Contact Angle and Electrochemical Characterization of Multicomponent Thiophene-Capped Monolayers

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We have investigated the wetting behavior and electrochemical response of self-assembled monolayers made from ω-(3-thienyl)-alkyltrichlorosilanes and alkyltrichlorosilanes on indium–tin oxide coated glass slides. Contact angle measurements and cyclic voltammetry show that the properties of the monolayers change as the relative loading of the two components is changed by altering the concentration of the deposition solution. The water contact angles indicate that a fully loaded hydrophobic layer is formed, and both water and hexadecane contact angle measurements show that the tethered thiophenes are at the periphery of the monolayer. However, the hexadecane contact angles also imply that the surface roughness exposes the methylene groups of the monolayer chains. Cyclic voltammograms obtained from mixtures of 11-(3-thienyl)undecyltrichlorosilane and decyltrichlorosilane and mixtures of 16-(3-thienyl)hexadecyl-trichlorosilane and hexadecyltrichlorosilane show that as the relative amount of thienyl-bearing chains in the monolayer decreases, the oxidation peak position shifts to higher potential and the peak area, which is related to the amount of charge transferred, decreases. Integration of the oxidation peak area from the cyclic voltammetry experiments yields a coverage that is consistent with a monolayer. Preliminary evidence for formation of a surface-tethered redox-active polymer is observed by cycling the self-assembled monolayers at low potentials.

Introduction

Modification of surfaces with self-assembled monolayers (SAMs) is one route to conferring desirable properties to the underlying substrate. In general, the assembly of these amphiphilic interfacial layers is driven by the affinity that the tethering group has for the surface (e.g., thiols for gold or silanes for oxide) and interchain interactions that drive packing of the chains into a dense surface layer. By controlling the size, structure, and composition of the monolayer, it is possible to manipulate the properties of the interfacial layer. One class of SAMs that are particularly interesting for their ability to create well-defined surface layers with controllable properties is ω-substituted monolayers, which present a functional group at the monolayer periphery.

In recent years, there has been widespread interest in using ω-substituted monolayers to create surface layers with tunable properties. Some of the targeted applications include promoting or preventing the adherence of materials to the substrate,[1–4] changing the wetting behavior,[5–12]

or altering the frictional properties of the surface.[13–15] In applications ranging from producing biocompatible layers to developing surfaces with specific wear properties, the ability to place a specific functional group at the periphery of the monolayer or mediate the surface density of active sites permits tailoring of the physicochemical properties of the surface. Directly related to the work presented in this paper are systems in which the groups in the monolayers impart electrical, optical, or photonic activity to the surface.

For example, using multicomponent SAMs made from *n*-alkyl and azobenzene-terminated chains, Evans and co-workers[16] were able to produce molecularly thin surface layers with reversible photoactivity. They found that the presence of the *n*-alkyl chains, which reduce the concentration of azobenzene-terminated chains, enabled the photoswitching of the azobenzene groups. Hayes et al.[17] utilized a mixed monolayer system consisting of dissimilar materials, octadecanethiol and 4-aminothiophenol (4-ATP), to produce phase-separated domains on electrode surfaces to nucleate the electropolymerization of aniline from the 4-ATP islands. SAMs made from alkanethiol chains capped with a redox group, such as ferrocene or viologen,[18–21] have been used to mediate the transfer of

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electrons to and from the surface. These systems are of interest because of their potential application as molecular electron relays for sensing and display devices. The electrochemical response of ω-substituted SAMs containing either pyrrole or thiophene headgroups has also been an area of intense study. Researchers have shown that thiol-based monolayers bearing pyrrole molecules[22-26] or silane-based monolayers capped with dimers or trimers of thiophene[27-29] or pyrrole[30] can be electrochemically or chemically oxidized. This can result in polymerization of the groups within the monolayer. Because these SAMs are capped with the constituents of electrically conductive polymers (polypyrrole or polythiophene), they promote the growth and adhesion of conductive polymer chains to the surface and can be used to template the electrochemical deposition of conductive polymers.

Conductive polymers are of key interest because of their electrical and optical activity. They are viewed as suitable materials for applications that include antistatic layers, organic electronic and nonlinear optical devices, and selective electrodes. Like other polymers, the conformation of the chains plays an integral role in dictating properties. Thus, the fabrication of organic electro-optic devices depends on precise control of the assembly process, chain growth mechanisms, and chain orientation. For example, Roncali and co-workers[31] have reported that polythiophene films with a thickness of approximately 200 nm prepared from anodic electropolymerization exhibited conductivities as high as 2000 S cm^{-1}. The high conductivity, which is an order of magnitude higher than that of bulk films, was attributed to a high degree of ordering and conjugation brought on by the compactness of the thin film. Gregory and co-workers[32] showed that the refractive indices in the three principle directions of a conductive polyaniline film became anisotropic when the film was biaxially stretched to induce orientation of the chains. Despite successes in developing conductive polymer films with anisotropic or enhanced properties, the most significant barrier to using conductive polymers in device applications is their intractability; they are difficult to dissolve, process, and polymerize because of their rigid aromatic structure, and they easily degrade. Highly reproducible, stable, and uniform thin films needed for device applications are difficult to achieve. Our work is aimed at overcoming some of these difficulties by using surface-anchored monolayers to promote the growth of tethered electrically conductive
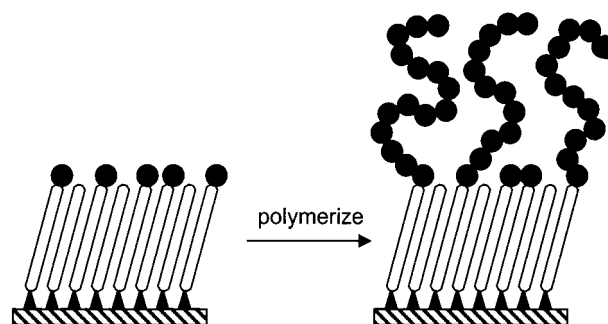

Figure 1. Schematic diagram showing the modification of a surface with a conductive polymer grown from a self-assembled monolayer. Polymerization is initiated from the group at the free end of the monolayer, and the distribution of groups along the periphery of the monolayer discourages polymerization within the monolayer.

chains from the monolayer. Specifically, we are interested in exploring whether multicomponent monolayers can be used to reduce the polymerization of groups within the monolayer and allow the chains to grow from the liquid–solid interface to create thin tethered films. A schematic diagram of this process is depicted in Figure 1.

In this paper, we report primarily on our activities to characterize the wetting behavior and electrical activity of pure and mixed monolayers made from ω-(3-thienyl)-alkyltrichlorosilanes on indium–tin oxide coated glass slides. Although metal-mediated Grignard couplings have been used by several groups to promote the coupling between alkyl halides and 3-bromothiophene,[27,33-36] we also report the routes used to synthesize the ω-(3-thienyl)-alkyltrichlorosilanes we have studied, including a pathway for making long-chain ω-substituted alkyltrichlorosilanes. The electrochemical properties of surface-bound monolayers capped with monomeric precursors of conductive polymers have been most recently reported on by Collard,[25-27] Kim,[26] and McCarley.[23,24] Our focus here is to understand how such monolayer assemblies can be manipulated in order to change the electrochemical activity of the system and also how the electrical activity is affected by the structure of the SAM. Mixed monolayers can be used to manipulate the electroactivity of the surface layer, with the composition of the monolayer being a very significant factor affecting oxidation potential and the amount of charge transferred. This is, to the best of our knowledge, the first such study of the electrochemical response of multicomponent monolayers made from this class of materials. We expect that the behavior of these mixed monolayers will ultimately affect the ability to grow the conductive polymer layer from the SAM.

Experimental Section

Synthesis. The ω-(3-thienyl)-alkyltrichlorosilanes used to make the monolayers were made by nickel phosphine complex catalyzed Grignard coupling of alkylbromides and 3-bromo-thiophene. This strategy has also been used by Mino and co-workers,[35] Inaoka and Collard,[27] and Appelhans and co-workers[36] to produce (3-thienyl)-alkyl-silane compounds. All reactions were performed in an inert atmosphere, and precursors were purified

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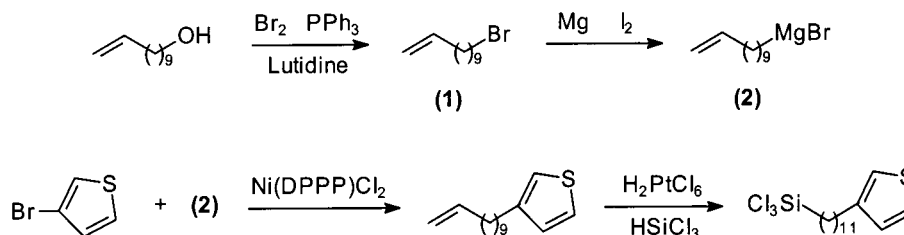
Figure 2. Synthetic scheme used to make 3TUTS. The alkyl chain (unsaturated at the ω-position) is joined to the thiophene ring by a metal-mediated cross coupling, and then the trichlorosilane functionality is added terminally across the double bond. This general scheme is used to make other chain lengths as well.

by standard laboratory techniques.[37,38] Unless otherwise noted, the materials needed to synthesize the ω-(3-thienyl)-alkyl-trichlorosilanes can be purchased from either Aldrich or VWR. Shown in Figure 2 is the scheme used to make 11-(3-thienyl)-undecyltrichlorosilane from 10-undecen-1-ol. This compound was brominated in the presence of triphenylphosphine and 2,6-lutidine, and the reaction was followed by thin-layer chromatography (TLC) to monitor the disappearance of 10-undecen-1-ol. 11-Bromo-1-undecene (**1**) was reacted with magnesium (in the presence of iodine) to form its Grignard reagent (**2**), and this was then coupled with 3-bromothiophene. A nickel phosphine catalyst was used to assist in the coupling. The 3-(10-undecenyl)-thiophene was verified by ^{1}H and ^{13}C NMR, and the coupling constant data is consistent with literature results[39] for 3-substituted thiophenes. All ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-300 at 300 and 75 MHz, respectively. Values of J are given in Hz. ^{1}H NMR (300 MHz, CDCl$_3$): δ_H 7.25−7.22 (dd, 1H, $J = 2.9$, $J = 4.8$), 6.95−6.92 (m, 2H), 5.98−5.77 (m, 1H), 5.05−4.94 (m, 2H), 2.64 (t, 2H, $J = 7.7$), 2.10−2.03 (q, 2H, $J = 6.9$), 1.61−1.53 (m, 2H), 1.37−1.24 (m, 12H). ^{13}C NMR (75 MHz, CDCl$_3$): δ_C 143.2, 139.2, 128.2, 125.0, 119.7, 114.1, 33.8, 30.6, 30.3, 29.52 (2×), 29.47, 29.3, 29.1, 28.9.

A method similar to that of Spier et al.[40] was used to add the trichlorosilane group terminally across the double bond. Excess trichlorosilane and a small amount of hydrogen hexachloroplatinate(IV) hydrate in 0.1 mL of 2-propanol were added into a reaction vessel that had been fitted with a dry ice/acetone condenser. The mixture was heated to 50 °C, at which point the 3-(10-undecenyl)thiophene was slowly added. The temperature of the reaction mixture was slowly increased to 90 °C, and the mixture was allowed to react for 1 h. The excess trichlorosilane was removed by short path distillation and the residual was purified by Kugelrohr distillation. The product was verified by NMR. ^{1}H NMR (300 MHz, CDCl$_3$): δ_H 7.26−7.23 (dd, 1H, $J = 2.9$, $J = 4.9$), 6.95−6.92 (m, 2H), 2.63 (t, 2H, $J = 7.7$), 1.65−1.55 (m, 2H), 1.43−1.23 (m, 18 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ_C 143.2, 128.3, 125.0, 119.7, 31.8, 30.5, 30.3, 29.5 (2×), 29.4, 29.3 (2×), 29.0, 24.3, 22.2.

Because of the limited availability of the ω-unsaturated primary alcohols needed for the above reaction sequence, a more involved synthesis was required to make longer-chain molecules such as 16-(3-thienyl)hexadecyltrichlorosilane (3THTS). Our scheme basically involved making the 16-bromo-1-hexadecene from two shorter alkyl chains and then doing a metal-mediated cross coupling to make 3-(15-hexadecenyl)thiophene. In the description of the reaction pathway that follows, we refrain from offering NMR data on intermediates. To make 16-bromo-1-hexadecene, we started with 11-bromo-1-undecanol and converted it to 11-bromo-1-undecanal in a suspension of pyridinium chlorochromate (PCC) in dry methylene chloride. The Grignard reagent of 5-bromo-1-pentene was made in dry ether and reacted with the 11-bromoundecanal to extend the chain length. For this reaction, the aldehyde was added slowly in a dropwise fashion to the reaction flask containing the Grignard reagent, and gentle refluxing was maintained. The coupling of the aldehyde and Grignard produced 16-bromo-1-hexadecene-6-ol.

To remove the secondary alcohol, the 16-bromo-1-hexadecene-6-ol was tosylated. Six equal portions of *p*-toluenesulfonyl chloride (tosyl chloride, TsCl) in pyridine (approximately 2 equiv of each) were added to a solution of 16-bromo-1-hexadecene-6-ol in dry methylene chloride. The reaction was monitored by TLC for disappearance of 16-bromo-1-hexadecene-6-ol. Additional portions of the pyridine/TsCl mixture were added as needed to drive the reaction to completion. The reaction was quenched with cold HCl and extracted using ether. During the extractions and washes, the system was held at a temperature of 0 °C. To cleave the tosyl group, 16-bromo-1-hexadecene-6-tosylate in ether was added in a dropwise fashion to a suspension of lithium aluminum hydride (LAH) in dry ether at 0 °C. TLC was used to monitor the reaction progress, and after approximately 12 h, when there was no indication of further progress, the reaction was stopped using ethyl acetate. After extracting with ether and washing the extracts, 16-bromo-1-hexadecene was isolated. This compound (analogous to **1**) was then used by following the reaction pathway displayed in Figure 2 to make 16-(3-thienyl)hexadecyltrichlorosilane. This product was verified by NMR. ^{1}H NMR (300 MHz, CDCl$_3$): δ_H 7.22−7.20 (dd, 1H, $J = 2.9$, $J = 4.9$), 6.92−6.89 (m, 2H), 2.61 (t, 2H, $J = 7.7$), 1.63−1.51 (m, 4H), 1.42−1.29 (m, 26H). ^{13}C NMR (75 MHz, CDCl$_3$): δ_C 143.2, 128.2, 125.0, 119.7, 31.8, 30.6, 30.3, 29.7 (4×), 29.6, 29.54, 29.45, 29.3 (3×), 29.0, 24.3, 22.3.

Preparation of Samples. Sample substrates of indium−tin oxide (ITO) coated glass slides (Delta Technologies, 0.7 mm thickness) were cut into rectangular pieces of 25 mm × 7 mm. The ITO-coated slides were cleaned by sonication in chloroform and a 20 wt % ethanolamine solution. The substrates were then rinsed, oven-dried, and used. The deposition solvent, methylene chloride, was freshly distilled prior to use, and decyltrichlorosilane (DTS) (United Chemical Technologies) and 11-(3-thienyl)-undecyltrichlorosilane (3TUTS) were vacuum distilled (0.1 mmHg) immediately before use. To make mixed monolayers, deposition solutions of the desired mole fraction of 3TUTS were made. All depositions were carried out under a nitrogen atmosphere. Each substrate was allowed to react with a 1 mM solution of the 3TUTS/DTS mixture for up to 72 h, and then the surfaces were thoroughly rinsed with methylene chloride and distilled water. Prior to analysis, the samples were rinsed with distilled water and dried with nitrogen. An analogous procedure was used when making monolayers containing 3THTS and hexadecyltrichlorosilane (HTS) (United Chemical Technologies).

SAMs on polished silicon were deposited in the same manner. The silicon surfaces were cleaned using fresh piranha etch (7:3 v/v concentrated H$_2$SO$_4$/H$_2$O$_2$), rinsed with copious amounts of distilled, deionized water, and then blown dry with nitrogen. These substrates were then immediately used. **Caution!** *Piranha solution should be handled with extreme care, as it reacts violently with most organic materials. Do not store piranha solution in a closed vessel.*

Contact Angle Measurements. Advancing and receding contact angles were measured using a Cahn Dynamic Contact Angle Analyzer (DCA-322). The contact angle liquids used were distilled water and hexadecane. Each contact angle measurement was repeated three times, and between each measurement the sample was dried under a stream of nitrogen.

Ellipsometry. The thickness of the monolayers on polished silicon was measured using a Rudolph AutoEL-II fixed angle, single-wavelength ellipsometer. The incident angle of the He−Ne laser beam was 70°. Multiple samples were prepared,

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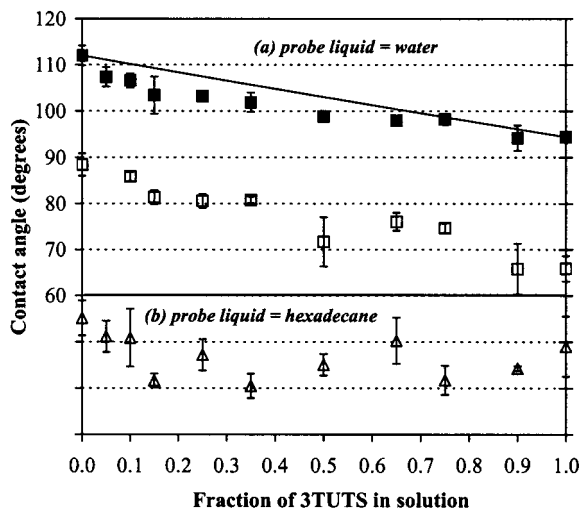
Figure 3. Contact angles as a function of the composition of the (deposition solution used to make) monolayers made from 11-(3-thienyl)undecyltrichlorosilane (3TUTS) and decyltrichlorosilane (DTS). (a) Advancing (■) and receding (□) water contact angles. The advancing water contact angle for SAMs made from only 3TUTS is similar to water contact angles on polythiophene (88°), and the contact angle for the pure alkyl chains is consistent with fully loaded hydrophobic surfaces. (b) Hexadecane contact angles (△). The low values are in line with the contact angle of hexadecane on polythiophene, but the roughness of the surface allows the probe liquid to contact the methylene groups of the alkyl chains too. The wetting behavior of the substrates modified with 3THTS and HTS SAMs is analogous.

including blanks, and thickness was calculated from the optical constants using a refractive index of 1.50.[41]

Electrochemistry. A single-compartment glass cell employing a standard three-electrode arrangement with a $Ag/AgNO_3$ nonaqueous reference electrode and a coiled platinum auxiliary electrode was used. The SAM-modified ITO slide serves as the working electrode. All cyclic voltammetry (CV) experiments were conducted at room temperature (24 ± 1 °C) on either a BioAnalytical Sciences (BAS-100) or a CH Instruments (model 600A) electrochemical analyzer. Electrolyte solutions of 0.1 M tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile were prepared and purged with nitrogen immediately before use. The supporting electrolyte was recrystallized from methanol and vacuum-dried for at least 48 h prior to use. A scan rate of 100 mV/s was used in all CV experiments.

Results and Discussion

The water contact angle data for monolayers made from DTS and 3TUTS is shown in Figure 3a. For a 100% DTS monolayer, advancing water contact angles of 112° were measured. This value is consistent with a fully loaded hydrophobic surface.[5–12,41,42] A monolayer composed solely of 3TUTS chains had an advancing water contact angle of approximately 92°. Because water prefers not to penetrate a hydrophobic layer, this value is a result of the thienyl groups (thiophene rings) located at the periphery of the monolayer. We made some sessile-drop measurements to determine the contact angle of water on a polythiophene film, and although the surface was rough, a value of approximately 88° was observed. The contact angle of water on the thienyl-bearing surfaces is similar to the contact angle for water on surfaces covered with phenyl groups, which is reported to be between 80 and
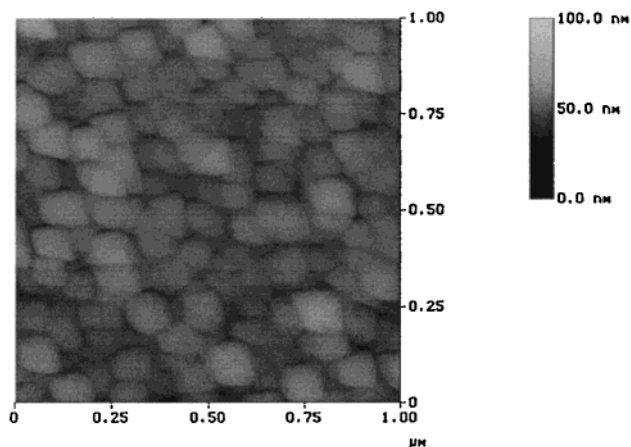
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Figure 4. Topographical image of an ITO substrate showing the rough, grainy nature of the ITO-coated glass substrates. The effect of the roughness can be seen in the hexadecane contact angle data (Figure 3b).

90°.[43–45] A line showing the equilibrium contact angles based on ideal mixing of the two components (Cassie's equation) is also plotted in Figure 3a. The receding contact angles are, on average, 20° lower than the advancing contact angles, and we attribute this hysteresis to surface roughness. As shown in Figure 3a, the advancing and receding water contact angles depend on the concentration of 3TUTS in the deposition solution and follow the trend of decreasing contact angle as the relative amount of thiophene-bearing chains (in the monolayer) increases. Also, the water contact angles of the mixed monolayers are distinctly different than those of either of the single-component SAMs. These observations suggest that the SAMs are not phase separated, as this situation would yield a contact angle independent of SAM composition.[10–12] Monolayers made from 3THTS and HTS on ITO exhibited similar results; we measured an advancing water contact angle of 105° for a monolayer made from only HTS and a value of 91° for a monolayer made of 3THTS. Although we do not presume that the concentration of the ω-(3-thienyl)-alkyltrichlorosilane in the monolayer is the same as in the deposition solution, we have two independent experiments, water contact angle and electrochemical measurements, that show that the properties of the monolayer assemblies change in a manner that follows the deposition solution concentration. This suggests that the monolayer composition also changes in a manner that follows the deposition solution composition.

An AFM image, produced in contact mode, of a cleaned, dried ITO surface is shown in Figure 4. The grainy nature of the surface is due to the method by which ITO is coated onto the glass surfaces; the ITO coating is formed by a reactive vapor-phase deposition of indium and tin oxide. Because there are many layers of ITO grains deposited on the surface, the widths and heights of the plateaus vary considerably. The influence of the surface roughness is seen quite strongly in the hexadecane contact angle data for these surfaces, which are shown in Figure 3b. For the entire range of deposition solutions used to make SAMs, we observe the hexadecane contact angles to be nearly constant, although in some cases there is significant variation between repeat samples. To put this behavior

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in the proper context, it is useful to review some limiting cases: (1) It is well-known that a highly ordered, well-packed monolayer terminated with methyl (CH_3) groups should have a hexadecane contact angle of approximately 45°.[10–12,41,42] (2) A surface that presents only methylene (CH_2) groups to the wetting liquid, for example, polyethylene, has a hexadecane contact angle of 0°.[41,46,47] (3) A surface of closely packed phenyl groups has a hexadecane contact angle of approximately 20°.[43–45] We have also measured the contact angle of hexadecane on electrochemically polymerized polythiophene films on ITO surfaces and found contact angles of 15.9 ± 2°.

On the basis of these last two pieces of data, the hexadecane contact angles we observe from SAMs containing a relatively high loading of thienyl groups appear to be consistent with what is expected. However, the low hexadecane contact angles measured for the *n*-alkyl SAMs and the SAMs that contain a relatively low loading of the thiophene groups would seem to indicate that the hexadecane probe liquid is also contacting a significant number of CH_2 groups. This, like the large hysteresis observed in the water contact angles, is probably a result of the surface roughness; the steps and edges of the ITO grains expose CH_2 groups to the contacting liquid. We anticipate that this happens for all SAM compositions, not just at low loadings of 3TUTS and 3THTS. Although the thienyl groups may prevent the SAMs from becoming well-ordered, similar to how bulky headgroups or side groups disrupt the packing of Langmuir monolayers,[48] it is impossible to judge the severity of any such disordering based solely on these hexadecane contact angles; the roughness of the ITO substrate seems to be the dominating factor in contact angle measurements. The effect that the *ω*-(3-thienyl)alkyltrichlorosilane has on the packing of the SAM is an issue that we are currently investigating spectroscopically. Despite the roughness that disrupts the structure of the SAM and complicates contact angle measurements, these substrates are important in electrochemical measurements.

The cyclic voltammograms of the monolayer-modified surfaces made from 3TUTS and DTS are shown in Figure 5a. In the case of the surface modified with only 3TUTS, a peak indicating oxidation is seen on the first cycle at a potential of approximately 1.4 V (vs Ag/AgNO$_3$). The oxidation potential is similar to that observed for 3-substituted thiophenes in free solution. This potential is lower than that at which monomeric thiophene would oxidize because of the electron-donating effect of the alkyl chain. As the relative amount of 3TUTS in (the deposition solution used to make) the monolayer decreases, the oxidation peak decreases in height and shifts to higher potential. The area under the peak, which is proportional to the amount of charge transferred, also decreases as the relative loading of 3TUTS drops. Similar behavior is observed for monolayers made from 3THTS and HTS, as shown by the voltammograms presented in Figure 5b. Additional experiments using the 3THTS/HTS system at a few other intermediate concentrations and a series of samples that were allowed to assemble for 48 h (as opposed to 72 h) also exhibited the pattern of behavior seen in Figure 5b.

In both the 3TUTS/DTS and 3THTS/HTS systems, strong oxidation peaks were visible on the first anodic charging and only when the concentration of thienyl-
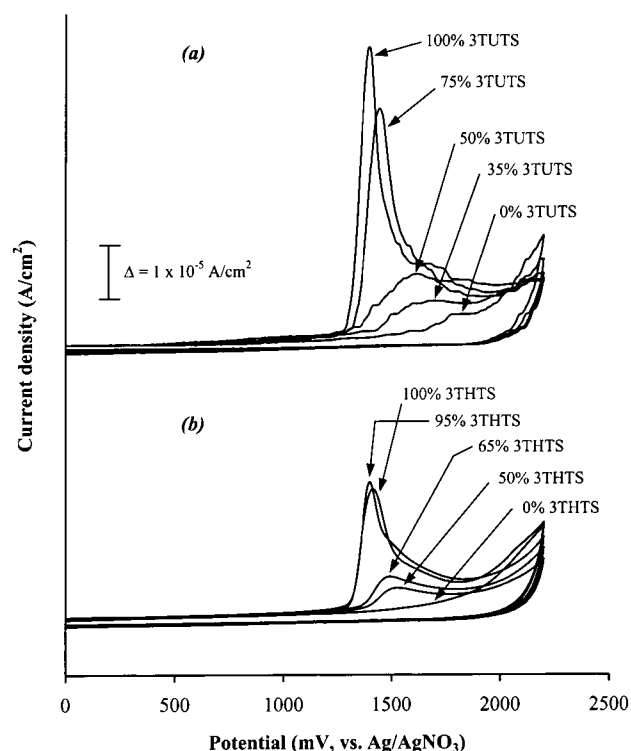

Figure 5. Cyclic voltammograms for SAMs made from (a) 3TUTS and DTS and (b) 3THTS and HTS. (Only the first scans are shown for clarity.) The oxidation potentials for the SAMs made from only 3TUTS or 3THTS are consistent with the oxidation potential of 3-substituted thiophenes. The shift in peak potential as the relative amount of thienyl-capped chains is decreased is attributed to the influence of a rapid chemical reaction that follows the electrochemical oxidation of the pendant thiophene rings. The current density is based on the apparent area of the working electrode (uncorrected for ITO roughness), and the sweep rate in all experiments was 100 mV s^{-1}.

capped chains (in the deposition solution used to make the samples) was at least 35%. The peaks seen at high potential (~2 V) in the CV sweeps of Figure 5 appear to be consistent with degradation of poly(3-alkylthiophenes),[49] but destruction of the SAM may also be occurring. At this juncture, it is not clear what any secondary peaks (e.g., in the 100% and 75% 3TUTS samples) or shoulders (e.g., in the 100% and 95% 3THTS systems) are, but possibilities include decomposition or deactivation of the thiophene rings of the monolayer. These issues are also being examined with follow-on electrochemical and spectroscopic experiments.

Although the apparent area of the working electrode was used in calculating the current density, we believe that variation in the actual surface area (i.e., roughness) of the ITO coating is the primary cause of the differences in peak heights between the 3TUTS/DTS and 3THTS/HTS systems at corresponding concentrations. A set of four ITO substrates that were modified with 3TUTS were prepared and subjected to CV experiments. We found that the peak heights varied by a factor of 1.6, whereas the oxidation peak potentials differed by less than 40 mV. In these experiments, the substrate cleaning, monolayer assembly, and electrochemistry procedures were identical. With the care taken during the monolayer formation step (rigorously dried solvents, nitrogen environment), we do not believe that the difference in peak heights between

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the two systems is due to the formation of multilayers. Our deposition procedure was applied to create SAMs of 3TUTS and 3THTS on polished silicon wafers so that the layer thickness could be measured using ellipsometry. Thicknesses in the range of 15−18 Å were measured for monolayers of 3TUTS, and thicknesses of 22−25 Å were obtained for monolayers of 3THTS. Both of these results seem quite reasonable for these monolayers, and the values for SAMs of 3TUTS agree with the findings of Appelhans and co-workers.[36]

The surface density of thienyl-bearing chains in the 3TUTS and 3THTS monolayers can be obtained from the area beneath the CV curve. From the area, which was calculated by numeric integration using an extrapolated baseline, the amount of charge transferred and the surface density of the electroactive molecules were determined. The surface densities obtained in this manner should be considered crude estimates; no adjustment was made for the actual surface area of the ITO electrode, and it was assumed that the electrochemical reaction was a one-electron process. For the SAM made from 3TUTS, a surface density of 3.8×10^{15} molecules cm^{-2} was calculated. This was based on the area (beneath the curve and above the extrapolated baseline) between the potential range of 1250−1900 mV. For the SAM made from 3THTS, a surface density of 1.4×10^{15} molecules cm^{-2} was calculated using the potential range of 1270−1820 mV. In both cases, the upper limit of the potential window used to determine the area was selected in order to eliminate the high potential region of the CV sweep where degradation of substituted thiophenes and polythiophenes is known to occur.[49,50] The surface densities reported above are about an order of magnitude higher than those other researchers have reported for other monolayer systems that contain an electroactive moiety at the periphery,[18,23,25,27] but tacit assumptions regarding the surface area of the ITO and the nature of the oxidative process have been made. The actual surface area of the ITO substrate is clearly greater than the apparent surface area, and over the potential window used, electrochemical processes that involve more than one electron are probably occurring. (As stated previously, the shoulder in the 3THTS cyclic voltammogram and the second peak seen in the 3TUTS cyclic voltammogram could be indicative of decomposition, which would involve multiple electrons.) Therefore, correcting for these simplifying assumptions would decrease the surface densities reported above. Because quantitative corrections cannot be made at this point, it is best to view these surface densities as crude estimates of the maximum number of molecules per *apparent* unit area of the electrode.

The relationship between the peak potential and the composition of the deposition solution used to make the monolayer is shown in Figure 6. The data for the 3THTS/HTS systems assembled for 48 and 72 h are displayed in this plot, and similar shifts are seen for the 3TUTS/DTS systems. There appears to be little change in the peak position until the fraction of alkyl chains exceeds approximately 0.10. The location of the oxidation peak may be influenced by a chemical reaction that follows the electrochemical oxidation of tethered thienyl groups. In bulk solutions, the coupling or polymerization reaction that follows the formation of the radical cation of thiophenes is rapid,[50] and a rapid chemical reaction that follows an electrochemical reaction tends to decrease the peak potential.[51,52] In our system, we suspect that the
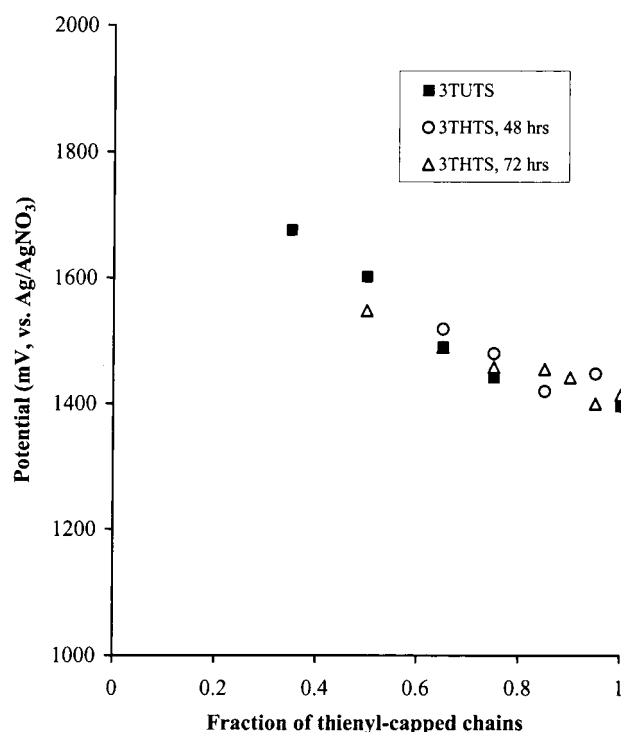

Figure 6. Oxidation peak potential as a function of the composition of (the deposition solution used to make) the monolayers for the 3TUTS/DTS and 3THTS/HTS systems. There is not a significant change in peak potential until the fraction of alkyl chains exceeds approximately 0.10.

surface density of tethered thiophenes along the monolayer plays a key role in affecting the chemical reaction that follows oxidation of thienyl groups; the coupling/polymerization reaction would be facilitated when the SAMs have a high loading of thiophenes, because of the close proximity of thiophenes that are available for reaction, but suppressed in the SAMs that have a low surface density of thienyl groups, because the tethered thiophenes are dispersed along the monolayer. Thus, the oxidation potential of SAMs with a low surface density of ω-(3-thienyl)alkyltrichlorosilanes would be higher than that of SAMs containing mostly thienyl-bearing chains. Also, this view of the increase in peak potential as the fraction of thienyl-bearing chains decreases provides further evidence that the constituents of the monolayers are not phase separated. The peak shift indicates that the local environment around the oxidizable thienyl groups is changing, presumably reflecting the change in monolayer composition. If the components of the monolayer were separating into microdomains, then we might expect that the potential at which we see oxidation would remain constant, with the peak size diminishing as the relative amount of thienyl-capped chains decreased.

For the 3TUTS/DTS and 3THTS/HTS systems, on the second and third CV scans small but broad oxidation and reduction waves were observed at potentials around 0.7 V for SAMs with high relative amounts of thienyl-bearing chains (around 65−75% and above). However, in these scans the potential was ramped to 2.2 V, and these peaks rapidly attenuated on successive cycles. This disappearance of the peaks could be due to destruction of the SAMs, but it also appears to be consistent with degradation of poly(3-alkylthiophenes).[49] Polythiophenes are known to

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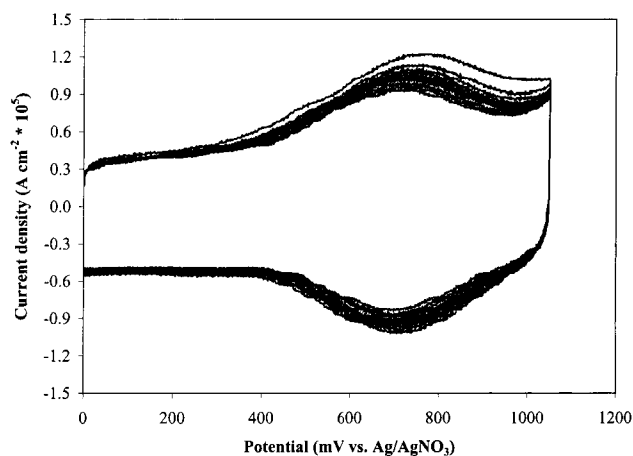
Figure 7. Cyclic voltammogram of a 100% 3TUTS monolayer that is cycled at a low potential after a single excursion to ~1.4 V. The small oxidation and reduction peaks suggest charging and discharging of a surface-tethered conductive polythiophene that may be formed when the pendant thiophene groups of the SAM undergo oxidative polymerization/coupling along the monolayer. The CV experiment was conducted at a sweep rate of 100 mV s^{-1}.

be unstable at the high potentials required for their formation, particularly when the monomer concentration is too low to sustain the rate of electropolymerization.[49,53] In an attempt to better capture this behavior, SAMs of 3TUTS were made and subjected to CV experiments at lower potentials; the first excursion to high potential was limited to 1.4 V, and then these samples were cycled 12 times between 0 and 1.05 V. Figure 7 shows the results from one of these experiments.

The redox peaks are relatively stable upon repeated cycling at low potential, although over the course of the cycling the peak height decreased by a factor of approximately 30%, with the largest attenuation in peak height occurring between the second and third sweeps. The fact that these waves are more stable than those observed when the potential was cycled to 2.2 V is probably due to the fact that there was less degradation because the system was not severely overoxidized. The ratio of the cathodic to anodic peak currents for each charge–discharge cycle is 0.90 ± 0.02, the peak widths at half-maximum remain fairly constant, and the redox peak potentials decrease by ~0.05 V during the cycling. Also, the oxidation waves are shifted, on average, +0.018 V relative to the reduction waves. We believe these redox waves are preliminary evidence that the thiophenes of the SAM have undergone oxidative coupling to form a surface-tethered polymer and that tethered polythiophene can be oxidized and reduced. Although full spectroscopic characterization is necessary to support this contention, the formation of a surface-bound polymer (or at least an oligomer) by oxidative electropolymerization has been reported by other groups as well; McCarley and Willicut[24]

have shown that pyrrole groups tethered to a surface through a monolayer can also be polymerized, and Inaoka and Collard[27] and Berlin and co-workers[54] have demonstrated that monolayers capped with bi- and trithiophene groups can undergo oxidative coupling to form more highly conjugated oligomeric or polymeric species.

Conclusions

We have shown that monolayers made from ω-(3-thienyl)-alkyltrichlorosilanes are electrically active, and the electrical activity of the system can be manipulated by incorporating a second component, *n*-alkyl chains, into the monolayer. Although the roughness of the substrates is a factor, the wetting and electrochemical behaviors of the monolayers change as the relative amount of *n*-alkyl and thiophene-bearing chains changes, indicating that the two components have not segregated. The loading of *n*-alkyl chains in the monolayer has a significant impact on the electroactivity of the layer; the oxidation potential shifts to higher values, and the peak height (and area) decreases as the relative amount of *n*-alkyl chains in the layer increases. We believe that the peak shift is due to and influenced by a rapid chemical reaction, perhaps coupling or polymerization of the thiophenes, that follows electrochemical oxidation of the thienyl-capped species; a high loading of 3TUTS or 3THTS facilitates the reaction, and thus the SAMs containing predominantly ω-(3-thienyl)-alkyltrichlorosilanes have lower oxidation potentials than those containing fewer tethered thiophenes. Although spectroscopic verification remains to be done, preliminary data suggest that a monolayer made of thienyl-bearing chains can be electropolymerized (within the monolayer), and when cycled at a low potential, the resultant polythiophene can be oxidized and reduced. However, when a significant fraction of *n*-alkyl chains are incorporated into the monolayer, we speculate that polymerization/coupling may not be possible because the *n*-alkyl chains disperse the thienyl-capped chains along the monolayer. We anticipate that this effect will be seen more clearly when monomer is added to the electrolyte solution and polymerization (in the bulk solution) is attempted with these systems.

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