Patterned Polymer Brushes from Surface-Initiated Polymerization Inside a Microchannel†

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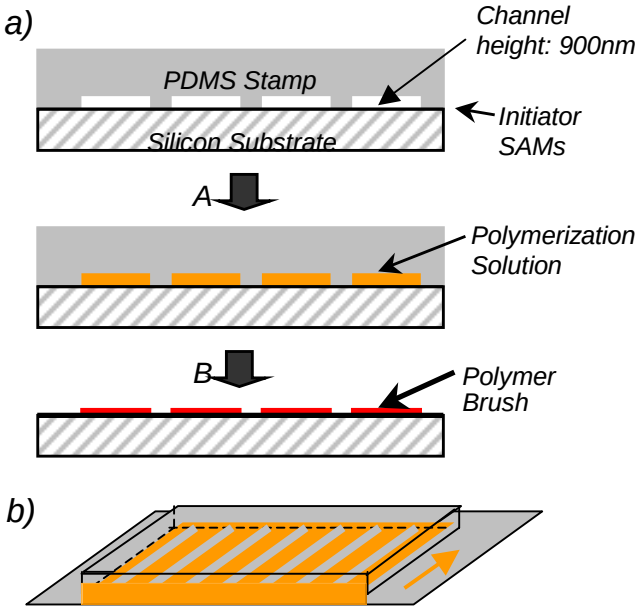
INTRODUCTION

Surface modification with covalently-bonded organic thin films provides a versatile method to tailor surface properties.[1] With recent advances in surface-initiated polymerization, a range of polymer brushes have been synthesized with controlled properties.[2]

The development of lithography techniques, especially soft lithography, provides facile ways to pattern surfaces with micron or sub-micron features.[3] One of the most common methods to pattern surfaces with polymer brushes is to polymerize from initiator-functionalized, patterned self-assembled monolayers (SAMs), which can be generated by micro-contact printing or e-beam lithography.[4,5] However, only limited substrates such as gold or silicon are suitable for micro-contact printing of SAMs and the quality of the formed SAMs can be hard to control.

In this work, we introduce surface-initiated polymerization inside a microchannel as an alternate method to pattern surfaces with polymer brushes. Instead of patterning the SAM layer, the pattern is formed during the polymerization process.

Scheme 1: Surface-initiated polymerization inside a microchannel



DISCUSSION

The basic procedure for surface patterning via surface-initiated polymerization inside a microchannel is illustrated in Scheme 1. The initiator-modified silicon substrate and the monomer / catalyst solution were prepared according to the literature procedures.[6,7] Microchannels were formed by placing a polydimethylsiloxane (PDMS) stamp on an initiator-SAMs modified substrate. The PDMS stamp was cut so that both ends of the channels were open. The final dimensions of the channel were about 900 nm thick, 40 µm wide and 3 mm long. In our experiment, surface-initiated atom transfer radical polymerization (ATRP)[8] of of 2-hydroxyethyl methacrylate (HEMA) was used to synthesize polymer brushes from the surface. For this purpose, the substrate, along with the PDMS stamp, was placed in a test tube and thoroughly degassed. To start the polymerization, a drop of solution was placed at one end of the channel. Immediately after the solution came in contact with the side of the stamp, it was pulled in to the channel via capillary force.

Once the polymerization was complete, the PDMS stamp was quickly removed from the surface and the surface was thoroughly rinsed with solvents to remove the residual monomer solution on the surface. Then the whole surface was dried under a flow of nitrogen.

Figure 1 shows an optical micrograph of the patterned surface resulting from polymerization of HEMA inside a microchannel. The dark regions in the picture correspond to the areas inside the microchannel. In contrast, regions covered by PDMS during the experiment remain white, suggesting no polymer brushes grow from that part of the surface. The patterns retain high fidelity with the PDMS stamps.

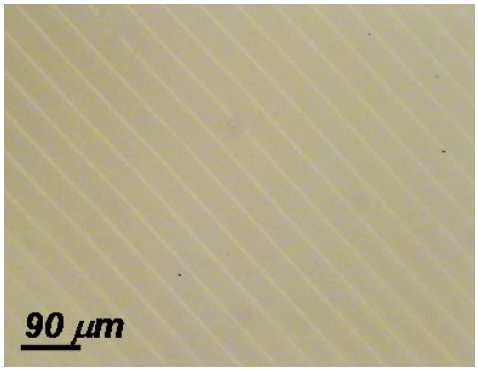


Figure 1. Patterned polymer brush of HEMA

CONCLUSIONS

In summary, we developed a new method to pattern a surface with polymer brushes via a microchannel formed between PDMS stamps and initiator-modified substrates. The polymerization solution was delivered into the channel through capillary force. Polymer brushes only grow on the surface areas that inside the microchannel. Since the whole surface retains reinitiating capacity,[7] this technique may provide a simple way to fabricate patterned polymer brushes with complex geometries.

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