

Supporting Information

Multi-Component Hierarchically-Structured Polymer Brushes

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An S1813 thickness of 1500 nm (thickness assumed based on the spin-coating speed) was chosen for the patterning procedure on the basis that there was no observed differences between the S1813 thicknesses as a barrier for brush reinitiation. S1813 is capable of restricting polymer brush growth to areas not coated by it and it is shown to be resilient in the brush polymerization solution. The insolubility of the different S1813 thicknesses also demonstrates the stability S1813 as a protective layer in mostly aqueous brush polymerization solutions. The solubility of S1813 was tested in varying solvents and concentrations that have possible use in brush polymerization solutions (Table S1). To test the solubility, S1813 was simply coated onto a silicon wafer and any visible dissolution of the photoresist was noted.

Table S1. Visual determination of solubility of S1813.

Solvent	Solubility
Milli Q Water (control)	Insoluble
Hexanes	Insoluble
Toluene	Insoluble
Acetone	Soluble
Methylene Chloride	Soluble
Methanol	Soluble
7:3 Methanol:Water	Soluble
5:5 Methanol:Water	Soluble
3:7 Methanol:Water	Insoluble
1:9 Methanol:Water	Insoluble

In addition to the solvent, other components of the polymerization mixture could also influence the quality of the pattern achieved. For example, if the concentration of the catalyst chelator (*N,N,N',N',N"-pentamethyldiethylenetriamine* (PMDETA)) was too high, while there was no obvious dissolution of the photoresist it was still evident that the PNIPAM grew in areas

that were supposed to be masked by the photoresist. As shown in Figure S2, a sloping transition from the PHEMA-PNIPAM interfaces represented by shadow is believed to be caused by the etching of the S1813 by PMDETA and the polymerization growth solution is able to access areas of PHEMA underneath the edges of S1813. When the PMDETA concentration was decreased, the polymerization solution did not appear to undercut the photoresist and grow in undesired areas.

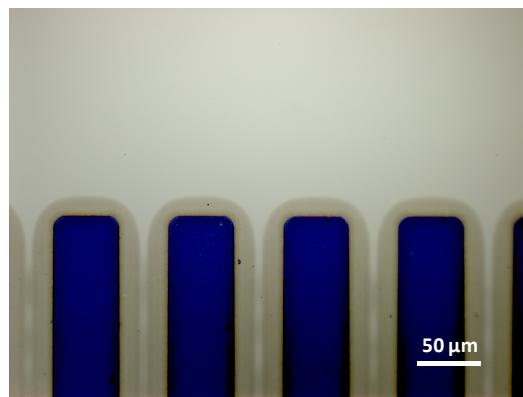


Figure S1. Microscopy image of brush in areas that are supposed to be blocked by the photoresist.

In addition to the polymer growth solution, the patterning of the photoresist can also affect the quality of the polymer brush patterns achieved. Figures S2a and S2b show the difference between two PNIPAM brushes grown under the same conditions but patterned at 20 second and 30 second UV exposures, respectively. The 20 second exposure resulted in a patterned brush with less curved corners than the 30 second. More optimization work needs to be done to find the appropriate exposure time for different pattern size scales.

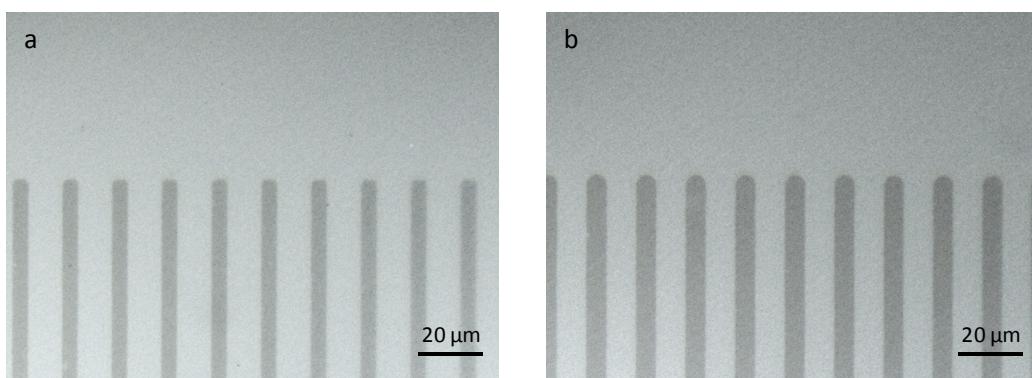


Figure S2. The dark areas are lines of PNIPAM patterned on PHEMA using S1813 that was exposed for a. 20 seconds and b. 30 seconds through a 5 μm mask.

The AFM of the multicomponent patterns (Figure S3) shows the four distinct regions of the multicomponent brush. An accurate comparison of the height of the PGMA growth on PHEMA and on PNIPAM-HEMA is difficult due to normalization of the heights from the flattening function performed in the AFM software.

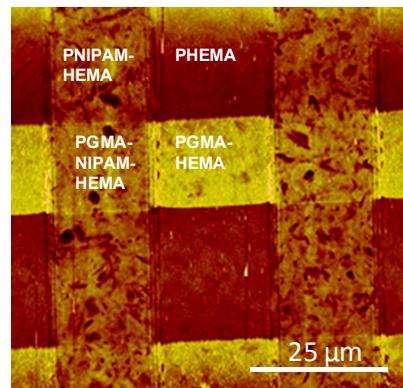


Figure S3. AFM image of PGMA-NIPAM-HEMA Pattern. While the four distinct regions are visible. The flattening function normalized the heights of objects that were parallel to the fast scan axis making it difficult to directly compare the different heights

For thin film interference, Newton's interference colors (Table S2) can be used to semi-quantitatively determine the thickness of the film. Others have used this method before to

determine the thickness of polymer films and this concept can be used for quantification of material binding to a surface.[1-2] The interference colors occur when white light is reflected off two interfaces of a thin film. When the light recombines some of the wavelengths constructively interfere while other wavelengths destructively interfere. Newton's interference colors are based on soap bubble films, where the light undergoes a phase shift of 180° when it is reflected off the air-film interface, due to the higher refractive index (n) of the film compared to the air. These colors are assigned a retardation number which equals $2nd$, where d is the thickness of the film.[3] Using the previous equation, the thickness of the film can be determined semi-quantitatively from the color. However in our case, both the light reflected off the air-brush interface and brush-silicon interface experience a phase change due to the higher n of the reflecting surface (Figure S4). Thus, in comparison to the polymer brushes, Newton's interference colors and respective retardations are off by $\lambda/2$ and we cannot use them directly to calculate the thickness of the brush. However, we can use the thickness difference between two colors in Newton's color chart to determine the difference in thickness between two colors in the polymer brush. Again, keep in mind that this technique is semi-quantitative. Based on the difference between the yellow-brown and orange-red retardation values and an average refractive index of 1.5, the difference in thickness between these two colors is approximately 20 nm.

Table S2. Newton's interference colors (partial list) and their retardations. [3]

Retardation (nm)	Color
0	Black
50	Iron gray
100	Gray
160	Gray blue
260	White
330	Yellow
440	Yellow brown
500	Orange red
540	Red
580	Violet
680	Blue
720	Blue green
750	Green
840	Yellow green
920	Yellow

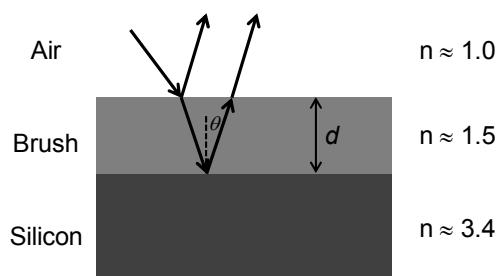


Figure S4. The different layers giving rise to the optical interference and their approximate refractive indices.

References:

1. P. F. Green, G. Coulon, T. P. Russell, V. R. Deline, *Macromolecules* 1989, **22**, 2581-2589.
2. E. Özkumur, J. W. Needham, D. A. Bergstein, R. Gonzalez, M. Cabodi, J. M. Gershoni, B. B. Goldberg, M. S. Ünlü, *PNAS* 2008, **105**, 7988–7992.
3. Nassau, K., *The Physics and Chemistry of Color*. 1983, New York: John Wiley & Sons, Inc.