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Surface Modification Using Thiol−Acrylate Conjugate Addition Reactions

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ABSTRACT: A novel method for forming surface-bound polymer films using amine-catalyzed thiol−acrylate reactions is investigated. The surface is modified with a thiol-terminated self-assembled monolayer (SAM) and treated with acrylate monomer in the presence of an amine catalyst. A conjugate addition reaction takes place at the surface, attaching an acrylate molecule to the surface. The fraction of attached acrylate on the surface was controlled by the reaction time, forming a gradient of acrylate surface density, and the acrylate fraction of the surface was changed from 0 to 0.6. An orthogonal gradient comprised of either the same acrylate functionality or multiple functionalities was also obtained on the same surface. The technique was further modified to yield acrylate surface density gradient on a polymer surface. Thicker films were grown in a controlled manner by polymerizing a dithiol−diacrylate mixture on a thiol-terminated surface, and the thicknesses of the films were controlled from 0.1 to 6 nm by changing the thiol−acrylate stoichiometry and the extent of reaction. In both cases the surface densities of the attached chains were theoretically calculated, and a model to predict them was proposed.

Introduction

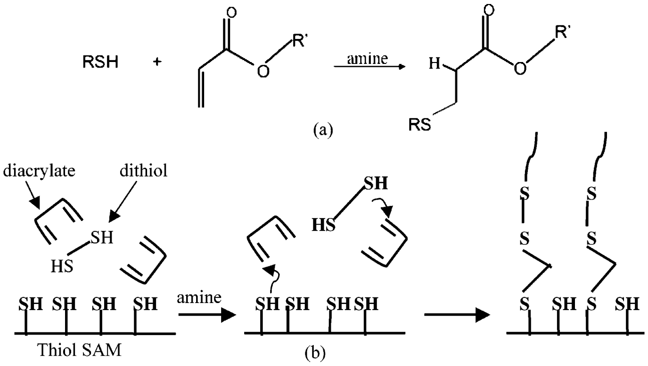
In recent years, various methods for attaching thin polymer films on surfaces have been developed.[1−6] The "grafting from" approach involves the attachment of an anchor molecule to the surface, which leads to a surface-initiated polymerization reaction, whereas the "grafting to" approach involves the attachment of a preformed polymer chain to anchor groups on surfaces. Several polymerizations such as free radical polymerization,[2,5,7] controlled or living radical polymerization,[8,9] and ionic polymerizations have been employed to form surface-bound polymers. Although radical polymerization methods are more common for the growth of surface-bound films, several studies using ionic polymerizations have also been conducted.[1]

In this work, amine-catalyzed thiol−acrylate reactions have been used for modification of surfaces. These reactions combine the distinct advantages of amine-catalyzed reactions[10] and step-growth thiol−acrylate reactions.[11−15] The basic mechanism for the polymerization step in a thiol−acrylate reaction is shown in Scheme 1.

Under the presence of a nucleophile such as an amine, a thiol group adds across a carbon−carbon double bond of the acrylate molecule, forming a thiol−acrylate dimer.[10,16] The surface is modified with a thiol-terminated self-assembled monolayer, and the thiol−acrylate reaction as shown above is performed on the surface. A portion of the surface thiols participates in the reaction, leading to the attachment of acrylate monolayers or thiol−acrylate polymers on the surface.

The use of an amine-catalyzed ionic reaction for surface modification possesses several unique advantages over other polymerization schemes.[17] Since the reaction proceeds via a catalyst, no initiator is required, which gives it the potential to form thick, clear films on the surface. Also, no external source of initiation such as light or heat is required making these systems suitable for biological applications. All reactions take place at ambient conditions without the use of any noncommercial catalysts.

Scheme 1. (a) Thiol−Acrylate Conjugate Addition Reaction: a Thiol Molecule Adds across the Carbon−Carbon Double Bond of the Acrylate To Form the Thiol−Acrylate Product; (b) Schematic of the Thiol−Acrylate Conjugate Addition Reaction on a Surface[a]



[a] The reaction shown in (a) is performed on a thiol-terminated surface, leading to the modification of the surface with linear thiol−acrylate polymers. The symbols shown in the figures are schematics and do not represent actual monomer molecules. All reactions were performed at room temperature, without the presence of solvents. Thiol and acrylate molecules were used in varying stoichiometric ratios as well as with different functionalities per molecule. Depending on the reaction, a primary or a secondary amine was used.

This work investigates the combination of amine-catalyzed reactions with the step growth thiol−ene polymerization scheme. In the past decade, there has been a renewed interest in the thiol−ene polymerization scheme,[13,14,18−24] which has been employed in various applications such as dental composites,[25,26] surface modification,[5,27−30] functionalization of nanoparticles,[31] formation of biomaterials for tissue engineering,[32] and formation of holographic gratings[3,18−20,33] and for preparation of microfluidic devices[34] and liquid crystalline components.[14,18−20,33,35]

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However, the thiol−ene reaction is mainly photoinitiated and requires the usage of ene functionalities to maintain its step growth nature.[11] In this work, the amine-catalyzed reactions mentioned earlier have been combined with a thiol−acrylate reaction, such that the step growth nature of the reaction is preserved.

A unique feature of the thiol−ene polymerization reaction is its step growth, radical-mediated polymerization mechanism, where a thiol molecule adds across a carbon−carbon double bond to form a thiol−ene product.[11,12,29,36−38] The step growth nature, the photoinitiated mechanism, and the ability to polymerize without the addition of an initiator provide distinct advantages for the application of this system as a tool for surface modification.[12,28] However, the addition of acrylates to a photopolymerized thiol−ene system results in a mixed step-chain growth mechanism as acrylate monomers homopolymerize in addition to reacting with the thiols.[11,12]

However, changing the reaction mechanism from photopolymerization to amine-catalyzed addition reaction results in a step growth thiol−acrylate conjugate addition reaction. As a result, several advantages of the step growth mechanism are preserved while incorporating an acrylate functionality in the polymer chain. Desired secondary functionalities such as biological peptides or poly(ethylene glycol) are modified more readily with an acrylate group as compared to an ene group such as vinyl ethers. Hence, using acrylates with a step growth mechanism for surface modification is very advantageous.

In this work, various aspects of surface modification using the thiol−acrylate conjugate addition reaction have been explored. Monolayers of acrylates with varying surface densities were deposited on both glass and polymer substrates. Orthogonal gradients were synthesized by depositing the same or different acrylate functionalities in a gradient fashion. Additionally, thicker films were synthesized by polymerizing dithiol−diacrylate mixtures, and the thickness of the formed films was changed by controlling the stoichiometric ratio of thiol and acrylate functionalities and/or the extent of reaction. A model to predict the surface density of the chains has been proposed and applied to each of these cases.

Experimental Section

Materials. The chemicals 3-mercaptopropyltrimethoxysilane (MPTMS), 1,6-hexanediol diacrylate, 1,6-hexanedithiol, poly(ethylene glycol) acrylate ($M_n = 375$), pentaerythritol tetrakis(3-mercaptopropionate) (tetrathiol), and hexyl acrylate were obtained from Aldrich and used as received. The UV photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (DMPA), was purchased from Ciba-Geigy (Hawthorn, NY). Substrates used were precleaned, plain microscope slides obtained from Gold Seal Products, Portsmouth, NH. Substrates used for all ellipsometric studies were polished, double-sided silicon wafers (Umicore Semiconductor Processing, Boston, MA). Wafers were in the (100) orientation and 760 μm thick.

Methods. a. SAM Deposition. All substrates were cleaned using "piranha" solution, which is a mixture of hydrogen peroxide and sulfuric acid (1:3 by volume), for 45 min, rinsed with deionized water, and then blown dry with a N_2 stream prior to SAM deposition. A vapor-based method was used for SAM deposition. Clean substrates were placed in a Teflon bottle with an open vial containing ~0.5 mL of 3-mercaptopropyltrimethoxysilane. The bottle was purged with argon for 5 min, sealed, and placed in an oven maintained at 90 °C for 2.5 h. After removal, the SAM-coated substrates were rinsed in toluene and then in acetone and blown dry with a nitrogen stream.

b. Deposition of Acrylate Monolayers. The thiol-terminated SAM substrates were treated with a 100 mM dithiothreitol (DTT) solution in a potassium phosphate buffer for 10 min to cleave the disulfide bonds formed on the surface, as detailed by Jonnson et al.[39] Acrylate monolayers were deposited by sandwiching a layer of acrylate monolayer and amine mixture between a thiol-terminated SAM and a glass surface for varying periods of time. A syringe pump was used to dip the thiol SAMs in an acrylate−amine mixture at varying speeds to obtain gradients with various slopes.[27] Typically, an acrylate−amine mixture containing 10 vol % amine was used, and the thiol SAM was immersed at a rate of 0.4 cm/min for 5 min for the deposition of an acrylate monolayer gradient. Orthogonal gradients were formed by repeating the same process with the same or different acrylate mixtures. An acrylate gradient on a polymer substrate was formed by repeating the same process with the polymer substrate. All reactions were carried out at room temperatures and using 10 vol % ethylenediamine. The reaction time was changed, and the effect of the same on acrylate coverage was investigated.

c. Deposition of Polymer Films. Various stoichiometric mixtures of dithiol and diacrylate were mixed with 2.5 mol % triethylamine and sandwiched between the thiol SAM and a glass substrate. The sides of the slides were sealed with silicone isolators and vacuum grease to prevent the evaporation of amine, and the setup was maintained overnight. After complete polymerization, the ungrafted polymer was removed by washing with acetone, and the substrates were washed in a methylene chloride Soxhlet for 12−24 h. The substrates were characterized using water contact angle goniometry and ellipsometry. All reactions were carried out at room temperature without the use of any solvents.

Thickness dependence on conversion of thiol−acrylate systems was studied by using a syringe pump to immerse a long thiol-terminated SAM substrate in a polymerizing mixture of thiol−acrylate in a 1:1 ratio. A real-time FTIR system was used to monitor the conversion of the monomer with time. For each point on the surface, the conversion at which the surface is immersed in the reacting mixture was thus calculated using the IR data. The samples were washed in a methylene chloride Soxhlet, and the thickness was measured using ellipsometry. The thickness of the polymer film vs conversion was then plotted.

Surface Characterization. The formed surfaces were characterized using water contact angle goniometry and ellipsometry. Water contact angle measurements were performed using a sessile drop method.[40,41] An ellipsometer (Multiskop, Optrel GBR, Berlin) was used to make all film thickness measurements. Background measurements of the oxide layer and the SAM layer were performed and used to measure the thickness of the formed acrylate monolayers or thiol−acrylate polymer films. All measurements were done at an angle of incidence of 70°. Five separate measurements were taken for each sample, and three repeats of each sample were performed to obtain an average thickness in each case.

To measure real-time conversion, an IR spectrometer was used (FTIR Magna 750, Series II, Nicholet Instrument, Madison, WI). Samples were placed in NaCl salt crystals. Thiol conversion was monitored by calculating the peak area at 2575 cm^{-1}, and the acrylate peak was monitored using the peak area at 1636 cm^{-1}.

A PicoPlus scanning probe microscope (SPM) (Molecular Imaging, Inc., Phoenix, AZ) was used to obtain all SPM images. All images were obtained in contact mode using silicon nitride cantilevers at a speed of 2 lines/s.

Results and Discussion

The formation and control of surface-attached films using thiol−acrylate conjugate addition reaction are investigated here. In this reaction, a thiol molecule adds across an acrylate carbon−carbon double bond to form a thiol−acrylate dimer, in the presence of an amine catalyst. This process is repeated many times in the reaction mixture and forms the basis of the thiol−acrylate polymerization. Since the reaction proceeds via a step growth mechanism, it has distinct advantages, including that the functionality and stoichiometry of the thiol−acrylate mixtures can be independently controlled to manipulate the final

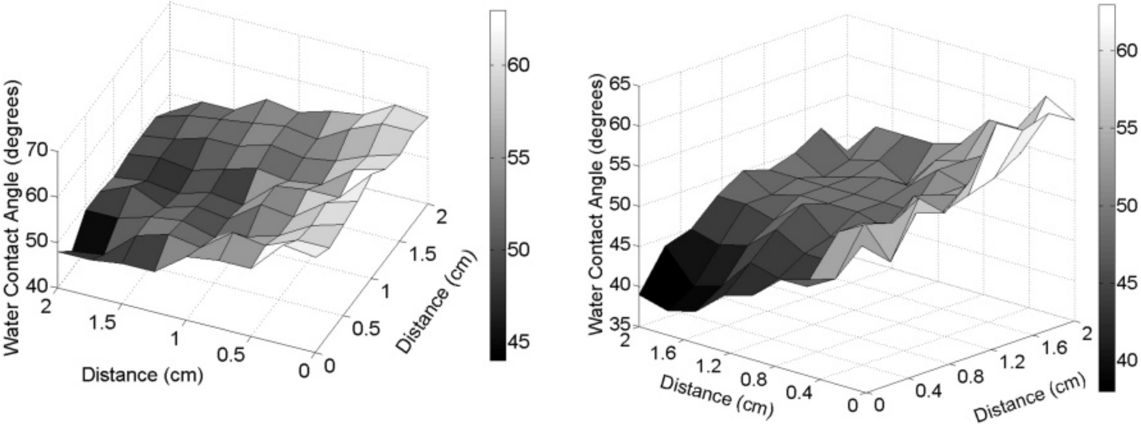

Figure 1. Water contact angle of a thiol-terminated surface modified with PEG gradient. (a) A thiol SAM was immersed in a solution containing PEG acrylate ($M_n = 375$) and 10 vol % ethylenediamine at a rate of 4 cm/min for 5 min and withdrawn at a rate of 24 cm/min. (b) The same sample was immersed in a similar solution in the orthogonal direction at the same rates.

polymer properties as previously shown for purely step growth thiol−ene photopolymerization reactions.[28] In addition, the use of acrylates in place of ene groups in thiol−ene polymerizations is a distinct advantage since, due to their frequent use in the polymerization industry, a wide variety of commercially available and industrially important compounds are available as acrylates. In this work, both these advantageous aspects of amine-catalyzed thiol−acrylate polymerizations have been exploited.

In the initial part of this work, the deposition of various acrylate monolayers is investigated. Recently, self-assembled monolayers (SAMs) have become a standard method for modifying a surface with a specific functionality.[42] Silane−hydroxide or gold−thiol bonds have been used to deposit a complete monolayer of a desired functionality on a surface.[43] However, it is often difficult to synthesize SAM-forming monomers modified with a specific functionality. Also, controlling the coverage of SAM molecules on a surface, although not impossible, is not trivial. Last, it is extremely difficult to modify a surface with multiple SAM monomers in a controlled fashion with changing surface densities in orthogonal directions. The current technique has been used to overcome each of these difficulties.

A mixture of acrylate and amine is placed on a thiol-terminated SAM deposited on a glass or silicon substrate, and a reaction as depicted in Scheme 1 takes place. The amount of surface coverage achieved depends primarily on the amine type and the contact time and to a small extent on the secondary functionality attached to the acrylate. It was found that the thiol−acrylate reaction proceeded faster in the presence of primary amine catalyst as compared to the presence of secondary and tertiary amines. When added in catalytic amounts (1 mol %), it took several hours for complete reaction to occur in the presence of triethylamine or a few minutes in the presence of diethylamine, whereas the reaction was complete almost as soon as the reactants and the catalyst were mixed in the case of ethylenediamine with no observable reactants remaining by the time the reacting mixture could be transferred to the infrared spectrometer. For the rapid attachment of acrylates to the surface, a 10 vol % ethylenediamine solution, a molecule containing two primary amine groups, was used. It might, however, be possible to use a stronger base to reduce this amount.

A side reaction of thiolate ions formed with the dissolved oxygen is possible. However, the oxygen concentration in the system is extremely low (10^{-3} M) relative to the reactants.[44] Hence, the extent of this possible reaction is minimal in the time frame of the reaction. Also, the effect of amine addition to acrylate was investigated using FTIR. Though a large amount of amine is indeed used, well beyond what would be normally considered a catalytic amount, we verified no significant addition of the amine to the acrylate occurred by evaluating nearly identical conditions except that the thiol was removed. Under these conditions, no acrylate amine reaction was observed for at least 18 h.

A 2.5 × 2.5 cm^2 thiol-terminated SAM substrate was immersed in a mixture of PEG acrylate ($M_n = 375$) and 10 vol % ethylenediamine using a syringe pump. The end of the substrate, which was immersed first, is in the reaction mixture for the longest time, and hence, maximum grafting takes place at that end. In this case the substrate was immersed at a rate of 0.4 cm/min for 5 min and withdrawn at a very high rate of 24 cm/min. This resulted in the deposition of acrylate over a 2 cm range, which was used for analysis by water contact angle goniometry. The substrate was washed thoroughly with water and acetone and dried subsequently with a stream of nitrogen gas. The samples were then characterized using water contact angle goniometry, and the results are presented in Figure 1a. As can be seen, the water contact angle increases from 46°, where the PEG deposition is maximum, to 62°, where there is least PEG deposition (and the thiol SAM is nearly unreacted).

The fraction of deposited PEG was calculated using Cassie's equation.[40] The water contact angle of PEG acrylate monolayer was taken as 34° and that of a thiol SAM as 63°. The results of the same are shown in Figure 2a. It can be seen that the fraction of PEG groups on the surface changes from 0 to 0.6 in 5 min.

The same process was repeated in the orthogonal direction to obtain a gradient in multiple directions. The sample was immersed in a similar mixture in an orthogonal direction, and the water contact angles were recorded for the surface and have been plotted in Figure 1b. The fractional coverage of PEG was calculated using the same technique as mentioned above, and the coverage of PEG is plotted in Figure 1b. It can be seen that the fractional PEG coverage increases from 0 to ~0.6 along the edges and to 0.84 along the diagonal.

In addition to forming gradients of the same functionality along two directions on a substrate, gradients of multiple acrylate functionalities have also been formed. To minimize the effect of the first gradient on the second step, the maximum surface coverage was kept at a lower value than in Figures 1 and 2. A thiol-terminated glass substrate was immersed in a mixture of PEG acrylate ($M_n = 375$) and 10 vol % ethylenediamine at the

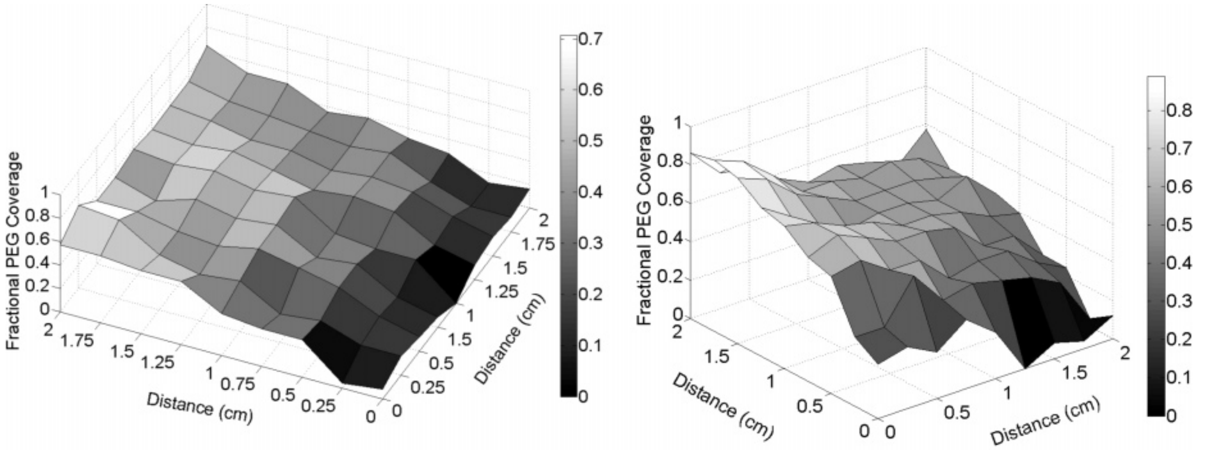

Figure 2. Fractional coverage of PEG acrylate calculated using water contact angle data. (a) A thiol-terminated glass substrate was gradually immersed in a solution containing PEG acrylate ($M_n = 375$) and 10 vol % ethylenediamine at a rate of 0.4 cm/min for 5 min and withdrawn at a rate of 24 cm/min. (b) The same substrate was immersed in a similar solution in the orthogonal direction at the same rates.

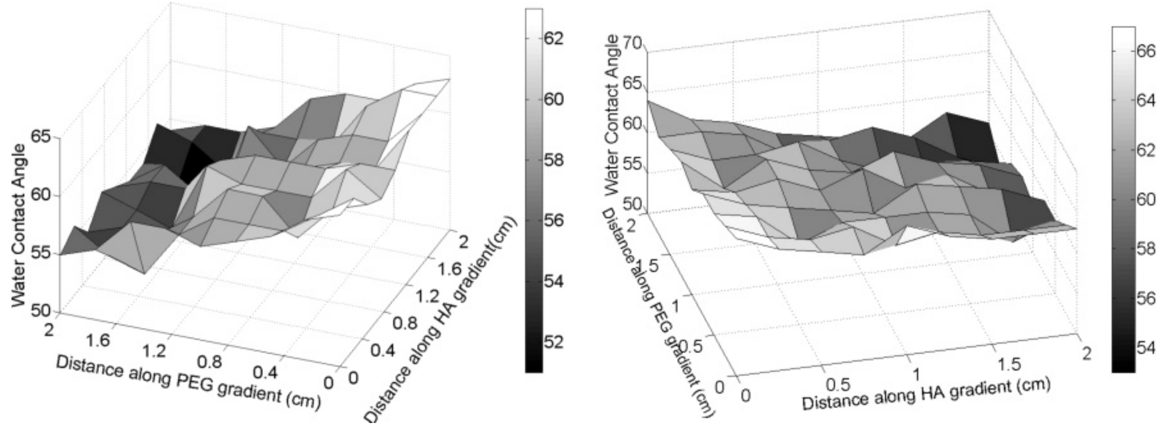

Figure 3. Water contact angle of a surface modified with a PEG acrylate and hexyl acrylate (HA) gradient. (a) A thiol SAM was immersed in a mixture containing PEG acrylate and 10 vol % ethylenediamine at the rate of 0.57 cm/min for 3.5 min and withdrawn at the rate of 24 cm/min. (b) The same sample from (a) was immersed in a solution of HA and 10 vol % ethylenediamine at the same rates.

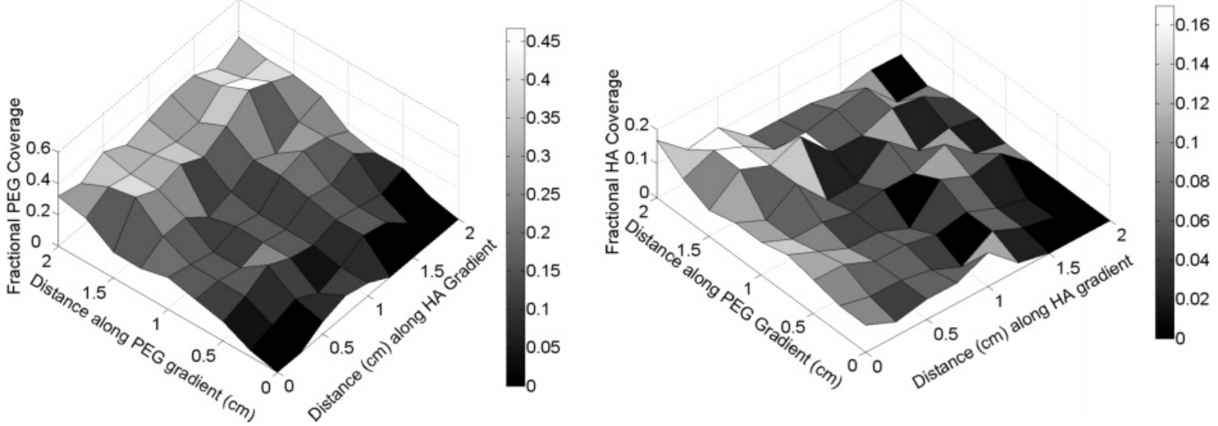

Figure 4. Orthogonal gradient on a thiol-terminated glass substrate with PEG acrylate ($M_n = 375$) and hexyl acrylate (HA). (a) A thiol-terminated glass substrate was immersed in PEG acrylate and 10 vol % ethylenediamine at the rate of 0.57 cm/min for 3.5 min and withdrawn at the rate of 24 cm/min. (b) The same sample from (a) was immersed in a solution of HA and 10 vol % ethylenediamine along the orthogonal direction at the same rates.

rate of 0.57 cm/min for 3.5 min and withdrawn at the rate of 24 cm/min. The water contact angle of the surface was measured at various points, and the results are plotted in Figure 3a. The PEG fractional coverage was calculated using Cassie's equation as described earlier, and the results are shown in Figure 4a. A maximum fractional surface coverage of 0.26 was achieved. The sample was then immersed in a mixture of hexyl acrylate (HA) and 10 vol % ethylenediamine at the same speed, and the water contact angles were measured and are plotted in Figure 3b. The fractional coverage of the resultant sample was calculated by extending the Cassie's equation to three components, namely, thiol, PEG, and HA. The water contact angle for a completely covered surface of HA was found to be 110°, and the fractional coverage of PEG for a specific point was assumed to be the same as in Figure 4a.

The maximum fractional coverage of HA was about 0.16, which is smaller as compared to the coverage of PEG in Figure 2a for the same reaction time and amine concentration. The

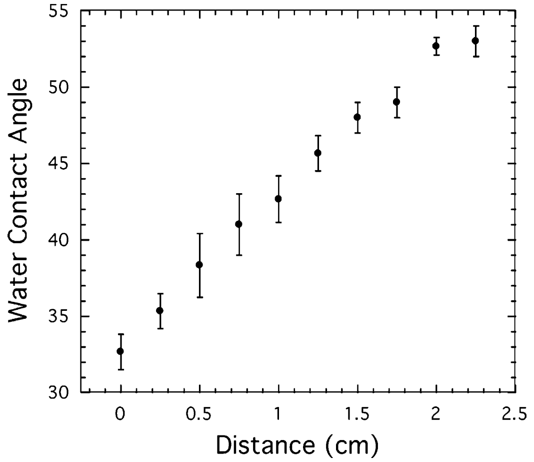

Figure 5. Water contact angle of a PEG-modified polymer surface. A mixture of hexanediol diacrylate and tetrathiol in the ratio of 1:1.1 of acrylate to thiol functionalities was photopolymerized with 0.1% UV photoinitiator, 2,2-dimethoxy-2-phenylacetophenone. The polymer was immersed in a mixture of PEG acrylate (M_n = 375) and 10 vol % ethylenediamine at the rate of 0.4 cm/min and withdrawn at the rate of 24 cm/min. Error bars denote the standard deviation from three samples.

result is partially explained by the lower reactivity of the HA as compared to PEG. Another factor that contributes to this outcome is the presence of a PEG layer when the HA deposition is taking place, making the deposition of HA on the surface more difficult since HA and PEG are hydrophobic and hydrophilic in nature, respectively. However, Figure 4a,b shows conclusively the deposition of two different acrylates on a surface in a spatially controlled two-dimensional gradient manner.

Thiol−acrylate reactions were also carried out to deposit an acrylate gradient on a polymer surface. Polymers with pendant thiol groups are readily synthesized by polymerizing a thiol−ene or a thiol−acrylate mixture with an excess amount of thiol monomers.[32] A mixture of HDDA and tetrathiol in the ratio of 1:1.1 of acrylate to thiol groups was photopolymerized with the addition of 0.1% DMPA as photoinitiator. HDDA undergoes homopolymerization and also reacts with tetrathiol in a step growth fashion; hence, the acrylate groups react to complete conversion, whereas a sufficient amount of thiol groups are pendant on the surface. The above process of gradient formation was repeated on this surface with PEG-375 and 10 vol % ethylenediamine with the same rates of immersion and withdrawal, and the water contact angles of the surface were recorded. The results of the same are shown in Figure 5. It can be seen that the water contact angle of the surface increases from 33° to about 53° from zero to 2 cm. The water contact angle of the bare polymer (before deposition of PEG gradient) is 55°, and that of a complete PEG layer is 34°. Thus, there is a deposition of nearly complete PEG layer on the polymer surface.

Effectively, this technique can be used for the deposition of an acrylate monolayer or an acrylate gradient on any polymer surface, since it is possible to attach a layer of thiol−ene or a thiol−acrylate polymer on a variety of polymer surfaces. With the use of a specific stoichiometry of the thiol−vinyl groups in the polymer mixtures, it is possible to readily modify a polymer surface with a wide variety of acrylate groups in a spatially controlled manner as shown in the previous results.

The proposed reaction scheme was also used for growing thicker polymer films on surfaces. A mixture of thiol and acrylate monomers with the amine catalyst is sandwiched between a thiol SAM and a glass slide and allowed to react. The surface thiols participate in the reaction, attaching thiol−acrylate chains on the surface. The thiol−acrylate coupling either initiates from the surface or polymer chains formed in the bulk attach to thiols on the surface. Hence, this surface modification scheme is an intermediate between “grafting to” and “grafting from” approaches. The thiol and acrylate monomers do not react with molecules of the same species, and hence the reaction follows a purely step growth mechanism. As a result of this behavior, the advantages of step growth polymerizations can be exploited for surface modification.

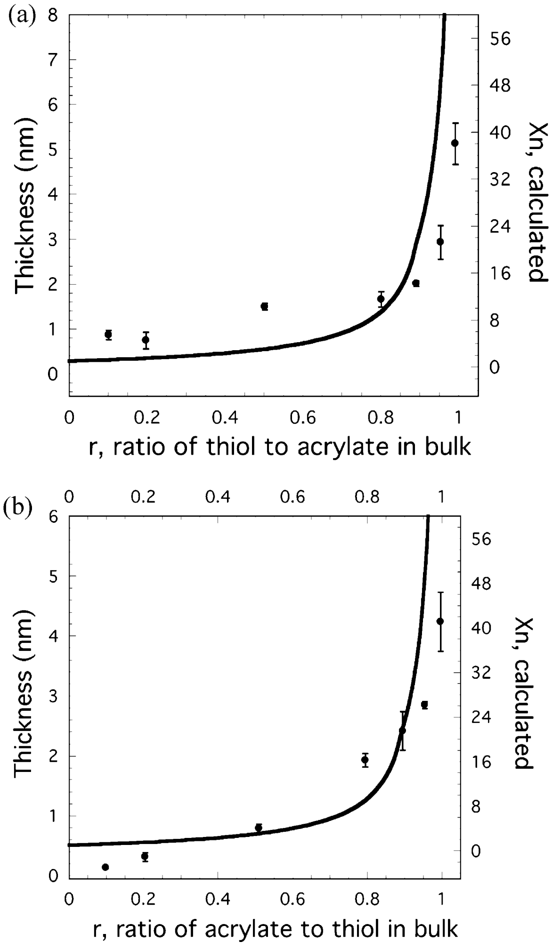

Figure 6. Thickness of thiol−acrylate films deposited using mixtures of 1,6-hexanediol diacrylate and hexanedithiol vs the stoichiometric ratios of thiol to acrylate functionalities. (a) Film thickness vs the ratio of thiol to acrylate functionalities in bulk, where thiol is the limiting reagent. (b) Film thickness vs ratio of acrylate to thiol functionalities in the bulk, where acrylate is the limiting functionality. Error bars denote the standard deviation from three samples. The solid line denotes the theoretical value of average chain length calculated for a nonstoichiometric step growth polymerization.

The ratio of thiol and acrylate functionalities in the bulk was changed from 0 to 1 to grow brushes on a thiol-terminated silicon substrate, and the thickness of the formed films was measured using ellipsometry. A 2.5 mol % triethylamine was added as a catalyst, and the whole setup was sealed to prevent the evaporation of amine. As the ratio of thiol to acrylate functionalities increased from 0 to 1, the thickness increased from 0.1 to 4 nm. The results for the same are depicted in Figure 6a. The solid black line in the graph shows the theoretical value of average chain length vs stoichiometric ratio of the reacting species for a step growth polymerization.[45] The observed thickness follows a similar trend to the theoretical chain length. The same process is repeated for the cases when the thiol is in excess and the acrylate functionality is the limiting reagent. The results are shown in Figure 6b.

The theoretical chain length in bulk gives the number-average polymer chain length, X_n, in bulk. At high values of the stoichiometric ratio, r, the theoretical value of X_n is much larger than the thickness. This result can be due either to the impurities in the monomer or to the increased viscosity in these systems at high chain lengths, which reduces grafting.

The surface chain density was calculated using the measured thickness and the calculated average chain length using the equation[5]

$$\sigma = \frac{h\rho N_A}{MX_{n,s}} \qquad (1)$$

where σ represents the number of chains/nm^2, h represents the measured thickness of the film, ρ represents polymer density, N_A represents Avogadro's number, M is the average molecular weight of monomers, and $X_{n,s}$ represents the average chain length of the polymer chains. It was assumed that the average chain length in the bulk (which was calculated) is the same as the chain length on the surface.[5]

The surface chain density is normalized against the coverage of the thiol SAM (which was assumed to be 5 chains/nm^2)[46] and is plotted in Figure 7a,b. The thiol SAM density is used only for normalizing purposes and not for the calculation of actual surface densities and is assumed to be constant for all samples. The profiles of the surface chain densities vs the stoichiometric ratio, r, exhibit interesting results with respect to the mechanism of thiol−acrylate polymerizations on surfaces. The probability of a chain attaching to the surface is directly proportional to the number of chains with acrylate end groups in the bulk and inversely proportional to the average chain length of the bulk polymer. As the value of r increases, the average chain length increases, and hence, it becomes increasingly difficult for the chains to reach and react with the surface.

In the case when the acrylate functional group is in excess (Figure 7a), the highest surface coverage is obtained for the lowest value of r and monotonically decreases as r increases. For all values of r, the chains with acrylate end groups are in excess, and hence the probability of a chain attaching to the surface depends on the average chain length. When the thiol functionality is in excess, for smaller chain lengths, the majority of chains in the bulk have thiol end groups, and hence the surface coverage is severely limited. As the ratio of acrylate to thiol increases, both the proportion of acrylate end groups and the chain length increase. The two factors have opposing effects on the surface coverage, and hence, the surface coverage increases initially and decreases subsequently. As the value of r increases further, the effect of increasing chain length dominates and the surface coverage starts decreasing.

It is also interesting to compare the values of surface chain densities with those routinely observed in "grafting to" and "grafting from" systems. Typically, "grafting to" systems show very low surface coverages of 0.005−0.03 chains/nm^2 since the chains formed in the bulk are long, and it is difficult for them to diffuse on the surface.[5,47,48] The "grafting from" systems have much higher coverage ranging from 0.25 to 1.3 chains/nm^2.[5,49−51] The current system has surface coverages spanning both these ranges since both "grafting to" and "grafting from" mechanisms take place in this system depending on the reaction conditions. In the case when the acrylate is in excess, the highest surface coverage is nearly 2 chains/nm^2, the first data point in Figure 7a, and it decreases to about 0.05 chains/nm^2, the last data point in Figure 7a. The very high surface coverage in the initial regime is due to the very small chain lengths of the attached polymer films. In the case when the thiol is in excess, the highest coverage achieved is 0.75 chains/nm^2, which is in the "grafting from" regime. It should be noted that the values used for comparison here are absolute values of surface densities whereas the ones in Figure 7 are normalized with respect to SAM coverage.

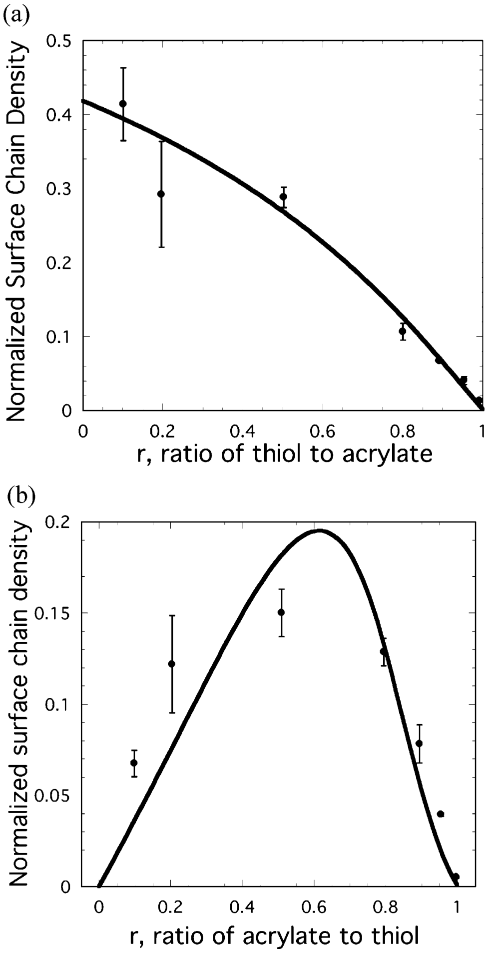

Figure 7. Normalized surface chain densities calculated using theoretical average chain length and assuming a surface coverage of 5 SH/nm^2 for the thiol SAM (a) for the case when thiol is a limiting reagent and r denotes the ratio of thiol to acrylate functionalities and (b) for the case when acrylate is the limiting reagent and r denotes the ratio of acrylate to thiol functionalities. Error bars denote the standard deviation from three samples. The solid line depicts the modeling predictions as calculated using eq 6 and described in detail in the text.

The normalized surface coverage was modeled using a model where the effect of the polymer chain length in the bulk and the bulk acrylate concentration were considered. The rate at which the chains formed in the bulk attach to the surface is proportional to the number of acrylate end groups in the bulk and the number of unreacted thiol groups on the surface:

$$\text{rate of attachment of chains on the surface} \propto (\text{no. of unreacted acrylate groups in the bulk}) \times (\text{no. of unreacted thiol groups on the surface})$$

The number of unreacted surface thiol groups decreases with every attached chain. It is assumed that each chain that is attached to one thiol group on the surface and coils on the surface to cover some of the adjacent thiol groups depending on the length of the chain. If SH_s^0 denotes the number of thiol groups present per unit area initially, N denotes the number of chains attached per unit area at time t, and X_n denotes the average chain length, then the number of unreacted thiol groups on the surface per unit area is given by

$$\mathrm{SH} = \mathrm{SH}_s^0 - N[z(X_n - 1) + 1] \tag{2}$$

where z is a modeling parameter. The term $[z(X_n - 1) + 1]$ gives the number of thiol groups covered per attached chain and is always greater than or equal to 1. Thus, the attachment rate of chains to the surface, dN/dt, is given by

$$\frac{dN}{dt} = k\{\mathrm{SH}_s^0 - N[z(X_n - 1) + 1]\} \times \text{(unreacted acrylate groups in the bulk)} \tag{3}$$

where k is the kinetic constant for the addition reaction between surface thiols and bulk acrylate groups.

The rate at which the reaction proceeds in the bulk is proportional to the unreacted thiol and acrylate groups in the bulk. Thus

$$\text{rate of reaction in the bulk} = k' \times \text{(unreacted thiol group in the bulk)} \times \text{(unreacted acrylate groups in the bulk)} \tag{4}$$

Here, k' denotes the kinetic constant for the addition reaction between bulk acrylate and thiol groups. When the thiol is the limiting functionality, p denotes the conversion of thiol groups in the bulk and SH_b^0 is the initial bulk thiol concentration

$$\frac{\mathrm{SH}_b^0\, dp}{dt} = k'\mathrm{SH}_b^0(1 - p) \times \text{(no. of unreacted acrylate groups in bulk)} \tag{5}$$

Dividing eq 3 by eq 5 and defining σ as the N/SH_s^0, the equations reduce to

$$\frac{d\sigma}{dp} = \frac{K\{1 - \sigma[z(X_n - 1) + 1]\}}{1 - p} \tag{6}$$

for the case when the thiol is the limiting reagent and $K = k/k'$. X_n is dependent on both the conversion of the limiting reagent and the stoichiometric imbalance as given by[45]

$$X_n = \frac{1 + r}{1 + r - 2rp} \tag{7}$$

Equation 6 was numerically integrated using the boundary condition that, at $p = 0$, $\sigma = 0$. The results of the same are plotted in Figure 7a as the solid line.

For the case when the acrylate is the limiting reagent, a similar analysis gives the equation

$$\frac{d\sigma}{dp} = \frac{Kr\{1 - \sigma[z(X_n - 1) + 1]\}}{1 - rp} \tag{8}$$

where r is the ratio of acrylate to thiol functionalities in the bulk. The equation is integrated similarly, and the results are plotted in Figure 7b. It can be seen that the modeling predictions follow a close trend with the experimental data.

The two factors that influence chain length in step growth polymerization are the stoichiometric imbalance and the extent of reaction.[45] The effect of the first factor on surface chain density was studied in the earlier section by growing polymer films with various stoichiometric ratios of thiol and acrylate. The effect of conversion is difficult to study for several reasons. The grafting process continues as long as the reacting mixture is in contact with the thiol SAM, making it difficult to stop the grafting accurately at a specific conversion. In addition, the reaction continues for long times (several hours in the above case) making continuous, real-time monitoring of the conversion difficult. Finally, the reaction starts as soon as the reactants and the catalyst are mixed; hence, accurately monitoring it in real time is difficult.

A gradient method used for studying monolayers was modified to overcome some of these difficulties. Diethylamine was used instead of triethylamine to increase the reaction rate and achieve near complete conversion within 50 min. A reacting mixture was prepared with a stoichiometric ratio of thiol and acrylate groups, and a thiol-terminated SAM substrate was immersed with such a speed that the entire substrate was immersed in the mixture in the time required for the completion of the reaction. Separately, the conversion vs time profile for the reaction sample was monitored using FTIR for 50 min. In both cases (grafting on the sample and IR monitoring), a time period of 1 min was allowed to elapse between the mixing of reactants and catalyst and the start of the experiment.

It was found that a stoichiometric mixture of hexane dithiol and HDDA, when polymerized in the presence of diethylamine, crystallized before the reaction could be completed. This outcome could be a result of very high molecular weight chains being formed in a short time due to the addition of a stronger catalyst. In order to overcome this, a small amount (30 mol %) of propanedithiol was added to the thiol−ene mixture, while the overall number of thiol and acrylate groups was maintained in a stoichiometric ratio.

The thiol SAM substrate was immersed in a reacting thiol−acrylate mixture at a rate of 0.04 cm/min, so that each point on the surface comes in contact with the reaction mixture at a specific conversion and remains in contact until maximum conversion is reached. The points on the surface which come in contact earlier have higher grafting since they are in contact with the reaction mixture for longer amounts of time, and there is more grafting when the average chain length is smaller, which is the case at lower concentrations. The points that come in contact at higher conversions have reduced thickness and smaller grafting densities. The average thickness of three samples vs distance is plotted in Figure 8a. The grafting density was calculated in the same manner as before and is plotted in Figure 8b. It can be seen that the grafting density decreases as expected with increasing initial conversion.

The same model as described earlier was used to model the surface chain densities in this case. The initial conversion for a particular point in the gradient was taken from the FTIR data (by matching time points), and the surface density at that conversion was taken to be zero. Equation 6 was numerically integrated with the initial conditions and fit to the observed value of normalized surface chain densities, as seen in Figure 8b. It can be seen that the model fits the data on surface chain density well.

Finally, the deposited films were investigated using scanning probe microscopy (SPM). A blank thiol SAM, a surface modified with PEG acrylate groups, and surfaces modified with brushes of dithiol−diacrylate in various stoichiometric ratios of thiol and acrylate group were observed under the contact mode of the SPM. The results of the same are presented in Figure 9. It can be seen that all the deposited films are uniform. Figure 9b,d,f shows the profile of the films across the line shown in the images. It can be seen that the average height for a thiol SAM as observed under AFM is 0.6 nm, which corresponds to

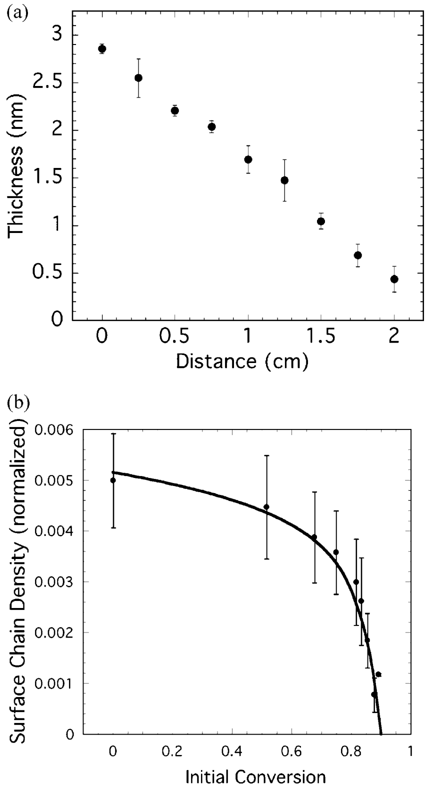

Figure 8. (a) Thiol−acrylate polymer film thickness along a thiol-terminated SAM substrate immersed in a reaction mixture of hexanediol diacrylate, hexanedithiol, and propanedithiol in a ratio of 10:7:3 (by moles) with 1.5 mol % diethylamine at the rate of 0.04 cm/min for 50 min. Error bars denote the standard deviation from three samples. (b) Normalized surface chain density was calculated using theoretical average chain length and using the initial surface thiol concentration as 5 SH/nm^2 on the SAM surface. The solid line denotes the modeling predictions obtained using eq 6 and described in detail in the text.

the expected value as per the ellipsometry results. A PEG acrylate monolayer was deposited by reacting the monomer with the thiol SAM in the presence of 10 vol % ethylenediamine for 10 min. The average height for the PEG acrylate film (Figure 9c,d), as seen in the SPM profile, is about 2.7 nm, which corresponds to the increase in thickness for the deposition of a monolayer. The average thickness as seen in the profile for a thiol−acrylate brush grown from a stoichiometric ratio of thiol and acrylate functionalities is 5.4 nm, which corresponds well to the from earlier ellipsometry results.

These results show that it is possible to modify glass, silicon, and polymer substrates with thin acrylate films in a controlled manner, where several properties such as surface density, thickness, and wettability of the deposited films are readily changed. The deposited films have certain unique advantages as compared to other methods for surface modification. Since the films are deposited in a noninvasive manner, without the use of severe reaction conditions, they can be used to modify suitable substrates for biological applications. Varying acrylate density can be employed to study the cell−material interaction where gradients of various acrylated biological functionalities are easily deposited on the surface. Gradients in multiple directions can be used for the investigation of the synergistic action of multiple functionalities with respect to their concentrations. The main advantage of this method is the ability to readily deposit acrylate films on a variety of substrates with controllable properties without harsh reaction conditions.

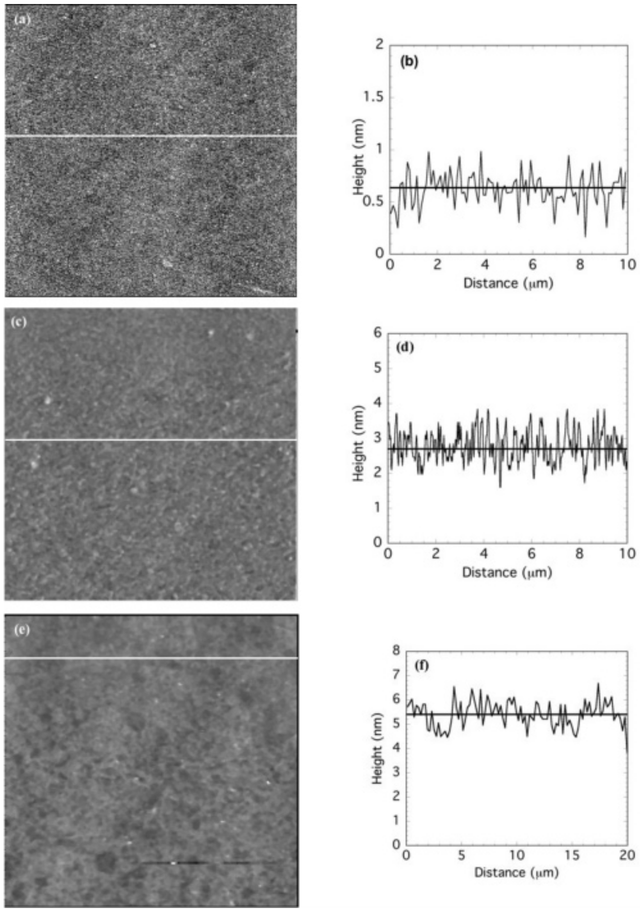

Figure 9. (a) SPM image of a thiol SAM deposited on a silicon wafer. (b) Cross section of thickness across the marked lines in (a). (c) SPM image of thiol SAM modified with poly(ethylene glycol) acrylate film deposited by reacting for 10 min with 10 vol % ethylenediamine. (d) Cross section of thickness across the marked lines in (c). (e) SPM image of a thiol SAM modified with a polymer brush deposited by reacting dithiol and diacrylate in a stoichiometric ratio. (f) Cross section of thickness across the marked lines in (e). All images were taken in contact mode at a speed of 2 lines/s with silicon nitride tips.

Conclusions

The application of the thiol−acrylate conjugate addition reaction for surface modification was developed and evaluated. Acrylate monolayers of varying surface densities were deposited on silicon, glass, and polymer surfaces. Repeating the process in multiple directions results in deposition of multiple acrylate functionalities in orthogonal directions. Ultrathin films were deposited with varying chain lengths by changing the stoichiometric ratio of thiol and acrylate functional groups and by controlling the extent of the reaction. A model was developed to predict the surface chain densities and applied to all the cases.

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