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Thiol−Ene Photopolymer Grafts on Functionalized Glass and Silicon Surfaces

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ABSTRACT: A simple and straightforward method for forming polymer grafts on glass and silicon surfaces using thiol−ene photopolymerizations is presented. A linear thiol−ene system composed of 1,6-hexanedithiol and triethylene glycol divinyl ether was photopolymerized over a silicon surface functionalized with a thiol-terminated self-assembled monolayer (SAM). Although the grafted thiol−ene films are thin, ranging from 0.1 to 9.6 nm, the thickness is linearly related to the molecular weight of the polymer formed in the bulk. Thus, the thickness is tunable simply by controlling the polymerization conversion or the stoichiometric excess of one component. By lithographically patterning the SAM chemistry on the surface prior to polymerization, 5 μm wide lines of grafted thiol−ene polymer were created. Thin, grafted acrylic films, from 0.5 to 1.7 nm in thickness, were formed by photopolymerizing *tert*-butyl acrylate with a small amount of thiol chain transfer agent to control chain length and facilitate radical transfer to the surface.

Introduction

Surface chemistry control is critical to numerous applications of both polymers and microelectronics, including sensors, microelectromechanical systems (MEMS), and other micro- and macrodevices. Surface chemistry control is critical to facilitate desired interactions, to catalyze reactions, to limit adsorption of undesirable species, and to alter friction and adhesion behavior. In particular, the surface properties of materials are effectively modified and enhanced by the formation of thin polymer films and coatings. A wide range of polymers are readily formed into thin films, allowing the surface hydrophobicity, wettability, lubricity, biocompatibility, or chemical reactivity to be designed appropriately. Surface-grafted polymer layers have the additional advantage of decoupling surface and bulk properties. Surface-grafting techniques are used to prepare very thin polymer layers with strong surface adhesion, usually by covalent linkages. The thickness of the film created by the polymer graft is defined by the molecular weight and the surface density of the polymer.[1,2]

The techniques available for the formation of polymer grafts are divided into two categories: "grafting to" and "grafting from".[3] In "grafting to" systems, preformed polymers are attached to a surface, either by forming a chemical bond between a polymer end group and a reactive surface site or by the physisorption of a block copolymer where one block preferentially "sticks" to the surface.[4−6] The "grafting to" approach is limited in that it generally cannot achieve high surface densities due to steric blocking of available surface sites by grafted polymer. For this reason, the film thickness is comparatively low. With the "grafting from" method, much higher polymer surface densities are possible. In these so-called surface-initiated polymerizations, initiator sites are generated at the surface, often from a self-assembled monolayer (SAM). The most common methods for SAM-based initiation use controlled-radical polymerization initiators, such as ATRP[3,7−9] or nitroxide-based[10,11] systems, or radical photoinitiators.[12−14]

Grafting on SAM-modified silica particles during radical polymerizations was observed by Tsubokawa et al.[15] Vinyl monomers were polymerized in the presence of the functionalized silica particles. Chain transfer of polymeric radicals to the surface allowed subsequent coupling with polymeric radicals in the bulk or the reinitiation of the polymerization from the surface. The grafted film quality, in terms of film thickness and graft density, was not reported.

Here, we discuss a novel method for rapidly forming oligomeric or polymeric films of relatively high density and uniformity through a previously unexplored technique for surface-induced polymerizations. Specifically, this paper explores the use of thiol−ene polymer systems for the creation of polymer grafts on functionalized silicon and glass surfaces. Thiol−ene polymers form by a radical-based, step-growth mechanism in which multifunctional thiol and ene (usually vinyl or allyl ether) monomers are coupled.[16−18] In these studies, a stoichiometric mixture of a dithiol and a divinyl ether (ene) are polymerized using a photoinitiator to form linear polymer. The polymerization propagates by the addition of a thiyl radical to a vinyl functional group (step 1). The carbon radical then abstracts a hydrogen from a thiol functional group, regenerating a thiyl radical (step 2).

step 1: propagation

$$\mathrm{RS^{\bullet} + R'CH{=}CH_2 \xrightarrow{k_{p,SC}} R'C^{\bullet}H{-}CH_2SR}$$

step 2: chain transfer

$$\mathrm{R'C^{\bullet}H{-}CH_2SR + RSH \xrightarrow{k_{CT}} R'CH_2{-}CH_2SR + RS^{\bullet}}$$

The alternating process of propagation and chain transfer, the basis of the step-growth thiol−ene polymerization, makes the

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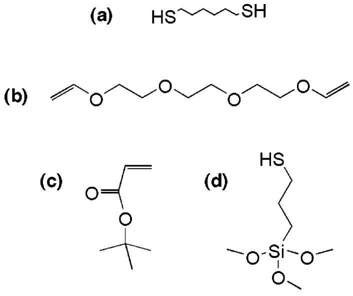

Figure 1. Chemical structures of monomer species (a) 1,6-hexanedithiol (HDT), (b) triethylene glycol divinyl ether (DVE-3), (c) *tert*-butyl acrylate, and SAM-forming species (d) 3-mercaptopropyltrimethoxysilane.

creation of a thiol−ene polymer graft a straightforward process. In general, the "enes" selected for these reactions tend to homopolymerize (i.e., the typical chain growth mechanism) only to a very limited extent.[19]

To form a graft, the thiol−ene polymerization is simply carried out over a silicon surface that has been functionalized with a commercially available, thiol-terminated SAM. The thiol groups on the surface readily participate in the thiol−ene reaction, serving as surface initiators once a hydrogen is abstracted from a surface bound thiol. Thus, for the case of a diene reacting with a dithiol, a linear polymer forms on the surface as the bulk polymerization proceeds, without the need for a special initiating SAM. Because of the step-growth nature of the thiol−ene polymerization, the grafting process cannot solely be considered a "grafting to" or "grafting from" process. Oligomer or polymer chains forming in the bulk readily react with surface-bound thiol or ene groups in the same way as monomeric species. At very high conversions, where the molecular weight of the bulk polymer increases rapidly in this step-growth system, the grafting process becomes more like a "grafting to" system. However, this system is less restricted because reactive functional groups remain accessible at the polymer surface, not just the original SAM surface, as in classical "grafting to" systems.

In this study, the viability of using a thiol−ene polymerization to form grafted films is explored. A variety of techniques are used to verify the presence of the thiol−ene grafts. In particular, the thickness of the grafted films as a function of conversion is tracked. Preliminary experiments demonstrate that acrylic monomers with small amounts of thiol (as chain transfer agent) present in the bulk also form thin polymer films.

Experimental Section

Materials. The thiol−ene monomer system used was a stoichiometric mixture of 1,6-hexanedithiol (HDT) and triethylene glycol divinyl ether (DVE-3). Acrylic grafts were formed from *tert*-butyl acrylate (tBa). HDT and tBa were purchased from Aldrich (Milwaukee, WI). The tBa was purified by running through a column of dried K_2CO_3 and aluminum oxide. DVE-3 was provided as a sample (Rapi-Cure DVE-3) from ISP Technologies, Inc. (Wayne, NJ). The UV photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (DMPA), was purchased from Ciba-Geigy (Hawthorn, NY).

Thiol-functionalized SAMs were formed from 3-mercaptotrimethoxysilane purchased from Aldrich. Amino-terminated SAMs were formed from (3-aminopropyl)triethoxysilane from Gelest, Inc. (Morrisville, PA). Chemical structures of monomer and SAM species are shown in Figure 1.

ACS reagent-grade toluene, acetone, methylene chloride, and *N*-methylpyrrolidinone (NMP), used for sample cleaning, were purchased from Aldrich. All chemicals, except tBa, were used without further purification.

Polished, double-sided silicon wafers (Umicore Semiconductor Processing, Boston, MA) were used as substrates for all but the micropatterning experiments, for which float glass was used. Wafers were in the (100) orientation and 200 μm thick. Prior to SAM deposition, the substrates were "piranha"-cleaned in a mixture of hydrogen peroxide and sulfuric acid (1:3 by volume) for 30 min, rinsed in DI water, and then blown dry with a N_2 stream.

SAM Deposition. A vapor-based method was used for SAM deposition on most samples.[20] Clean pieces of Si were placed in a Teflon bottle with an open vial containing ~0.5 mL of 3-mercaptopropyltrimethoxysilane. The bottle was purged with argon, sealed, and then placed in a 90 °C oven for 3 h. After removal, the SAM-coated Si (SH-Si) pieces were rinsed in toluene and acetone and then blown dry with a nitrogen stream.

For the solution-based method, used for the micropatterned sample detailed below, samples are immersed into a toluene solution of 1.5 wt % tri(m)ethoxysilane and 0.5 wt % *n*-butylamine at room temperature.[21,22] The *n*-butylamine was omitted for (3-aminopropyl)-triethoxysilane due to the presence of the primary amine functionality. After 45 min, the slides were removed from the solution and immediately rinsed with toluene and acetone. The SAMs were cured under vacuum at room temperature for 48 h.

SAM Micropatterning. Photoresist micropatterns were formed according to processing conditions supplied by MicroChem Corp. for use with the S1805 positive photoresist and MF series developer. Spin-coated photoresist films were exposed to 365 nm UV light (Blak-Ray B 100 AP; UVP, Inc., San Gabriel, CA) though a chromium-on-quartz mask. Following photoresist development, the samples were etched in an H_2/SF_6 plasma using a Surface Technology Systems MESC Multiplex ICP (Newport, UK). The conditions used were sufficient to etch a short distance (0.5−1 nm) into the glass substrate, thus completely removing the underlying SAM and exposing bare SiO_2. Immediately following etching, the photoresist was removed by sonicating for 10 min in NMP and then scrubbing for 1 min under NMP with a cotton-tipped applicator; both steps were repeated twice. The stripped sample was finally rinsed and sonicated in toluene before being transferred to a fresh SAM deposition solution for backfilling a second SAM into the etched pattern.

Photopolymer Graft Formation. For experiments in which the polymerization conversion was controlled, the thiol−ene monomer mixture was a 1:1 stoichiometric ratio of HDT and DVE-3, with 0.1 wt % DMPA. Other experiments varied the stoichiometric ratio and were conducted to achieve 100% conversion of the limiting reagent. Before polymer graft formation, the thiol-terminated SAM (SH-Si) is treated with a solution of dithiothreitol (DTT) which reduces disulfide bonds to thiols. Following Jönsson et al., 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 with nitrogen.[23] The polymerization was carried out immediately following DTT treatment.

For some experiments, the polymerization conversion was monitored in real time by in situ infrared (IR) spectroscopy. By using thin, double-polished silicon wafers, it is possible to collect a transmission IR spectrum directly through the sample. A small drop of monomer plus initiator solution was sandwiched between the DTT-reduced SH-Si and a polished NaCl salt crystal. A custom-built horizontal sample mounting accessory was used with the IR spectrometer (FTIR Magna 750, Series II, Nicolet Instrument, Madison, WI), allowing consistent, simplified data collection of liquid samples.[24] The photopolymerization was initiated by an Acticure UV light source (EXFO, Mississauga, Ontario) providing a light intensity between 5 and 10 mW/cm^2 with a 320−550 nm filter. All reported conversions are for the "ene" groups (from the DVE-3). The peak area across the region from 1740 to 1555 cm^{-1} was monitored at a resolution of 8 cm^{-1}. After the UV exposure was initiated, the peak area drops until the maximum conversion is reached or the light is extinguished.

If a precise conversion measurement was unnecessary for a particular sample, the SH-Si was immersed in a vial containing the monomer plus initiator solution. The photopolymerization was

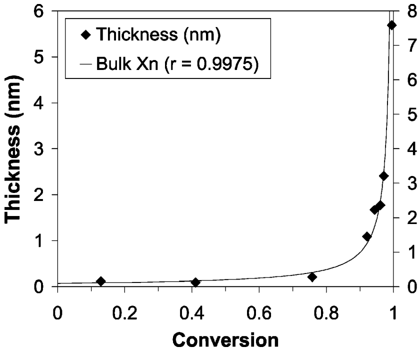

Figure 2. Grafted thiol−ene polymer film thickness vs bulk polymer conversion for a stoichiometric mixture of HDT and DVE-3. The solid line plots the calculated chain length, X_n, for the step-growth polymerization.

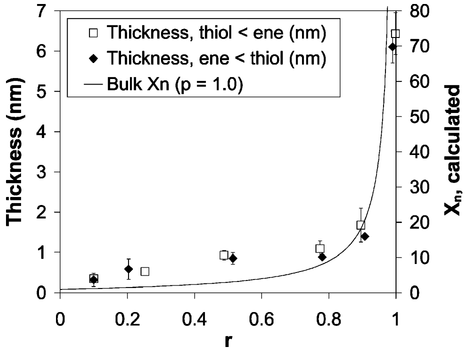

Figure 3. Grafted thiol−ene polymer film thickness vs monomer ratio for fully reacted ($p = 1.0$) mixtures of HDT and DVE-3. The solid line plots the calculated chain length, X_n, for the step-growth polymerization.

initiated with an EFOS Novacure UV light source (EFOS USA, Williamsville, NY) with a 320−550 nm filter. Conversion estimates were made by collecting IR spectra (between salt crystals) for the mixture before and after polymerization. However, thickness variations make such calculations relatively inaccurate.

Following polymerization, a relatively thick coating of the bulk thiol−ene polymer remains on the sample surface. To remove bulk polymer that is not covalently bound to the surface, the samples were rinsed for a minimum of 48 h in a Soxhlet extraction apparatus running with methylene chloride.

Polymer Film Analysis. An ellipsometer (Multiskop, Optrel GBR, Berlin) was used to perform all film thickness measurements. The background measurement of the oxide layer on the silicon and the bare SAM were made using samples from the same batch of Si or SH−Si as used for the polymer brushes. Five measurements in separate spots on each sample were averaged for the thickness calculations.

Topographic images of the sample surfaces were collected using a PicoPlus scanning probe microscope (SPM) (Molecular Imaging, Inc., Phoenix, AZ) operating in contact mode.

Results and Discussion

The thickness of a grafted polymer film is a function of two variables: the molecular weight and the surface density of the polymer. In this study, the molecular weight of the surface-attached polymer was not measured. However, for a step-growth polymerization, the chain length of the bulk polymer as a function of conversion is well-known.[25] In particular

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

where r is the ratio of ene to thiol functional groups and p is the conversion. Several groups have demonstrated that the thiol−ene polymerization does proceed in a stepwise manner with respect to molecular weight evolution and gel point conversion.[26,27] Because the conversion of the bulk polymerization was measured using IR spectroscopy, the chain length of the bulk polymer is calculated from the above equation.

Several grafted polymer films of varying thickness were formed by polymerizing samples to different conversions, as monitored by in situ IR. The thickness of the films (measured by ellipsometry) is plotted as a function of conversion in Figure 2. The graph of eq 1 is also shown on the plot ($r = 0.9975$). The observed trend in thickness growth matches the calculated growth of the chain length with conversion with dramatic increases in film thickness and expected molecular weight occurring only at high conversions beyond 90−95%.

Following eq 1, the ratio of thiol to ene functional groups, r, is also an effective means for controlling the chain length and, thus, the thickness of the grafted films. This technique has the added advantage of being a self-limiting process that does not require monitoring of the conversion. Rather, the desired film thickness is simply achieved at compete conversion of the limiting functional group. The film thickness is plotted as a function of the stoichiometric ratio in Figure 3 where each sample was polymerized to 100% conversion ($p = 1.0$).

In general, the thickness of the grafted thiol−ene films is less than that typically seen in ATRP brush systems. Because of the step-growth nature of the thiol−ene system, the molecular weight develops more slowly and uniformly. Likewise, the thiol−ene grafts are expected to develop uniformly, even at low conversions. Although an ATRP system will form very thin brushes with the addition of increased amounts of initiator, the polydispersity of the system is also increased.[28] The "controlled" growth of the ATRP system depends on the continuous activation and deactivation of the propagating end group of the growing polymer chain. During the growth of shorter chains, fewer activation−deactivation steps have occurred, reducing the number of opportunities for controlled growth and increasing the polydispersity of the grafts. Thus, in the limit of very thin films composed of only a few repeat units, it is expected that the ATRP system will not be as uniform as the thiol−ene system. An empirical comparison of the uniformity/roughness of very thin thiol−ene and ATRP films is left for future study.

If the chain length of the surface-attached polymer, $X_{n,s}$, is assumed equal to the chain length of the bulk polymer, X_n, the surface density (i.e., coverage) of polymer grafts can be estimated from the equation

$$\sigma = \frac{h \rho N_a}{M X_{n,s}} \tag{2}$$

where r is the polymer density (1.08 g/cm^3), N_a is Avogadro's number (6.022×10^{23}), and M is the average molecular weight of each repeat unit (176.3 g/mol). The polymer density was estimated from the monomer densities ($\rho_{HDT} = 0.983$ g/cm^3, $\rho_{DVE-3} = 0.99$ g/cm^3)[29] and an assumed volume shrinkage of 15 cm^3/mol.[17,30,31] The average σ for all points in Figure 2 is 0.26 ± 0.09 chains/nm^2. Interestingly, this value is intermediate to the surface densities seen in "grafting to" and "grafting from" systems. In the grafting of poly(2-vinylpyridine-*b*-styrene) block copolymers to silicon and mica surfaces, significantly lower surface densities in the range of 0.005−0.03 chains/nm^2 have been reported.[4−6] In contrast, surface densities are higher for ATRP polymerizations from organosilane and thiol-on-gold SAMs, yielding between 0.25 and 1.3 chains/nm^2.[7−9,32] Thus, the thiol−ene polymer grafting density is in the low range of those commonly seen with ATRP. The surface density of a high-quality organosilane SAM is 6.0 molecules/nm^2, assuming a hexagonal lattice.[33] Hence, even in the highest density ATRP systems, fewer than 1 in 5 SAM molecules participate in the polymerization. In the thiol−ene system, assuming the molecular weight of the surface-attached polymer is equal to that of the bulk polymer, only 5% of the available SAM molecules are attached to a polymer chain.

While the initial seven points from Figure 2 give an average σ of 0.28 ± 0.08 chains/nm^2, the final point at 99.5% conversion drops off considerably to 0.13 chains/nm^2. A decrease in graft density with increasing conversion is not realistically occurring in this system. The error has two possible explanations, both of which relate to the accuracy with which the molecular weight of the grafted polymer chains can be determined. The first explanation is that a small error in the conversion measured by in situ IR would cause a significant deviation in the calculated chain length at high conversions. For example, at 99.5% conversion, X_n (the bulk chain length) is 160, which yields a σ of 0.13 chains/nm^2. However, using a value of 99.0%, X_n is reduced to 89 and σ increases to 0.24 chains/nm^2, which is within the error of the other points. This sensitivity to small conversion changes occurs only at the very high degrees of conversion attained in the last sample.

Although deviations in the measured conversion could easily account for variations in the calculated coverage, a mechanistic explanation is also possible. A breakdown in the assumption that the molecular weight of the surface-attached polymer is equal to that of the bulk polymer may occur at high conversion. If it is assumed that the final point at 99.5% conversion has a surface density equal to that of the average of the previous seven points (0.30 chains/nm^2), $X_{n,s}$ (the surface chain length) is only 75, significantly lower than the bulk X_n of 160. As $X_{n,s}$ increases, steric blocking of active surface sites and end groups will increase, limiting the final molecular graft weight. Uniquely, the polymer molecular weight on the surface might also be limited by the formation of loops. A growing polymer chain attached to the surface could as easily react with a thiol on the surface as a thiol in the bulk, effectively terminating the growth of the chain. If loop formation predominates in this system, very high surface densities could be attained, while maintaining very low molecular weights.

From the existing data, it is impossible to distinguish between the case of high surface molecular weight and low coverage and vice versa. A direct measurement of the surface molecular weight by a chromatographic method, following detachment of the chains from the surface, would be required to obtain an accurate calculation of the surface density.

Parts a and b of Figure 4 show SPM images of a sample before and after polymerization (∼100% conversion, 1:1 thiol:ene), respectively. Large globules visible in both images are siloxane polymer from a flawed SAM deposition. A few of the globules are marked with arrows in Figure 4a. In general, the SPM results do not indicate a significant topographic change following polymerization, although the postpolymerization features appear more fine-grained. To establish further that polymer was present on the surface, the polymer-coated sample shown in Figure 4b was immersed in toluene and rubbed in one direction with a cotton-tipped applicator. After drying, the sample was imaged by SPM. Figure 4c clearly shows the grooves created by rubbing, indicating that there is polymer on the surface. Bare SAMs do not show any surface morphology changes following rubbing, as in Figure 4a, in which the sample was rubbed unidirectionally before imaging. As such, the morphology change with rubbing may be an indication that the polymer on the surface is of at least intermediate molecular weight and low surface density. In the opposite case of high coverage and low molecular weight, the short chains on the surface, resembling a SAM, would not undergo an observable transformation.

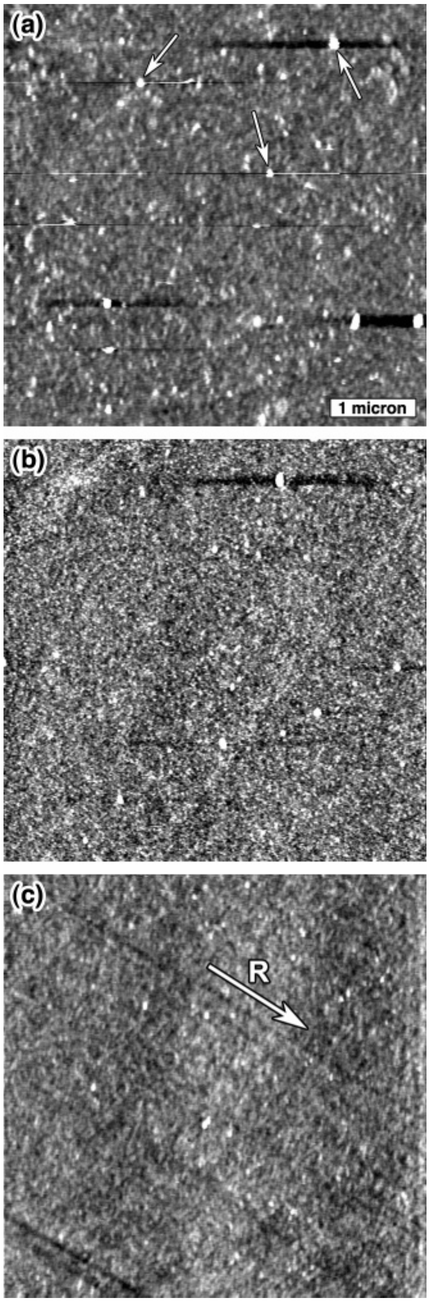

Figure 4. SPM topographic images. (a) SH-Si SAM before polymerization. Arrows indicate examples of siloxane globules. (b) Grafted thiol−ene polymer film. (c) Grafted thiol−ene polymer film after rubbing in toluene. Arrow “R” indicates the rubbing direction.

An amino-terminated SAM on glass was micropatterned with 5 μm wide lines of a thiol-terminated SAM. Specifically, following the procedure explained in the Experimental Section, a microlithographic technique was used to remove 5 μm wide lines of the amino-terminated SAM from the glass surface by plasma etching. The exposed lines of bare glass were subsequently backfilled with 3-mercaptopropyltrimethoxysilane, yielding lines of a thiol-terminated SAM separated by an amino-terminated SAM. The etching process left the top of the thiol-terminated SAM ∼1 nm below the amino-terminated surface,

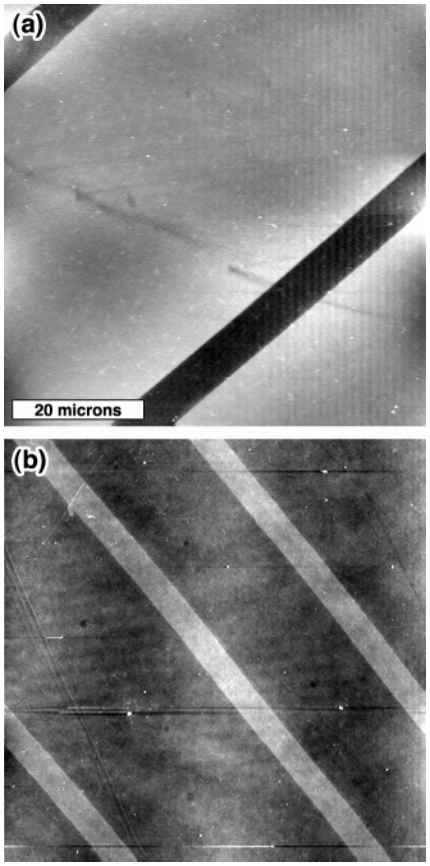

Figure 5. SPM topographic images. (a) Micropatterned amino-terminated SAM on glass with 5 μm wide thiol-terminated SAM lines. The thiol lines (black) are 1 nm below the amino surface (gray). (b) Same micropatterned sample following thiol−ene polymer graft formation. The grafted regions (white) are raised ∼1.5 nm above the amino surface (gray).

Table 1. Thickness of Thiol−Ene Films Grafted during and after Photopolymerization

	thickness (nm)	
approx conversion	A (during)	B (after)
0	0	0
0.45	1.0	2.2
0.96	2.7	1.8
1.00	3.5	1.2

as visualized in Figure 5a. The thiol−ene polymerization was carried out on this sample. Figure 5b shows the pattern following rinsing. Because of the growth of thiol−ene grafts from the thiol-terminated SAM, the lines are raised ∼1.5 nm above the amino surface. The experiment verifies that the thiol−ene grafts will only grow from the thiol surface and not from the amino surface. Beyond its experimental utility, the micropatterning of grafted thiol−ene polymer films provides a useful method for controlling surface properties in 2-D. Following thiol−ene graft formation, the remaining amino groups are available for further functionalization by a variety of organic coupling reactions. For instance, if an ATRP initiator were attached to the amino surface, a patterned surface composed of both thiol−ene and vinyl polymer grafts could be created.

Table 2. Film Thickness and Chain Length of Poly(*tert*-butyl acrylate) Grafts Formed with HDT as Chain Transfer Agent

[HDT] (wt %)	thickness (nm)	calcd chain length	normalized thickness	normalized chain length
1.0	1.8	89	1.0	1.0
1.9	0.85	45	0.47	0.51
3.8	0.51	23	0.28	0.26

A second set of thickness vs conversion data for thiol−ene grafts on SH−Si is shown in Table 1. The grafts were formed from a stoichiometric mixture of HDT and DVE-3 with 0.1 wt % DMPA photopolymerized at 23 °C using a Novacure UV light source at ∼8 mW/cm^2. These samples were not prepared using in situ IR, so the conversions measured are only approximate values. At each conversion, a thickness is shown for both an A and B sample. The A samples were in contact with the solution from the beginning to the end of polymerization. The B samples were immersed in the viscous polymer after the UV light was extinguished and then allowed to react for several minutes. Indeed, a polymer film is also formed with the B samples. Residual radical activity in the polymer mixture enables the reaction of polymeric vinyl ether molecules with the SAM surface.

Interestingly, for the B (postpolymerization) samples, the film thickness decreases with increasing conversion. In this case, adsorbed polymer chains would sterically block surface functionality. At higher conversions, the presence of longer chains would make this effect more pronounced. Additionally, the reduced ene concentration at higher conversions decreases the reaction rate. Finally, at higher conversions, and, thus, higher molecular weights and viscosities, the mobility of reactive end groups is lower, making diffusion to the surface occur more slowly. Solvent addition to this almost purely “grafting to” system would enhance mobility and potentially increase film thickness.

The thiol−ene grafts studied in this paper are all initiated by the formation of a thiyl radical on the SAM. However, other types of radical polymerizations, namely acrylic, are also readily initiated by that radical. In this study, a set of samples were made using *tert*-butyl acrylate as the monomer, with HDT added as a chain transfer agent. The acrylic monomer polymerizes by a radical chain growth mechanism, which would predominantly result in a “grafting from” growth mechanism. The bulk chain length, X_n, of polymer formed in this system is calculated as

$$X_n = f + \frac{k_{p,CC}}{k_{p,CT}}\frac{[C{=}C]}{[SH]} = 2 + 1.5\frac{[C{=}C]}{[SH]} \qquad (3)$$

where f is the thiol functionality, $k_{p,CC}$ and $k_{p,CT}$ are the propagation constants of the monomer and the chain transfer agent, respectively, [C═C] is the concentration of double bonds, and [SH] is the concentration of thiol groups (i.e., chain transfer agent). On the basis of real-time Fourier transform infrared spectroscopy of thiol−acylate polymerizations, Cramer and Bowman developed kinetic expressions to determine that the acrylate propagation constant is 1.5 times larger than the rate constant for hydrogen abstraction from the thiol.[34] Thus, the molecular weight of the polymer is easily controlled by the ratio of monomer to chain transfer agent. Three acrylic graft samples were prepared using three concentrations of HDT (1%, 2%, and 4%), with 0.5 wt % DMPA. The samples were photopolymerized at 23 °C using a Novacure UV light source with an intensity of ∼60 mW/cm^2 for 60 s. As shown in Table 2, the thickness of the grafted acrylic films decreases with increasing concentrations of chain transfer agent. In fact, the normalized thickness decreases by the same fraction that the normalized chain length drops with added thiol. As with the step-growth system, the film thickness is directly proportional to the chain length of the polymer.

Conclusions

The thiol−ene polymerization technique detailed in this study is a simple and straightforward method for forming surface-grafted polymer films on glass and silicon surfaces. Although the grafted thiol−ene polymer films are thin, the thickness directly correlates with the molecular weight of the polymer formed in the bulk. Thus, the thickness is tunable by controlling the polymerization conversion or the ratio of thiol to ene functional groups in the monomer mixture. The low thickness of the films suggests that the surface density and/or molecular weight of the surface-attached polymers are lower than could be expected.

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References and Notes

(1) de Gennes, P. G. *Macromolecules* **1980**, *14*, 1069−1075.
(2) Alexander, S. *J. Phys. (Paris)* **1977**, *38*, 983−987.
(3) Edmondson, S.; Osborne, V. L.; Huck, W. T. S. *Chem. Soc. Rev.* **2004**, *33*, 14−22.
(4) Belder, G. F.; ten Brinke, G.; Hadziioannou, G. *Langmuir* **1997**, *13*, 4102−4105.
(5) Webber, R. M.; Anderson, J. L. *Langmuir* **1994**, *10*, 3156−3160.
(6) Parsonage, E.; Tirrell, M.; Watanabe, H.; Nuzzo, R. G. *Macromolecules* **1991**, *24*, 1987−1995.
(7) Matyjaszewski, K.; Miller, P. J.; Shukla, N.; Immaraporn, B.; Gelman, A.; Luokala, B. B.; Siclovan, T. M.; Kickelbick, G.; Vallant, T.; Hoffman, H.; Pakula, T. *Macromolecules* **1999**, *32*, 8716−8724.
(8) Husseman, M.; Malmstrom, E. E.; McNamara, M.; Mate, M.; Mecerreyes, D.; Benoit, D. G.; Hedrick, J. L.; Mansky, P.; Huang, E.; Russell, T. P.; Hawker, C. J. *Macromolecules* **1999**, *32*, 1424−1431.
(9) Shah, R. R.; Merreceyes, D.; Husemann, M.; Rees, I.; Abbott, N. L.; Hawker, C. J.; Hedrick, J. L. *Macromolecules* **2000**, *33*, 597−605.
(10) Mansky, P.; Liu, Y.; Huang, E.; Russell, T. P.; Hawker, C. *Science* **1997**, *275*, 1458−1460.
(11) Husemann, M.; Morrison, M.; Benoit, D.; Frommer, J.; Mate, C. M.; Hinsberg, W. D.; Hedrick, J. L.; Hawker, C. J. *J. Am. Chem. Soc.* **2000**, *122*, 1844−1845.
(12) Prucker, O.; Naumann, C. A.; Ruhe, J.; Knoll, W.; Frank, C. W. *J. Am. Chem. Soc.* **1999**, *121*, 8766−8770.
(13) Prucker, O.; Ruhe, J. *Langmuir* **1998**, *14*, 6893−6898.
(14) Prucker, O.; Schimmel, M.; Tovar, G.; Knoll, W.; Ruhe, J. *Adv. Mater.* **1998**, *10*, 1073−1077.
(15) Tsubokawa, N.; Kimoto, T.; Koyama, K. *Colloid Polym. Sci.* **1993**, *271*, 940−946.
(16) Kharasch, M. S.; Read, J.; Mayo, F. R. *Chem. Ind. (London)* **1938**, *57*, 752.
(17) Jacobine, A. F. In *Radiation Curing in Polymer Science and Technology III, Polymerisation Mechanisms*; Rabek, J. F., Ed.; Elsevier Applied Science: London, 1993; p 219.
(18) Woods, J. G. In *Radiation Curable Adhesives in Radiation Curing: Science and Technology*; Pappas, S. P., Ed.; Plenum: New York, 1992; pp 333−398.
(19) Cramer, N. B.; Reddy, S. K.; O'Brien, A. K.; Bowman, C. N. *Macromolecules* **2003**, *36*, 7964−7969.
(20) Sugimura, H.; Hozumi, A.; Kameyama, T.; Takai, O. *Surf. Interface Anal.* **2002**, *34*, 550−554.
(21) Mooney, J. F.; Hunt, A. J.; McIntosh, J. R.; Liberko, C. A.; Walba, D. M.; Rogers, C. T. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 12287−12291.
(22) Walba, D. M.; Liberko, C. A.; Korblova, E.; Farrow, M.; Furtak, T. E.; Chow, B. C.; Schwartz, D. K.; Freeman, A. S.; Douglas, K.; Williams, S. D.; Klittnick, A. F.; Clark, N. A. *Liq. Cryst.* **2004**, *31*, 481−489.
(23) Jönsson, U.; Malmqvist, M.; Rönnberg, I. *Biochem. J.* **1985**, *227*, 363−371.
(24) Lovell, L. G.; Berchtold, K. A.; Elliott, J. E.; Lu, H.; Bowman, C. N. *Polym. Adv. Technol.* **2001**, *12*, 335−345.
(25) Odian, G. *Principles of Polymerization*, 3rd ed.; John Wiley & Sons: New York, 1991.
(26) Morgon, C. R.; Magnotta, F.; Ketley, A. D. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 627−645.
(27) Cramer, N. B.; Davies, T.; O'Brien, A. K.; Bowman, C. N. *Macromolecules* **2003**, *36*, 4631−4636.
(28) Patten, T. E.; Matyjaszewski, K. *Adv. Mater.* **1998**, *10*, 901−915.
(29) *Aldrich Catalog Handbook*; Aldrich Chemical Co.: Milwaukee, WI, 2005−2006.
(30) Jacobine, A. F.; Glaser, D. M.; Nakos, S. T. In *Radiation Curing of Polymeric Materials*; Kinstle, J. F., Ed.; American Chemical Society: Washington, DC, 1990; pp 161−175.
(31) Lu, H.; Carioscia, J. A.; Stansbury, J. W.; Bowman, C. N. *Dent. Mater.*, in press.
(32) Jones, D. M.; Brown, A. A.; Huck, W. T. S. *Langmuir* **2002**, *18*, 1265−1269.
(33) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533−1554.
(34) Cramer, N. B.; Bowman, C. N. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 3311−3319.

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