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Ultrathin Patterned Polymer Films on Surfaces Using Thiol−Ene Polymerizations

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ABSTRACT: A simple and straightforward method for growing ultrathin, micropatterned polymer films on surfaces with precise thickness and spatial control is presented. A difunctional ene monomer and a difunctional thiol were photopolymerized on a surface terminated with thiol groups. The surface thiols participate in the polymerization, and a linear polymer is formed on the surface. Brush growth was spatially controlled by selectively polymerizing the monomers through a photomask, while the brush thickness was controlled by changing the ratio of thiol and ene monomers or by changing the monomer functionality. Further, the surface was passivated by attaching a patterned, cross-linked polymer film, which was then backfilled with another monomer, demonstrating the attachment of multiple functionalities on the surface in a controlled, photolithographically patternable manner. Thiol−ene polymerizations were carried out without an initiator and used to graft patterned, polymer films. The films were observed using scanning probe microscopy and characterized using ellipsometry.

Introduction

Modification of surface properties is critical in several fields including MEMS, biotechnology, and nanotechnology. Covalent attachment of polymer films to substrates provides an effective method for altering surface characteristics. Depending on the type of polymer film attached, several characteristics such as biocompatibility, adhesion, corrosion and friction resistance, and sensing capabilities of a surface can be modified.[1,2] Techniques used to attach polymer films covalently to a surface are mainly divided into "grafting to" and "grafting from" techniques. The "grafting to" involves attaching an already formed polymer chain to a surface and yields nonuniform films with very low grafting densities.[1] The "grafting from" approach consists of initiating a polymerization reaction from initiator molecules attached to the surface, which yields more control over surface properties.[3−6] Self-assembled monolayers (SAMs) have become a very convenient and effective method for attaching initiators of various types of polymerization reactions to a surface.[1,7−12] Depending on the monomer system used and the polymerization mechanism, either a linear polymer, called a "polymer brush", or a cross-linked polymer film is formed and attached to a surface.

Attaching a linear polymer brush is particularly attractive since several film properties are tunable. For example, a specific functionality like an antibody[13,14] or a sensor molecule[15] can be attached on the polymer brush terminus to obtain a surface presenting that particular functionality. Other film properties that are controllable in a polymer brush include uniformity, stability, thickness, and the spatial growth of the brush. Several polymerization mechanisms have been used to form polymer brushes including traditional free radical polymerization, living or controlled radical polymerization (LRP), and atom transfer radical polymerization (ATRP).[1,2,16] Over the past decade, ATRP, in particular, has become a popular technique for growing polymer brushes due to its precise control over thickness and the ability to control the lengths of blocks in the films.[2,17] However, the ATRP technique often requires synthesis of specialized SAM-forming initiators.

The two important properties of polymer brushes grown on surfaces include thickness and spatial control. Primarily, the chain length of the attached polymer chains and/or the surface density of chains are controlled. While controlling the surface chain density is not trivial, the chain length of attached polymer chains is usually controlled by changing the polymerization time in most types of polymerizations.[10,16,18] The ability to spatially control the attachment of polymer chains helps in selectively modifying polymer properties and the attachment of multiple functionalities. Prucker et al. employed multiple photolithographic techniques to pattern surfaces including photopatterning of a SAM layer followed by surface-initiated polymerization, exposing unpatterned polymer films to UV light and etching selectively, and selectively initiating polymerization by using a photomask.[19] Other groups have used microcontact printing techniques to obtain a patterned SAM, followed by brush growth to obtain selective brush formation.[20] A range of polymerization mechanisms such as ATRP,[21] ring-opening polymerizations,[22] ring-opening metathesis polymerization,[20] and free radical polymerizations[23] have been combined with microcontact printing technique to form patterned films.

In this work, two aspects, namely, the formation of ultrathin films (<10 nm) with control over film thickness and growing films with spatial control, have been combined. Thiol−ene photopolymerizations were combined with self-assembly techniques to attach polymer thin films with thickness control achieved in a *self-limiting* manner. Photolithography was used to spatially pattern the polymer grafts, and patterned, ultrathin

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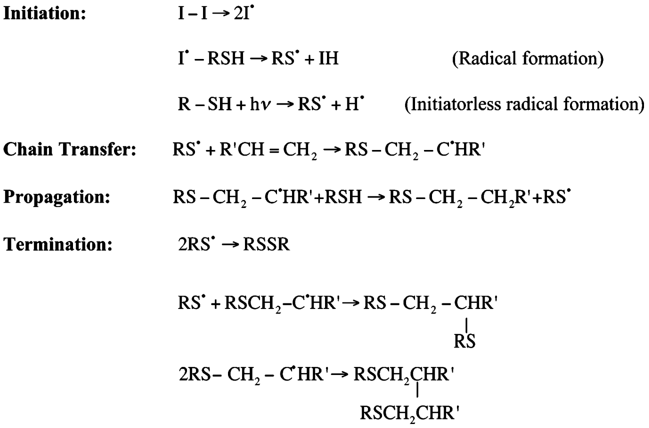
Scheme 1



Initiation: $I - I \rightarrow 2I^{\bullet}$

$I^{\bullet} - RSH \rightarrow RS^{\bullet} + IH$ (Radical formation)

$R - SH + h\nu \rightarrow RS^{\bullet} + H^{\bullet}$ (Initiatorless radical formation)

Chain Transfer: $RS^{\bullet} + R'CH = CH_2 \rightarrow RS - CH_2 - C^{\bullet}HR'$

Propagation: $RS - CH_2 - C^{\bullet}HR' + RSH \rightarrow RS - CH_2 - CH_2R' + RS^{\bullet}$

Termination: $2RS^{\bullet} \rightarrow RSSR$

$RS^{\bullet} + RSCH_2{-}C^{\bullet}HR' \rightarrow RS - CH_2 - \underset{\displaystyle RS}{\underset{|}{CHR'}}$

$2RS - CH_2 - C^{\bullet}HR' \rightarrow \underset{\displaystyle RSCH_2CHR'}{\underset{|}{RSCH_2CHR'}}$

films with a thickness ranging from 1 to 5 nm were grown using this technique.

Thiol−ene polymerizations are radical-mediated, step-growth polymerization systems, where chain transfer and propagation steps take place in an alternating manner. Initiation usually takes place under UV light in the presence of a cleavage-type initiator, although these polymerizations are regularly performed in the absence of any distinct initiator species.[24−27] In these systems the thiyl radical propagates across the carbon−carbon double bond, forming a carbon radical and a carbon−sulfur bond. This carbon radical abstracts a hydrogen from another thiol moiety, regenerating the thiyl radical. These propagation and chain transfer steps occur recursively and form the basis of the thiol−ene polymerization. Termination in these systems is dominated by radical−radical recombinations where carbon−carbon, sulfur−sulfur, or carbon−sulfur radicals combine to terminate.[25,27] Steps in a thiol−ene polymerization are shown in Scheme 1.

To graft thiol−ene based films to a surface, the surface is first modified with a thiol-terminated silane, 3-mercaptopropyltrimethoxysilane, and a thiol−ene reaction as shown above is performed on and above the surface. The surface thiols become part of the polymer network (or chain if it is a linear polymer), thereby covalently attaching the film to the surface. Since polymerization initiation takes place on the surface and bulk oligomers/polymers can also be reacted to the surface, this approach to surface modification is an intermediate between the "grafting to" and "grafting from" approaches.[18] A difunctional thiol and a difunctional ene are reacted on a thiol-terminated surface to form linear polymer grafts attached to the surface, while higher functionality thiols or enes are used to graft a cross-linked polymer film on the surface. In addition, an acrylate monomer will undergo thiol−acrylate polymerization to form a polymer film.

Thiol−ene systems have several advantages as compared to traditional acrylate systems for surface modification.[6,25,27] Since it is a step-growth mechanism, where thiol and ene groups add stoichiometrically to each other, it is possible to change the ratio of thiol and ene monomers in the bulk to control the molecular weight of the attached chains in a *self-limiting* manner.[18] Also, by changing the functionalities of thiol and ene used, it is possible to graft monolayers, brushes, or cross-linked films on a surface.

An important advantage of using thiol−ene polymerizations is the possibility of initiation in the absence of an added photoinitiator.[24,26] Initiatorless systems are particularly attractive since thick, clear coatings can be formed without concerns associated with light attenuation caused by initiator absorption. In addition, thiol−ene chemistry is highly versatile, and a variety of functional groups are readily incorporated in the grafted film.[6,25] Another advantage of thiol−ene systems is that they are photoinitiated systems, and hence photolithographic techniques are appropriate for forming spatially patterned films. Last, thiol−ene polymerizations are insensitive to the presence of oxygen, and hence very thin films can be formed, which is not possible in acrylate polymerizations. These advantages make thiol−ene systems unique for surface modification applications offering precise control over film properties.

In this work, patterned thiol−ene films were grafted on a surface by using an optical mask alignment system. A chrome mask with 50 μm squares is used to obtain a model, patterned film. The ratio of thiol to ene functionalities present in the bulk was changed to control the thickness of the grafted films. The thickness of the films was also controlled by the addition of a small amount of a monofunctional ene. The thickness of the formed films was measured using scanning probe microscopy (SPM) and ellipsometry, and the values from the two measurements were compared.

Cross-linked polymer films were attached using thiol−acrylate polymerizations and shown to passivate the surface. A fluorescent dye, hematoxylin, was used to stain films formed from a poly(ethylene glycol) acrylate−thiol mixture to demonstrate the presence of PEG only in the regions which were exposed to light, where the film formation takes place. To demonstrate the grafting of multiple functionalities, patterned acrylate films were backfilled with PEG brushes and dyed with hematoxylin. Photoinitiatorless thiol−ene polymerizations were carried out to obtain patterned films attached to the surface.

Experimental Section

Materials. The thiol−ene monomer system used was a mixture of 1,6-hexanedithiol (HDT) and triethylene glycol divinyl ether (DVE-3). DVE-3 was provided as a sample (Rapi-cure DVE-3) from ISP technologies, Inc. (Wayne, NJ). HDT, dodecyl vinyl ether (DoDVE), poly(ethylene glycol) monoacrylate ($M_n = 375$), and trifluoroethyl acrylate were purchased from Aldrich. 1*H*,1*H*,6*H*,6*H*-Perfluoro-1,6-hexyl diacrylate was purchased from Exfluor Research Corp. (Round Rock, TX). The UV photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (DMPA), was purchased from Ciba-Geigy (Hawthorn, NY). Thiol-functionalized SAMs were formed from 3-mercaptopropyltrimethoxysilane purchased from Aldrich. All chemicals were used as obtained.

SAM Deposition. *Substrates.* Polished, double-sided silicon wafers (Umicore Semiconductor Processing, Boston, MA) were used for all brush growth studies. Wafers were in the (100) orientation and 760 μm thick. Substrates used to obtain fluorescent images were precleaned, plain microslides obtained from Gold Seal Products (Portsmouth, NH). 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.

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.[18,28]

Patterned Photopolymer Brush Formation. Monomer mixtures were prepared using HDT and DVE-3 mixed in various ratios of thiol and ene functionalities. Before polymer brush formation, the thiol-terminated SAM is treated with a solution of dithiothreitol (DTT), which reduces disulfide bonds to thiols. Substrates were immersed in a 100 mM DTT solution in 10 mM phosphate buffer for 10 min, then rinsed with DI water and acetone, and blown dry

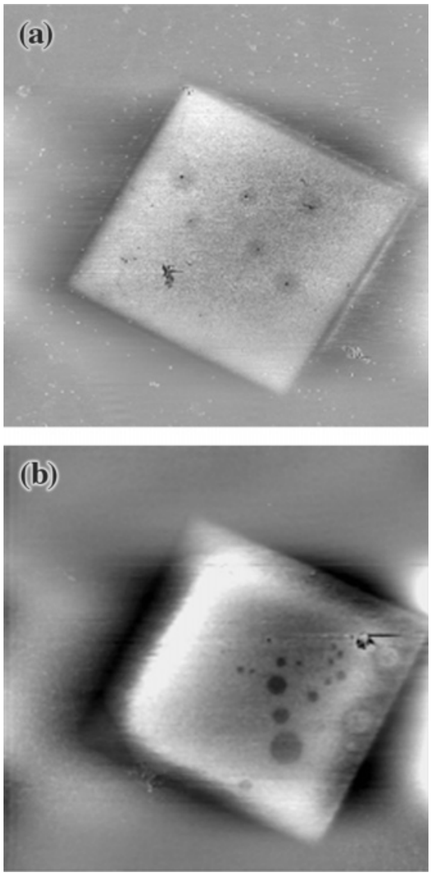


Figure 1. Friction mode SPM image of a patterned thiol−ene brush: (a) obtained with a silicon nitride tip and (b) obtained with a gold-coated tip. The region inside the square has bare thiol-terminated SAM and shows higher friction, whereas the regions outside have brush formation and show lower friction. The side of the square is 50 μm.

with nitrogen. The polymerization was carried out immediately following DTT treatment.

To form patterned brushes, an optical mask alignment system (Optical Associates, Inc., San Jose, CA) coupled to a 5 cm collimated flood exposure source that generated 60 mW/cm^2 of 365 nm radiation was used. Conceptually, the system provides a simple method to expose precisely certain regions of a surface to UV light. A surface is covered with a monomer, and an optical mask is placed on it. The distance between the mask and the sample is changed as required by moving the sample stage in the vertical direction. A chrome-on-quartz mask was used which had 50 μm squares of chrome that prevented the UV light from reaching the sample. The sample and mask were brought as close to each other as possible so that only a thin monomer layer remains between the two. The light was switched on for sufficient time for the monomers to react to complete conversion, which was approximately 10−20 s. The polymerization, and hence grafting, took place only in the regions exposed to UV light.

Following brush formation, a thick coating of the unattached thiol−ene polymer remained on the sample surface. To remove this unattached polymer, the samples were rinsed in a Soxhlet extraction apparatus running with methylene chloride for 48 h.

Polymer Brush Characterization. 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. All images except Figure 1b were obtained at a constant force at a scan speed of 2 lines/s with silicon nitride tips. A gold-coated tip was used in Figure 1b to enhance the friction between the tip and sample and used as a sensor for detection of surface thiol groups. In all cases both topographic and friction mode images were obtained.

An ellipsometer (Multiskop, Optrel GBR, Berlin) was used to make all thickness measurements, which were done at an angle of incidence of 70°. Five separate measurements were conducted at different spots for each sample. Three repeats for each sample were made to obtain an average thickness for each case.

Patterned PEG films were stained with hematoxylin for 5 min and washed in a PBS solution. Fluorescent images were obtained using a Zeiss Pascal LSM5 confocal microscope (Carl Zeiss, Thornwood, NY) with a 40× oil immersion objective. The dye was excited using a 543 nm helium−neon laser, and fluorescence was collected through a 560 nm long-pass filter.

Results

Harant et al. have recently demonstrated that thickness control in grafted thiol−ene films is achieved by controlling two variables, namely the ratio of thiol and ene functionalities in the bulk monomer and the conversion to which the monomers are reacted.[18] They showed that by altering these two factors the brush thickness could be controlled from 0.1 to 6 nm. Controlling the polymerization up to a certain conversion is nontrivial since the samples must be monitored continuously using real-time conversion measurement techniques such as real-time infrared spectroscopy. Controlling the ratio of the monomers, on the other hand, is simple and does not require any additional equipment. In this work, this technique of thickness control is employed along with photolithographic methods to obtain ultrathin micropatterned polymer films with a thickness ranging from 0.1 to 5 nm.

Patterned films were formed using an optical mask alignment system. Thiol−ene comonomer solution was sandwiched between a chrome mask with 50 μm squares and a thiol-terminated SAM and exposed to collimated UV light. Polymerization and hence grafting take place only in regions exposed to light, and a patterned surface is formed.

Typical friction mode SPM images of the patterned samples are shown in Figure 1. The friction image in contact mode SPM detects the lateral force experienced by the SPM tip moving along the surface. This force depends on the chemical groups present on the surface, and hence the friction image is a useful method for detecting changes in surface chemistry. Thiol groups show a high value of friction in SPM images as shown previously.[29] In Figure 1a, it is seen that the regions inside the square, which are unexposed to UV light, show a high friction value, indicating the presence of thiol groups. The regions exposed to light, where brush formation has taken place, show a lower friction value, since there exist both thiol and ene groups at the terminating end of the chains in these regions, along with the exposed methylene or ether groups present in the chains. Further, the chain density in these regions is reduced as compared to the density of SAM molecules in the unexposed regions. The increased mobility of the brushes, as compared to the SAMs, further reduces the interaction between the tip and the sample, which also results in lower friction. The friction images were obtained using both silicon nitride and gold-coated tips. Gold-coated tips possess higher affinity for thiol groups and were used as a means to detect the presence of surface thiols.[29] The gold-coated tips show higher friction, as seen in Figure 1b. As is seen in Figure 1a, the edges of the square appear sharp, indicating that brush formation takes place only in the exposed regions with little blurring of features due to light diffraction during the formation of these samples.

The topographic images of the patterned samples for various thiol:ene ratios are shown in Figure 2. The thickness of the brushes is controlled by changing the thiol-to-ene ratio used in the bulk monomer solution. Here, the ratio of thiol-to-ene

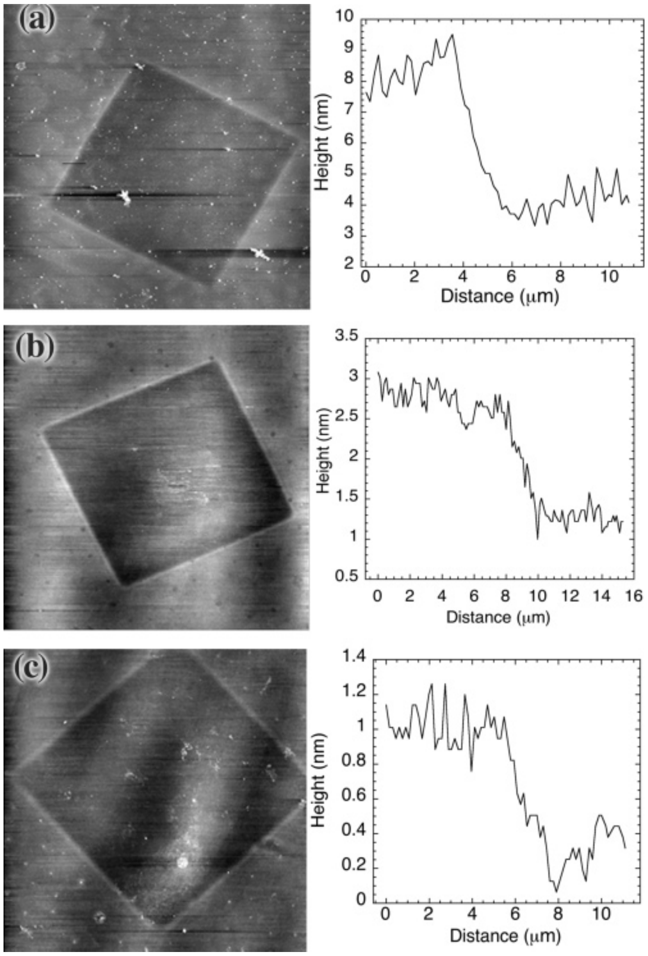


Figure 2. Contact mode SPM topography images of patterned thiol−ene brushes with various thiol:ene ratios obtained using a silicon nitride tip. Insets show the height profiles across an edge of the square. Each side of the square is 50 μm. (a) Thiol:ene = 1:1 in bulk. Step height is 4.1 nm. (b) Thiol:ene = 0.95:1 in bulk. Step height is 1.51 nm. (c) Thiol:ene = 0.9:1 in bulk. Step height is 0.7 nm.

functionalities was changed from 0.9 to 1.0. The brush thickness was measured by finding the step height change in SPM height images. Several factors influence the height measured by the SPM tip during scanning.[30] As mentioned earlier, bouncing of the tip at very high edges distorts the height measurement. Also, the brush height changes in the presence of solvents or with changes in atmospheric conditions. However, it is possible to compare the relative heights of the brushes formed when all the scanning parameters and the physical properties of the film remain nearly constant. The thickness of the patterned films was also measured using ellipsometry, and the values from the two methods are compared in later sections.

All measurements here are made at a constant force and a constant scanning speed of 2 lines/s. The height profiles across an edge are shown in the inset of Figure 2. It can be seen that the height difference in the modified and the unmodified regions is around 4.1 nm for a 1:1 ratio of thiol and ene monomers, which decreases to around 1.5 nm for a ratio of 0.95 and becomes 0.7 nm for a ratio of 0.9 of thiol to ene. The three images clearly show that it is possible to control brush height in a self-limiting manner by changing the thiol-to-ene ratio. It should be noted that on reducing the ratio further to a value less than 0.9 the roughness in the height of the brushes and the SAMs becomes similar, and the brushes cannot be observed in the topographic images. However, the friction mode image still detects the difference in the exposed and the unexposed regions.

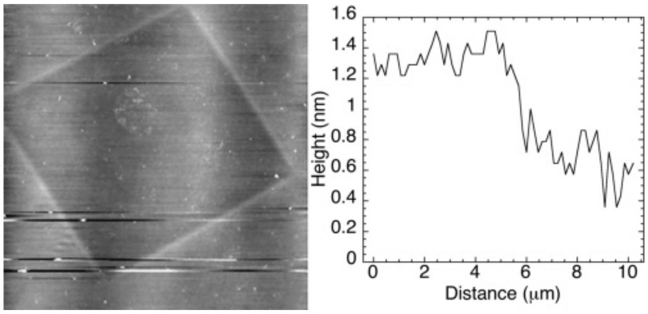


Figure 3. Contact mode SPM topography image of a patterned thiol−ene brush obtained using a silicon nitride tip. Thiol:ene = 1:1 with 1% dodecyl vinyl ether in bulk. Inset shows the height profile across the edge of the square. Each side of the square is 50 μm. Step height is 0.7 nm.

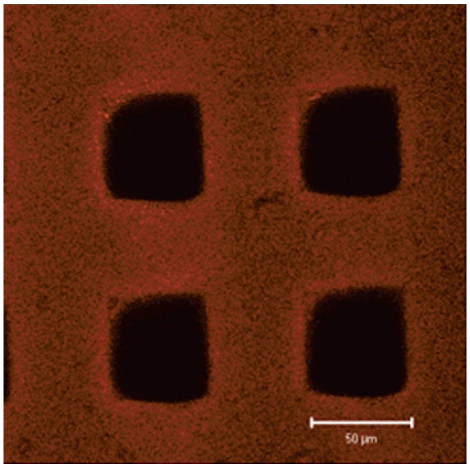


Figure 4. Confocal fluorescent image of a patterned film. The fluorescent regions contain PEG monoacrylate (M_n = 375) and propanedithiol in the ratio 4:1 of acrylate and thiol functional groups. The sample was dyed with hematoxylin and imaged under a confocal microscope.

Since thiol−ene systems react via a step-growth mechanism, the chain lengths of the oligomers formed are controlled by changing the ratio of the two functionalities taking part in the polymerization reaction. It is also possible to add a small quantity of monofunctional monomer of either the thiol or ene used to achieve control over the chain length.[31] Patterned films were formed by adding a small amount of dodecyl vinyl ether to a thiol−ene monomer solution. The SPM images of the same are shown in Figure 3. The step height of the brushes is now reduced to around 0.7 nm, despite the equivalent molar concentrations of thiol and ene functional groups.

To demonstrate that grafting occurs only in the exposed regions, fluorescent techniques were used. A cross-linked film of PEG acrylate and dithiol was polymerized on a thiol-terminated glass surface under an optical mask. The sample was dyed with hematoxylin, which is readily absorbed in PEG containing films. A fluorescent image of the sample is shown in Figure 4. The image was obtained by imaging layers of the sample from the top of the film to the bottom using a confocal microscope. The fluorescence was observed only in the exposed regions of the sample throughout the film, indicating that there was minimal PEG present in the unexposed regions.

It can also be seen from Figure 4 that the surface is passivated by forming the cross-linked films on the surface. The thiols on the surface are, however, still active in the unexposed regions, and it is possible to graft oligomers with a different chemistry in these regions. Figure 5 shows the fluorescent image of a

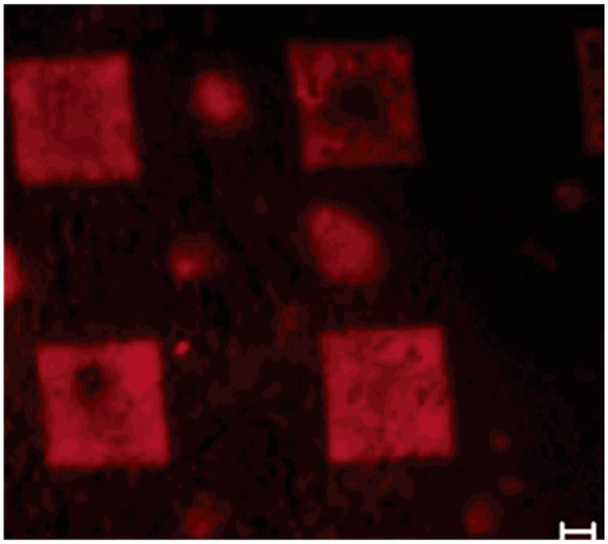


Figure 5. Fluorescent image of a backfilled sample. The regions outside the squares were patterned with a mixture of perfluorohexyl diacrylate and trifluoroethyl acrylate (1:10) to obtain a cross-linked film. The squares were backfilled with PEG monoacrylate. The sample was dyed with hematoxylin and imaged under a fluorescent microscope. The length of the bar shown is 10 μm.

surface formed by backfilling a cross-linked film grafted on to a surface. A cross-linked film consisting of a mixture of fluorinated acrylates was grown on a thiol-terminated surface. PEG acrylate was then polymerized on the surface, and the sample was washed with methanol and dyed with hematoxylin. It can be seen that the hematoxylin fluorescence is seen in the regions, which had the remaining surface active thiols from regions that were unexposed in the first step. This result shows that PEG was grafted only on the thiol-terminated region, as expected.

An important advantage of using thiol−ene polymerizations for surface modification is the possibility of carrying out initiatorless polymerizations. Thiol−ene polymerizations take place without the addition of an initiator under 365 nm light. This process was used to attach patterned thiol−ene films on the surface without any added initiator. A mixture of tetrathiol and DVE-3 was polymerized through a photomask on a thiol-terminated SAM for 15 min. The SPM image of the resultant film is shown in Figure 6. A tetrathiol was used in this case instead of a dithiol since the reaction in this case is faster as compared to a dithiol, DVE-3 mixture. The need for longer exposure times for the initiatorless reaction reduces the resolution of the patterned films, as observed in Figure 6. Another effect observed in initiatorless polymerizations is the small amount of polymerization taking place in the unexposed regions. This reaction occurs as a result of the small amount of light reflecting back from the surface, which polymerizes the monomer in the unexposed regions.

Thickness Comparison of Patterned Films. As mentioned earlier, thickness control by changing the monomer solutions and polymerization conditions is an important advantage of thiol−ene films. In addition to characterizing the films with SPM for various thiol:ene ratios (Figure 2), the thickness of the films was also measured using ellipsometry. Several factors influence the thickness value obtained by using the SPM topographic images as mentioned earlier. A comparison of the values of the thickness obtained for samples with changing ratios of thiol and ene functionalities by these two techniques is shown in Figure 7.

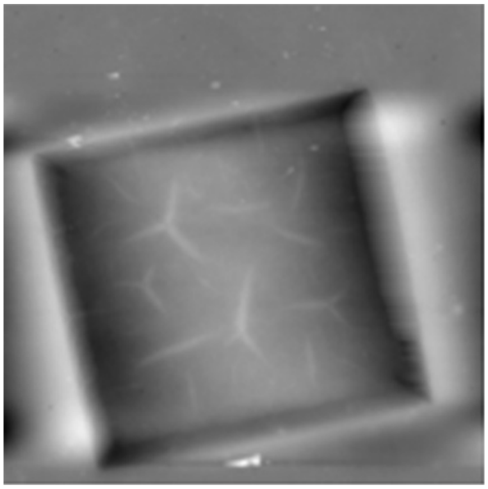


Figure 6. SPM topography image of a patterned film formed using a stoichiometric mixture of DVE-3 and tetrathiol without an added photoinitiator. The sample was exposed to UV light with an intensity of 60 mW/cm^2 for 15 min. The side of the square is 50 μm, and the z-scale is 1.5 μm.

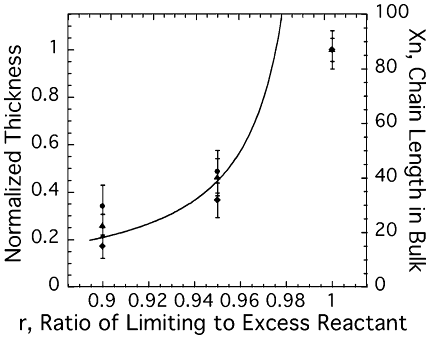


Figure 7. Comparison of film thicknesses measured using various techniques. Normalized thickness of patterned samples obtained using ellipsometry (●), normalized step height obtained in SPM measurements (◆), and normalized ellipsometric thickness of unpatterned samples (▲). Calculated average chain length for a step-growth polymerization (—). The data points are normalized for $r = 1.0$ value in each case.

Since the thickness is measured by different techniques, the values of thickness are different. Whereas ellipsometry gives an average value of the film thickness, SPM gives the change in the thickness of the film from the bare SAM to a polymer brush. To compare the thickness values, the measurements were normalized with respect to the film thickness obtained when the ratio of limiting to excess reagents, r, is equal to 1. In addition, experiments were performed under the same conditions described in the Methods section, without the presence of the optical mask, thereby forming unpatterned films. The thicknesses of these films were also measured using ellipsometry, normalized similarly, and are presented in Figure 7 (data set represented by ▲). In all cases, three different values were taken, and the standard deviation was plotted as error bars. It can be seen that the values obtained for all the three cases are the same within experimental errors. The difference in the thicknesses for various ratios is due to the difference in chain length of the films attached to the surface, which is a function of the ratio in which the two monomers are mixed in the bulk. The value of the average chain length, X_n, calculated for various values of thiol−ene ratios is plotted in Figure 7. It can be seen that the theoretical value of X_n increases in a manner similar to the observed thickness increase. At values of r close to unity, the theoretical chain length tends toward infinity, and the observed thickness values are below the theoretical ones due to monomer impurities and other side reactions. Figure 7 shows conclusively that it is possible to change the ratio of thiol and ene functionalities in the bulk and change the thickness in the patterned brushes.

Conclusions

Thiol−ene polymerizations were used to pattern ultrathin polymer films spatially on a surface with control over the thickness of the films at a sub-10 nm level. The thickness of the formed films was readily altered by changing the ratio of thiol and ene functionalities in the bulk monomer solution. Further, the thickness was also controlled by adding a small amount of monofunctional ene monomer in the bulk. Patterned, cross-linked films were suitable to passivate a surface, which was then backfilled with a different monomer solution to obtain a surface presenting multiple functionalities. Finally, patterned thiol−ene grafted films were readily formed without the addition of a photoinitiator.

Several important advantages of thiol−ene polymerizations for surface modification are demonstrated in this work. The ability to design monomer solutions for a desired thickness offers unique control over film properties not possible in systems involving chain addition polymerization. The actual polymerization time in each of the samples shown here is 10−20 s with the addition of only 0.1 wt % of the photoinitiator. This time is an order of magnitude smaller than most other polymerization mechanisms, making this technique a rapid surface modification procedure. Also, the possibility of initiatorless polymer grafting makes thick, clear coats on a surface a potential application of the technique.

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