Photochemistry

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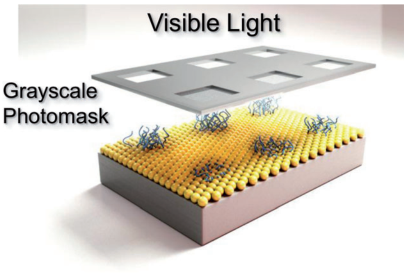

A facile approach to unique 3D, patterned polymer brushes is based on visible-light-mediated controlled radical polymerization. The temporal and spatial control of the polymerization allows the patterning of polymer brushes from a uniform initiating layer using a simple photomask (see picture). Furthermore, gradient polymer brushes, patterned block copolymers, and complex 3D structures can be obtained by modulating light intensity.

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Fabrication of Complex Three-Dimensional Polymer Brush Nanostructures through Light-Mediated Living Radical Polymerization**

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Surface-initiated polymerizations (SIPs) have received significant attention as a robust and effective strategy for the fabrication of polymer brushes.[1,2] These polymerizations are generally performed on substrates modified with a self-assembled monolayer of initiators, giving polymer chains that are tethered to the substrate by one end. By employing controlled radical polymerization techniques, such as atom-transfer radical polymerization,[3] reversible addition-fragmentation chain transfer polymerization,[4] and nitroxide-mediated polymerization,[5] brush architectures, such as block copolymer brushes and a variety of polymer brushes patterned in the *x*- and *y*-dimensions,[6] are accessible.[7] The versatility of these synthetic routes has led to a wide range of applications, including antifouling coatings,[8,9] chemical sensing,[10] biofunctional interfaces,[11,12] and stimuli-responsive materials.[13,14]

While progress has been made toward advanced brush architectures, current surface initiation strategies lack temporal and spatial control and, therefore, rely on a prepatterned initiator layer to template brush formation. Prepatterning has been demonstrated on a variety of substrates using top-down lithographic techniques,[15] such as photo- and interference lithography,[6] electron-beam lithography,[16–18] scanning-probe lithography,[19–21] and soft lithography.[22] In these cases, polymerization only occurs in regions where the initiator is present, resulting in patterned polymer brushes.[22]

With greater difficulty, the patterning of polymer brushes can be extended to three-dimensional (3D) nano- and microstructures by patterning a concentration gradient of the initiating species by lithographic techniques or through controlled vapor deposition of initiators.[23–25] Steric interactions between chains cause densely packed areas to be highly extended when compared to sparsely grafted areas, resulting in varying brush heights on the substrate. A key characteristic of these routes to patterned and gradient brushes is the uniform distribution of initiators on the substrate. Though less common, gradient brushes have also been obtained from a uniform layer of the initiators by varying the chain density through the time of exposure to UV light,[26,27] or by manipulating the contact time of the surface with the monomer and catalyst solution.[28] While these approaches can readily give rise to gradient surfaces, it is technically challenging to produce complex 3D structures.

Recently, our group reported the living radical polymerization of methacrylates regulated by visible light using an Ir-based photoredox catalyst.[29,30] In this system the propagating polymer chains are efficiently returned to their dormant state when the light source is removed, and can be reinitiated upon subsequent exposure to light, affording temporal control over chain growth.

Herein, we demonstrate facile, temporally and spatially controlled brush formation from a uniform initiating layer through a visible light-mediated radical polymerization, and illustrate a set of key differentiating features of this approach compared with previous strategies (Figure 1a). For example, the use of light to control the polymerization allows the brush height to be determined by the exposure time. Through the use of a traditional photomask, brush growth can also be spatially confined to exposed regions (Figure 1b), however,

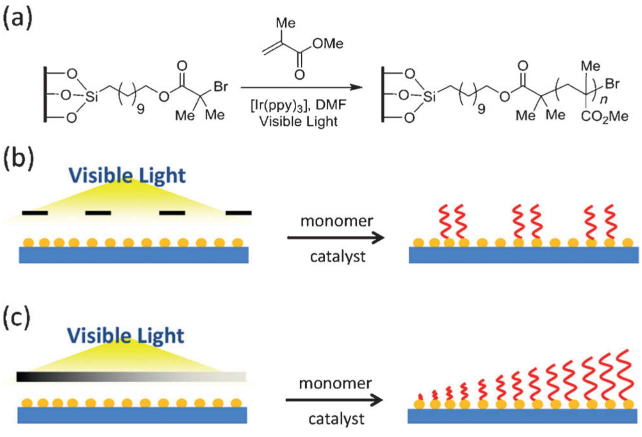

Figure 1. Patterning of polymer brushes from substrates uniformly functionalized with trichlorosilane-substituted α-bromoisobutyrate-based initiators (a) using b) a photomask for patterns or c) a neutral density filter for gradient structures. DMF = *N*,*N*-dimethylformamide, ppy = 2-phenylpyridine.

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the unexposed regions still contain active initiating species that can be utilized for subsequent polymerizations. In prior studies, the initiating groups were typically destroyed in areas where the polymer brushes were not grown. Finally, neutral density filters can be used to modulate the intensity of incident light and, therefore, the kinetic rate of polymerization from the surface. These factors allow the direct formation of gradient brush structures and arbitrary 3D features in a single step over large areas (Figure 1 c).[31] In combination with the uniform density of initiating groups, this method leads to homogeneous stretching of the polymer chains with varying molecular weights, in direct contrast to the variable stretching in prior studies. The unique properties of this process, which leads to nanoscale features that are molecularly distinct from those achieved previously, offer significant scope for applications ranging from photolithography to one-step, high-throughput fabrication of patterned substrates.

To demonstrate the capabilities of this new concept, silicon oxides were uniformly functionalized with trichlorosilane-substituted α-bromoisobutyrate-based initiators (Figure 1 a).[7] Initially, the relationship between film thickness and irradiation time was determined by a series of separate, yet comparable experiments, in which exposure time to the light of a commercial 26 Watt fluorescent lamp (available from any hardware store) was varied for a solution of methyl methacrylate (MMA), DMF, and *fac*-[Ir(ppy)$_3$] in contact with silicon wafers uniformly functionalized with a covalently bound initiating species. Film thickness increased linearly with time upon continuous irradiation (Figure 2). Significantly, the use of light as an external mediator of polymerization enables the control of film thickness without the addition of a "sacrificial" untethered initiator or a deactivating species to the monomer and catalyst solution. To further confirm the facile nature of this process and establish that brush growth only occurs when irradiated by light, a series of "on"–"off" experiments were conducted. First, a sample was irradiated for 20 minutes, left in the dark for 10 minutes, and then re-exposed to light for 10 minutes, resulting in a total exposure time of 30 minutes. Similarly, a substrate was cycled between three dark periods of 5 minutes and two intervals of 5 minutes of exposure to light (10 minutes total exposure to light). In all cases, brush thickness was determined only by the total irradiation time (Figure 2, □). This ability to "pause" and "restart" surface-initiated polymerizations has profound implications for patterning polymer brushes and clearly demonstrates that iridium-based photocontrolled polymerization affords excellent temporal control of brush growth from a surface.

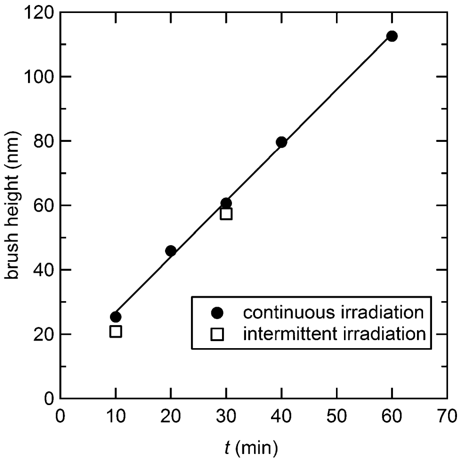

Figure 2. Brush height as a function of irradiation time measured by spectral reflectance. ●: continuous irradiation, □: brushes that were obtained by "on"–"off" cycles (see text for details).

One of the most attractive features of a photochemically controlled route to polymer brushes is the potential for direct spatial control over brush growth. As a simple illustration, initiator-functionalized substrates in a solution of MMA and [Ir(ppy)$_3$] in DMF were irradiated through photomasks containing rectangular patterns of different sizes. Optical micrographs show clear patterning of the poly(methyl methacrylate) (PMMA) brushes (Figure 3), thus demonstrating spatial control over brush formation from a uniform initiating layer and the ability to pattern a range of features over large areas. Patterning could be achieved at submicrometer levels and was only limited by the wavelength of the light. The key to minimizing the impact of diffusion on the resolution in this system is the short excited state lifetime of the [Ir(ppy)$_3$] catalyst(ca. 50 ns). Based on an upper limit for the diffusion coefficient of the Ir catalyst, which is the self-diffusion coefficient of water ($D = 2.3 \times 10^{-9}\ \mathrm{m^2\,s^{-1}}$), the catalyst is expected to diffuse less than approximately 20 nm during its excited-state lifetime. This distance is significantly shorter than the wavelength of light and leads to the high degree of fidelity observed in this system.

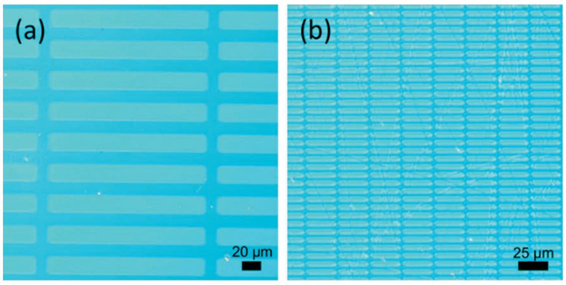

Figure 3. Optical microscopy image of patterned PMMA brushes obtained using a negative photomask with a) 20 µm by 200 µm and b) 2.5 µm by 25 µm rectangles.

The ability to spatially control brush formation also opens up the intriguing possibility of combining spatial (x,y dimensions) with intensity (z dimension) modulation to produce well-defined three-dimensional nanostructures in a single step. When compared to previous strategies, this represents a more practical and versatile synthetic approach. As an initial example, a grayscale photomask that contains an array of squares of varying optical density was used to probe the relationship between brush height and light intensity for a given exposure time. The brush height was found to be inversely proportional to the optical density of the mask (Figure 4). Regions of the substrate that are exposed to more

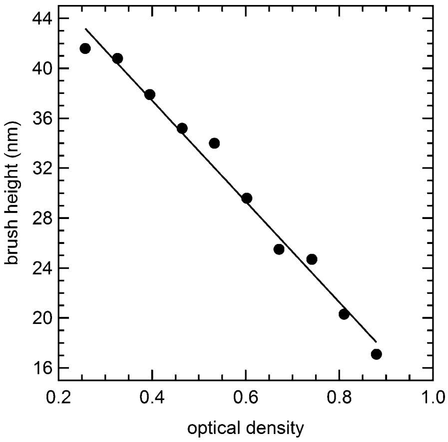

Figure 4. Brush height as a function of optical density of the photomask, as measured by profilometry.

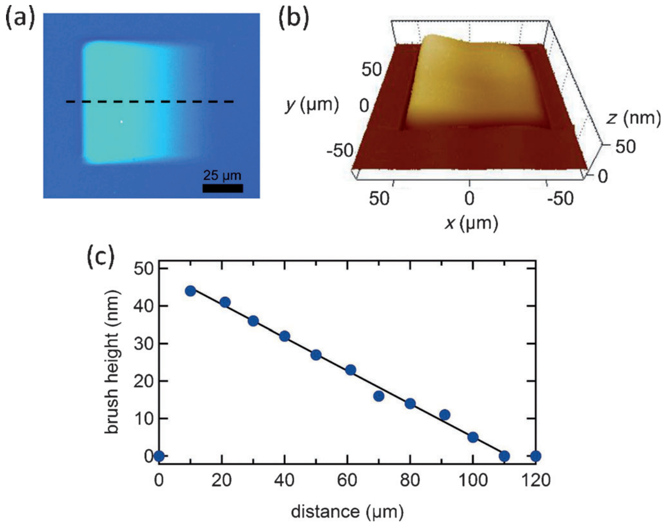

Figure 5. a) Optical micrograph of nanoscale-inclined plane formed from a 3D polymer brush; b) 3D AFM image of nanoscale-inclined plane, and c) height along hashed line across feature as shown in (a).

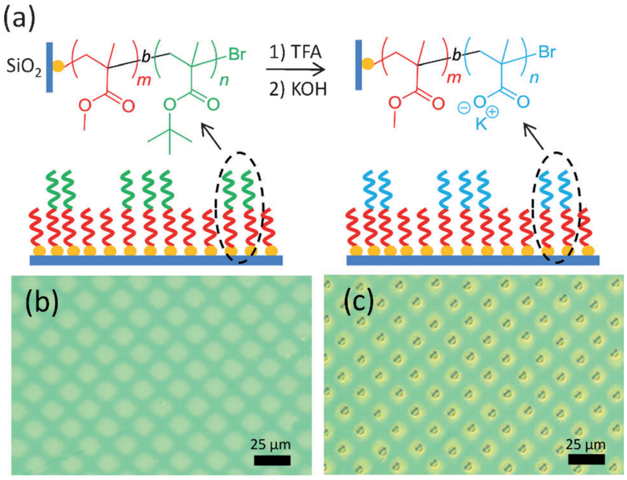

Figure 6. a) Schematic of patterned block copolymer brushes and conversion of PMMA-*b*-P*t*BuMA to PMMA-*b*-PMAA. b) Optical micrograph of PMMA-*b*-P*t*BuMA brushes patterned from a uniform PMMA initiating layer. c) Selective wetting of PMMA-*b*-PMAA regions after exposure to water vapor.

light experience an increase in the kinetic rate of brush formation, resulting in higher molecular weight brushes and, as a result, an increase in polymer brush thickness. Because the initiator density is uniform over the entire substrate, variances in brush thickness are a result of variations in the molecular weights of the polymer brushes in different regions. To support this hypothesis, the grafting densities were determined to be consistent (0.27 ± 0.02 chains nm^{-2}) for a range of different features/samples, as well as within the same sample, regardless of light intensity or exposure time.[26] These grafting densities compare favorably with reported values for moderately dense polymer brushes.[32]

A powerful consequence of this novel mechanism is the possibility to fabricate complex and arbitrary three-dimensional patterns by modulating the intensity of light to control the molecular weight of the brushes rather than the density of the initiator. Using a grayscale lithography mask, a variety of features could be prepared, including inclined planes, microprisms, gradients, and arrays of microlenses (Figure S3). The optical micrograph and 3D atomic force microscopy (AFM) image of an inclined plane (Figure 5) illustrate the compelling nature of this technique for patterning 3D polymer brush structures from a uniform initiating layer in a single step. Importantly, the linear relationship between feature height and the optical density of the mask is maintained, as evidenced by a height profile along the length of the structure (Figure 5c).

An additional attractive feature of this strategy is the nondestructive nature of the patterning process, which allows retention of initiator activity after initial polymer brush formation. As a result, this technique represents a facile route to patterned block copolymer brushes in which both chemical functionality and surface topography can be tuned (Figure 6a). To investigate this capability, a uniform PMMA brush with a height of approximately 40 nm was initially prepared. Exposure of this surface through a TEM grid as a photomask was then used to grow poly(*tert*-butyl methacrylate) (P*t*BuMA) chains specifically in the irradiated areas. This technique gives regions of PMMA-*b*-P*t*BuMA where the P*t*BuMA domains are 12 nm thicker than the PMMA initiating layer with these block copolymer domains clearly being visible by optical microscopy (Figure 6b).

The ability to selectively initiate the fabrication of a second block shows that the first PMMA layer still contains active alkyl bromide chain ends, which can be efficiently reinitiated to afford spatially defined block copolymer brushes. As with the temporal control observed by cycling between light and dark periods, no untethered initiator or deactivating species was required to maintain control over the polymer chain ends. To illustrate the variations of surface properties that can be readily obtained, P*t*BuMA was converted to polymethacrylic acid (PMAA) by immersion in a 1:1 mixture of dichloromethane and trifluoroacetic acid (TFA) for 30 minutes. After deprotonation with a 0.1 molar aqueous

KOH solution, selective wetting of the PMAA regions was observed by optical microscopy (Figure 6c), further verifying the presence of the patterned block copolymers.[1,2,33] The ability to pattern block copolymer brushes through sequential polymerization of monomers from a uniform initiating layer represents significant progress in the fabrication of 3D features for tuning surface properties.[3,34]

In summary, a facile approach to patterned polymer brushes has been developed by taking advantage of the temporal and spatial control afforded by a "living" visible light mediated radical polymerization. Through modulation of the light intensity, complex and arbitrary 3D structures can be fabricated. Furthermore, patterned block copolymer structures can be formed for tuning surface properties.

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