

Facile Synthesis of Thick Films of Poly(methyl methacrylate), Poly(styrene), and Poly(vinyl pyridine) from Au Surfaces

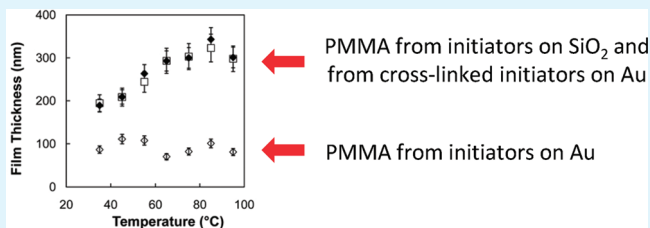
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S Supporting Information

ABSTRACT: Atom transfer radical polymerization (ATRP) is commonly used to grow polymer brushes from Au surfaces, but the resulting film thicknesses are usually significantly less than with ATRP from SiO₂ substrates. On Au, growth of poly(methyl methacrylate) (PMMA) blocks from poly(*tert*-butyl acrylate) brushes occurs more rapidly than growth of PMMA from initiator monolayers, suggesting that the disparity between growth rates from Au and SiO₂ stems from the Au surface. Radical quenching by electron transfer from Au is probably not the termination mechanism because polymerization from thin, cross-linked initiators gives film thicknesses that are essentially the same as the thicknesses of films grown from SiO₂ under the same polymerization conditions. However, this result is consistent with termination through desorption of thiols from noncross-linked films, and reaction of these thiols with growing polymer chains. The enhanced stability of cross-linked initiators allows ATRP at temperatures up to ~100 °C and enables the growth of thick films of PMMA (350 nm), polystyrene (120 nm) and poly(vinyl pyridine) (200 nm) from Au surfaces in 1 h. At temperatures >100 °C, the polymer brush layers delaminate as large area films.

KEYWORDS: polymer brush, ATRP, surface-initiated polymerization



INTRODUCTION

Self-assembled monolayers (SAMs) on Au serve as a prototype surface because they provide closely packed, well-ordered, and reasonably stable films. Au substrates are ideal since they are chemically homogeneous, virtually free of contamination, easy to clean, and compatible with a wide variety of analytical techniques for thin film characterization. Elaboration of SAMs with polymers can occur when the self-assembling thiols contain initiating groups at their termini. Although surface-initiated radical polymerization takes place on a broad range of substrates, most studies have focused on Au and silica.^{1–9}

Nevertheless, the Au–S bond that links initiator-containing SAMs to the surface is labile above 60 °C,^{10–15} so atom transfer radical polymerization (ATRP) and other polymerizations from Au typically occur at <60 °C. However, at such low temperatures important monomers such as styrene and 4-vinyl pyridine have low radical propagation rates, which limit their growth. Moreover, even at temperatures <60 °C, polymerization is slower from SAMs on Au than from monolayers on SiO₂-coated substrates.¹⁶ Several factors may lead to different polymerization rates from monolayers on Au and silica. For example, the number and density of sites available for immobilizing initiators on Au and SiO₂ surfaces are different. Studies of silica surfaces provide a limiting area/chain of 0.6 nm²,¹⁷ with typical values of ~0.65 nm² or ~1.54 chains/nm². This is roughly 40% of the density for a SAM on Au, and the higher initiator density on Au surfaces may lead to greater termination of growing chains. Additionally, gold is a transition metal capable of quenching radicals,^{18–20} which could

reduce the number of growing chains to give reduced growth rates and thin films.

Huang et al.¹² investigated polymerization of styrene from azo-initiators immobilized on flat Au substrates and concluded that the instability of alkanethiol monolayers limits free-radical polymerization. They suggested that solvent-phase free radicals accelerate thiol desorption from Au, and desorbed alkanethiols appear to be efficient chain-transfer reagents that terminate brush growth. A simple cross-linking procedure, however, can stabilize the SAM to enable thermal radical polymerization from Au. In other strategies to stabilize Au-supported polymers at elevated temperatures, Roux et al.²¹ coated gold electrodes with a carboxylic acid-functionalized polypyrrole to restrict thiol desorption, and Matyjaszewski et al.¹³ formed a cross-linked polymer shell to prevent dissociation of linear brushes from gold nanoparticles.

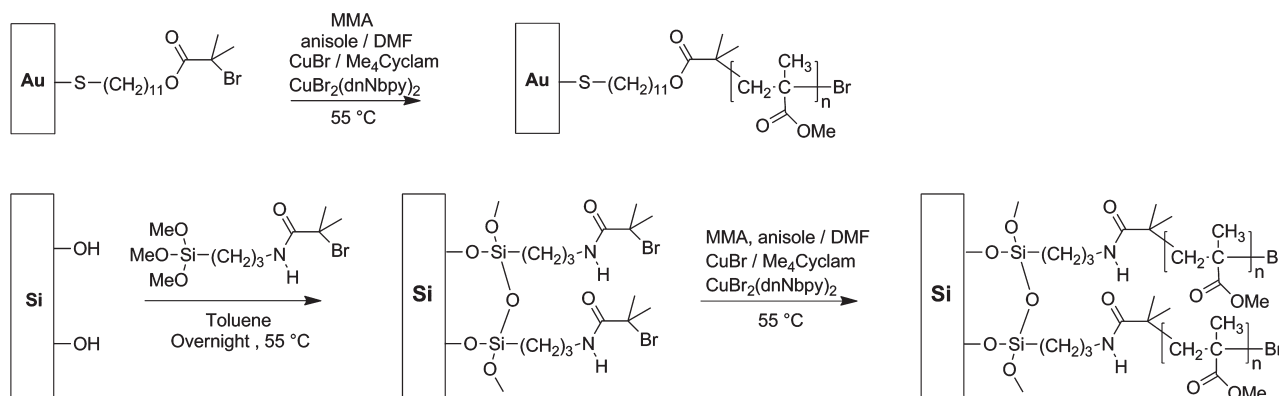
This report explores factors that may be responsible for retarding film growth rates in ATRP from gold: (1) differences in the initiator densities for gold and silica substrates, (2) radical quenching by the gold surface, and (3) termination resulting from desorption of thiols from SAMs on gold surfaces. We believe that the latter is most important, and that the use of cross-linked thiol initiators prevents thiol desorption from Au, and enables polymer growth rates comparable to those from SiO₂ substrates. In addition, cross-linked thiol initiators extend surface-initiated polymerizations from Au to temperatures >100 °C, well above

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Scheme 1. Surface-Initiated Polymerization of MMA from Silicon and Gold Surfaces



the normal 60 °C stability limit for SAMs on Au. The enhanced initiator stability enables the growth of thick films of poly(methyl methacrylate) (350 nm), polystyrene (120 nm), and poly(vinyl pyridine) (200 nm) from Au surfaces in 1 h.

EXPERIMENTAL SECTION

Materials. Unless otherwise noted, all chemicals were obtained from Aldrich and stored under nitrogen. 11-Mercapto-1-undecanol (MUD, 97%), 2-bromo-2-methylpropionyl bromide (97%), 3-mercaptopropyltrimethoxysilane (MPS), anisole (99.7%), *N,N*-dimethylformamide (DMF, 99.8%), Cu(I)Br (99.999%), Cu(II)Br₂ (99.999%), Me₄Cyclam (99%), and 4,4'-dinonyl-2,2'-bipyridine (dnNbpy, 97%) were used as received. (3-Aminopropyl)trimethoxysilane was distilled under vacuum prior to use. Triethylamine was distilled from calcium hydride under a nitrogen atmosphere, and stored under nitrogen. *tert*-Butyl acrylate (tBA, 98%), methyl methacrylate (MMA, 99%), and styrene (99%) were passed through a 10 cm long, 0.5 cm diameter column of activated basic alumina and then distilled from calcium hydride to remove inhibitors. The disulfide initiator, 11-[(2-bromo-2-methyl)propionyloxy]undecyl-disulfide,²² and the trimethoxysilane initiator, 2-bromo-2-methyl-*N*-(3-trimethoxysilylpropyl)propionamide, were synthesized using slightly modified versions of literature procedures.^{23,24} All silane compounds were used and stored under nitrogen. Toluene was distilled from sodium/potassium alloy under nitrogen, using benzophenone as an indicator. After purification, the monomers, liquid chemicals, and solvents were transferred to Schlenk flasks, degassed by three freeze–pump–thaw cycles, and then transferred into a drybox. Au-coated silicon wafers were prepared by electron-beam evaporation of 200 nm of Au on 20 nm of Cr on Si (100) wafers. Silicon (SiO₂ surface) and Au-coated wafers were cleaned in a UV/O₃ chamber for 30 min prior to use.

Characterization Methods. Ellipsometric measurements were obtained with a rotating analyzer spectroscopic ellipsometer (model M-44, J. A. Woollam) using WVASE32 software. The angle of incidence was 75° for all experiments, and a refractive index of 1.50 was used when calculating film thicknesses. Reflectance Fourier Transform Infrared (reflectance FTIR) spectra were obtained from a Nicolet Magna-560 FTIR spectrometer with a MCT detector and a PIKE grazing angle (80°) attachment. Typically, 128 scans were collected for each spectrum. Thermally induced morphology changes of films grown from Au substrates were observed using a Keyence Digital Microscope equipped with a video camera.

Preparation of Immobilized Initiators on Gold and Silicon Substrates. Gold-coated wafers, cleaned for 30 min in UV/O₃, were washed with water and ethanol, and then transferred into a glovebag

purged with N₂. The wafers were immersed in a 1 mM ethanolic solution of the disulfide initiator, (Br–C(CH₃)₂–COO(CH₂)₁₁S)₂, for 24 h to form a self-assembled initiator monolayer, and then the films were washed with ethanol and dried under a stream of N₂. Cross-linked initiator monolayers were formed in a N₂-purged glovebag, by immersing Au-coated substrates in a vial containing a 2 mM methanolic solution of MPS for 12 h at room temperature. After deposition, the substrates were rinsed three times with 2 mL of methanol and dried with a stream of nitrogen. The attached silane monolayer was then hydrolyzed at room temperature with 0.1 M HCl for 15 h to afford a cross-linked-hydroxylated surface. The modified Au substrates were treated with a 10 mM solution of the trimethoxysilane initiator, 2-bromo-2-methyl-*N*-(3-trimethoxysilylpropyl)propionamide, in toluene at 55 °C for 12 h. Following the deposition, the substrates were rinsed repeatedly with toluene and isopropanol, and then dried in a stream of nitrogen. The typical ellipsometric thickness of the cross-linked initiator layer on gold was 1.0–1.5 nm.

The trimethoxysilane initiator was immobilized on UV/O₃-cleaned silicon wafers by immersing substrates in a 10 mM solution of 2-bromo-2-methyl-*N*-(3-trimethoxysilylpropyl)propionamide in toluene at 55 °C under nitrogen. After 12 h, the wafers were rinsed repeatedly with toluene and isopropanol, sonicated in toluene for 1 min and dried in a stream of nitrogen. The ellipsometric thickness of the cross-linked initiator layer on silicon surfaces was 1.0–1.5 nm.

Surface-initiated Polymerization. In a N₂-purged drybox, CuBr (5.7 mg, 0.040 mmol), CuBr₂ (4.5 mg, 0.020 mmol), Me₄Cyclam (10.3 mg, 0.040 mmol) and dnNbpy (16.4 mg, 0.040 mmol) were added to a round-bottom flask containing 20 mL of a degassed solution of monomer in DMF/anisole (monomer/DMF/anisole) 2:1:1 v:v:v, [monomer] ~4.0 M. The mixture was heated with an oil bath to 50 °C and stirred until it formed a transparent light green solution. The solution was transferred into a vial containing an initiator-modified substrate, Au or SiO₂, to start the surface-initiated polymerization. After a predetermined reaction time at 50 °C, the substrate was removed from the vial, washed with ethyl acetate and THF sequentially, and then dried under a stream of N₂.

RESULTS AND DISCUSSION

Surface-Initiated Polymerization from Gold and SiO₂ Substrates. Bao et al. reported that “identical” polymerizations of MMA from initiators on Au and SiO₂ gave different polymer film thicknesses, and that PMMA films grown from SiO₂ are systematically thicker than those grown from Au substrates.¹⁶ To confirm this observation, we polymerized MMA and styrene under

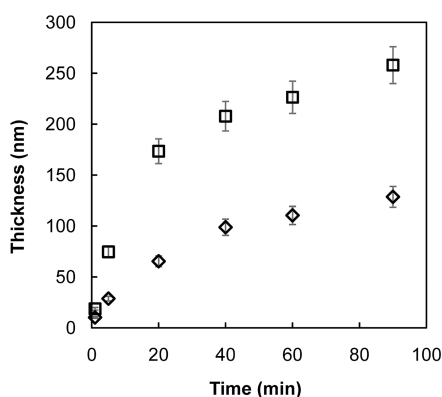


Figure 1. Evolution of the ellipsometric brush thickness with time for the polymerization of MMA from \diamond gold and \square SiO_2 surfaces at 50°C . The data points are the average of two independent trials, and the limits of the error bars are the measured film thicknesses from the two runs.

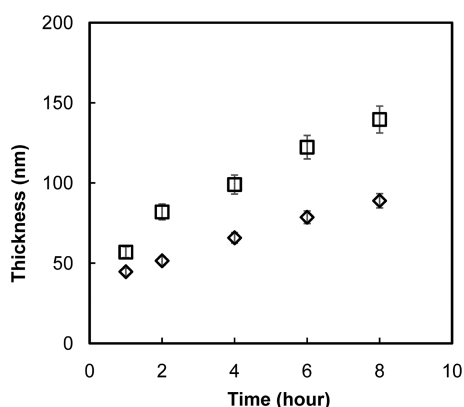
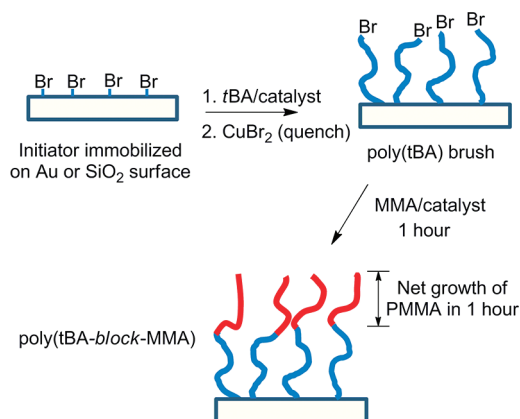


Figure 2. Evolution of the ellipsometric brush thickness with time for the polymerization of styrene from \diamond gold and \square SiO_2 surfaces at 50°C . The data points are the average of two independent trials, and the limits of the error bars are the measured film thicknesses from the two runs.

Scheme 2. Block Copolymer Formation on Au and SiO_2 Surfaces



identical conditions from initiators anchored on Au and SiO_2 surfaces (Scheme 1), and compared the evolution of the film thickness with time. As Figures 1 and 2 show, regardless of the

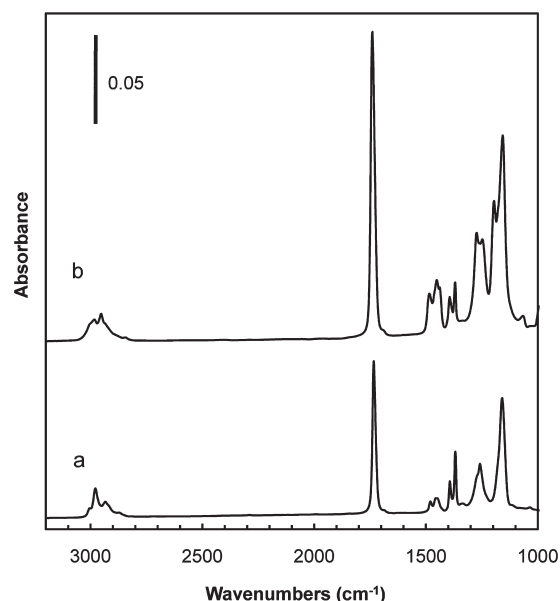


Figure 3. Reflectance FTIR spectra of (a) a 100 nm PtBA film grown from an initiator layer on a gold substrate and (b) a PtBA-block-PMMA copolymer brush, synthesized by growing 210 nm of PMMA from the 100 nm PtBA film.

monomer, ATRP from SiO_2 provides thicker films and higher apparent growth rates than polymerization from Au surfaces under similar conditions. However, the shapes of the film thickness vs time profiles are similar, suggesting that the primary difference between polymerization from gold and from silica is that there are fewer active chains when brushes grow from gold surfaces.

Block Copolymer Formation on Au and SiO_2 Substrates. If the difference between polymerization rates on Au and SiO_2 substrates occurs due to a reaction or interaction at the substrate–film interface, such an effect might diminish as the films grow thicker. We tested this notion by placing the initiator at increasing distances from the Au surface simply by using ATRP to grow polymers from the surface, and then quenching the growing chain by adding a large excess of Cu(II)Br_2 .²⁵ As Scheme 2 shows, the resulting Br-terminated chains can then initiate further polymerization. To that end, we grew poly(*tert*-butyl acrylate) (PtBA) brushes from initiators anchored to Au surfaces and quenched the growing chains at various times. After washing to remove excess monomer, we dried the substrate under a stream of N_2 , removed it from the drybox, and characterized the film by ellipsometry and FTIR spectroscopy. We then returned the substrates to the drybox and initiated polymerization of MMA for 1 h from the dormant PtBA chains. The same process on SiO_2 substrates served as a control.

Figure 3 shows FTIR spectra of a 97 nm PtBA film and the PtBA-block-PMMA copolymer that resulted from growing 210 nm of PMMA from the initial PtBA film. Upon addition of the PMMA block the intensity of the ester carbonyl increased 2-fold, and the relative intensity of the *t*-butyl doublet (1365 , 1375 cm^{-1}) decreased compared to the CH_2 and CH_3 deformation bands at ~ 1440 – 1460 cm^{-1} .

The ellipsometric data in Figure 4 show that PtBA brushes grew to ~ 200 nm thick films in 1 h from Au substrates and ~ 400 nm from SiO_2 . Remarkably, when thickness data from Au substrates are doubled and replotted (open squares), the data

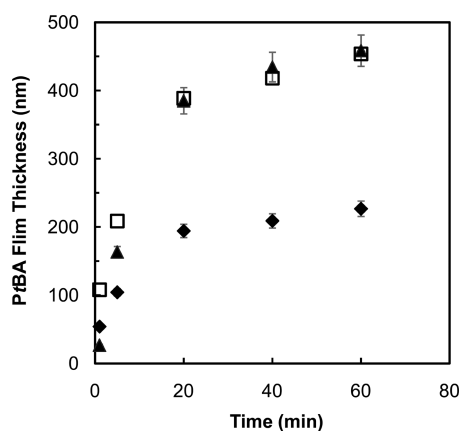


Figure 4. Formation of PtBA from SiO₂ and gold surfaces; \blacklozenge thickness of PtBA brushes grown from thiol initiators anchored on gold as a function of time; \blacktriangle thickness of PtBA brushes grown from initiators anchored on SiO₂ substrates as a function of time; \square $2 \times$ the thickness of PtBA brushes grown from thiol initiators anchored on gold.

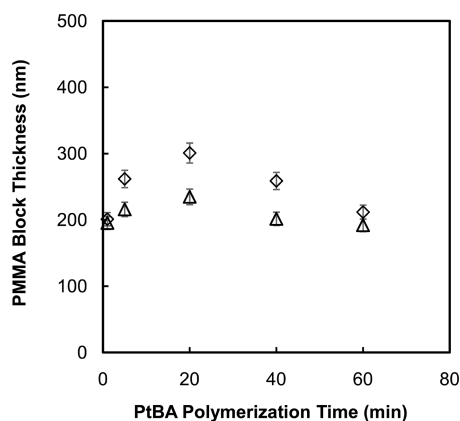


Figure 5. Formation of PtBA-block-PMMA films on Au and SiO₂ surfaces. \diamond Net growth of PMMA from PtBA (Au surface); \triangle Net growth of PMMA from PtBA (SiO₂ surface). The polymerization time for the PMMA block was 1 h for all samples.

from SiO₂ and Au substrates nearly coincide. From this analysis, we conclude that under comparable conditions, the number of chains growing from Au surfaces is half of those growing from SiO₂, but both have comparable termination rates. Figure 4 also argues that lower growth rates on Au surfaces stem from termination events in close proximity of the Au surface, presumably by radical quenching through electron transfer, or by the loss of growing chains via desorption of thiols from Au surfaces. Desorbed thiols may act as a chain transfer agent, and for polymer brush syntheses, chain transfer is equivalent to termination. Alternatively, polymers anchored through Au–S bonds may be mechanically unstable, especially for highly solvated polymers of high molecular weight.²⁶

MMA polymerizations were initiated from PtBA brushes that had been grown for 1 to 60 min (see Figure 5). The added PMMA layers are ~ 2 times thicker than PMMA films grown for 1 h directly from gold surfaces, but comparable in thickness to PMMA blocks grown directly from SiO₂ in 1 h (see Figure 1). The resulting ~ 200 – 300 nm PMMA layers were similar for both substrates, initially increasing in thickness, but decreasing in

thicknesses for longer PtBA polymerization times. This trend likely reflects fewer dormant PtBA chains available to form the PtBA-block-PMMA copolymer due to termination during the growth of PtBA brushes. These results suggest that a significant fraction of the growing chains are active after polymerization of the initial PtBA block, and confirm that being in close proximity to the Au surface reduces the rate of film growth from immobilized initiators.

Polymerization from a Cross-Linked Initiator. The previous data cannot distinguish whether radical quenching or thiol desorption cause decreased film growth on Au compared to SiO₂. However, preventing desorption of thiols from the Au surface would test the validity of the thiol desorption mechanism. To that end, we formed cross-linked ATRP initiators on gold by an method analogous to that of Huang et al.,¹² and compared polymerizations from these initiators with corresponding polymerizations from standard thiol initiators. Scheme 3 depicts the formation of the cross-linked initiator. During hydrolysis, the trimethoxysilane groups of the MPS monolayer condense to form a dense poly(siloxane) network, which provides lateral stabilization through interchain cross-linking and generates a hydroxylated surface for the subsequent attachment of the trimethoxysilane-ATRP initiator. The cross-linked and standard thiol initiator (Scheme 1, top left) layers have comparable ellipsometric thicknesses, and therefore, radical quenching by the gold surface should be similar for both layers.

FTIR spectroscopy and ellipsometry verify the attachment of the ATRP initiator to MPS. The reflectance FTIR spectrum of the MPS layer on Au (not shown here) shows vibrational bands characteristic of MPS (2938 cm^{-1} for overlapping CH₃ and CH₂ bands, 2846 cm^{-1} for CH₂ symmetric stretching, and 1114 cm^{-1} for Si–O–C stretching). After hydrolysis, the methyl peaks disappeared and the peak at 1114 cm^{-1} greatly decreased, indicating nearly complete hydrolysis of the trimethoxysilanes. The 1.0 nm ellipsometric thickness of the hydrolyzed MPS and the IR spectra agree well with literature data.^{12,27–29} After subsequent reaction with the trimethoxysilane initiator, the film thickness increased to 2.2 nm and amide peaks (1652 and 1548 cm^{-1}) appear in the reflectance FTIR spectrum, confirming successful attachment of the ATRP-initiator.

Figures 6 and 7 show the evolution of ellipsometric film thickness with polymerization time for the surface-initiated polymerization of MMA and styrene from gold surfaces (both standard and cross-linked initiators) and SiO₂. For both MMA and styrene, the film growth rates from cross-linked initiators on Au were essentially identical to those of films grown from silane initiators on SiO₂ and 2–3 times the growth rate from noncross-linked thiol initiators on Au surfaces. Additionally, increases in the characteristic IR peaks of the respective polymers are consistent with the ellipsometry data (see the Supporting Information, Figures S1 and S2). Therefore, stabilizing the initiator layer via cross-linking efficiently restricts thiol desorption, and there is no evidence for radical quenching by gold.

To explore the thermal stability of the cross-linked thiol initiator, we polymerized MMA at temperatures ranging from 35 to $115\text{ }^{\circ}\text{C}$ using standard initiators on Au and SiO₂ surfaces. The data (Figure 8), which show that thinner films form on Au substrates at all temperatures, suggest that thiol desorption is important even at low temperatures. Increases in polymerization rates at higher temperatures may offset the accompanying increases in thiol desorption and chain transfer to give a film thickness that is relatively independent of polymerization

Scheme 3. Formation of Cross-Linked Initiators on Gold Surfaces

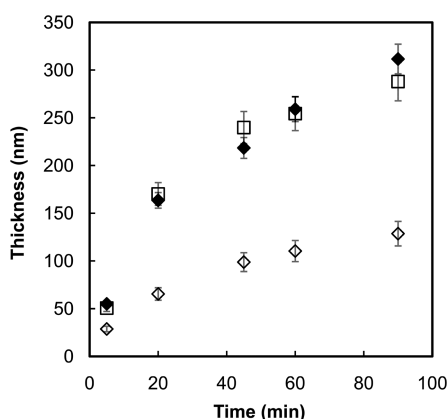
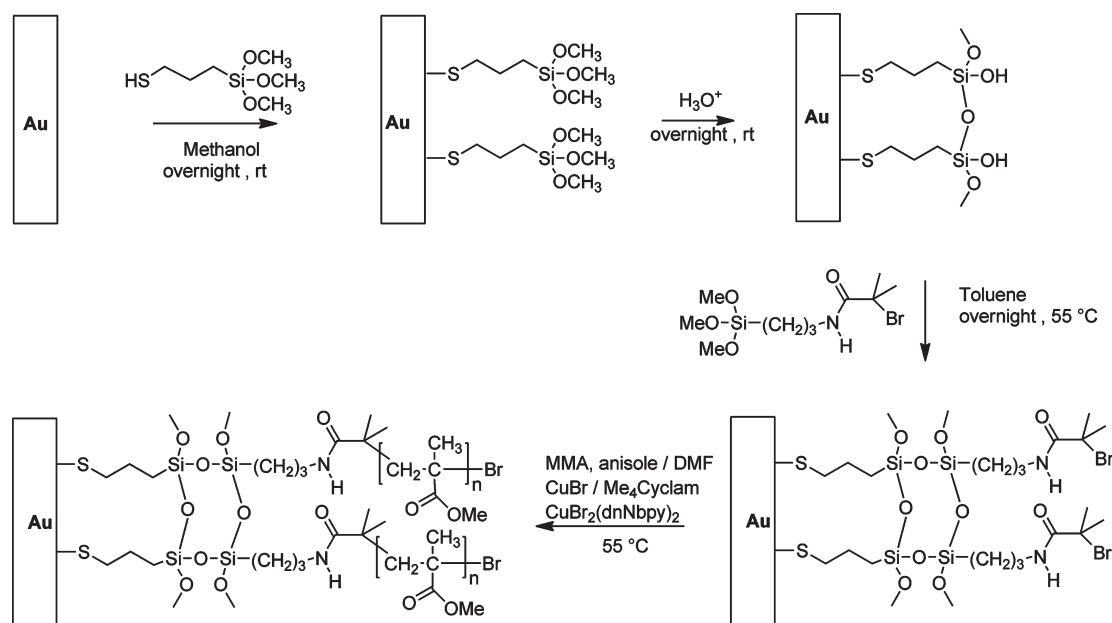


Figure 6. Surface-initiated polymerization of MMA from gold and SiO₂ surfaces. \diamond PMMA grown from a standard (noncross-linked) initiator on gold; \blacklozenge PMMA grown from a cross-linked thiol initiator; \blacksquare PMMA grown from a silane initiator layer on SiO₂. The points are the average of data from three independent runs, and the limits of the error bars are the measured film thicknesses from the three runs.

temperature. In contrast, polymerizations using the cross-linked initiator were identical to polymerization on SiO₂. Furthermore, the use of the cross-linked initiator enabled the polymerization of MMA from Au surfaces at temperatures up to ~ 100 °C, providing 300 nm films in 1 h.

Polymerization of styrene gives similar results, except the thickness of films grown from the thioinitiator initially showed some increase with temperature (Figure 9). The rate constant for styrene polymerization likely increases faster with temperature than the corresponding rate constant for MMA. The apparent temperature limit for growth from Au surfaces is ~ 110 °C. Above 90 °C, film thickness begins to decline even on SiO₂ substrates. Inspection of a polystyrene film grown at 115 °C showed large-scale delamination of the polymer films

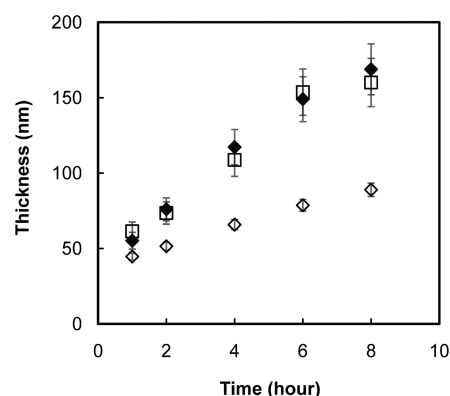


Figure 7. Surface-initiated polymerization of styrene from gold and SiO₂ surfaces. \diamond Polystyrene grown from a normal thiol initiator on gold; \blacklozenge polystyrene grown from a cross-linked thio initiator; \square polystyrene grown from SiO₂. The points are the average from three independent runs, and the limits of the error bars are the measured film thicknesses from the three runs.

(Figure 10), which is absent in films grown at 90 °C. Kim et al. made similar observations for poly(hydroxyethyl methacrylate) brushes grown on Au.³⁰

The improved polymer film growth from Au provided by cross-linked initiators can be generalized to other monomers such as poly(vinyl pyridine) (PVP). Despite its potential utility as a polyelectrolyte brush, we are unaware of examples of thick PVP brushes grown from Au surfaces (20 nm in 2 h by Bao et al.³¹ and 6 nm in 5 h by Husson et al.³²). However, R  he³³ grew 430 nm thick PVP films from surface-anchored azo initiators on SiO₂ in 14 h, and growing PVP from the cross-linked initiator should provide films on Au with similar thicknesses. As Figure 11 shows, polymerization of vinyl pyridine for 8 h at 50 °C gave 200 nm films from both Au and SiO₂ surfaces. This thickness is approximately 10 times the thickness of previous examples on Au. The

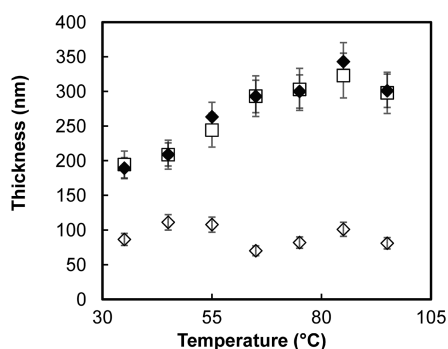


Figure 8. Temperature-dependent surface-initiated polymerization of MMA from various initiators; \diamond PMMA grown from standard thioinitiators (Scheme 1) anchored to Au surfaces; \blacklozenge PMMA grown from the cross-linked thioinitiator shown in Scheme 3; and \square PMMA grown from SiO_2 as shown in Scheme 1. Each data point indicates the film thickness after 1 h of growth. The points are the average of data from two independent trials, and the limits of the error bars are the measured film thicknesses from the two runs. All polymerization times were 1 h.

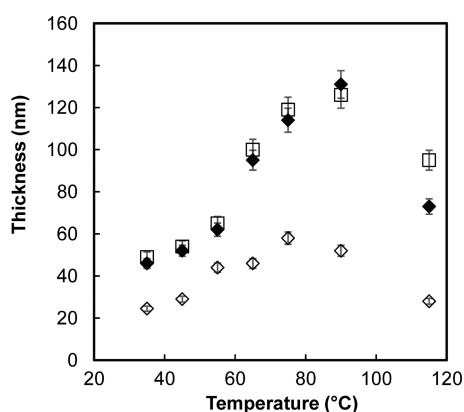


Figure 9. Temperature-dependent surface-initiated polymerization of styrene from various initiators; \diamond polystyrene grown from standard thioinitiators (Scheme 1) anchored to Au surfaces; \blacklozenge polystyrene grown from the cross-linked thioinitiator shown in Scheme 3; and \square polystyrene grown from SiO_2 as shown in Scheme 1. Each data point indicates the film thickness after 1 h of growth. The points are the average of data from two independent runs, and the limits of the error bars are the measured film thicknesses from the two runs. All polymerization times were 1 h.

increase in IR intensities (see the Supporting Information, Figure S3) is consistent with the ellipsometric data.

Our experiments using cross-linked initiators indicate thiol desorption as the main limitation to growing thick polymer brushes on Au. However, the precise desorption mechanisms are unknown. Scheme 4 depicts some pathways that may lead to termination of surface-bound radicals on Au surfaces. Thiol desorption, especially at $>60^\circ\text{C}$, is probably important. Radical-induced desorption of thiol SAMs from growing chains can be important over a broad temperature range, and the copper catalyst also may contribute to thiol desorption. While modifying polymers grown on Au using “click chemistry”, the Cu-catalyzed cycloaddition of azides with alkynes, we observed decreases in film thickness at high Cu concentrations and long reaction times, suggesting desorption of polymer brushes from Au substrates.³⁴ Although the copper concentration in ATRP is relatively low, its effect may not be negligible because partial desorption of

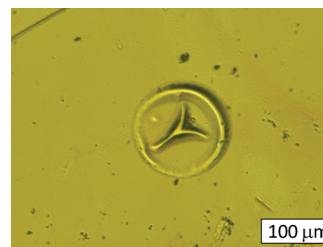


Figure 10. Optical micrograph of a 70 nm thick polystyrene brush, showing delamination of the polymer film from the substrate. The film was grown for 1 h at 115°C from cross-linked initiators immobilized on Au.

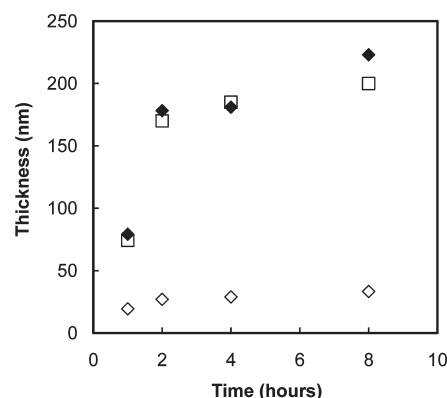
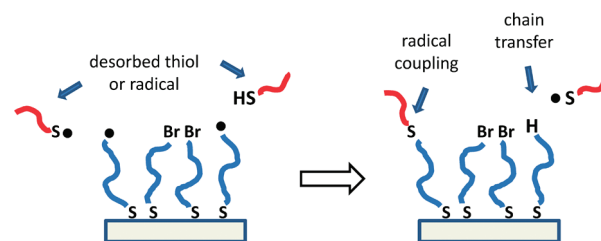


Figure 11. Evolution of film thickness with time during surface-initiated polymerization of vinyl pyridine from various initiators at 50°C ; \diamond poly(vinyl pyridine) grown from a noncross-linked thioinitiator on gold; \blacklozenge poly(vinyl pyridine) grown from a cross-linked thioinitiator on gold; \square poly(vinyl pyridine) grown from a SiO_2 surface.

Scheme 4. Proposed Pathways for Terminating Surface-Bound Radicals on Au. Thermal- or Radical-Induced Desorption of Surface Thiols or Thiol Radicals Terminate Growing Chains by Radical Coupling or by Chain-Transfer, Which Is Equivalent to Termination for Brushes



initiator-containing monolayers from the Au surface would result in a decrease in surface initiator concentration.

CONCLUSIONS

At temperatures ranging from 23 to 100°C , radical polymerizations initiated from Au surfaces generally provide thinner polymer brushes than comparable polymerizations initiated from SiO_2 . A cross-linked poly(siloxane) primer layer on gold surfaces eliminates this disparity. These results implicate thiols in terminating

growing polymer brushes to give polymer chains with low molecular weights and low film thicknesses. These results also exclude radical quenching by gold or the difference in initiator density between gold and silicon as significant factors. Cross-linked initiators extend the temperature range for polymerizations initiated from Au to 100 °C, enabling rapid polymerization of monomers less active than methacrylates, e.g. styrene and vinyl pyridine. Above 100 °C, we observed macroscopic delamination of polymer films grown on Au.

■ ASSOCIATED CONTENT

S Supporting Information. IR data for polymers grown from surfaces (Figures S1 – S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ REFERENCES

- (1) Milner, S. T. *Science* **1991**, *251*, 905–14.
- (2) Huang, X.; Doneski, L. J.; Wirth, M. J. *Anal. Chem.* **1998**, *70*, 4023–4029.
- (3) Bruening, M. L.; Zhou, Y.; Aguilar, G.; Agee, R.; Bergbreiter, D. E.; Crooks, R. M. *Langmuir* **1997**, *13*, 770–778.
- (4) Sidorenko, A.; Minko, S.; Schenk-Meuser, K.; Duschner, H.; Stamm, M. *Langmuir* **1999**, *15*, 8349–8355.
- (5) Prucker, O.; Naumann, C. A.; Ruhe, J.; Knoll, W.; Frank, C. W. *J. Am. Chem. Soc.* **1999**, *121*, 8766–8770.
- (6) Edmondson, S.; Osborne, V. L.; Huck, W. T. S. *Chem. Soc. Rev.* **2004**, *33*, 14–22.
- (7) Li, D. X.; He, Q.; Cui, Y.; Wang, K. W.; Zhang, X. M.; Li, J. B. *Chem.—Eur. J.* **2007**, *13*, 2224–2229.
- (8) Li, D. X.; He, Q.; Cui, Y.; Li, J. B. *Chem. Mater.* **2007**, *19*, 412–417.
- (9) Li, D. X.; Cui, Y.; Wang, K. W.; He, Q.; Yan, X. H.; Li, J. B. *Adv. Funct. Mater.* **2007**, *17*, 3134–3140.
- (10) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533–1554.
- (11) Schlenoff, J. B.; Li, M.; Ly, H. *J. Am. Chem. Soc.* **1995**, *117*, 12528–12536.
- (12) Huang, W. X.; Skanth, G.; Baker, G. L.; Bruening, M. L. *Langmuir* **2001**, *17*, 1731–1736.
- (13) Dong, H. C.; Zhu, M. Z.; Yoon, J. A.; Gao, H. F.; Jin, R. C.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2008**, *130*, 12852–+.
- (14) Shan, J.; Nuopponen, M.; Jiang, H.; Kauppinen, E.; Tenhu, H. *Macromolecules* **2003**, *36*, 4526–4533.
- (15) Fan, X. W.; Xia, C. J.; Fulghum, T.; Park, M. K.; Locklin, J.; Advincula, R. C. *Langmuir* **2003**, *19*, 916–923.
- (16) Bao, Z. Y.; Bruening, M. L.; Baker, G. L. *Macromolecules* **2006**, *39*, 5251–5258.
- (17) Sander, L. C.; Wise, S. A. *J. Chromatogr.* **1984**, *316*, 163–181.
- (18) Henglein, A.; Lilie, J. *J. Am. Chem. Soc.* **1981**, *103*, 1059–1066.
- (19) Ganesh, V.; Lakshminarayanan, V. *J. Phys. Chem. B* **2005**, *109*, 16372–16381.
- (20) Imahori, H.; Norieda, H.; Nishimura, Y.; Yamazaki, I.; Higuchi, K.; Kato, N.; Motohiro, T.; Yamada, H.; Tamaki, K.; Arimura, M.; Sakata, Y. *J. Phys. Chem. B* **2000**, *104*, 1253–1260.
- (21) Roux, S.; Duwez, A. S.; Demoustier-Champagne, S. *Langmuir* **2003**, *19*, 306–313.
- (22) Shah, R. R.; Merrezees, D.; Husemann, M.; Rees, I.; Abbott, N. L.; Hawker, C. J.; Hedrick, J. L. *Macromolecules* **2000**, *33*, 597–605.
- (23) Yoon, K. R.; Chi, Y. S.; Lee, K. B.; Lee, J. K.; Kim, D. J.; Koh, Y. J.; Joo, S. W.; Yun, W. S.; Choi, I. S. *J. Mater. Chem.* **2003**, *13*, 2910–2914.
- (24) Mulvihill, M. J.; Rupert, B. L.; He, R. R.; Hochbaum, A.; Arnold, J.; Yang, P. D. *J. Am. Chem. Soc.* **2005**, *127*, 16040–16041.
- (25) Kim, J. B.; Huang, W. X.; Miller, M. D.; Baker, G. L.; Bruening, M. L. *J. Polym. Sci. Polym. Chem.* **2003**, *41*, 386–394.
- (26) Zhang, Y. X.; He, J. A.; Zhu, Y.; Chen, H.; Ma, H. W. *Chem. Commun.* **2011**, *47*, 1190–1192.
- (27) Yan, Y. G.; Bein, T. *J. Phys. Chem.* **1992**, *96*, 9387–9393.
- (28) Mihailova, B.; Engstrom, V.; Hedlund, J.; Holmgren, A.; Sterte, J. *J. Mater. Chem.* **1999**, *9*, 1507–1510.
- (29) Mintova, S.; Schoeman, B.; Valtchev, V.; Sterte, J.; Mo, S. Y.; Bein, T. *Adv. Mater.* **1997**, *9*, 585–&.
- (30) Kim, J. B.; Wang, C. L.; Bruening, M. L.; Baker, G. L. In *Polymer Brushes*; Advincula, R. C.; Brittain, W. J.; Caster, K. C.; Rühle, J., Eds.; Wiley-VCH: Weinheim, Germany, 2004; pp 105–117.
- (31) Bao, Z. Y.; Bruening, M. L.; Baker, G. L. *J. Am. Chem. Soc.* **2006**, *128*, 9056–9060.
- (32) Li, X.; Wei, X. L.; Husson, S. M. *Biomacromolecules* **2004**, *5*, 869–876.
- (33) Biesalski, M.; Ruhe, J. *Langmuir* **2000**, *16*, 1943–1950.
- (34) Saha, S. Surface-Initiated ATRP of Substituted Styrenes and Functional Monomers on Flat Surfaces. Ph.D. Thesis, Michigan State University, East Lansing, MI, 2010.