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Stimuli-Responsive Surfaces Utilizing Cleavable Polymer Brush Layers

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ABSTRACT: A new set of materials has been developed that allow for the preparation of coatings with stimuli-responsive surfaces relying on acid-sensitive polymer brush layers. A functionalized methacrylate monomer, 5-(2-bromo-2-methylpropanoyloxy)-2,5-dimethylhexan-2-yl methacrylate, was synthesized and added to a photopolymerizable solution consisting of ethoxylated bisphenol A dimethacrylate, *N*-vinylpyrrolidone, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol trimethacrylate, and 2,2-dimethoxy-2-phenylacetophenone. Thin films of this solution were spin-coated onto silicon wafers and cured. These substrates were placed into a reactor under atom transfer radical polymerization conditions which accomplished the growth of a polystyrene polymer brush layer from the photopolymer surface. Because of the acid-sensitive nature of the brush tether group, the brush layers could be selectively cleaved from the surface by treatment with a *p*-toluenesulfonic acid/dioxane solution. All surfaces were fully characterized before and after modification. The cleaved polymer from the brush layer was collected and characterized using gel permeation chromatography (GPC) and nuclear magnetic resonance (NMR).

Introduction

The term polymer brush refers to an assembly of polymer chains tethered at one end to a surface or interface.[1] When initiating sites on the surface are close to each other, the resulting polymer chains grown from these surfaces are forced into close proximity. To avoid each other, they must stretch away from the surface they are attached, yielding a dense polymer brush layer. Consequently, the thickness of the brush layer is larger than the radius of gyration of the grafted molecule so chain overlapping can be avoided. The study of polymer brushes synthesized by surface-initiated polymerization (SIP) reactions continues to be an active research area due to the fascinating nature of these materials.[2−7] Polymer brushes have potential applications in a large number of areas including, but not limited to, control of stimuli-responsive surfaces,[8] tunable biological interfaces,[9] release and adhesive surfaces,[10,11] generation of hydrophobic/hydrophilic surfaces,[12] and lithographic patterning.[13] We are interested in brush layers where the polymer chains are covalently attached to the underlying surface by "grafting from" techniques where polymer chains are grown from the surface of the substrate.[14−16] These dense brush layers can consist of a wide variety of homopolymer and copolymers and have been made via controlled polymerization methods such as atom transfer radical polymerization (ATRP),[17−21] reversible addition−fragmentation chain-transfer polymerization (RAFT),[22−24] and nitroxide-mediated polymerization (NMP).[25,26]

In order to grow polymer brush layers, thin films consisting of a mixture of acrylate/methacrylate monomers containing a cross-linking agent were photochemically attached to modified silicon wafer surfaces. Embedding reactive functionality into the photopolymer film by addition of inimers (*ini*tiator/mono*mer*) facilitates polymer brush growth in subsequent polymerization reactions (Figure 1).[27]

This process is a simple and powerful method of growing brushes of controlled thickness, and a wide variety of monomers have been successfully polymerized into brush layers. A careful examination of each of the steps has been performed, from substrate preparation to photopolymer attachment and polymer brush growth.[28] Patterning the inimer-embedded layer prior to brush growth via imprint lithographic techniques and then growing brushes from these nanopatterned features allowed for effectively changing the size, shape, and chemistry of these nanostructures.[27] To date, work in this area has concentrated on brush layers that are permanently attached to the photopolymer matrix, while we desire a methodology for the controlled detachment of these brush layers to allow us to understand surface changes introduced by the brush layer and their removal.

Harsh methods exist to cleave polymer brushes from silicon or glass surfaces including dipping them to HF solution. Unfortunately, this not only strips the brushes but also has the potential to damage and change the substrate surface.[29] In other words, these treatments are not targeting the polymer brush layer themselves, but the underlying substrate. With our new methodology, polymer brushes can be grown from the desired substrate, and when the polymerization is complete, the brushes can be cleaved from the surface at their attachment site and, in principle, the degrafted surface can be functionalized again and later the surface can initiate further polymer brush growth, if desired. A targetable linkage that is sensitive to mild conditions is required to cleave the polymer brushes. Previous work has shown that tertiary ester linkages derived from 2,5-dimethylhexane-2,5-diol can be hydrolyzed under mild acidic conditions.[30] Acid-cleavable esters such as *tert*-butoxycarbonyl (*t*-BOC) esters and their derivatives have found widespread application in organic synthesis as protecting groups for nucleophilic functional groups such as alcohols, phenols, amines, and thiols.[31] These esters are quantitatively cleaved in the presence of catalytic quantities of acids such as trifluoroacetic acid (TFA)[32] or *p*-toluenesulfonic acid.[33] To facilitate brush removal, a new acid-sensitive inimer based upon 2,5-dimethylhexane-2,5-diol has been designed and synthesized.

Herein, we report a new approach for the synthesis of stimuli-responsive polymer surfaces relying on acid-sensitive polymer brush layers. By synthesizing a new acid-sensitive, bifunctional

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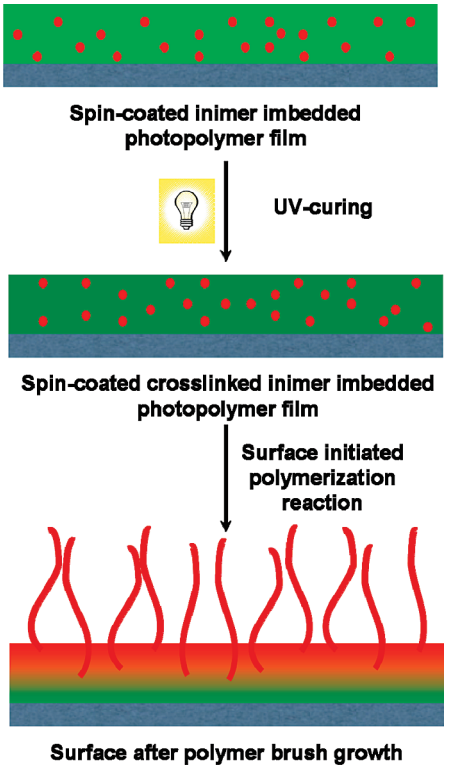


Figure 1. Surface-initiated polymerization (SIP) of polymer brushes from inimer-embedded polymer films.

inimer and incorporating it into a photopolymer film, we have created a layer that can be modified by simple polymer brush reactions. These polymer brush layers can later be selectively cleaved by treatment with acids. This allows us not only to prepare these new stimuli responsive layers but also to easily collect and examine the cleaved polymer chains and use this data to better understand the polymer brush growth processes.

Experimental Section

Materials. Styrene and triethylamine (Aldrich) were dried over CaH_2 overnight, and distilled under reduced pressure before use. Ethoxylated bisphenol A dimethacrylate (Sartomer), *N*-vinylpyrrolidone (Aldrich), and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol trimethacrylate (TMPA) (Aldrich) were used as received. 2,2-Dimethoxy-2-phenylacetophenone (DMPA) was recrystallized from ethanol prior to use. Electronic grade propylene glycol methyl ether acetate (PGMEA) (Aldrich) was used to make solutions for the thin film photopolymer resins. All other chemicals were used as received and all reactions were run under dry N_2 unless otherwise noted. The polished 3 in. silicon wafers were purchased from University Wafers (Boston, MA).

Characterization. The thickness of the polymer layers was determined with a Dektak^3 profilometry instrument (Veeco Instruments). Measurements were obtained at two different locations on each wafer with three measurements per spot. The molecular weights of the free and cleaved brushes were analyzed with gel permeation chromotography (GPC) on a Waters chromotograph (four Water Stryragel HR columns HR1, HR2, HR4, and HR5E in series) connected to a Waters 410 differential refractometer with THF as the eluent. Molecular weight standards were narrow polydispersity polystyrenes. NMR spectra (in DMSO-d_6 or $CDCl_3$) were recorded on a Bruker DPX300 spectrometer operating at 300 MHz (^{1}H) and 75.5 MHz (^{13}C) with chemical shifts reported in ppm downfield from tetramethylsilane.

Synthesis of 5-Hydroxy-2,5-dimethylhexan-2-yl 2-Bromo-2-methylpropanoate (1). 2,5-Dimethylhexane-2,5-diol (70 mmol, 10.2 g), 2-bromoisobutyryl bromide (104.1 mmol, 23.9 g), and triethylamine (104.1 mmol, 10.5 g) in 60 mL of THF were charged to a 150 mL three-neck flask and placed into an ice bath, and the reaction mixture was stirred overnight at room temperature. The mixture was filtered to remove salts and washed twice with water after THF was removed. Purification was accomplished by flash chromatography with CH_2Cl_2:ethyl acetate (9:1) as the eluent. 5-Hydroxy-2,5-dimethylhexan-2-yl 2-bromo-2-methylpropanoat (**1**) was obtained in 50% yield as light brown liquid (52 mmol, 15.3 g). ^{1}H NMR (400 MHz, $CDCl_3$): 3.65 (bs, 1H, OH), 2.02 (s, 6H, CH_3), 1.49 (m, 2H, CH_2), 1.43 (m, 6H, CH_3), 1.40 (m, 2H, CH_2), and 1.24 (s, 6H, CH_3).

Synthesis of 5-(2-Bromo-2-methylpropanoyloxy)-2,5-dimethylhexan-2-yl Methacrylate (2). Methacryloyl chloride (26.8 mmol, 2.8 g) was added to a 100 mL three-neck flask and placed into an ice bath with a mixture of **1** (20.4 mmol, 6.0 g) and triethylamine (27.7 mmol, 2.8 g) in 40 mL of THF, and the mixture was stirred overnight at room temperature. After filtration to remove the white salt, the THF was removed, and the product was washed with water three times, and the product was purified by flash chromatography with CH_2Cl_2:hexane to give the product of **2**, which is a colorless liquid. The yield was 53% (10.9 mmol, 3.8 g). ^{1}H NMR (400 MHz, $CDCl_3$): 6.03 (s, 1H, CH), 5.55 (s, 2H, CH) 2.21 (s, 3H, CH_3), 2.02 (s, 6H, CH_3), 1.89 (m, 4H, CH_2CH_2), and 1.43 (m, 12H, CH_3).

Preparation of 5-(2-Bromo-2-methylpropanoyloxy)-2,5-dimethylhexan-2-yl Methacrylate (2) Embedded Photopolymer Film. Polished 3 in. silicon wafers were used as a substrate for the functional photopolymer film layer. The wafers were washed with acetone and dried under a stream of N_2 and then cleaned by exposure to an oxygen plasma for 8 min. An adhesion promoter, 3-(trimethoxysilyl)propyl methacrylate, was then applied and spin-coated at 3000 rpm for 10 s, and the wafer was baked at 130 °C for 2 min. A PGMEA solution consisting of a ethoxylated bisphenol A dimethacrylate (52 wt %), 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (16%), 2,2-dimethoxy-2-phenylacetophenone (1%), 1-vinyl-2-pyrrolidone (16%), and inimer **2** (15%) was spun-cast for 15 s at 3000 rpm on the substrate. After applying the photopolymer solution, the substrate was exposed to UV light (365 nm) for 10 min, curing the photopolymer mixture into a hard, robust network thin film.

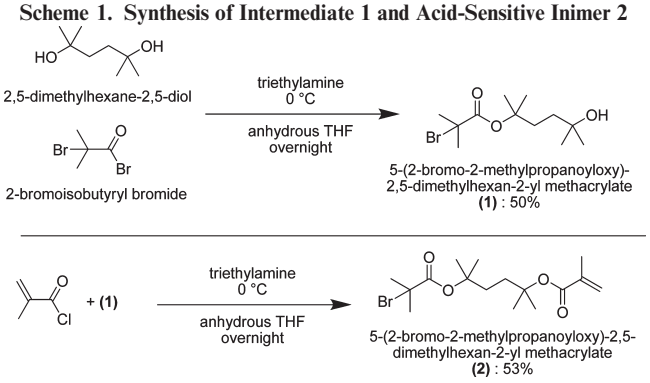
Polystyrene Brushes by Surface-Initiated Polymerization of Styrene. A 50 mL reaction vessel containing a photopolymer-coated wafer was charged with styrene (28.8 mmol, 6 g), ethyl 2-bromoisobutyrate (0.29 mmol, 0.056 g), CuBr (0.43 mmol, 0.06 g), PMDETA (0.43 mmol, 0.075 g), (ratio 200:1:1.5:1.5) and 7 mL of anisole (50% v/v). The reaction mixture was carefully degassed by three freeze−pump−thaw cycles to remove dissolved oxygen. Polymerization was carried out at 100 °C for 12 h. The reaction was terminated by precipitation of the reaction mixture into a 30 mL methanol solution. The polymer precipitated from solution was washed, filtered, and dried. The substrate was removed from the reactor and washed extensively by Soxhlet extraction using THF as a solvent for 24 h to remove any adsorbed polymer from the photopolymer surface. A series of reactions were performed with varying concentrations of styrene in order to determine the effect on the molecular weight of the polymer (ratios of 300:1:1.5:1.5 and 400:1:1.5:1.5, respectively).

Cleavage and Removal of Polystyrene Brushes. The brush-modified silicon wafers were immersed in a solution of *p*-toluenesulfonic acid (0.09 mol, 15 mg) in dioxane (2 mL) with stirring for 12 h under nitrogen flow. After treatment, the wafer was removed and the dioxane solution was poured into 30 mL of methanol, resulting in the precipitation of the cleaved polymer brushes. This cleaved polymer was filtered, washed with water and methanol, and dried.

Results and Discussion

Synthesis of Inimer. 2,5-Dimethylhexane-2,5-diol was sequentially esterified with two acid chlorides, 2-bromoisobutyryl bromide and methacryloyl chloride, in order to prepare the acid cleavable inimer **1**. Initially, synthesis was attempted by first reacting the diol with methacryloyl chloride at 0 °C. However, methacryloyl chloride is very reactive, and as a result it quickly esterified both −OH groups, regardless of the stoichiometry. This lead to a mixture of the difunctional adduct and unreacted alcohol and little (< 10%) of the desired monosubstituted product. Attempts were made to improve the yield by changing the reaction conditions with no appreciable improvement in the yield. However, if instead of reacting with methacyloyl chloride first, the diol was first reacted with 2-bromoisobutyryl bromide, good yields of the monosubstituted alcohol (**1**) were obtained. Accordingly, 2,5-dimethylhexane-2,5-diol and 2-bromoisobutyryl bromide were allowed to stir overnight and then purified by flash chromatography giving the desired intermediate product (**1**) in 50% yield. Next, methacryloyl chloride was added to a solution of **1** and allowed to react overnight, and the product was purified by flash chromatography to give **2** in 53% yield. Scheme 1 shows the overall route used for the synthesis of **1** and **2**. ^{1}H NMR analysis of **2** was performed with peaks and integration, which confirmed the structure of the desired product. The singlets at 1.43 and 1.89 ppm were assigned to H_a and H_b, respectively. The signals for H_b were overlapped with the signal of H_d, but the difference between these peaks was easily distinguished. The protons on the double bond give two different peaks where the hydrogen on trans position (H_f) gave a signal at 6.03 ppm where the other two assigned to H_e gave another singlet at 5.55 ppm.

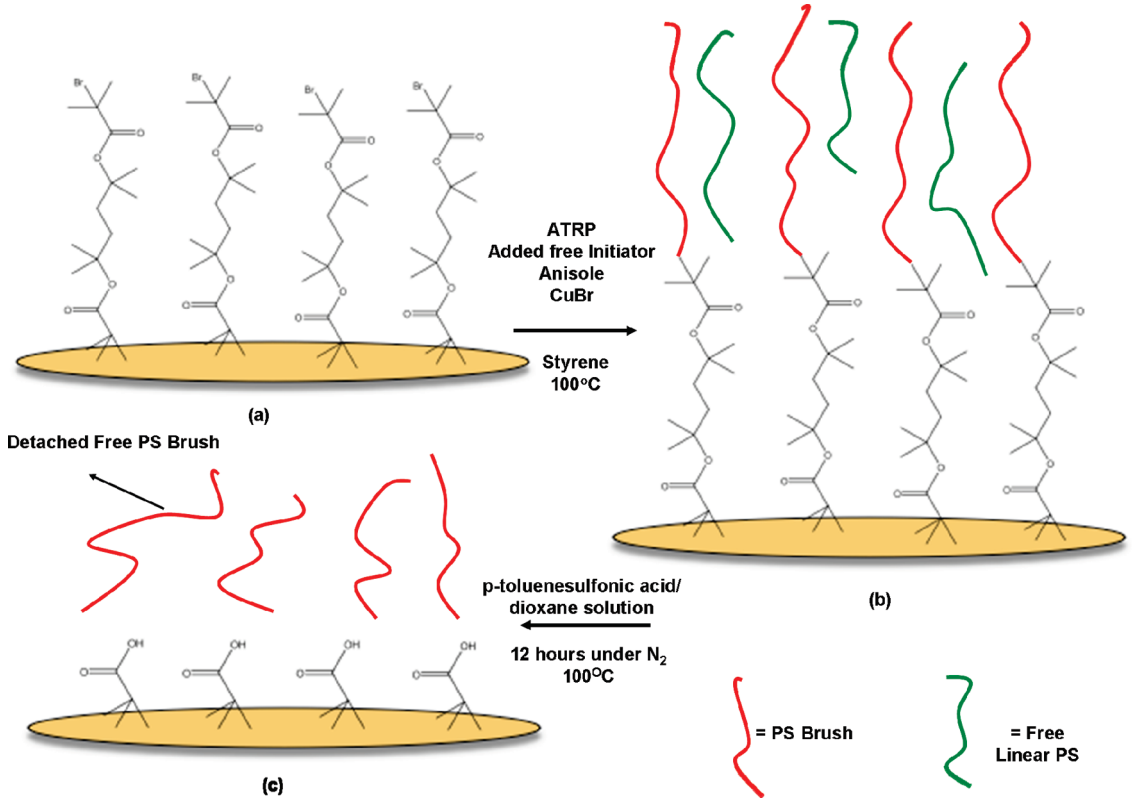
Scheme 1. Synthesis of Intermediate 1 and Acid-Sensitive Inimer 2



The high-resolution mass spectrum of **2** gave the expected parent peak at 364 *m*/*z* (see Supporting Information). It was expected that the easily ionizable tertiary ester group may be lost during the desorption/ionization step, and indeed a strong peak observed at 197 *m*/*z* was assigned to the cleaved-inimer fragment.

Synthesis of Polymer Brush Layers. A cleaned silicon wafer was treated with an adhesion promoter, 3-(trimethoxysilyl)-propyl methacrylate, and baked at 130 °C in order to prepare it for treatment with the functional photopolymer solution. In order to promote the surface-directed growth of polymer brushes from the photopolymer network, an initating site must be present within the resin. This was accomplished by incorporating the inimer **2** into the photopolymer. After coating the wafer with the inimer-containing photopolymer solution, the wafer was irradiated with 365 nm light to affect the cross-linking of the resin. After this curing, the wafer was washed with isopropyl alcohol in order to remove any residue and unreacted monomer from the surface. The wafer was placed in a polymerization reactor, and a mixture of ethyl 2-bromoisobutyrate, CuBr, PMDETA, and styrene was added. After three freeze−thaw−pump cycles the reactor was placed into an oil bath at 100 °C for 12 h. Ethyl

Scheme 2. Preparation of Cleavable Polymer Brushes and Removal



2-bromoisobutyrate served as a "free" initiator since it has been reported that the addition of free initiator is desirable as the molecular weight of the surface-initiated polymer brushes has often been assumed to be similar to that of the free solution polymer grown in the same reaction.[27] Later we discuss how this is not necessarily the case as the new cleavable brushes allowed for a direct comparison of the molecular weight and PDI of the solution polymer and cleaved brush polymer. After precipitating the reaction mixture into methanol, the free solution polymer was collected and isolated, and its molecular weight was determined by GPC. The wafer, now coated with polymer brushes, was extracted extensively with THF and washed with water.

The modified surfaces were characterized by a number of techniques including contact angle measurement and ellipsometry. The ellipsometry data showed that there is a thickness change on the surface after brush growth. The change was closely related to photopolymer solution composition (how many initiating sites present on the surface) and the inimer:monomer ratio. Table 1 shows the thickness before and after brush growth. As the inimer:monomer ratio increases, the thickness of the brush layer increases as well since there are more monomers available for each initiating sites.

Water contact angle measurements were used to monitor the changes to the surface of the thin films and the uniformity of functionalization. Profiles of the water contact angle measurements are shown in Figure 2. Before brush growth the photopolymer film (Figure 2a) was slightly hydrophilic (~82°), and after growing PS brushes (Figure 2b) the surface was rendered more hydrophobic (~97°). The uniformity of these measurements over large areas indicated good, consistent brush growth over the surface of the wafer. These values are in agreement with previously reported PS brush surfaces.[27,28]

Cleavage of Polymer Brushes. In order to remove the PS brush layers, the brush-modified wafers were put into a *p*-toluenesulfonic acid/dioxane solution for 12 h under nitrogen flow. *p*-Toluenesulfonic acid was chosen to cleave polymer brushes since it will attack the tertiary ester group of the tethering site but will not aggressively attack the silicon surface. The color of the acid solution changed from colorless to light brown as the cleaving reaction proceeded. The treated wafer was removed from the solution and washed with THF. The dioxane solution containing the cleaved PS chains was poured into methanol to precipitate the polymer. This cleaved polymer was saved for later analysis. After removal of the brushes, the substrate surface was washed, dried, and characterized by water contact angle measurement and ellipsometry. A change in film thickness and water contact angle due to the new chemical composition of the film was observed. Table 1 contains the thickness data of the films observed at the different steps: (1) the imimner-embedded photopolymer film, (2) polymer brush attached to photopolymer layer, and (3) after cleaving the brushes from the surface. The thickness due to the growth of the brush layer was 30−68 nm depending upon brush growth conditions. After brush cleavage, the films returned to the original thickness of the photopolymer film. Water contact angle of the surfaces after brush cleavage (Figure 2c) dropped to ~73°, which is more hydrophilic than both the photopolymer film and PS brush. This is due to the carboxylic acid groups which are present on the surface after hydrolysis of the tertiary ester groups. The *p*-toluenesulfonic acid attacks the tethering site (tertiary ester) and does not remove the underlying photopolymer layer. In principle, it should be possible to take advantage of this mild cleaving reactions and use the residual carboxylic acid groups to chemically modify the surface if desired.

The cleaved polymer brushes were characterized by GPC and NMR. The NMR spectrum of the cleaved polystyrene brushes displayed the characteristic broad peaks of the polystyrene (see Supporting Information). The data obtained from GPC was used to directly compare the molecular weight of the solution polymer and the polymer grafted from the surface. At lower molecular weights (samples with monomer:initiator ratio of 200:1; Table 2, polymer samples A), the molecular weight and the PDI of the polymer brushes were very similar to the relative free polymer (solution polymerization). As the monomer-to-initiator ratio was increased with the expected result of increasing MW, an increasing deviation between the solution polymer and brush

Table 1. Thickness Data of the Surfaces before Brush Growth, after Brush Growth, and after Brush Cleavage[a]

	photopolymer layer (nm)	after brush growth (nm)	after brush cleavage (nm)
sample A	130	160	135
sample B	140	199	144
sample C	135	203	138

[a] Sample A: styrene (28.8 mmol, 6 g), ethyl 2-bromoisobutyrate (0.29 mmol, 0.056 g), CuBr (0.43 mmol, 0.06 g), PMDETA (0.43 mmol, 0.075 g) (ratio 200:1:1.5:1.5) in anisole (50% v/v), 100 °C for 12 h (for samples B and C, ratios of 300:1:1.5:1.5 and 400:1:1.5:1.5, respectively).

Table 2. GPC Data of the Solution Polymer and the Corresponding Cleaved Polymer Brushes[a]

	M_n	M_w	PDI	conversion (%)
solution polymer A	11 400	12 000	1.04	55
cleaved polymer A	11 000	11 300	1.03	53
solution polymer B	21 500	23 600	1.1	69
cleaved polymer B	29 100	37 000	1.27	93
solution polymer C	26 600	34 200	1.28	64
cleaved polymer C	37 300	47 100	1.26	90

[a] Sample A: styrene (28.8 mmol, 6 g), ethyl 2-bromoisobutyrate (0.29 mmol, 0.056 g), CuBr (0.43 mmol, 0.06 g), PMDETA (0.43 mmol, 0.075 g) (ratio 200:1:1.5:1.5) in anisole (50% v/v), 100 °C for 12 h (for samples B and C, ratios of 300:1:1.5:1.5 and 400:1:1.5:1.5, respectively).

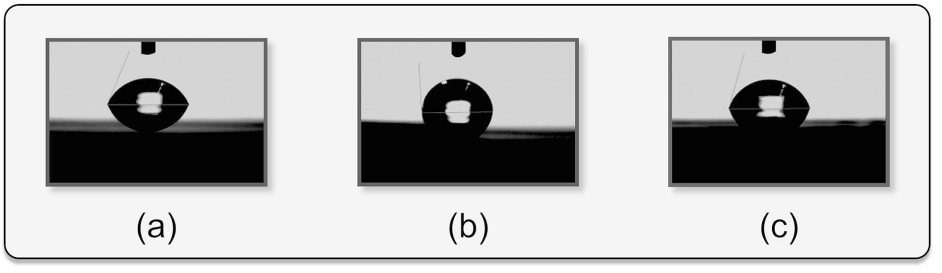


Figure 2. Water contact angle analysis of the various surfaces: (a) photopolymer surface before PS brush growth, 82° water contact angle; (b) PS brush surface, 97° water contact angle; and (c) polymer surface after brush cleavage, 73° water contact angle.

Table 3. Calculated Grafting Density and Distance between Grafting Points

	grafting density (chain/nm^2)	distance (nm)
cleaved polymer A	1.4	0.95
cleaved polymer B	0.94	1.16
cleaved polymer C	0.83	1.24

polymer molecular weight was observed. In sample B, the M_n of the solution polymer (21 500 g/mol) was 7600 g/mol less than the corresponding cleaved polymer brush (29 100 g/mol). The PDI of the cleaved polymer was also greater—1.27 compared to 1.1. This effect became more apparent as molecular weight was increased with sample C solution polymer 26 600 g/mol compared to the cleaved polymer at 37 300 g/mol with the cleaved polymer being 40% larger than the solution polymer. This is an interesting observation since it is widely reported that the molecular weight of the polymer brushes grown from the surface are the same or almost the same as the molecular weight of the solution polymer prepared with free initiator.[34,35] Clearly, there is not a linear relationship between the molecular weight of the solution polymer and cleaved polymer in this system.

In an effort to better understand this behavior, we calculated the surface coverage, graft densities, and distance between brush chains for these systems. The surface coverage, Γ (mg/m^2), was calculated from thickness of the layer h (nm) by the following equation:

$$\Gamma = h\rho \quad (1)$$

where ρ (1.05 g/cm^3) is the density of polystyrene.

The grafting density, Σ (chain/nm^2), was determined by the formula below where N_A is Avogadro's number and M_n (g/mol) is the number-average molecular weight of the grafted polymer.

$$\Sigma = \Gamma N_A \times 10^{-21}/M_n = (6.023\Gamma \times 100)/M_n \quad (2)$$

Finally, the distance between grafting sites, D, (nm) was calculated using the following equation:

$$D = (4/\pi\Sigma)^{1/2} \quad (3)$$

Table 3 contains the calculated grafting density data (chains/nm^2) and distance between grafting sites (nm) for several samples. As the molecular weight of the brushes increases, the observed grafting density decreases. Additionally, the distance between brushes increases with increasing molecular weight. These results can be explained by taking into account the 3-D nature of the brush growth. In this study, the brush growth starts not from a planar monolayer of initiating sites but from the sites both at the surface and at some depth inside the inimer-embedded photopolymer layer. Increasing brush molecular weight makes it more difficult for monomers to diffuse through brushes into the photopolymer layer, which eventually leads to an observed decrease in the grafting density. This effect can also be seen in the changes in the distance between brushes as well as at higher molecular weight the brushes have longer distances between each other.

Conclusion

We have demonstrated a new and facile approach to preparing cleavable polymer brushes by surface-initiated atom transfer radical polymerization (ATRP). A new inimer containing an acid-labile group was synthesized and incorporated into a thin photopolymer film, allowing for the subsequent growth of polymer brushes. Styrene was used as the monomer for polymer brush growth, and a free initiator was added to the polymerization solution in order to grow free polymer chains concurrent with surface brush growth. The grafted layers could be easily removed by treatment with acid solutions, and the cleaved PS chains were collected and analyzed. This allowed for the comparison of the molecular weight of the free polymer to polymer brushes later cleaved from the photopolymer film. It was determined that the molecular weight of the polymer brushes is higher than the free polymer. As the molecular weight of the polymers increases, the difference between solution polymer molecular weight and the cleaved polymer brush weight becomes more dramatic. This suggests that it cannot be universally assumed that the kinetics of surface brush growth and solution polymerization are the same when using a free initiator during the reaction. In fact, due to the difficulty that past studies have had in carefully analyzing the exact molecular weight of tethered polymer brush layers, little has been explored in this area. Most surface brush studies have not performed any analysis of their brush molecular weight in favor of the more convenient assumption of parity to solution polymer molecular weight. Albeit our brush system is slightly different from those grown directly from monolayer initiating sites, a careful reexamination of surface polymer brush molecular weight for all systems may be warranted.

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Supporting Information Available: Figures containing the mass spectrum of inimer **2** and the ^{1}H NMR of **2** and the cleaved polymer. This material is available free of charge via the Internet at http://pubs.acs.org.

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