Controlled Assembly of Silane-Based Polymers: Chemically Robust Thin-Films

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We describe the controlled assembly of silane-based copolymers on various interfaces that have surface silanol groups. This assembly occurs as a result of the formation of very robust siloxane bonds (Si—O—Si) due to a condensation reaction between the alkoxysilane groups of the polymers and surface hydroxyl groups of the substrates. Deposition of these copolymers is not self-limiting; therefore, they could not be assembled into discrete monolayers. However, UV-visible data collected as a function of deposition cycle reveals a linear relationship, confirming the deposition of a constant amount of polymer in each deposition cycle. A linear variation of layer thickness with deposition cycles is also observed. The assembled polymer layers are found to be very robust and resistant even when exposed to piranha solution for several hours.

Introduction

The need to assemble1,2 thermally,3,4 and chemically robust5,6 materials has led to the development of numerous controlled assembly methods. The assembly of materials into predictable thickness layers employing a layer-by-layer scheme7–11 results in a higher levels of control over the properties12 of the resulting polymer when compared to other bulk preparation methods. Functional films produced by a layer-by-layer process are being used for a variety of applications including drug delivery,13,14 solid battery electrolyte,15 molecular sensing,16 and membranes.17,18 Commonly employed layer deposition schemes include Langmuir–Blodgett (LB) films,19–22 metal phosphonates23,24 and other covalent linkage strategies.25–27 However, some of them suffer from a fundamental lack of robustness, or complex/multistep assembly processes to realize initial and subsequent layer deposition. The LB scheme provides a facile route to the preparation of systems where weak van der Waals interactions allow the species being adsorbed to retain their functionality. However, such interactions are susceptible to disruption on rinsing with polar solvents and preclude the use of these systems in harsh environments.28,29

The metal phosphonate route to prepare thin films20,31 organizes molecules into lamellar structures very similar to those formed by the LB technique. Although the metal-phosphonates exhibit enhanced chemical and thermal stabilities over the LB films, they are susceptible to disruption under acidic conditions.32

The Gold-alkanethiol32,33 self-assembly method, extensively studied for the preparation of thin-film modified interfaces is often limited to the assembly of one molecular layer due to

selective interaction of the head groups with the substrate. Multilayer assembly is only possible if the distal end of the molecule bears a moiety capable of further reaction. This method is also restricted to a few substrates (gold/silver), which imposes cost related constraints.

In this work we report the facile self-assembly of a group of silane-based polymers into thin-films. These polymers can be self-assembled onto substrates such as silicon, glass, and quartz by a simple dip-coating technique, without the need for any surface priming steps other than cleaning with piranha solution, which is more of a surface cleaning step mandatory for such surfaces. One of the monomers in the copolymers incorporated into the polymer backbone is an allyl- or a vinyl-functionalized alkoxysilane. The other comonomer is a functionalized maleimide which allows for more control over the distribution of functional groups within the polymer backbone. Additionally, the use of maleimides makes it easier to monitor the material assembly by spectroscopic techniques described later in the text. Though the idea of preparation of films using silane chemistry is not new, it has proven to be a very difficult task, often requiring well-controlled conditions and most often, little control over the loading density. In this work we describe a route for the construction of polymer thin-films through the judicious incorporation of the functional entities employed in the design of the polymers. We have achieved control over the materials that go onto the substrate with each deposition cycle. The resulting assembly due to the formation of chemically and thermally robust siloxane bonds have been found to be resistant to harsh acidic, basic, and oxidizing conditions. We believe that this level of structural control and chemical stability will find use in the design of chromatographic stationary phases, sensors, and other assemblies such as coatings for use in harsh environments.

Experimental Section

Materials. Dimethyl formamide (DMF), acetonitrile, acetone, toluene, and chloroform (all HPLC grade) were purchased from Fisher Scientific (Fair Lawn, NJ). Ethanol (200 proof) was purchased from Pharmo Products (Brookfield, CT). Maleic anhydride (>98%, Fluka, Seelze, Germany), 4-bromoaniline (98%, Alfa Aesar, Ward Hill, MA), aniline (Matheson, Coleman & Bell, Rutherford, NJ), 4-fluoroaniline, 4-chloroaniline (>97%, Fluka), sodium acetate (99%+, ACROS Organics, Geel, Belgium), and acetic anhydride (99%, ACROS Organics) were used in the synthesis of the maleimides. Alkoxysilanes (vinyltrimethoxysilane (VTMS), allyltriethoxysilane (ATES), and allyltrimethoxysilane (ATMS) which was accomplished using 2,2’-azobisisobutyronitrile (AIBN) as radical initiator, the details of which have been reported elsewhere. All polymers prepared by this procedure were collected as precipitates from hexanes and purified by dissolving the polymers in the polymerization solvent and recollecting the precipitates prior to their use in this study. It should be noted that the N-phenylmaleimide group was specifically chosen to allow for spectral confirmation of polymer layer deposition onto the substrates. The structures of these various monomers are depicted in Figure 1. A schematic of the polymers has been represented in Figure 2. For simplicity we have developed acronyms for each of the polymers. For example, the copolymer of N-phenylmaleimide and allyltrimethoxysilane is given the acronym NPM-ATMS. Thence the polymers prepared and used in this study are NPM-ATMS, NPM-ATES, NPM-VTMS, and NPM-VTES. This simplified naming scheme has been employed for the remainder of this paper with reference to each polymer system. Though polymers with varying initiator percentages such as 1 mol %, 5 mol %, and 10 mol % were prepared, we employed the 10 mol % polymers throughout this study. In all cases we recovered yields in excess of 85% for all of the polymers prepared, and the molecular weights depended on the amount of initiator used.

Polymer Deposition. Prior to polymer deposition, the substrates (quartz, silicon, and glass) were cleaned in a piranha solution (3:1 concn H2SO4:30% H2O2). Polymer solution was prepared by dissolving 10 mg of the different polymers in 10 mL of various solvents (acetone, DMSO, chloroform and toluene). No surface priming steps (other than cleaning with piranha solution) were required prior to polymer deposition. These substrates were then introduced into solutions of the four polymer systems described above for 4–8 deposition cycles. After each deposition cycle the surfaces were withdrawn from the polymer solution, cleaned with acetone and dried with air. Two different substrates were employed in this study. One was a glass microscope slide treated with an oxide layer using a standard thermal oxidation process. The other was a silicon wafer with a native oxide layer. Both substrates were cleaned with piranha solution in order to remove the overlying hydrocarbon contamination and oxygen plasma etched for 30 sec. The oxide was then removed using buffered oxide etch (BOE) in order to obtain a clean hydroxylated silicon surface.

Figure 1. Structures of various monomers used in this study. (a) NPM, (b) VTES/VTMS, (c) ATES/ATMS. [R = H in structure a, R = CH3 or CH2=CH3 in structures b and c].

Figure 2. Schematic of the synthesis of polymers where R = –CH3 or –CH2=CH3.

Polymer Preparation. The polymers employed in this study were all designed and prepared by radical copolymerization of N-phenylmaleimide monomer with the various alkoxysilane monomers–vinyltrimethoxysilane (VTES), vinyltrimethoxysilane (VTMS), allyltrimethoxysilane (ATES), and allyltrimethoxysilane (ATMS) which was accomplished using 2,2’-azobisisobutyronitrile (AIBN) as radical initiator, the details of which have been reported elsewhere. All polymers prepared by this procedure were collected as precipitates from hexanes and purified by dissolving the polymers in the polymerization solvent and recollecting the precipitates prior to their use in this study. It should be noted that the N-phenylmaleimide group was specifically chosen to allow for spectral confirmation of polymer layer deposition onto the substrates. The structures of these various monomers are depicted in Figure 1. A schematic of the polymers has been represented in Figure 2. For simplicity we have developed acronyms for each of the polymers. For example, the copolymer of N-phenylmaleimide and allyltrimethoxysilane is given the acronym NPM-ATMS. Thence the polymers prepared and used in this study are NPM-ATMS, NPM-ATES, NPM-VTMS, and NPM-VTES. This simplified naming scheme has been employed for the remainder of this paper with reference to each polymer system. Though polymers with varying initiator percentages such as 1 mol %, 5 mol %, and 10 mol % were prepared, we employed the 10 mol % polymers throughout this study. In all cases we recovered yields in excess of 85% for all of the polymers prepared, and the molecular weights depended on the amount of initiator used.
dried under nitrogen, and then cleaned by carefully dipping in acetone bath to ensure that the deposited film is not destroyed and only the excess polymer not linked to the substrate is removed. These substrates were then thoroughly dried under nitrogen and were then characterized using UV–vis spectroscopy, ellipsometry, and scanning electron microscopy (SEM). Deposition of films was studied by varying parameters such as the time of exposure and temperature. The surfaces were exposed to the polymer solutions for either 2 or 4 h with heating and 12 or 24 h at room temperature.

Exploring the role of solvents played a major role in the deposition of these polymers at the interfaces as the main issue with respect to solvents was solubility of the polymer. The solvent systems studied included ethanol/water mixtures, DMSO, acetonitrile, chloroform, and toluene. In the case of the ethanol/water mixture the polymer precipitated and hence was considered unsuitable for further deposition. This could be due to the hydrolysis of the alkoxy groups and self-linking of the polymer via siloxane bonds while being in solution. While DMSO, acetonitrile, and chloroform were found to be good with respect to solubility, deposition of the polymers from these solvents onto the substrates was found to be very poor. The most ideal solvent system was a 1:4 mixture of acetone and toluene which not only showed good solubility but also yielded the best observed deposition of the polymers and is the solvent system employed throughout this study, as described in detail below.

Characterization

A Perkin-Elmer UV–vis spectrophotometer in the range of 200–600 nm was used to monitor the UV–vis absorption spectra of the films for each deposition layer. Values of ellipsometric thickness of the deposited polymer multilayer assemblies were acquired using a J. A. Woollam M2000 spectroscopic ellipsometer. Park Scientific AutoProbe CP/MT (MultiTask) scanning probe with linearized 100 and 5 μm scanners were used to obtain the topology of the substrates. SEM images were obtained using a Hitachi S-5500 SEM and a resolution of 0.4 nm resolution at 30 KV. XPS (X-ray photoelectron spectroscopy) analysis was performed on the polymer films using a Kratos AXIS Ultra DLD XPS equipped with a 180° hemispherical energy analyzer. Photoemission was stimulated by a monochromated Al Kα radiation (1486.6 eV) at an operating power of 150 W. It was operated in the analyzer mode at 20 eV for detailed scans of core level lines. Binding energies were referenced to the C 1s binding energy set at 284.5 eV. The substrates with same films (before and after treatment) were directly loaded onto the sample bar for analysis.

Results and Discussion

The assembly of these polymers onto various substrates was studied by controlling parameters such as (1) solvent system, (2) polymer chain termination (methoxysilane versus ethoxysilane), (3) temperature (room temperature versus heating at ~55 °C), and (4) time of deposition cycle. NPM-VTES and NPM-VTMS were chosen for detailed studies for understanding deposition trends and stability of polymer films. Deposition trends for all the four polymers are detailed in Table 1 and have been discussed below.

Typically, polymer deposition was realized through a condensation reaction between the surface silanol groups and the alkoxy silane side-group of the polymers resulting in the formation of very stable siloxane (Si–O–Si) bonds. Deposition of further polymer layers was the result of a similar condensation reaction between the alkoxy silane side groups of the polymer from solution and the one already deposited polymer. Deposition of these polymers onto quartz substrates (1 × 1 cm²) allowed monitoring of the aromatic band associated with the N-phenylmaleimide moiety by UV–vis spectroscopy.

As mentioned earlier, several solvents were employed in this study and a binary mixture of acetone and toluene (1:4) was found to be the most ideal. While the polymers dissolved readily in acetonitrile and DMSO, both solvents proved poor candidates for the deposition of these polymers onto substrates. In the case of the toluene alone, the polymer was completely insoluble and therefore not suitable. When a small amount of acetone was first used to dissolve the polymer followed by addition of toluene this binary mixture proved not only adequate with respect to solubility, but also led to good polymer deposition. These findings are rationalized in the context of polymer, solvent, and surface polarity. It may be possible that the polar nature of acetone allows the polymer to exhibit a random coil conformation that exposes silanol reactive groups which would otherwise be protected inside a helical polymer molecule (Figure 3). The random coil polymer conformation may exhibit a lower persistent length giving the polymer the flexibility to overcome surface repulsion due to the reflectance principle. It can be argued that the silanization of these polymers and hence cross-linking can also occur without deposition onto the substrates. However, the stability of these polymers in ambient conditions has already been reported. Hence, a solvent system is mandatory for initiation of silanization of these polymers onto the substrates. All the solvents used were HPLC grade but not anhydrous, hence the small percentage of water in the solvents could also have assisted in the initiation of attachment of these polymers onto the substrates.

Figure 4 shows the UV–vis absorbance data of NPM-VTMS as a function of deposition cycle. The inset is a plot of the absorbance of the aromatic moiety of the polymer as a function of deposition cycle. Figure 5 represents the AFM image of the ethoxy polymer (NPM-VTMS) which seemed to form islets initially, rather than forming a continuous overlayer. The same trend was observed for NPM-ATES as well. This is in perfect accordance with the thickness measurements obtained by ellipsometry. Figure 6 shows the comparative thickness variations of the polymers NPM-VTES and NPM-VTMS which revealed a linear relationship when plotted as a function of deposition cycle, with a slope of approximately 9 nm/deposition cycles. Layer-by-layer deposition at these initial stages is governed by nonequilibrium condensation reactions between the surface silanol groups and the alkoxy silane side groups of the polymer

Table 1. Slopes and Corresponding Correlation Coefficients ($R^2$) of Various Polymers as a Function of Deposition Cycle under Various Conditions

<table>
<thead>
<tr>
<th>conditions</th>
<th>NPM-VTES</th>
<th>NPM-VTMS</th>
<th>NPM-ATES</th>
<th>NPM-ATMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>no heat</td>
<td>0.0019 ($R^2 = 0.99$)</td>
<td>0.0244 ($R^2 = 0.99$)</td>
<td>0.0015 ($R^2 = 0.99$)</td>
<td>0.0088* ($R^2 = 1$)</td>
</tr>
<tr>
<td>2 h heat</td>
<td>0.0019 ($R^2 = 0.98$)</td>
<td>0.0121 ($R^2 = 0.99$)</td>
<td>0.0033 ($R^2 = 0.98$)</td>
<td>0.0146 ($R^2 = 0.97$)</td>
</tr>
<tr>
<td>4 h heat</td>
<td>0.0065 ($R^2 = 0.97$)</td>
<td>0.0053 ($R^2 = 0.99$)</td>
<td>0.0053 ($R^2 = 0.99$)</td>
<td>0.0055 ($R^2 = 0.99$)</td>
</tr>
</tbody>
</table>

The data point marked with the asterisk (*) (NPM-ATMS) is the value of slopes of the absorbance data for cycles 1–3. The value of the slope for cycles 4–8 was found to be approximately 4 times this value.

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kinetics, thereby exhibiting a nonexponential scaling. It may be possible that due to the new binding sites introduced in every chain, these polymer coatings may never reach equilibrium. It is clearly observed that the thickness of the first four layers in the case of the NPM-VTMS increased very slowly (in increments of approximately 2 nm) until a full coverage of the substrates was observed. Once the substrate gets completely covered, the subsequent layers showed a regular increase of \(\sim 10\) nm per deposition cycle. As surface coverage increases, surface reaction sites may decrease, but the perturbation of the polymer chain near the surface will dominate making polymer aggregation likely. After complete coverage a new deposition rate is exhibited which is dependent only on available polymer sites for polymer interaction. This finding coupled with the requisite for two or three deposition cycles to observe further increase in the absorbance suggests that the ethoxysilane polymers possibly fill in the areas around the islands preferentially to layering which follows Langmuir absorption dynamics. It is worth noting that subsequent polymer deposition beyond the early cycles reveals a smooth well-covered interface. It appears that, after filling in the areas around the islands, layering occurs. This finding suggests that there might be a stronger driving force for the polymers to react with the surface silanol groups before reacting with themselves. The formation of islets follows the reflectance principle. This principle describes why these polymers will have binding preference for other polymers already grafted and/or to stay in solution due to chain perturbation near a surface. Hence, once the polymers in solution react with polymers already deposited on the substrate surface, they will next react with the substrate resulting in the formation of an expanding, but chemically bonded, islet, not a free-floating one with minimal polymer-substrate interaction. This also explains the linear deposition of polymers with a high degree of silane moieties, in which once an end of the polymer is grafted to the surface the rest of the chain will be projected away from the surface exposing new polymer-borne silanol groups. We also rationalize the observed difference between the methoxysilane and ethoxysilane in the context of the reactivity of these groups. As observed in sol-gel chemistry, methoxysilanes have been shown to be more reactive than ethoxysilane leading to different properties between sol-gels prepared of the two different groups. Figure 7 shows a schematic representation of the islets formed on the substrates once some of the polymer chains react with the surface, the chains in solution are more likely to form bonds with polymer already reacted with the surface thereby forming islets that will coalesce into continuous film with additional deposition cycles. This appears to be consistent with our earlier observations that the methoxy-terminated polymers appear to be far more reactive and lead to more uniform coverage for the initial layers. The thickness measurements as seen in Figure 6 also imply that the NPM-VTMS shows a regular increase in thickness of the order of \(\sim 9\) nm/deposition cycle. In both cases however, the total thickness of the films was close to 60 nm after 8 deposition cycles, averaging to 7.5 nm per deposition cycle.

Table 1 shows the slopes and corresponding correlation coefficients \(R^2\) for UV-vis absorbance as a function of deposition
In most cases we carried out 4–8 deposition cycles for the copolymer. The polymer NPM-VTMS follows bimodal growth kinetics with two linear growth regimes when compared to NPM-VTES. Upon further examination of the data, an interesting trend was discovered. If the early deposition cycles (e.g., cycles 1 to 3) were plotted separately from the later cycles (4–8) we recovered correlation coefficients of unity or nearly so for the two plots. This finding seems to suggest that there may be two distinct growth regimes. For the two regions we recover very different slopes, with the slope of cycles 4–8 being roughly four times that of deposition cycles 1–3. This finding seems to suggest that there is a region of slow growth (cycles 1–3) followed by a region of fast growth (cycles 4–8). The explanation for this observation is that while NPM-ATMS does not show islet formation as in the case of NPM-VTES and NPM-ATES, there is still not complete coverage in the initial layer. When the substrate with the initial layer was introduced into the polymer solution it would have been possible that while there was some reaction between the deposited polymer and the polymer in solution there was also the possibility that some polymer reacted with the surface first. After about three layers the surfaces were well covered beyond which there was rapid cross-linking between the silane side groups of the polymer leading to the region of rapid growths. This finding appears to be somewhat consistent with the ethoxysilane polymers as discussed above that required two or three subsequent cycles before any further absorbance was observed. The difference here is undoubtedly due to the fact that the methoxysilane is more reactive leading to more material being deposited than the ethoxysilane polymer.

Another interesting feature of these polymer films is that they can withstand highly oxidizing and acidic conditions. Figure 8a shows a typical SEM plan-view micrograph (NPM-VTMS) film with 10 layers deposited on quartz substrate where uniform coverage can be seen. Figure 8b shows an SEM micrograph after exposing the same polymer film to the piranha solution for 48 h. The polymer films were first air-dried for 24 h and then dried with nitrogen before proceeding with further treatment and
characterization. Figure 8b clearly shows that the polymer was removed from some areas (though not very uniformly, as indicated by white arrows), and there was also an overall decrease in the film thickness as proven by UV–vis and XPS. Figure 8c shows an SEM image of the edge of the polymer film, taken at an angle to characterize the cross section of the polymer film (10 layers). Since these polymers were prepared by dip-coating technique, there was no distinction of the polymer film from the substrate. Hence to get insight into the film thickness, the polymer film was scratched, and the thickness of the film at the scratch was observed. It is evident from Figure 8c that the polymer film deposition was very uniform on the substrates (see Table 2) which is very important for applications as mentioned below. Figure 8d shows the comparative UV–vis spectra of the untreated polymer film, one treated for 24 h, and another treated for for 48 h. It clearly showed a decrease in the absorbance indicating a decrease in the film thickness. However the fact that a peak at 220 nm was present proved that the polymer film was still present on the substrate. This observation was also supported by XPS as shown in Figure 8e which represents the C 1s spectra of the films before and after treatment with piranha solution for 48, 72, and 96 h. XPS clearly shows that the intensity of C1s reduces on the first exposure to piranha solution (also supported by UV–vis). This might be due to the

Table 2. Surface Roughness (nm) with Increase in Layer Number

<table>
<thead>
<tr>
<th>polymer</th>
<th>layer 1</th>
<th>layer 2</th>
<th>layer 3</th>
<th>layer 4</th>
<th>layer 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPM-VTMS</td>
<td>9.3</td>
<td>8.8</td>
<td>8.4</td>
<td>7.1</td>
<td>6.8</td>
</tr>
<tr>
<td>NPM-VTES</td>
<td>20.0</td>
<td>16.1</td>
<td>10.5</td>
<td>8.3</td>
<td>8.1</td>
</tr>
</tbody>
</table>

Figure 8. (a) SEM plan-view of untreated polymer film with 10 layers. (b) SEM plan-view of polymer film after 48 hours of treatment in piranha solution. Although most of the film is still present after the treatment, there are regions from where the polymer has been removed (white arrows). (c) SEM image showing the top and cross-section of the film. The magnified image in the inset shows a relatively uniform surface, which is representative of a uniform deposition. (d) UV-Visible absorbance of the aromatic group in the polymer as a function of acid treatment for 48 hours. (e) C 1s spectrum of the polymer film before and after treatment with piranha solution for 48 hrs showing a decrease in intensity after 48 hours.
removal of the excess polymer not covalently bonded to the surface. However, on further exposure, for extended periods (48 and 72 h), there was some more removal of the polymer, but beyond that, the removal of polymer on piranha treatment plateaus (96 h and above). This is due to the fact that the polymer coverage might have reached to a point where any unlinked polymer is completely removed, and only the covalently bound polymer remains on the substrate. The fact that there is still some C1s signal pertaining to the polymer indicates that the polymer is not completely stripped off the substrate. Since XPS is a surface technique, it is likely that the oxidizing groups from the piranha might have oxidized the surface which is seen as an increase in the intensity of oxidizing groups in the C1s spectrum. However, the UV-vis which is a bulk technique does not show any shift in the absorption of the polymer, confirming that this is only a surface issue and not bulk degradation of the polymer. This clearly proves that the polymer films are stable and can withstand very harsh oxidizing conditions.

There are several advantages to employing a layer-by-layer approach such as exquisite control over the dimensions of the resulting system and control over what goes into each layer. As a consequence of this, there is control over the physical dimensions of the resulting assembly. The ability to control the physical dimension, that is, the depth at which a particular functionality can be placed within an interface, may prove very useful in the design of sensors where the reporting group may be influenced by the substrate. In this way controlling the dimension of the polymer film may allow one to place the reporter group at an appropriate distance from the substrate to minimize surface influence. Additionally, multiple sensing functionalities can be incorporated into a sensor assembly by placing different reporter/sensing entities into different layers. This can easily be accomplished by preparing polymers that bear different sensing groups and then layering them as described.

**Conclusion**

A very simple technique for the modification of interfaces using silane-based polymers, where the functional groups employed in the design allow for a facile deposition scheme and do not involve cumbersome procedures of prior surface preparation has been demonstrated. The polymers prepared in-house proved very robust and stable not only under conditions of temperature but also under very harsh acidic and oxidizing conditions. Plots of thickness data as well as UV–vis data both reveal a linear relationship consistent with deposition of a constant amount of polymer per deposition cycle/layer. In all cases it was observed that the ethoxysilane-based polymer was the most difficult to deposit, most likely due to differences in reactivity relative to the methoxysilane-based polymers. The stability of these polymer-modified interfaces under harsh oxidizing conditions renders them as possible candidates for tailored coatings, sensors, and to direct the assembly of ordered nanoparticle sensing arrays.

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