Patterning of Polymer Brushes as Membranes and Investigating the Effects

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Principal Investigator: Christopher K. Ober
Users: M. Elizabeth Welch, Christian Ohm, Bernd Deffner

Affiliations: 1) Department of Materials Science and Engineering, 2) Department of Chemistry and Chemical Biology; Cornell University
Primary Source of Research Funding: National Science Foundation
Contact: cko3@cornell.edu, mew239@cornell.edu, co237@cornell.edu

Abstract:

Patterning of polymer films has been an area of great interest due to the broad range of applications including bio-related and medicinal research. Consequently, the nature of patterned polymer brushes as removable thin films was explored. Both an etching and polyvinyl alcohol dissolution process has enabled us to lift off very thin membranes for further characterization with the potential of using them as Janus membranes for biological applications. Furthermore, the repolymerization of monomer on brushes that had previously been exposed and patterned was explored.

Summary of Research:

Polymer brushes can be formed by densely attaching polymer chains to a substrate. They have garnered much attention due to the need for systems in the fields of microelectronics, nanofluidic devices, biosensing, and other areas of nanotechnology [1-4]. Another application of interest is the production of Janus membranes. We have begun to explore different means for detaching polymer brush membranes from a surface. Previous work on polymer brush nanochannels led us to question the robustness of the bridging polymer film that stretched over distances ranging from 100 nm to a few microns. The first method involved a silicon oxide layer upon which the polymer brushes were grown from via atom transfer radical polymerization (ATRP) to thicknesses ranging from 30 to 70 nm. The polymer brushes were then patterned and crosslinked by a UV source and etched with HF to produce very thin membranes. HF was chosen because it etches only the silicon oxide and does not harm the polymer brush membranes, and because silicon oxide is a conventional surface for polymer brush growth. Thus we are not limited to the types of brushes membranes that can be produced.

Membrane characterization included TEM and optical microscopy (Figure 1). Results indicate the membranes retain a significant amount of strength even at very thin thicknesses. Folding, wrinkling, and bending are commonly observed instead of tearing or falling apart and therefore imply that membranes are robust enough to undergo further functionalization to produce Janus membranes. Additionally, this technique can provide information regarding ATRP initiator immobilization as well as the brush polymerization process to answer questions about the nature of brush films.

A second method for the controlled release of polymer brushes from a silicon substrate involves crafting the polymer film from a sacrificial layer of poly (vinylalcohol) (PVA). For this, thin layers of PVA were spin-coated on bare silica and were subsequently functionalized with an ATRP starter in a gas phase reaction. ATRP polymerization of monomers like styrene or methylmethacrylate yielded homogenous polymeric films with thicknesses between 20 and 200 nm linked to the PVA. Subsequent polymerization of a second monomer allowed producing Janus films consisting of two different brush layers. After patterning these films into isolated squares with lateral dimensions of 10 × 10 µm using photolithographic techniques, the PVA layer was dissolved in water. Thereby, the patterned polymer brushes were lifted.
off the substrate and formed a dispersion in the water. Due to entanglements between remaining PVA chains and the polymer brush, the resulting particles were stable without further crosslinking. They were characterized using optical-, fluorescence- and electron microscopy (Figure 2). Currently, we are investigating the possibility to use these nanofilms as encapsulation agents.

In order to expand our range of patterning techniques, we investigated the possibility of patterning positive tone polymer brushes using deep-UV photolithography. In comparison to recent experiments using e-beam lithography [5], this approach allows patterning larger brush areas at lower costs. In first experiments, we exposed brushes from several materials like poly (methylmethacrylate), poly (isobutylmethacrylate) and poly (neopentylmethacrylate) at different doses of 220 nm irradiation. After development, optical and scanning probe microscopy proved that the patterning was successful. Additionally, we investigated the effect of irradiation on the brush’s ability to reinitiate ATRP polymerization. For this, we polymerized styrene on deep-UV patterned brushes. We found that the ATRP polymerization runs much slower in exposed areas of the brush, thus drastically increasing the contrast of the first pattern. Consequently, this new patterning technique allows the patterning of negative tone materials like polystyrene without the application of photoresists. Finally, applying a gray-scale exposure gradient enabled us to produce interesting thickness gradients in polymer brushes.

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