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ARTICLE

Grafting Polymer Brushes from Nylon Surfaces via Hydrogen Atom Transfer

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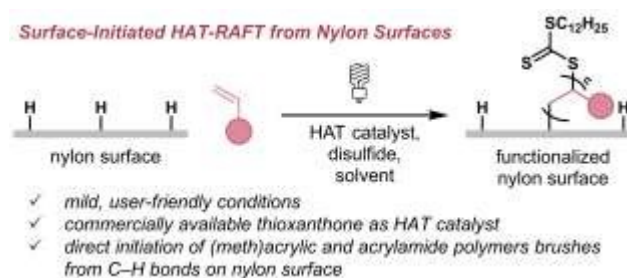
The direct functionalization of nylon surfaces with well-defined polymer brushes would enable access to functional materials for advanced biomedical and industrial applications. To this end, we developed a surface-initiated hydrogen atom transfer reversible addition fragmentation chain transfer (SI HAT-RAFT) polymerization to directly graft from nylon surfaces under mild conditions. Hydrogen abstraction by a triplet-excited thioxanthone catalyst initiates polymer chains, which are capped by a bistrithiocarbonate moiety. Our method is amenable to (meth)acrylic and acrylamide monomers and various commercially relevant nylon substrates, and we demonstrate spatial control over the polymerization by patterning nylon surfaces with polymer brushes. Finally, we explored the ability of our method to modify surface properties by measuring water contact angles with select polymer grafts and demonstrate that hydrophilic polymer brush modifications inhibit bovine serum albumin adhesion.

Introduction

Aliphatic polyamides (i.e. nylons) are ubiquitous polymers with tuneable crystallinities,^{1–3} attractive material properties,⁴ and biocompatibility resulting from strong hydrogen bonding in the polyamide crystal structure.⁵ However, the applications of nylons as advanced materials are hindered by their surface wettability, biological inertness, and susceptibility to fouling.^{6–8} Functionalization of nylon surfaces is a key strategy to broaden the utility and robustness of these materials.

Various methods have been employed to chemically modify nylon surfaces, including plasma treatment,^{6,9} UV-irradiation,¹⁰ *N*-alkylation,^{11,12} and polymer-graft modifications. Current methods for grafting from the surfaces of nylons and other polymeric surfaces are limited to uncontrolled polymerization strategies under harsh conditions^{13–15} or require lengthy synthetic routes to attach initiators/chain-transfer agents to polymer surfaces to achieve well-defined brushes.^{8,16–20} While diaryl ketones have been extensively studied as photosensitizers for surface functionalization, these studies have largely been limited to the initiation of free-radical polymerization via hydrogen atom transfer (HAT),²¹ require prior impregnation of the polymer surface with a photosensitizer,²² or graft a polymer network to the surface via C,H-insertion.^{23–26} A direct method of initiating controlled radical polymerization from nylon surfaces would be ideal.

In 2024, our group reported surface-initiated hydrogen atom transfer radical addition fragmentation chain-transfer (SI HAT-RAFT) polymerization, for grafting from polyethylene surfaces.²⁷ We found that under visible light irradiation in the presence of a benzophenone-derived HAT photocatalyst and a bis(trithiocarbonate) disulfide, thick and dense polymer brushes could be directly grafted from polyethylene surfaces. We posited that nylons would be amenable to SI HAT-RAFT due to the presence of hydridic hydrogen atoms on the polymer backbone which could be efficiently abstracted by the HAT catalyst to initiate polymerization. We envisaged that the wide scope of monomers amenable to SI HAT-RAFT would enable access to nylon materials with diverse surface properties. Herein, we develop a SI HAT-RAFT method as a mild, one-step method for functionalizing nylon surfaces (Scheme 1).



Scheme 1. Surface-initiated HAT-RAFT via a thioxanthone derivative enables the direct functionalization of nylon surfaces.

Results and discussion

We began our investigation by screening a set of diaryl ketones as HAT catalysts for SI HAT-RAFT from nylon-6,6. A solvent-cast nylon-6,6 film was layered with a solution of HAT catalyst, bis-

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dodecyltrithiocarbonate disulfide (BisTTC), and ^tbutyl acrylate in 1,4-dioxane, covered with a glass slide, and irradiated with a compact fluorescence lamp (CFL) for 18 hours (Figure 1a). After sonication of the irradiated films in dichloromethane to remove non-grafted polymer, FT-IR analysis revealed the appearance of a new carbonyl stretch at 1730 cm⁻¹ corresponding to the C=O stretch of grafted poly(^tbutyl acrylate) (P^tBA) (Figure 1b). The ratio between the area of the C=O stretch of P^tBA (1730 cm⁻¹) and the C=O stretch of nylon-6,6 (1630 cm⁻¹) (R_A) was used as a qualitative proxy for grafting efficiency. Benzophenone-derived (4-methoxyphenyl)(4-(trifluoromethyl)phenyl)methanone

(MTBP), which was the catalyst used for functionalization of polyethylene surfaces, yielded a modest amount of P^tBA grafting ($R_A = 0.13$). We hypothesized that thioxanthone-derivatives would result in a greater degree of grafting than benzophenone-derivatives due to their relatively long triplet lifetimes.^{28,29} In support of this, switching to thioxanthone (TX) increased the amount of grafted P^tBA significantly ($R_A = 0.33$). Commercially available 2,2'-dimethoxy-9H-thioxanthene-9-one (2,2'-diOMeTX) resulted in the most intense FT-IR stretch after grafting with ^tBA ($R_A = 1.01$); this is likely due to its increased absorbance in the visible region ($\lambda_{max} = 415$ nm) compared to TX,³⁰ as the CFL has a strong emission at 435 nm (Figure S1). Based on these high levels of grafting, 2,2'-diOMeTX was used for further optimization.

To confirm that the observed polymer is covalently attached to the nylon-6,6 surface, nylon films were subject to a series of controls deviating from our standard SI HAT-RAFT conditions (Table 1, entry 1). When nylon-6,6 was drop-cast with a solution of P^tBA, the P^tBA was washed away by sonication of the film in dichloromethane (Table 1, entry 2). Covalent attachment of the generated P^tBA to nylon-6,6 after SI HAT-RAFT conditions was further verified by subjecting a film to standard reaction conditions and then subjecting to a Soxhlet extraction in THF, after which R_A remained 1.30 (Figure S5).

Next, we conducted experiments to probe the mechanism of SI HAT-RAFT. When Ir(ppy)₃ catalysed photo-induced electron transfer RAFT (PET-RAFT) polymerization was conducted in the presence of a nylon-6,6 film (Table 1, entry 3) minimal P^tBA grafting was observed, confirming that HAT is necessary for efficient polymer grafting and non-HAT radical generation is insufficient. Additionally, when subjected to standard conditions without light or without a photocatalyst, no grafting from nylon-6,6 was observed (Table 1, entries 4 and 5). Removal of the chain transfer agent precursor, BisTTC, does not completely inhibit grafting, but the intensity of the P^tBA C=O stretch is diminished (Table 1, entry 6), suggesting that the bis(trithiocarbonate) is important for achieving efficient grafting. X-ray-photoelectron spectroscopy (XPS) data taken after subjecting a sample to our standard conditions revealed that sulfur remained in the sample after washing with DCM (Figures S21 and S22). Additionally, subjecting an SI HAT-RAFT grafted sample (Table 1, entry 7) to thermal RAFT chain extension conditions with AIBN and methyl acrylate (MA) (Table 1, entry 8) resulted in an increased R_A from 0.28 to 0.53, indicating that the disulfide species is capping polymer chains and can be used in chain-extension reactions.

We theorize that a solvent with hydridic C–H bonds is necessary to provide a source of radicals in solution to enable efficient chain transfer with surface-bound chains.^{27,31} To investigate this, we screened solvents with a range of C–H electron densities and bond dissociation energies (Table 1, entries 9–12). Cyclohexane and dichloroethane (DCE), which lack activated C–H bonds (cyclohexane C–H BDE = 99 kcal/mol²⁹) resulted in greatly diminished surface grafting compared to standard conditions with 1,4-dioxane. Toluene (C–H BDE = 88 kcal/mol),²⁹ with slightly activated benzylic hydrogens, showed

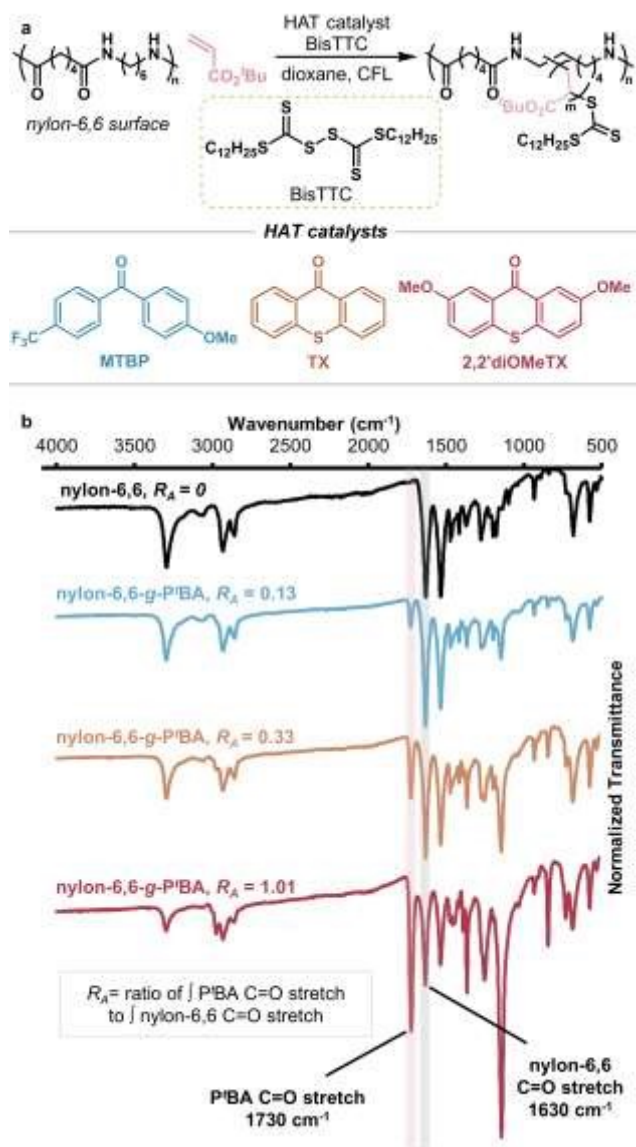
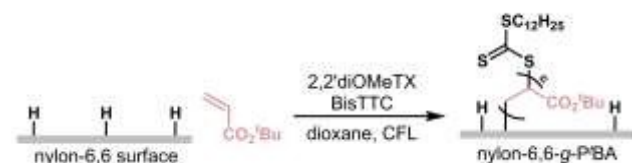


Figure 1. (a) General reaction scheme for the catalyst screen of SI HAT-RAFT from nylon-6,6: ^tBA (200 equiv), HAT catalyst (1 equiv), and BisTTC (1 equiv) dissolved in dioxane (0.04 M in catalyst) and irradiated from 4 cm with a CFL in a nitrogen filled glovebox. (b) FT-IR spectra (normalized to the C=O stretch of nylon-6,6) of pristine nylon-6,6 (black) and nylon-6,6-g-P^tBA generated after subjecting to SI HAT-RAFT conditions with MTBP (blue), TX (orange), and 2,2'-diOMeTX (pink).



increased surface grafting relative to unactivated solvents. In THF, which has C–H bonds of comparable electron-density to 1,4-dioxane and a lower BDE (92 kcal/mol compared to 96 kcal/mol),²⁹ surface grafting is only slightly diminished. Based on these results, we propose that a combination of the increased polarity of dioxane^{28,22} relative to unactivated solvents and the hydric nature of the C–H bonds of dioxane aids in radical generation for the facilitation of chain transfer to promote chain growth from the nylon surface.

Table 1. Optimization and control experiments.



entry	variation	R_A
1 ^a	standard conditions	1.01
2 ^b	dropcast P ^t BA onto nylon-6,6	0.06
3 ^c	PET-RAFT in the presence of nylon-6,6	0.02
4	no light	—
5	2,2'-diOMeTX removed	—
6	BisTTC removed	0.20
7	3 h irradiation	0.28
8 ^d	thermal RAFT chain extension from 7	0.53
9	cyclohexane instead of 1,4-dioxane	0.23
10	DCE instead of 1,4-dioxane	0.16
11	toluene instead of 1,4-dioxane	0.48
12	THF instead of 1,4-dioxane	0.65

^aStandard conditions: ^tBA (200 equiv), 2,2'-diOMeTX (1 equiv), and BisTTC (1 equiv) dissolved in 1,4-dioxane (0.04 M in catalyst) and irradiated from 4 cm with a CFL in a nitrogen-filled glovebox for 18 h. ^bDrop-cast with 200 mg/mL P^tBA ($M_n = 30$ kDa, $\bar{D} = 1.4$) in DCM. ^cIr(ppy)₃-catalyzed PET-RAFT of ^tBA in DMSO. ^dThermal RAFT chain extension from P^tBA brushes using methyl acrylate (MA).

A proposed mechanistic scheme for SI HAT-RAFT from nylon-6,6 surfaces is provided in the supporting information (see Section S10 for details). We propose that visible light irradiation excites 2,2'-diOMeTX to generate an electrophilic diradical, which abstracts a hydrogen from the nylon backbone to generate an initiating radical species along the polymer backbone. Small-molecule studies employing electrophilic radicals as HAT mediators from amides have reported chemoselectivity for the hydric hydrogen atom α to the nitrogen;^{32,33} we posit that radical generation primarily occurs at this hydric position, but abstraction from unactivated methylene units could also be occurring. Concurrent homolysis of bis(trithiocarbonate) disulfide by visible light yields two trithiocarbonyl radicals, one of which can combine with growing polymer chains. Importantly, without the ability to directly measure the dispersity of surface-attached polymer chains it is difficult to assess the degree of control attained by SI HAT-RAFT. While we have provided evidence that some population of surface-attached polymer chains are capped by a trithiocarbonate end-group, it is entirely possible that the surface polymerization is not well-controlled or that control is lost over time which may lead to branching.

We theorize that the kinetic selectivity of the electrophilic catalyst for electron-rich, hydric hydrogen atoms precludes unwanted side reactivity, such as C–H abstraction from the electron-deficient polymer backbone.³⁴ Our previous SI HAT-RAFT studies have shown that polymers with electron-poor, acidic C–H sites on the backbone are inaccessible.²⁷ This is in accordance with our prior work grafting from small-molecules in solution to yield linear polymer chains³⁵ as well as the lack of observable crosslinking in grafted nylon films (Figure S24). We propose that the photocatalyst is regenerated by single-electron transfer and proton transfer with a trithiocarbonyl

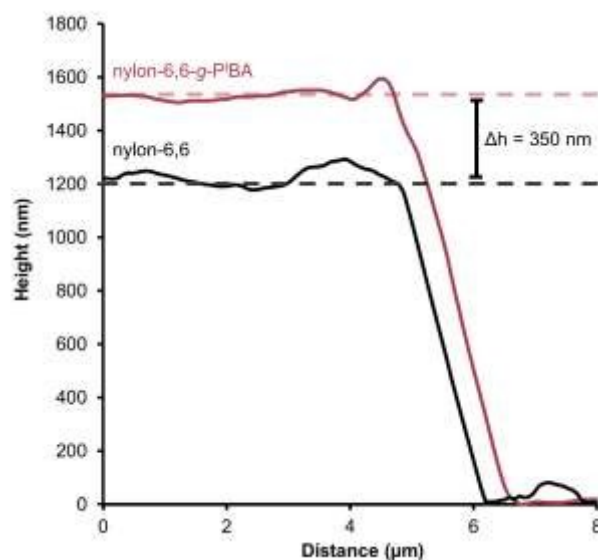


Figure 2. AFM measurement of nylon-6,6-g-P^tBA. Brush thickness was assessed by comparing the depth of a scratch on a nylon-6,6 film before and after grafting under standard reaction conditions.



radical to generate trithiocarbonic acid, enabling continued radical generation.

Having provided strong evidence that the P^tBA brushes are covalently bound to the nylon surface, we sought to characterize P^tBA brush thickness. Atomic force microscopy (AFM) was used to measure brush thicknesses via a change in step-height before and after grafting. Silicon wafers spin-coated with nylon-6,6 in HFIP were subjected to standard reaction conditions to grow P^tBA brushes. Under our optimized conditions with 2,2'-diOMeTX, P^tBA brushes were 350 nm thick (Figure 2). This figure was verified by optical profilometry, in which brush thicknesses of 300 nm were measured (Figures S25 and S26). Comparatively, ATRP polymerizations initiated from nylon 6,6 surfaces modified with alkyl bromide initiators report brush thicknesses of up to 80 nm³⁶ and RAFT polymerizations initiated from SiO₂ surfaces generally report brush thicknesses below 100 nm.^{19,31,37} Due to the inability to directly evaluate

polymer dispersity, it is possible that the thick graft layer observed in our system is a result of minimal control over polymerization. It is also possible that the thicker brushes obtained in our SI HAT-RAFT system are a result of the highly active thioxanthone catalyst and swelling of the nylon substrate by monomer and solvent leading to increased access to initiation sites. This is in agreement with a polyethylene surface-grafting system wherein increased swelling time led to a greater percent grafting,¹⁵ as well as an ATRP system using surface-attached poly(vinyl chloride) as an initiator wherein it is proposed that thicker initial films resulted in increased graft thickness due to swelling of the substrate and increased access to initiation sites.³⁸ Notably, pre-swelling a nylon-6,6 film with polymerization mixture for 14 hours prior to irradiation without excess solution present resulted in a similar degree of functionalization as standard reaction conditions for the same irradiation time (Figure S29).

Based on the change in R_A observed upon switching the photocatalyst used for SI HAT-RAFT and the increase in R_A after subjecting to chain extension conditions, we sought to investigate whether brush thickness measurements would correlate with FT-IR intensities. Indeed, MTBP resulted in a P^tBA brush thickness of 74 nm ($R_A = 0.13$) and TX in a brush thickness of 130 nm ($R_A = 0.37$) by optical profilometry (Figures S30-S33), suggesting that R_A functions as a reasonable proxy for polymer brush thickness. Additionally, subjecting a spin-coated nylon-6,6 sample to SI HAT-RAFT conditions for 2 hours to yield a nylon-6,6-*g*-P^tBA sample with a brush thickness of 33 nm by optical profilometry to thermal RAFT chain extension conditions resulted in an increased brush thickness to 88 nm (Figures S34-36). This result aligns with the increase in R_A observed by FT-IR and indicates that some polymer chains are capped by a trithiocarbonate moiety.

To investigate the breadth of polymer brushes accessible via SI HAT-RAFT, nylon-6,6 was subjected to our standard conditions with a diverse set of vinyl monomers (Figure 3a). (Meth)acrylic brushes are easily accessible under standard SI HAT-RAFT conditions; methyl acrylate (MA), methyl methacrylate (MMA), (trimethoxysilyl)propyl methacrylate (TMSPMA), and (hydroxyethyl)methacrylate (HEMA) brushes can be directly grafted from the surface of nylon-6,6. Additionally, P^tBA can be hydrolysed under basic conditions to yield poly(sodium acrylate) (PNaA) brushes. Interestingly, polyacrylamide (PAAm) brushes have been shown to introduce flame-retardant characteristics to nylon-based textiles;^{14,39} as a result, we were curious if SI HAT-RAFT would be amenable to PAAm brush growth. After subjecting nylon-6,6 to modified SI HAT-RAFT conditions with AAm in a mixture of DMSO and dioxane, we observed the appearance of a characteristic PAAm N–H stretch at 3183 cm⁻¹ by FT-IR (Figure S43) indicating successful grafting. Due to their thermoresponsive nature,^{13,40,41} we were also interested in polymerizing poly(N-isopropyl acrylamide) (PNIPAm) brushes. Standard reaction conditions with NIPAm yielded nylon-6,6-*g*-PNIPAm, based on the appearance of a characteristic N–H stretch at 2970 cm⁻¹ and C–H bend at 1385 cm⁻¹ (Figures S45 and S46). Due to the high selectivity of electrophilic diaryl ketones for hydridic C–H bonds,³⁴ monomers with electron-rich, hydridic C–H positions, such

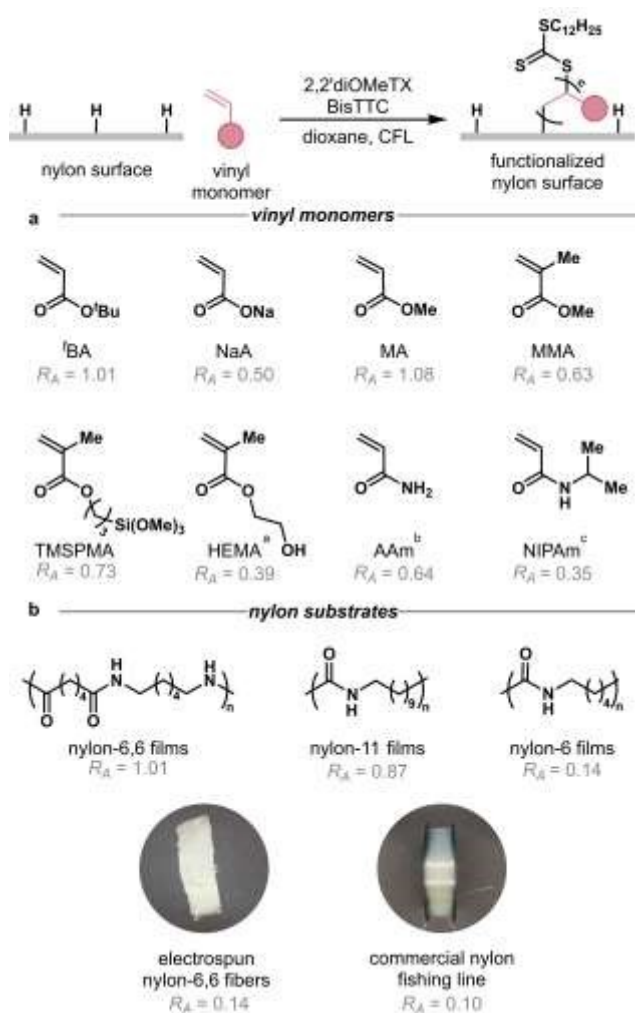


Figure 3. Scope of SI HAT-RAFT with (a) vinyl monomers and (b) various nylon substrates. ^aWashed with DMF instead of DCM. ^bDMSO/dioxane (50% v/v) used as solvent. R_A calculated as the ratio between the area of N–H stretch at 3183 cm⁻¹ before and after grafting. ^c R_A calculated as the ratio between the area of the C–H stretch at 2970 cm⁻¹ before and after grafting.



as HEMA and NIPAm, may result in a branched brush morphology or a crosslinked network. The polymer brushes reported here showcase the utility of SI HAT-RAFT for accessing a broad range of functional groups.

Next, we turned our attention to the scope of the nylon-surface (Figure 3b). Interestingly, P^tBA brushes can be efficiently initiated from nylon-11 surfaces, whereas nylon-6 resulted in a significantly depressed R_A . We theorize that the decreased grafting observed from solvent-cast nylon-6 compared to nylon-11 and nylon-6,6 could be due to slight differences in crystallinity. Electrospun nylon-6,6 fibres, used in composites for filtration⁴² and for biomedical applications,^{43,44} were also accessible and SEM images revealed that SI HAT-RAFT reaction conditions did not impact the integrity of the fibres (Figure S50). Interestingly, electrospinning nylon fibres has been reported to result in a predominately γ -crystal structure compared to the α -structure obtained from solvent-casting.^{45,46} Further studies relating substrate crystallinity and processing conditions to grafting efficiency are warranted. Subjecting commercially available nylon fishing line to SI HAT-RAFT conditions resulted in grafting ($R_A = 0.10$), but was less efficient, likely due to the presence of radical inhibitors in commercial samples.

An advantage of using light to initiate controlled surface grafting is the ability to exert spatial control over the polymerization. To probe the potential of SI HAT-RAFT to pattern surfaces with polymer brushes, we subjected a nylon-11 film to SI HAT-RAFT conditions with P^tBA and covered the sample with a photomask patterned with 500 by 500 μm transparent squares, as depicted in Figure 4a. Upon washing the sample and irradiating with 390 nm light, we were able to visualize the patterned brushes macroscopically and under a fluorescence microscope (Figure 4b). FT-IR measurements confirmed that brush growth only occurred where the sample was irradiated (Figure S57) and we hypothesize that the observed fluorescence can be attributed to trace amounts of photocatalyst. Having verified the

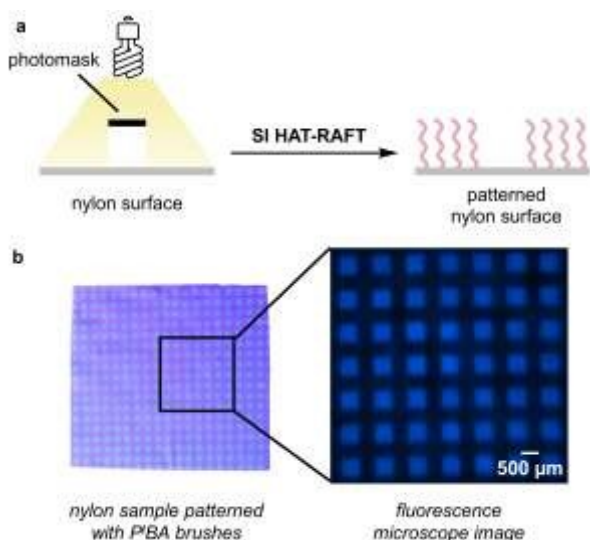


Figure 4. (a) Scheme depicting the spatial control attainable using SI HAT-RAFT when layered with a photomask. (b) Patterned nylon-11 -g-P^tBA surface imaged under 390 nm light and under a fluorescence microscope.

ability to exert spatial control over the polymerization, we envision that SI HAT-RAFT could be used to access to complex surface architectures via patterning of polymer surface modifications

The hydrophilicity of nylon surfaces has been reported to influence the fouling and adhesive behaviour of the material.^{47–49} Water contact angles of select hydrophobic and hydrophilic polymer grafts were measured to showcase the ability of SI HAT-RAFT to alter the surface properties of nylons (Figure 5a). PTMSPMA brushes increased the water contact angle (θ) of nylon-6,6 from 79° to 130°, whereas PHEMA and PEGA brushes resulted in hydrophilic surfaces ($\theta = 43^\circ$ and 58°).

While nylons are commonly employed for biomedical applications, such as sutures and cell scaffolding, their utility is hindered by non-specific protein and cell adhesion.¹⁷ PHEMA and PEGA brushes have been reported to inhibit protein adhesion on

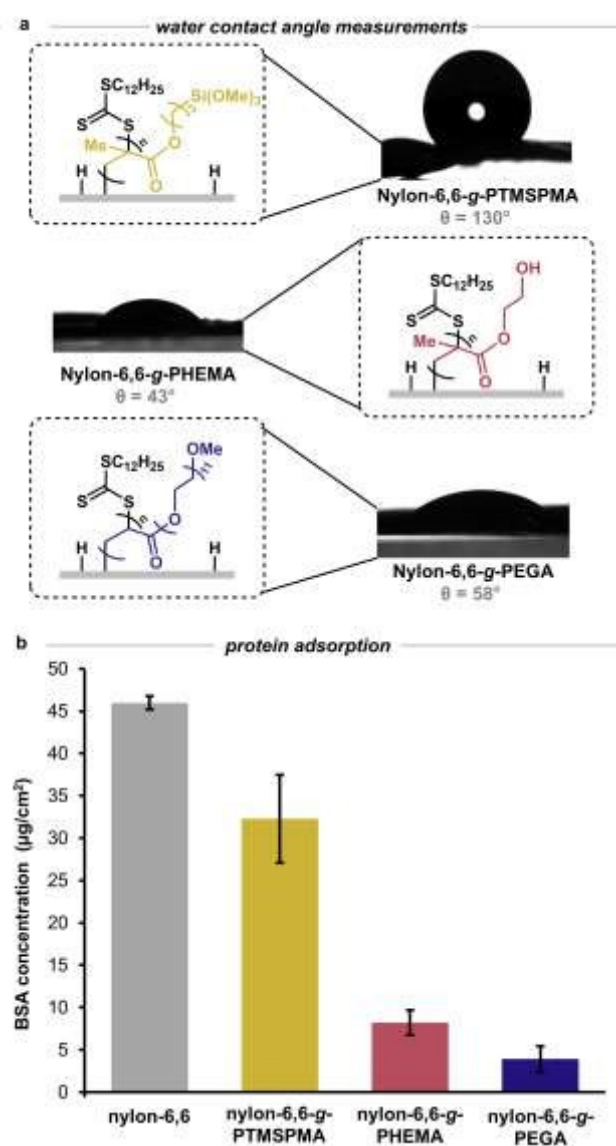


Figure 5. (a) Nylon-6,6-g-TMSPMA, nylon-6,6-g-PHEMA, and nylon-6,6-g-PEGA water contact angle measurements. (b) BSA adsorption on a pristine nylon surface and nylon surfaces modified with hydrophobic and hydrophilic polymer brushes.



polymer surfaces,⁴⁸ and we theorized that hydrophobic PTMSPMA brushes would function as a positive control and would not inhibit protein adhesion due to the low surface energies of silicone surfaces.⁴⁹ To test how polymer brushes grown via SI HAT-RAFT alter protein adhesion, we submerged nylon 6,6-*g*-PTMSPMA, nylon 6,6-*g*-PHEMA, and nylon-6,6-*g*-PEGA in a solution of bovine serum albumin (BSA) (see Section S15 of supporting information for details). As depicted in Figure 5b, the amount of adsorbed BSA slightly decreased from $46 \pm 1 \mu\text{g}/\text{cm}^2$ on pristine nylon-6,6 to $32 \pm 5 \mu\text{g}/\text{cm}^2$ on a PTMSPMA grafted sample. As expected, hydrophilic PHEMA and PEGA surface modifications greatly decreased the amount of protein that adhered to the substrate, with measured BSA concentrations of $8 \pm 2 \mu\text{g}/\text{cm}^2$ and $4 \pm 2 \mu\text{g}/\text{cm}^2$, respectively. This experiment demonstrates the potential for SI HAT-RAFT to modulate surface hydrophilicity and inhibit non-specific protein adhesion using BSA as a model protein.

Conclusions

This study demonstrates the utility of SI HAT-RAFT for directly functionalizing nylon substrates with a diverse array of polymer brushes. Using a commercially available thioxanthone catalyst, we have obtained a P^tBA brush thickness of ~300 nm, which could result from either monomer swelling into the nylon substrate or a lack of control over the polymerization. We have shown that SI HAT-RAFT is amenable to both (meth)acrylic and acrylamide monomer classes and that we can graft from commercially relevant nylon substrates. We explored the application of SI HAT-RAFT to access nylon surfaces patterned surfaces with polymer brushes. Additionally, we showed that we could tune the hydrophilicity of the polymer surface by changing the monomer employed. Hydrophilic PHEMA and PEGA grafted samples resulted in greatly diminished BSA adsorption, whereas hydrophobic PTMSPMA only slightly decreased the amount of adsorbed protein. We envision that SI HAT-RAFT will enable access to functional nylon surfaces for biomedical and industrial applications.

Author contributions

B. P. F. and G. W. C. supervised and provided guidance to the project. T.E.B. prepared all samples and analysed the data. A.E.R. carried out water contact angle measurements. J.R.K. conducted BSA adhesion tests. G.A.E. measured step heights via AFM measurements. S.K. obtained fluorescent microscope images of patterned nylon substrates. Y.W. and C.K.O. provided the necessary instrumentation and supervision for characterization of polymer brushes. T.E.B. prepared the manuscript and ESI.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this study have been included as part of the supplementary information (SI). Supplementary information is available.

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The data supporting this study have been included as part of the supplementary information (SI).
Supplementary information is available.

