Two-Dimensional Polyaniline Thin Film Electrodeposited on a Self-Assembled Monolayer

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Received March 23, 1998

Abstract: A two-dimensional conducting polyaniline (PAN) monolayer has been formed on an electrically insulating monolayer. The approach is based on the electrochemical polymerization of surface-confined anilinium ions that were electrostatically attached to a negatively charged self-assembled monolayer of ω-mercaptodecanesulfonate (MDS), $HS(CH_2)_{10}SO_3^-$, on a gold surface. The formation and characterization of the two-dimensional film and the MDS monolayer have been examined by cyclic voltammetry, Fourier transform IR spectroscopy, X-ray photoelectron spectroscopy, wettability, and scanning electrochemical microscope. The formation of a capacitor-like assembly, in which electron transfer was blocked between PAN and the gold surface, was accomplished by electrochemically incorporating hexadecanethiol (C_{16}) into the MDS monolayer. The PAN monolayer exhibits properties similar to those of a thin polymer film.

Introduction

The discovery of electrically conducting polymers made of organic monomers has encouraged the development of new materials envisioned to eventually replace metals and semiconductors in solid-state devices. However, despite the tremendous efforts in this area, conducting polymers have been introduced in only a few applications such as synthetic membranes, nonlinear optical elements, and sensors.[1] The obstacles that prevent their wide application stem from the relatively poor adhesion of polymeric films onto metal surfaces, the lack of fine control on the film thickness, and the need to develop methods for their micro- and nanopatterning. These limit the thickness, stability, and machining of polymer films, which are usually deposited upon electropolymerization.

An elegant approach that has been demonstrated as a means of increasing the adhesion of the metal−polymer interface involves the electropolymerization of the monomers on a self-assembled monolayer (SAM) containing an electropolymerizable unit.[2−4] Thus, for example, Wrighton and co-workers[2] formed a stable thick polypyrrole film on an *n*-Si surface modified with *N*-(3-trimethoxysilylpropyl)pyrrole. On the other hand, Rubinsteinet al.[3] studied the electropolymerization of aniline and the properties of the resulting polyaniline on a 4-aminothiophenol monolayer. Kowalik et al.[4a] reported that the polymer resulting from the electropolymerization of *N*-(3-sulfhydrylpropyl)-bisthiophenepyrrole on Pt and Au electrodes showed remarkable mechanical stability. These and other studies[5−7] also showed that the SAM (even in cases where it does not participate in the electropolymerization process) has a pronounced effect on the morphology and density of the bulk-deposited polymer. For example, Uchida and co-workers[5] nicely demonstrated that polypyrrole film is preferentially deposited on hydrophobic monolayers. Moreover, the fact that the thickness and the terminal group of the SAM can be used for controlling the rate of electron transfer across the monolayer has been recognized as an attractive approach for the selective deposition of conducting polymers and surface micropatterning.[6,7] Accordingly, two-dimensional (2-D) patterns of polypyrrole were formed by Whitesides and colleagues,[6a] who used the microcontact printing technique, in which a long-chain *n*-alkanethiol prevented the deposition of the polymer onto the areas covered by the thiol. On the other hand, Sayre and Collard showed that *n*-alkanethiols retard the deposition of polypyrrole, whereas positively charged monolayers efficiently block aniline electrochemical oxidation.[7a] The latter effect has been exploited by those authors,[7b] also using the microcontact printing technique, as well as by Rozsnyal and Wrighton,[6b−d] who used photopatterning for the selective deposition of polyaniline.

Recently, Willicut and McCarley[8] and Collard et al.[9] adopted another approach to accomplish the formation of a monomolecular layer of a conducting polymer, based on the electropo-

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10.1021/ja9809760 CCC: $15.00

lymerization of a self-assembled monomer layer. Both groups studied the formation of pyrrole-substituted alkanethiols on gold surfaces. However, whereas Collard et al. claimed that the monolayer of ω-(N-pyrrolyl)alkanethiol could not be electropolymerized, presumably because of the requirement of an anti-orientation of the pyrrole rings that is not obtained in the monolayer, Willicut and McCarley provided evidence for the formation of a 2-D polypyrrole film.

Ringsdorf and colleagues,[10f] and more recently Crooks and co-workers,[10b−e] as well as Mowery and Evans[10g−h] developed a strategy for the formation and patterning of polymeric SAMs through the 2-D photopolymerization of diacetylenic-containing monolayers. Their results indicated that the incorporation of a polymeric backbone within the monolayer structure significantly increased the stability of the film. Proceeding along this avenue, Garnier and colleagues[11a] and lately Bäuerle and co-workers[11b] assembled an organized monolayer consisting of oligomeric units that were oriented normally toward the surface.

Monolayers consisting of conducting polymer units can be formed also through the adsorption of polymers. For example, Gao and Siow reported the reversible chemical doping monolayers of poly(3-octylthiophene).[12a] A somewhat different approach for the formation of 2-D conducting polymers was demonstrated by Rubner and co-workers[12b−d] and others[12e−h] and has been successfully applied to assembling multilayer thin films of electroactive polymers. This concept, which is not limited to a single monolayer, is based on the spontaneous adsorption of alternate monolayers of ionically charged conducting polymers driven by electrostatic interactions.

The 2-D conducting polymers present very interesting systems with many possible applications, depending primarily on the conducting properties of the monolayer. Hence, the electrical conductivity of such thin film is of major importance. The 2-D conducting polymers could benefit from the advantages of SAMs. For example, the conductivity of a 2-D conducting organized layer might be anisotropic as a result of a preferred orientation of the monomer. Nevertheless, the conducting properties of such monolayers, which will not be pinhole-free, are questionable. In fact, this concept has already been tested by the LB technique. Several studies have focused on the polymerization of LB films.[13] Thin polymeric LB films of polypyrrole, polythiophene, polyaniline (PAN), and polydiacetylene have been prepared by various methods.[13] In the two major methods, a “bulk” chemically made, insoluble polymer was spread on pure water and transferred onto a solid substrate,[13b−d,j] or a hydrophobic monomer film was either chemically polymerized in the liquid−air interface or electropolymerized after it was transferred onto the conducting substrate.[13a,e−i] Although the first approach results in nonhomogeneous films, the latter requires the monomer to be functionalized (to increase its hydrophobicity), which reduces the conductivity of the polymer.

We report here on the formation and characterization of a 2-D PAN monolayer on a gold surface. The film was formed upon electropolymerization of anilinium ions that had been electrostatically attached onto a mixed SAM of ω-mercaptodecanesulfonic acid (MDS) and hexadecanethiol (C_{16}). The C_{16} was crucial for blocking the pinholes in the MDS monolayer and was electrochemically incorporated in the monolayer (see below). Various surface techniques, such as cyclic voltammetry(CV), external reflection IR, X-ray photoelectron spectroscopy (XPS), and wettability measurements, were used for studying this system. In particular, we used scanning electrochemical microscopy (SECM) to verify the formation of this capacitor device, in which the conducting PAN is electrically isolated from the gold substrate.

Experimental Section

Instrumentation. Electrochemical measurements were conducted with a BAS100B electrochemical analyzer using a conventional three-electrode cell. All potentials are quoted vs Ag/AgCl. Fourier transform IR (FTIR) spectra were obtained with a dry-air-purged Nicolet 740 spectrometer (Nicolet) at a resolution of 2 cm^{-1} with mercury−cadmium−telluride and indium−antimony detectors. Usually 1024 scans were collected of the sample vs a reference. The latter was either a per-deuterated 10-decanethiol or a bare gold surface that was treated in piranha solution [a solution of sulfuric acid (Merck, Ultrapure, 96%) and hydrogen peroxide (Merck, 30%) in a 3:1 ratio] *(Caution: Peroxysulfuric acid should be used carefully since it reacts violently with organic molecules)* just before insertion into the spectrometer. A p-polarized light with an incident angle of 80° was used. XPS measurements were conducted with a Kratos, AXIS−HS spectrometer having an Al Kα monochromatized source of 1486.6 eV. The pressure in the analysis chamber was $\sim 10^{-9}$ Torr. The stoichiometry of the elements on the surface was obtained from the ratio of the peak areas in the spectra. Advancing and receding contact angles were measured with a Ramé−Hart model 100 contact-angle goniometer, two measurements being made on opposite edges. The charging currents of the different systems were measured at 0.05 V by CV at various scan rates in 0.1 M phthalate buffer (pH 3) plus 0.5 M Na_2SO_4.

SECM experiments were performed on a micropositioning device (Burleigh Instruments, Fishers, NY) with a CE-7000 controller, which

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has been previously described.[14] A homemade potentiostat was applied to control the potential of the microelectrode. In cases where the potential of the gold substrate had to be controlled as well, we used a bipotentiostat (EI-400, Ensman Instrumentation). Ultramicroelectrodes of 25-μm-diameter platinum wire were constructed by conventional methods.[15] The microelectrodes were polished with 0.05 μm alumina prior to each experiment. Only in the case where *N,N′*-dimethyl-4,4′-bipyridinium (MV^{2+}) was used, a mercury film had been electroplated onto the Pt microelectrode at −1.0 V vs Ag/AgCl from a solution of 0.1 mM $Hg(NO_3)_2$ and 10 mM HNO_3.[16] A three-electrode Teflon cell was used with a Pt counter electrode and an Ag/AgCl reference electrode.

Chemicals. All chemicals were purchased from Aldrich. *n*-Hexadecanethiol (Aldrich, 95%) and aniline (Mallinckrodt, AR) were distilled under reduced pressure. Tris-9,10-phenanthroline iron(II) dichloride, $Fe(phen)_3Cl_2$, was prepared as previously described.[17] Solutions of aniline in phthalate buffer (0.1 M, pH 2.5) were prepared daily.

MDS, sodium salt, was synthesized from 1,10-dibromodecane in a modified two-step procedure.[18] A mixture of 30 mL (0.132 mol) of 1,10-dibromodecane, 100 mL of ethanol, and 40 mL of water boiling in 250-mL flask fitted with a reflux condenser, magnetic stirrer, and a separatory funnel. A solution made of 5.04 g (0.04 mol) of dry sodium sulfite in 40 mL of water was added through the separatory funnel to the well-stirred boiling mixture over a period of 2 h. The solution was refluxed for 4 h after all the sulfite solution was added. The lower phase (unreacted 1,10-dibromodecane) was removed while still warm (to avoid solidification of the unreacted 1,10-dibromodecane), and the upper aqueous phase was washed three times with petroleum ether. Then, the aqueous phase was concentrated by rotary evaporation at 50 °C to ∼50 mL, and the solid residue obtained was twice recrystallized from hot water and dried. Microanalysis of 10-bromosulfonic acid, sodium salt ($C_{10}H_{20}BrNaO_3S$), gave the following results (found/calculated): C, 37.4/37.2; H, 6.2/6.2; Br, 22.5/24.8. The thiol group was introduced after nucleophilic substitution with thiourea. Specifically, a mixture of 0.872 g (0.0027 mol) of the bromo compound, 0.205 g (0.0027 mol) of thiourea, 25 mL of water, and 25 mL of 95% ethanol was refluxed with continuous stirring at 95 °C for 3 h. 10-*S*-Thiouronium decanesulfonate separated as a white, crystalline solid, which we isolated and twice washed with water. Microanalysis of the thiouronium salt ($C_{11}H_{24}N_2O_3S_2$) gave these results (found/calculated): C, 44.4/44.6; H, 8.4/8.1; N, 9.3/9.5. We then added 5 mL of a 10% NaOH solution to 0.379 g of 10-*S*-thiouronium decanesulfonate and refluxed the mixture for 2 h. Crystals were obtained by cooling overnight. After acidifying the solution (to pH 6) with dilute sulfuric acid (0.7 mL of concentrated acid to 5 mL of water), the residue was isolated upon cooling, followed by double recrystallization from a water:ethanol solution. Microanalysis of the final product, i.e., MDS, sodium salt ($C_{10}H_{21}NaO_3S_2$) gave (found/calculated): C, 43.6/43.5; H, 7.7/7.6; and no nitrogen.

Per-deuterated 10-decanethiol, $C_{10}D_{21}SH$, was synthesized from deuterated 10-bromodecane, $C_{10}D_{21}Br$ (Cambridge, 98%), with thiourea followed by base hydrolysis.

Procedures. Gold film substrates (1000 Å of Au) were prepared by thermal evaporation (3×10^{-6} Torr) of gold (99.99%) on AG 45 glass slides (1.5 × 1 cm; Berliner Glass, Berlin, Germany) that had been previously coated with a layer of chromium, ∼20 Å thick. Before evaporation, the slides were cleaned in ethanol and piranha solution (*Caution*), rinsed with Millipore H_2O, and dried in an oven. Freshly prepared gold samples were kept in an inert atmosphere. The gold samples were flame-annealed in a hydrogen flame prior to modification with the thiols.

Monolayers of ω-mercaptoalkanesulfonic acid, sodium salt, were assembled by immersing for at least 6 h the gold substrates in $HClO_4$ (0.1 M) containing 1 mM of the thiol and then rinsing with water and drying under nitrogen. Mixed monolayers of MDS and C_{16} were formed by applying 0.8 V vs AgQRE for 40 min to a gold substrate covered with an MDS monolayer in an ethanolic solution of 1−2 mM C_{16} and 0.1 M $LiClO_4$ or 0.1 M $TBANO_3$.

Preconcentration of aniline was carried out by immersing a modified electrode in 0.01 M aniline solution (in 0.1 M phthalate buffer, pH 2.5) for 10 min. Then the electrode was carefully rinsed with water and immersed in an aniline-free solution of 0.1 M phthalate buffer (pH 3.0) and 0.5 M Na_2SO_4. Aniline was electropolymerized by scanning the potential between −0.2 and 1.1 V vs Ag/AgCl at 50 mV s^{-1}. Samples for IR measurements were prepared by extracting aniline from 0.1 M $NaHSO_4$ (pH 2.0), whereas electropolymerization was carried out in 0.1 M H_2SO_4 and 0.5 M Na_2SO_4. The final potential was 0.2 V. The following redox couples was examined by CV with MDS and MDS/PAN-modified electrodes: $Fe(CN)_6{}^{3-}$ in 0.1 M Na_2SO_4 and in 0.1 M ammonium buffer (pH 8.3); $Ru(NH)_3{}^{3+}$ in 0.1 M acetate buffer (pH 4.0) and in 0.1 M ammonium buffer (pH 8.3); MV^{2+} in 0.1 M Na_2SO_4; $Fe(phen)_3{}^{2+}$ in 0.1 M HCl and 0.1 M acetate buffer (pH 4.0); I^- in 0.1 M H_2SO_4; and Fe^{3+} in 0.1 M HCl. The area of the electrode surface was determined by chronocoulometry with a $Ru(NH_3)_6{}^{3+}$ solution.

Two sorts of SECM experiments were performed: typical feedback current−distance measurement, in which the current of an ultramicroelectrode was recorded while approaching the substrate, and tip−substrate CV, where the current at the tip was measured (at a fixed position above the substrate) while the potential of the substrate was being changed. The current of the microelectrode and the distance from the substrate were normalized by dividing them by the steady-state current far from the substrate and by the microelectrode radius, respectively. The solutions used in the SECM experiments were either $Fe(phen)_3{}^{2+}$ in 0.1 M HCl or MV^{2+} in 0.01 M H_2SO_4.

Results and Discussion

The essence of this work was to form a monolayer of polyaniline by electropolymerizing a monolayer of electrostatically bound anilinium ions. Although aniline is protonated at pH < 4.5, the electropolymerization of aniline is better carried out at relatively low pH, e.g., in 0.1 M sulfuric acid. Therefore, the first step was to form a monolayer that is negatively charged even at low pH to prevent depletion of the bound aniline prior to electropolymerization. ω-Mercaptoalkanesulfonic acid monolayers are ideal candidates since the sulfonic acid group is dissociated at very low pH. The only commercially available thiol of this homologous family is the 2-mercaptoethanesulfonic acid, which was used by Fawcett and colleagues[19] as an example of a highly charged monolayer. Our decision to synthesize a medium-length thiol, i.e., MDS, was a compromise between two opposite requirements; Although longer thiols would form more-organized monolayers, shorter thiols would not block electron transfer efficiently (which would be required to electropolymerize the monomer) across the layer.

Figure 1A shows the CV of an MDS-modified gold electrode after preconcentrating anilinium ions. The CV was carried out in an anilinium-free solution. A clear anodic wave was observed at 0.8 V during the first sweep. Whereas this anodic wave was detected only in the first cycle, a reduction peak ($E_{pk,c}$= 0.34 V) followed by a new oxidation wave ($E_{pk,a}$= 0.41 V) appear during the back-scanning. These waves do not change upon continuously electrocycling the electrode in this potential window. Control experiments showed that no peaks were observed with either an MDS-modified electrode when the preconcentration step was precluded, or after a preconcentration

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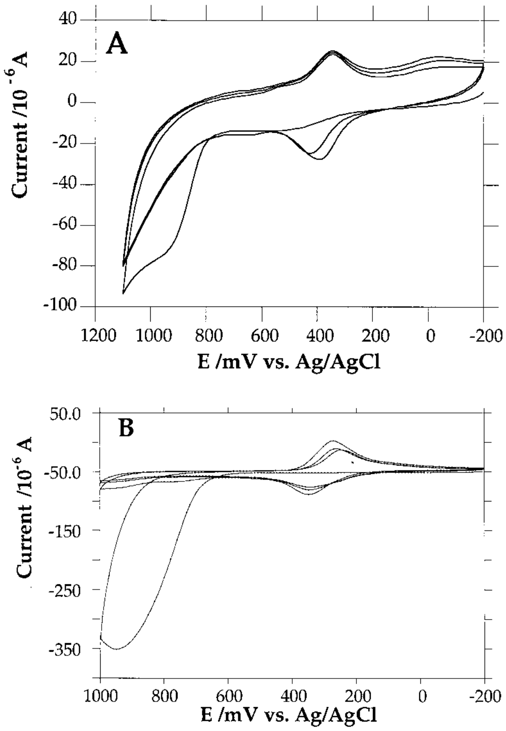

Figure 1. Cyclic voltammetry of (A) an MDS-modified gold electrode recorded in a solution of 0.1 M phthalate buffer (pH 3.0) plus 0.5 M Na_2SO_4 after preconcentrating anilinium ions and (B) a bare gold electrode recorded in a solution of 0.1 M phthalate buffer (pH 3.0) and 0.5 M Na_2SO_4 containing 0.01 M anilinium ions. Scan rate 50 mV•s^{-1}.

step using a bare gold electrode. Figure 1B shows the CV of a bare gold electrode recorded in the same solution as Figure 1A but with added 0.01 M aniline. In extensive studies of the electrochemical polymerization of aniline at gold electrodes,[20] the anodic wave at ~0.8 V has been associated with the irreversible oxidation of anilinium ions, whereas the reversible peaks at ~0.3 V are related to doping and undoping the polymeric film (see below). The close resemblance of Figures 1A and 1B strongly suggests that the voltammograms describe similar electrochemical processes. Because the electrooxidation in Figure 1A was carried out in an aniline-free solution, the anilinium ions, which are electrostatically attached by the negatively charged monolayer, conceivable electropolymerize on the electrode surface. The charge associated with the oxidation process equals 6.15 μC, which corresponds (assuming a one-electron process[21]) to 0.26 ± 0.04 nmol cm^{-2} (64 A^2 molecule^{-1}). Recently, we showed that MDS molecules on gold adopt a disorganized structure because of the bulkiness and charge of the sulfonate functional groups.[22] This results in a low surface coverage of MDS SAM ($\theta = 0.25-0.40$), which we determined, using Amatore's model,[23] from the change of electron transfer as a result of the presence of the monolayer. On the other hand, the excess surface coverage of a densely packed ($\theta = 0.99$) *n*-decanethiol SAM on Au equals 0.76 nmol cm^{-2},[24] which suggests that a monolayer of anilinium ions would be likely to form upon extraction by the negatively charged groups. A more accurate determination of the ratio between the MDS and aniline monomers was derived from XPS measurements, discussed later.

Further evidence for the formation of PAN is obtained from a close inspection of the oxidation−reduction waves that correspond to the doping−undoping process. Compared with other conducting polymers, PAN exhibits special electrochemical characteristics because its conductivity is proton-dependent. Therefore, the oxidation−reduction waves that are due to partially charging the polymer and transforming it from its insulating to conducting state are affected by the electrolyte and pH of the medium. The redox behavior of electrochemically deposited polyaniline has been the subject of numerous studies.[25] We find that the oxidation−reduction waves of the PAN monolayer are, indeed, sensitive to the electrolyte and in particular to the pH of the medium. For example, Figure 2A shows the CV of the film in 0.1 M HCl, which is in complete agreement with the literature.[20b,25b] The linear dependence of the peak currents on scan rate is indicative of a surface-confined process of the film (Figure 2B). Note that the PAN monolayer loses its electroactivity at pH > 4, as has been reported for PAN films on bare electrodes.[20a−b,25d,i]

We have examined and optimized the various parameters that affect the extraction of anilinium ions by the charged monolayer, e.g., pH and time of extraction. We found that the best conditions for extracting aniline with a 2-mercaptoethanesulfonate and an MDS-modified electrode are at pH 1.5−2.5. Obviously, this is a pH range in which aniline is well protonated and, at the same time, the sulfonate groups are deprotonated. The effect of the preconcentration time on the amount of aniline extracted shows time-saturation behavior, which reaches an asymptotic value of 0.26 ± 0.04 nmol cm^{-2} of aniline within 10 min.

The extraction of aniline and the formation of a PAN monolayer have been examined by additional surface techniques. Figure 3 shows the reflection−absorption IR of a PAN monolayer electropolymerized onto an MDS monolayer and of a much thicker film of PAN electrodeposited on a bare gold electrode under the same conditions. The spectrum of MDS is also shown, which clearly indicates that all the bands in this wavenumber range are due to PAN. The potential applied by the end of electropolymerization assured that the polyaniline was in its emeraldine form. Given the C−H stretching bands of the MDS at 2800−3000 cm^{-1}, the assignment of PAN is based on the C−C and C−N vibrations at lower wavenumbers, i.e., 1200−1700 cm^{-1}. Clearly, the PAN monolayer reveals IR bands similar to those of PAN on gold, a spectrum that has been studied extensively.[26] In general, the IR spectrum of PAN

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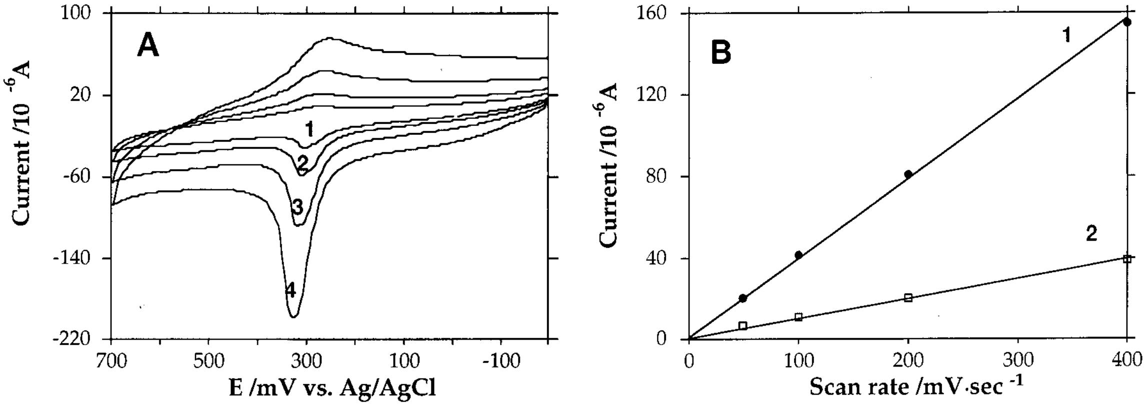

Figure 2. (A) Cyclic voltammetry of PAN/MDS modified electrode in a 0.1 M HCl solution at different scan rates (mV s^{-1}): (1) 50; (2) 100; (3) 200; (4) 400. (B) Dependence of the anodic (1) and cathodic (2) peak currents on the scan rate.

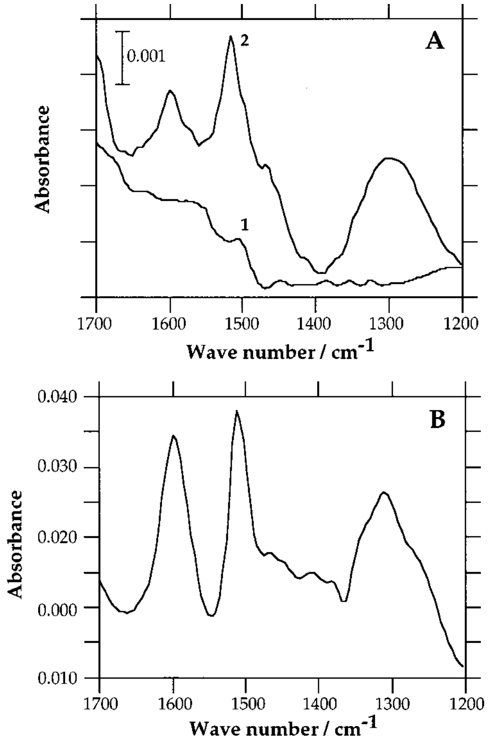

Figure 3. Reflection−absorption IR spectra of (A) MDS (1) and PAN/MDS (2) layers, and (B) a thicker film of PAN electrodeposited on a bare gold electrode under the same conditions.

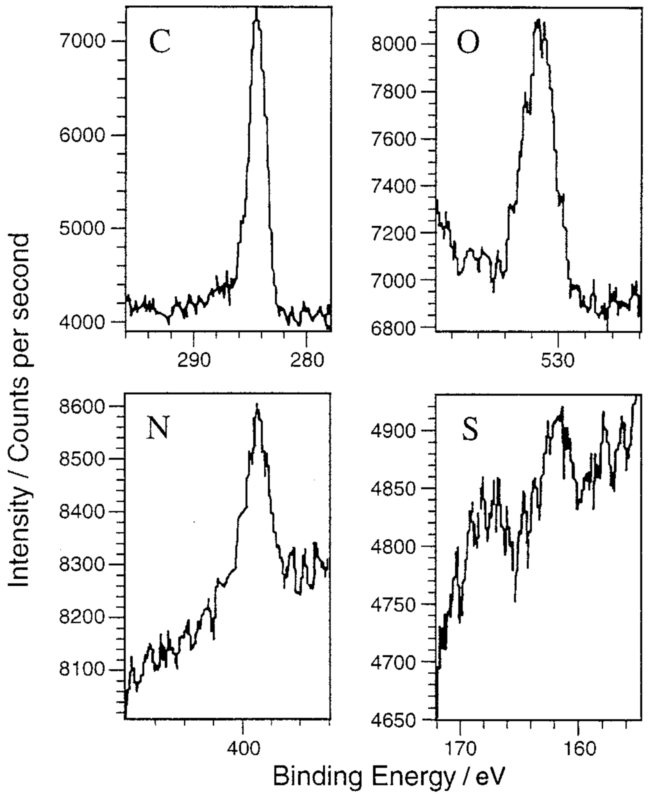

Figure 4. C 1s, N 1s, O 1s, and S 2p XPS spectra of a PAN/MDS monolayer on a gold substrate.

Table 1. Atomic Composition of the Elements of a PAN/MDS Interface

elements	PAN-MDS, %	elements	PAN-MDS, %	elements	PAN-MDS, %
Au (4f)	32.25	N (1s)	3.57	S (2p)	0.78
C (1s)	53.55	O (1s)	8.23		
F (1s)	0.33	S (2p)	1.30		

on gold surfaces exhibits several signals in the mid-IR that depend substantially on the electropolymerization conditions. More specifically, the two vibrations of PAN at 1599 and 1517 cm^{-1} are assigned to the υ(C=C) modes, while the bands between 1265 and 1315 cm^{-1} are attributed to the stretching of the C$_{\text{aromatic}}$−N bonds.[26] These signals are detected in the monolayer of PAN at almost the same wavenumbers (Figure 3A). Sometimes an additional band is detected at ~1700 cm^{-1} in the MDS/PAN spectrum, which might be from overoxidized PAN.

The stoichiometric ratio between aniline and the MDS in the monolayer can be obtained from XPS measurements. XPS has widely been used for studying PAN films.[27] Figure 4 shows the XPS spectrum of the relevant elements, and Table 1 summarizes the atom percent of all the elements that were measured. Note that the aniline was preconcentrated and electropolymerized in fluoride buffer solutions to avoid incor-

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Table 2. Theoretical (Assuming a 1:1 ratio) and Experimental Ratios between the Elements in the PAN/MDS Monolayer

	theoretical	experimental
C:N	16:1	15.0:1
O:N	3:1	2.3:1

poration of ions (e.g., phthalate) that contain elements already included in the monolayer. The samples were measured after doping the PAN at potential of 0.2 V. The XPS spectra confirm that anilinium ions are indeed preconcentrated onto the electrode surface before their polymerization, as indicated by the N^{1s} signal at 398.8 eV. Several researchers have shown that the nitrogen signal can be used upon deconvolution to assign the different amine and imine species in the polymer.[27a−c] Basically, the neutral imine and amine appear at 398.5 and 399.5 eV, respectively, whereas protonated N-species are located at higher energies and result in a shoulder. Therefore, the asymmetric peak of N^{1s} detected in the PAN monolayer (Figure 4) provides a distinct indication of the polymerization of aniline and the existence of a partially charged nitrogen. The counterions in this case might be either the sulfonate groups, as in sulfonated PAN,[28] or fluoride ions. Traces ($<0.5\%$) of fluoride ions were detected in the XPS spectrum. Finally, and as expected, two different sulfur signals at 168.2 and 162.1 eV were clearly visible; they were assigned to the sulfonate and thiol groups, respectively.

The data presented in Table 1 require a deeper inspection. Basically, the oxygen and sulfur originate from the MDS monolayer, whereas the nitrogen is contributed by the aniline only. In the case of a 1:1 ratio between the MDS and the anilinium ions, as would be anticipated on charge considerations, the carbon percent originated from MDS should be 33.5% (of 53.55%) and that of PAN 20%. Table 2 summarizes the theoretical (assuming a 1:1 ratio) and experimental ratios between the elements in the PAN/MDS monolayer. The experimental ratios between carbon/nitrogen and carbon/oxygen originating from PAN and MDS, respectively, are close to the theoretical ratios, but the experimental ratio for carbon/sulfur is substantially higher than the theoretical value, presumably because of the location of a sulfur buried deep at the substrate−monolayer interface. A lower than expected value for the S(thiolate)/C ratio has been reported by Bain et al.,[29] which they ascribed to inelastic scattering by the molecules in the monolayer. In fact, integration of the two sulfur peaks does not yield the same atomic percent (Table 1) because of the same effect, namely, that the thiol is located deeper in the film than the sulfonate group. Therefore, determination of the ratio between MDS and aniline should be derived from the ratio for oxygen/nitrogen as well as from the ratio between the total carbon content and either nitrogen or oxygen. To conclude, the data of Table 1 indicate that the ratio for MDS/PAN is slightly <1, or in other words, more anilinium is extracted than expected.

All these results verify the formation of PAN; however, they do not provide any structural detail about the nature of the assembly (Figure 5). Although our wish was to form a capacitor-type assembly in which the gold substrate would be separated from the PAN conducting layer by an insulating layer, such a structure is still to be proven. Moreover, the fact that the PAN/MDS ratio is >1 might indicate that aniline is incorporated inside the MDS monolayer rather than on it.

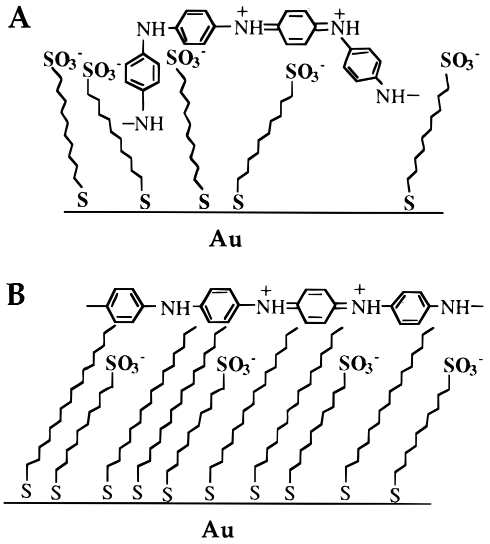

Figure 5. Schematic representation of (A) PAN monolayer penetrating into an MDS SAM, (B) 2-D PAN monolayer deposited on a mixed SAM of MDS/C_{16}.

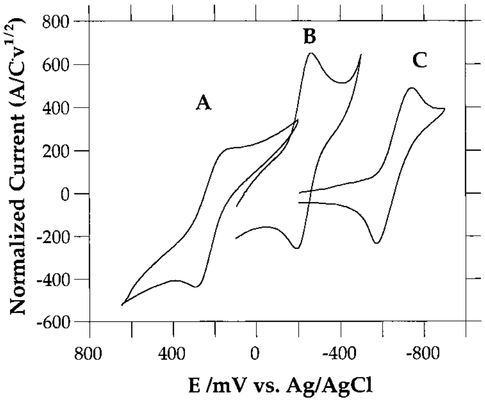

Figure 6. Cyclic voltammetry of (A) 2 mM $Fe(CN)_6^{3-}$, (B) 2 mM $Ru(NH_3)_6^{3+}$, and (C) 2 mM MV^{2+} recorded with PAN/MDS modified electrodes. The electrolyte was 0.1 M Na_2SO_4 and the scan rate was 100 mV·s^{-1}.

The first step toward addressing this structural question involved examining the electrochemistry of redox couples at MDS and MDS/PAN monolayers. We studied the CV of $Fe(phen)_3^{2+}$, $Fe(CN)_6^{3-}$, $Ru(NH_3)_6^{3+}$, MV^{2+}, I^-, and Fe^{3+}. Figure 6 shows as examples the CV of $Ru(NH_3)_6^{3+}$, $Fe(CN)_6^{3-}$, and MV^{2+} at an MDS/PAN electrode. In essence, we found[22] that, although an MDS monolayer blocks inorganic anions very efficiently, it does not at all affect electron transfer of positively charged or neutral inorganic species. This clearly suggests that MDS only partially covers the gold substrate, forming a disorganized layer. As mentioned before, the surface coverage derived from electrochemical measurements[22] was estimated as $\theta \approx 0.25-0.4$. On the other hand, we found that the CV of all the species studied at an MDS/PAN interface is almost identical to that observed on a bare gold electrode (Figure 6). The electrochemistry of redox couples on PAN films has been well studied and depends on the potential window, electrolyte, and pH.[30] Electroactivity of redox couples can be observed only

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[28] For example: Barbero, C.; Miras, M. C.; Kötz, R.; Haas, O. *J. Electroanal. Chem.* **1997**, *437*, 191−198.

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in a limited potential window in which PAN is in its conducting (i.e., doped) state. Hence, for example, although the reduction of $Fe(CN)_6^{3-}$ is detectable at PAN-coated electrodes, neither $Ru(NH_3)_6^{3+}$ nor MV^{2+} is electroreducible on PAN films. The fact that the CV of the various redox couples was not affected by the MDS/PAN monolayer can be explained by the disorganized MDS monolayer, which enables anilinium ions to penetrate and polymerize into the layer. This results in a nonuniform monolayer of PAN (as shown schematically in Figure 5A) that is too thin to prevent direct electron transfer from the gold surface. As a consequence, the monolayer–electrolyte interfacial electrochemistry is not governed by PAN.

These results imply that to form a better PAN monolayer that will be separated from the Au substrate and at the same time control the electrochemical properties of the surface, one must increase the packing of the organic spacer, i.e., the MDS layer. This, in turn, will prevent the anilinium ions from penetrating the monolayer and will enhance formation of a 2-D PAN layer on top of the insulating spacer. Interestingly, our attempts to form a more-packed monolayer via the spontaneous adsorption of C_{16} on an initially self-assembled MDS monolayer failed. We observed no changes in electron-transfer rates of redox couples, e.g., $Fe(phen)_3^{3+}$, after leaving an MDS monolayer in an ethanolic solution of C_{16} for as long as one week. In other words, the C_{16} did not block the pinholes in the MDS monolayer. This is itself an interesting observation, which we have further examined elsewhere.[22] We found that because of their high negative charge and hydrophilicity, long-chain ω-mercaptoalkanesulfonic acid monolayers are almost impermeable to inorganic anions as well as to organic molecules. Therefore, we had to incorporate an hydrophobic thiol into the MDS monolayer by other means. Recently, Ron and Rubinstein[31] have found that a highly organized SAM of alkanethiol was formed as a result of applying a positive potential to a bare gold electrode in an ethanolic solution of the thiol at mM concentration. Although the mechanism of this electrochemically induced adsorption and organization is not completely understood, they claimed that the monolayer formed was as dense as those assembled by the conventional method. Accordingly, we found that applying 0.8 V vs AgQRE to an MDS-modified gold surface in an ethanolic solution of 1 mM C_{16} significantly affected the solid–liquid interface. One indication that the surface was blocked by the thiol was the dramatic decrease of the current when a positive potential was applied in the C_{16} solution. The anodic current decreased to ~1% of its initial value during 40 min of electrolysis in a nonstirred solution. In addition, the charging current measured in 0.1 M phthalate buffer (pH 3.0) containing 0.5 M Na_2SO_4 was substantially smaller than that with the MDS monolayer (Figure 7). Control experiments in which a positive potential was applied to an MDS-modified gold surface in the same ethanolic solution but in the absence of C_{16} caused the partial desorption of the MDS monolayer. Figure 8 shows the CV of $Fe(phen)_3^{2+}$ recorded with an MDS/C_{16} and MDS-modified electrode. Clearly, the rate of electron transfer of the iron complex is significantly influenced by the MDS/C_{16} monolayer in comparison with that rate for a bare or MDS-coated electrode.

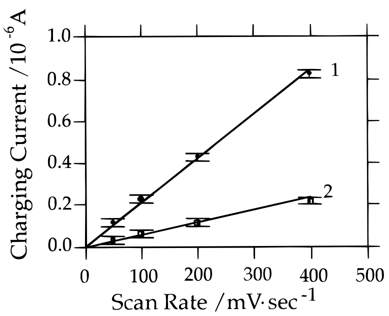

Figure 7. Charging currents as a function of scan rate measured in a solution of 0.1 M phthalate buffer (pH 3.0) and 0.5 M Na_2SO_4 with MDS- (1) and MDS/C_{16}- (2) modified electrodes.

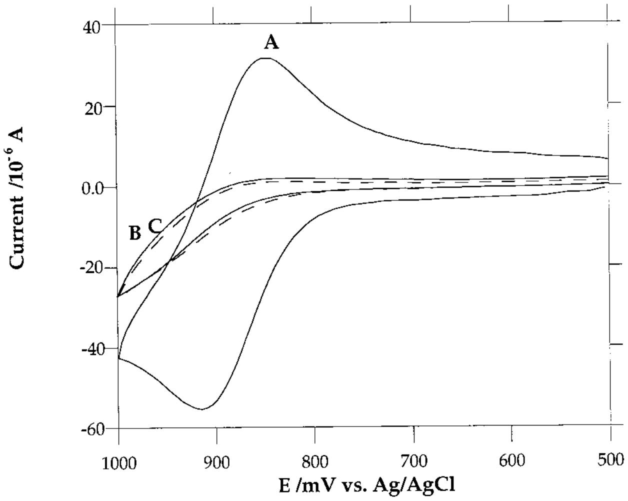

Figure 8. Cyclic voltammetry of 2 mM $Fe(phen)_3^{2+}$ in 0.1 M HCl recorded with (A) MDS, (B) MDS/C_{16}, and (C) (dotted line) MDS/C_{16}/PAN-modified gold electrodes. Scan rate 50 mV·s^{-1}.

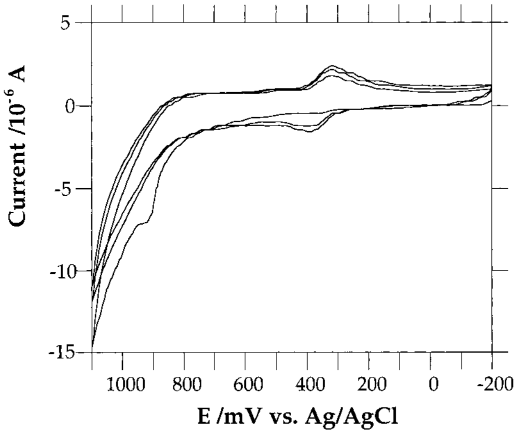

Figure 9. Cyclic voltammetry of MDS/C_{16}-modified gold electrode recorded in a solution of 0.1 M phthalate buffer (pH 3.0) and 0.5 M Na_2SO_4 after preconcentrating anilinium ions. Scan rate 50 mV·s^{-1}.

One of our concerns when using Ron and Rubinstein's method was the stability of the MDS monolayer. In other words, incorporation of the C_{16} must not result in desorption of the MDS monolayer. Two sets of independent experiments were conducted to address this concern. The first involved the extraction of anilinium ions by the MDS/C_{16} monolayer, followed by electropolymerization of the ions. Figure 9 shows the CV of an MDS/C_{16} in phthalate buffer (pH 3.0 and 0.5 M Na_2SO_4) after the extraction of anilinium ions. The CV is similar to that obtained with an MDS monolayer, showing a distinct electropolymerization of surface-confined anilinium in the mixed monolayer. Nevertheless, measuring the charge associated with the electropolymerization process revealed that the excess of surface coverage of aniline was 0.061 ± 0.02 nmol cm^{-2}, compared with 0.26 nmol cm^{-2} for an MDS monolayer. This drastic decrease is presumably the result of two effects: First, less anilinium is adsorbed because it cannot penetrate into

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(31) Ron, H.; Rubinstein, I. *J. Am. Chem. Soc.*, in press.

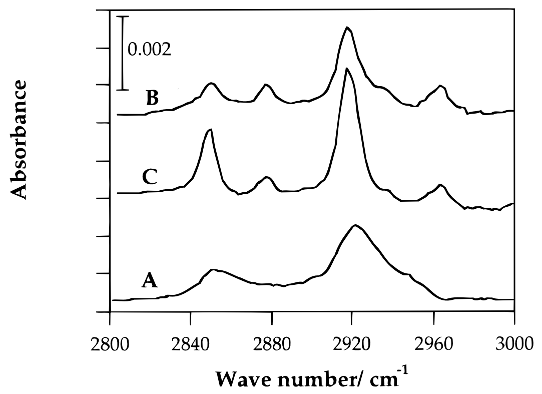

Figure 10. Reflection−absorption IR spectra of (A) MDS, (B) C_{16}, (C) MDS/C_{16} monolayers.

the mixed monolayer; second, the MDS monolayer is partially desorbed as a result of the potential-induced adsorption of C_{16}. Nonetheless, this excess of surface coverage is sufficient to form a PAN film (see below).

For a more detailed investigation on the MDS/C_{16} monolayer we used reflection−absorption IR. Figure 10 shows the IR spectra (only the 2800−3000 cm^{-1} range) of monolayers of MDS, MDS/C_{16}, and C_{16} obtained by using a *p*-polarized light incident at 80° to the normal. The reflection−absorption IR of thiols on metallic surfaces, especially on gold, has been treated theoretically and experimentally.[32] The methylene groups of the alkyl chains absorb at ~2850 and 2920 cm^{-1}, which correspond to symmetric and asymmetric C−H vibrations, respectively. These signals are sensitive to the degree of organization of the monolayer; i.e., a shift to higher frequencies of both bands is indicative of a disorganized layer. The symmetric and asymmetric C−H vibrations of a methyl group at the end of an alkyl chain absorb at 2878 and 2963 cm^{-1}, respectively. Accordingly, the MDS shows two bands at 2852 and 2921 cm^{-1}, which are assigned to the symmetric and asymmetric C−H vibrations (Figure 10A). The position of these bands strongly suggests that the MDS monolayer is disorganized, in agreement with our electrochemical experiments (Figure 6), which showed that the MDS monolayer is permeable to inorganic cations. For comparison, the methylene groups of an organized C_{16} monolayer absorb at 2850 and 2918 cm^{-1} (Figure 8B). That four C−H bands are detectable in the mixed monolayer (Figure 10C) suggests that C_{16} is indeed adsorbed on the surface and is responsible for the methyl signals.

The methylene symmetric and asymmetric vibrations of the mixed monolayer appear at 2850 and 2918 cm^{-1}, respectively. This shift in the frequencies can be attributed to either an average of the C_{16} absorbance in an organized layer and in the disorganized MDS monolayer, or to an induced organization of the MDS monolayer caused by the incorporation of C_{16}. To confirm that C_{16} increases the organization of the MDS monolayer, we carried out a similar experiment in which a perdeuterated 10-decanethiol was electrochemically incorporated onto an MDS monolayer. A similar shift in the C−H bands that are totally ascribed to the MDS was observed, indicating that the methylene groups of the MDS undergo an induced organization as a result of incorporating an alkanethiol into the monolayer. At the same time, we suggest that C_{16} does not change its orientation as a result of incorporation into the MDS monolayer.

The three spectra (Figure 10) make it possible to determine the molecular surface coverage of the MDS monolayer, θ, as was recently suggested by Kauffmann and colleagues.[33] According to their approach, θ is proportional to the integrated intensity of a specific band, *A*, multiplied by its proportionality factor, f. Thus, θ is expressed by the integrated intensity of the asymmetric methylene band, $(A_{\mathrm{MDS}})_{\mathrm{CH_2}}$ at 2924 cm^{-1} and a corresponding proportionality factor, f_{MDS} (eq 1). The assumptions needed are that $\theta = 1$ for the MDS/C_{16} mixed monolayer and for a C_{16} monolayer (eqs 2 and 3), where $(A_{\mathrm{C_{16}}})_{\mathrm{CH_3}}$ and $(A^*_{\mathrm{C_{16}}})_{\mathrm{CH_3}}$ represent the integrated intensities of the symmetric methyl stretching in pure C_{16} and MDS/C_{16}, respectively, and $(A^*_{\mathrm{MDS}})_{\mathrm{CH_2}}$ stands for the partially integrated intensity of the asymmetric methylene of MDS in the mixed monolayer.[34] The partial contribution of C_{16} to the symmetric or asymmetric methylene signals in the mixed monolayer can be calculated from the ratio between the methylene/methyl signals in the C_{16} pure monolayer (eq 4). From that, the integrated intensity attributable to the MDS in the mixed monolayer, $(A^*_{\mathrm{MDS}})_{\mathrm{CH_2}}$, can be found (eq 5), where A^* is the total integrated intensity of the asymmetric methylene band in the mixed monolayer.

$$\theta = f_{\mathrm{MDS}}(A_{\mathrm{MDS}})_{\mathrm{CH_2}} \tag{1}$$

$$1 = f_{\mathrm{C_{16}}}(A_{\mathrm{C_{16}}})_{\mathrm{CH_3}} \tag{2}$$

$$1 = f_{\mathrm{C_{16}}}(A^*_{\mathrm{C_{16}}})_{\mathrm{CH_3}} + f_{\mathrm{MDS}}(A^*_{\mathrm{MDS}})_{\mathrm{CH_2}} \tag{3}$$

$$(A^*_{\mathrm{C_{16}}})_{\mathrm{CH_2}} = (A^*_{\mathrm{C_{16}}})_{\mathrm{CH_3}}(A_{\mathrm{C_{16}}})_{\mathrm{CH_2}}/(A_{\mathrm{C_{16}}})_{\mathrm{CH_3}} \tag{4}$$

$$(A^*_{\mathrm{MDS}})_{\mathrm{CH_2}} = A^* - (A^*_{\mathrm{C_{16}}})_{\mathrm{CH_2}} \tag{5}$$

θ can be derived from this set of equations as follows (eq 6).

$$\theta = [(A_{\mathrm{C_{16}}})_{\mathrm{CH_3}} - (A^*_{\mathrm{C_{16}}})_{\mathrm{CH_3}}](A_{\mathrm{MDS}})_{\mathrm{CH_2}}/[A^*(A_{\mathrm{C_{16}}})_{\mathrm{CH_3}} - (A^*_{\mathrm{C_{16}}})_{\mathrm{CH_3}}(A_{\mathrm{C16}})_{\mathrm{CH_2}}] \tag{6}$$

Estimating θ from both the asymmetric and the symmetric vibrations gave $\theta = 0.35 \pm 0.05$. This relatively low value of θ is not surprising and is in excellent accordance with our electrochemical measurements[22] that suggest that MDS only partially covers the gold substrate.

We also used wettability measurements for following the changes that resulted from incorporating the C_{16}. A clear increase in the advancing contact angle of water on the mixed monolayer (to 98° from the 43° for the highly hydrophilic MDS monolayer) was observed. On the other hand, the formation of a thin PAN film on the mixed monolayer resulted in a decrease of 20° in the advancing contact angle of water, presumably because of full coverage of the monolayer by PAN.

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[34] The model is based on the assumption that the proportionality factors f_{MDS} and $f_{\mathrm{C_{16}}}$ are identical for both the pure and the mixed monolayers. While the change in $f_{\mathrm{C_{16}}}$ between the pure C_{16} and the mixed layer is negligible, based on the similarity of peak position in spectra (Figure 10B and C), f_{MDS} might be somewhat different in the pure vs the mixed monolayer. f_{MDS} is expected to increase with an increasing of the tilt angle of the alkyl chain from the normal. The resulting θ would be smaller than the experimental value. The agreement between the calculated value from IR measurement and that obtained fron electrochemical experiment suggests that the uncertaintly in f_{MDS} is relatively small.

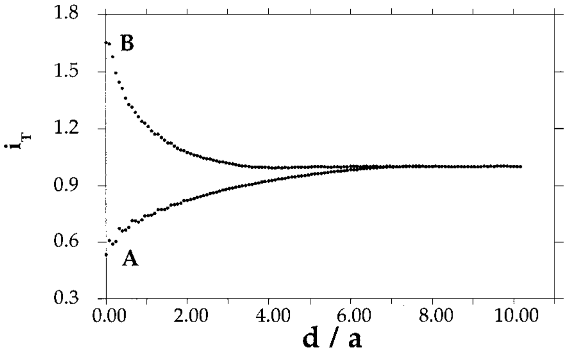

Figure 11. SECM-normalized feedback current−distance curves obtained with a 25-μm-diameter Pt tip in a solution of 2 mM Fe(phen)$_3^{2+}$ and 0.1 M HCl, approaching (a) MDS/C$_{16}$ substrate; (A) or PAN/MDS/C$_{16}$ substrate (B).

All these results suggest that the mixed monolayer of MDS and C$_{16}$ is still capable of extracting anilinium ions and that the latter can be electropolymerized to form a thin PAN film. Nevertheless, this still does not prove that the PAN monolayer maintains its high conductivity or that it is electronically separated from the gold surface (Figure 5). To characterize the thin PAN film, we used (SECM), a technique already used for studying ionically and electronically conducting polymers.[35−39] The conductivity and redox behavior of polypyrrole films has been studied by Bard and co-workers,[35] and the incorporation of cations was verified by SECM measurements of tip current−time curves or by tip/substrate CV. Direct evidence of ingression and egression of protons and anions during the oxidation of leucoemeraldine to emeraldine and pernigraniline was obtained by Frank and Denualt[36] from the tip response to changes in the potential of PAN films. On the other hand, Heinze and co-workers[37] recently presented an example of a "microwriting" and "reading" process of an undoped PAN film deposited on poly(ethylene terephthalate)-glycol substrate. Finally, SECM has been utilized in both direct and feedback mode for driving the local electropolymerization of polypyrrole and other conducting polymers.[35a,38−39]

The SECM is based on approaching a surface with an ultramicroelectrode (UME) while measuring its faradaic current. In most cases an electroactive species is added to the solution and is electrochemically oxidized or reduced at the UME under diffusion-controlled conditions. The electrochemical properties of the substrate affect the current of the UME and therefore can be studied by monitoring the UME current as a function of the distance from the surface or of its potential.

Figure 11 presents two SECM-normalized feedback current−distance curves obtained with a 25-μm-diameter Pt UME in a solution of 2 mM of Fe(phen)$_3^{2+}$ and 0.1 M HCl while approaching an MDS/C$_{16}$ monolayer before (curve A) and after (curve B) extracting and electropolymerizing aniline. In both experiments, the gold surface was not attached to an external power source. A clear negative feedback is observed upon approaching the MDS/C$_{16}$ monolayer, indicating that the Fe(phen)$_3^{3+}$ generated at the UME is not efficiently regenerated at the mixed monolayer. This is in agreement with CV of the same redox couple (Figure 8, curve B), which shows that the mixed monolayer behaves like an insulating layer that substantially decreases the rate of electron transfer across it. At the same time, a positive-feedback current and an almost reversible CV are observed while approaching a monolayer of MDS alone because of the partial coverage of the surface by MDS. A positive feedback current is also detected above an MDS monolayer after the extraction and electropolymerization of anilinium ions. Obviously, this does not indicate that PAN is electronically separated from the gold surface. On the other hand, curve B in Figure 11 shows that a positive feedback current is observed as the UME approaches a PAN film that was formed after extracting anilinium ions by an MDS/C$_{16}$ mixed monolayer. The 2-D PAN film was electropolymerized in pH 3.0, after which the resulting film was electrocycled in pH 1.0 (0.1 M HCl) to increase its conductivity. At the same time, the CV of Fe(phen)$_3^{2+}$ is irreversible on this surface, similar to the CV observed before the anilinium ions are extracted (Figure 8). When we examined a variety of redox couples, e.g., Ru(NH$_3$)$_6^{3+/2+}$, Fe(CN)$_6^{3-/2-}$, Fe$^{2+/3+}$, and dipropyl viologen sulfonate$^{0/-1}$, at this interface, their behavior resembled that of a partially blocked interface. That is, although the CV of positively charged redox couples was almost unaffected by the PAN in comparison with the CV for MDS/C$_{16}$, negatively charged species such as Fe(CN)$_6^{3-}$ showed higher currents at an MDS/C$_{16}$/PAN interface, which can be explained by the neutralization of the negative charge of the MDS by PAN.

These results can be explained only if we assume that the 2-D PAN is electronically isolated from the gold substrate. The positive feedback current that is observed on such film is attributable to the relatively high conductivity of the film (which serves as a conducting surface on which electrons can diffuse from other parts of the surface that are not located beneath the UME and regenerate the redox couple). That is, the PAN film acts as an inert conducting surface in which the positive feedback current is driven by the difference in the Ox/Red ratio beneath the UME and the solution.[40] On the other hand, we cannot entirely exclude the existence of defects in the organic spacer through which the redox couple exchange (to some extent) electrons with the gold surface. Nevertheless, the irreversible electron transfer observed for all redox couples examined on this interface cannot explain the positive feedback current of the SECM experiment, which must be due to the formation of large areas of conducting PAN on top of the organic insulating layer.

Additional evidence for the hypothesis that the electrochemical properties of PAN control the regeneration of the redox couple is provided by studying the effect of pH on this process. The positive feedback current that is observed while approaching a PAN monolayer formed on an MDS/C$_{16}$ spacer changes to a negative feedback current at pH 4.0 (in 0.1 M acetate buffer). We attribute this change of the magnitude of the feedback current to the strong dependence of the conductivity of PAN on pH. Wrighton and colleagues[20a] reported that the conductivity of PAN is reduced markedly as the pH is changed from 1 to 6.

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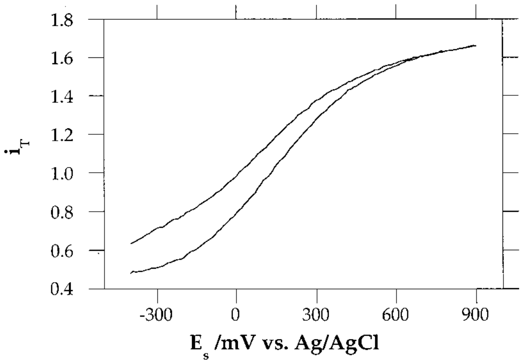

Figure 12. Tip current vs substrate potential. The microelectrode (a 25-μm-diameter Pt tip precoated with Hg) was held at a constant potential of -0.7 V above ($\sim$10 μm) a PAN/MDS/C_{16} substrate in a solution of 2 mM MV^{2+} and 0.01 M H_2SO_4. The potential of the substrate was scanned at 25 mV·s^{-1}.

The feedback current is expected to vary as a function of the substrate potential since the conductivity of PAN changes dramatically when the polymer is doped. Figure 12 shows the UME−substrate CV obtained while holding the UME at a constant height above the PAN monolayer in a solution of 2 mM MV^{2+} and 0.01 M H_2SO_4. The normalized UME current, i_T, was recorded as a function of the substrate potential, E_S. The UME was a 25-μm-diameter Pt disk on which a thin Hg film was electrodeposited. The latter was essential to prevent hydrogen evolution since the UME potential was held at -0.7 V to ensure that the MV^{2+} was reduced under diffusion control. The CV in Figure 12 clearly shows that the feedback current changed from negative, ($i_T < 1$) to positive ($i_T > 1$) while the substrate potential was scanned from -0.6 V to 0.9 V. The transition from negative into positive feedback current occurred at $E \approx 0$ V, which nicely correlates with the switching potential of PAN.[20a] Note that a positive feedback current would have been observed at somewhat more-negative potentials on a bare gold substrate ($E^{\circ\prime}_{MV^{2+}/MV^{+\cdot}} = -0.65$ V). In other words, the efficient oxidation of $MV^{+\cdot}$ at the surface started as soon as the PAN monolayer was doped, which increase its conductivity and enabled electrons to diffuse laterally across the 2-D PAN monolayer.

Conclusions

A novel approach for the formation of a 2-D conducting polymer on top of an insulating layer has been demonstrated. This approach, based on electrostatically binding a monomer to a charged monolayer followed by its electrochemical polymerization, has at least two significant advantages. It represents a generic and versatile concept that is not limited to PAN but can easily be exploited in other systems as well. Second, the electrostatic attachment does not “freeze” the orientation of the monomer but leaves it a sufficient degree of flexibility that is essential for the electropolymerization process. We believe this is the major reason why the 2-D conducting polymer exhibited similar chemical and electrochemical properties to those of conventional electrochemically deposited PAN. We are currently exploiting the same approach for assembling a PAN monolayer on an insulator by using silane chemistry and patterning it with use of SPM techniques.

Acknowledgment. This research was supported by the German-Israeli Foundation (grant no. I-0310) and the Volkswagen Foundation (grant no. I/68223).

JA9809760