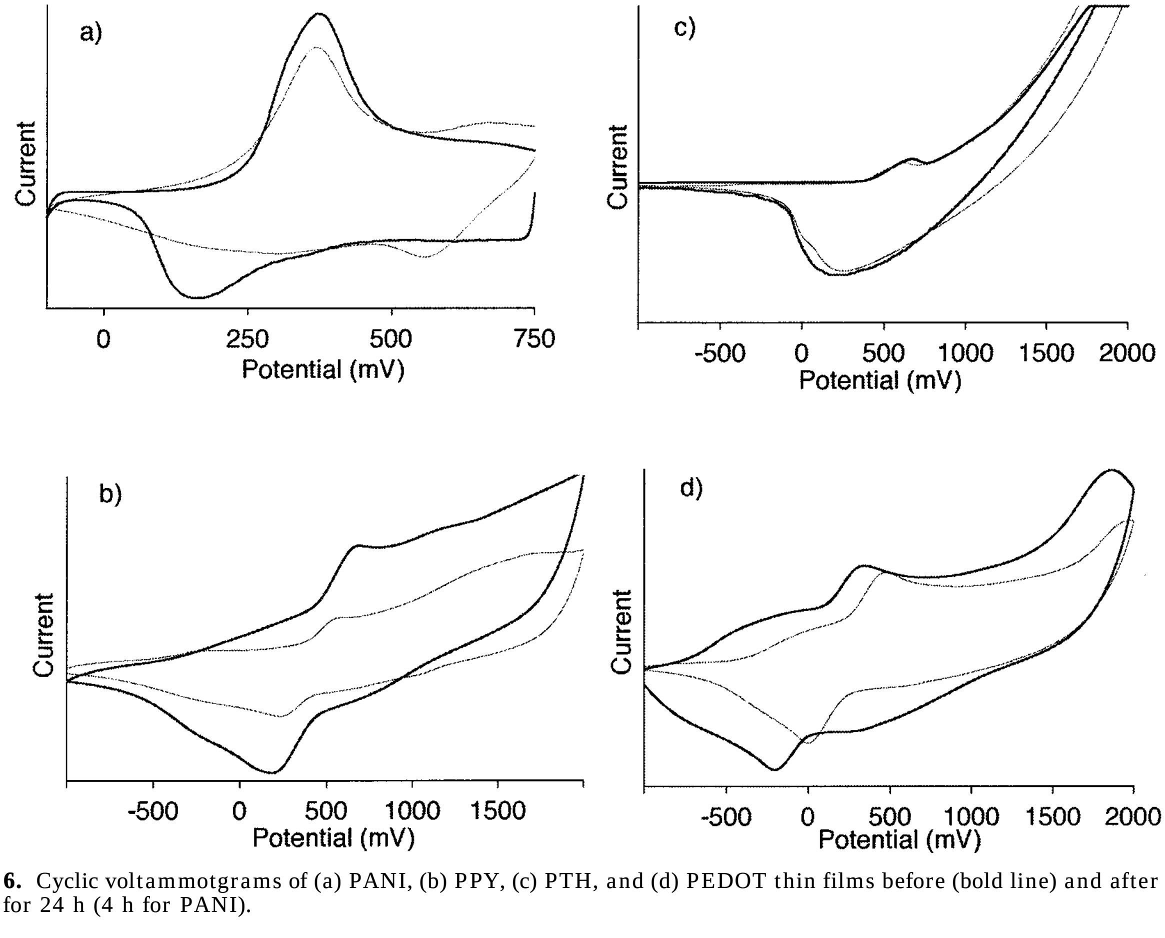

Figure 6. Cyclic voltammotgrams of (a) PANI, (b) PPY, (c) PTH, and (d) PEDOT thin films before (bold line) and after exposure to DDT for 24 h (4 h for PANI).

extent, the other polymers suffer structural degradation on prolonged exposure to thiols in organic solvents. PANI is the most interesting of the polymers studied. The PANI films had good stability, achieved very high nucleophile loading, and maintained electroactivity.

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Supporting Information Available: Table of contact angles, surface energies, and polarities, table of relative EDS signal intensities, and figures showing high-resolution XPS spectra of pristine and coated PANI films. This material is available free of charge via the Internet at http://pubs.acs.org.

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