Manipulating Polymer Interfaces: Adaptive Morphology of Mixed Brushes in a Selective and Non-selective Surrounding

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INTRODUCTION

The conformation of a polymer chain is very sensitive to changes in the surrounding environment.[1] Polymer surface and interface science, for the past two decades, has led to advances in colloidal stabilization, control of lubrication and adhesion, as well as the coating and paint industry.[2-4] One of the primary directions of current polymer surface modification is to create versatile interfaces that goes beyond these applications. Indeed, polymer surfaces must now be engineered to both protect a substrate and adapt its conformation, or respond to environmental conditions.

Advances in nanoscale fabrication have led to the development of nanodevices in which the surface properties can be manipulated in order to perform complex sensing functions. Such an example may be microfluidic devices in which thermal, pressure, or pH sensitive surfaces inside these systems allow for the control of flow rate and direction.[5,6] These systems require adaptive surfaces that have the built in ability to possess "on-demand" properties based on external conditions. Polymer brush systems are regarded as ideal materials for these applications since the high grafting density and uniformity in chain length inherent in a brush allows for rapid, communal changes in the layer even upon subtle fluctuations of local pH, temperature, and solvent quality.[7,8]

Mixed brushes, especially when composed of incompatible species, further enhances the responsive range of a polymer surface due to more possible surface chemistry configurations, which is directly a result of having a larger combination of chain morphology and segregation modes within the brush.

EXPERIMENTAL

Materials and Synthesis. Detailed explanation of the grafting from procedure and molecular weight characterization is given elsewhere.[9] Briefly, poly(methyl acrylate) (PMA) (M_w = 505,000 g/mol) was grafted at the first polymerization step, and next poly(styrene-co-2,3,4,5,6-pentafluorostyrene) (PSF) (M_w = 372,000 g/mol) at the second step using the residual amount of the azo - initiator on the silicon substrates. Oxygen was removed from the methyl acrylate (MA) monomer solution in toluene, 5 mol/L, or a mixture of styrene (PS) and 2,3,4,5,6-pentafluorostyrene (FS) in ratio 4:1 wt % in THF, 5 mol/L, and AIBN, 4.4×10^{-4} mol/L) using five freeze-pump-thaw-cycles. The silicon wafers with the chemically attached azo initiator were placed into a reactor with the monomer solution under Argon atmosphere. The reactor was immersed in a water bath (60 $\pm$ 0.1º C) for 12 hours. The silicon wafers were rinsed several times with toluene. The non – grafted polymer was removed by cold Soxhlet extraction in THF for 1 hour. The same procedure was used to graft the second polymer. The non – grafted amount of the second polymer was removed by a hot Soxhlet extraction in THF for 12 hours. Since complete extraction of any ungrafted chains is a critical issue in this type of system, we have extensively studied the extraction and found that layer thickness does not change significantly after 4 hours of extraction time. Grafted amount of the polymers was monitored after each polymerization step with ellipsometry.

Method. The binary brush morphology was altered with exposure to a selective solvent (toluene for PSF and acetone for PMA), and non-selective good (ethyl acetate) and non-selective bad (Nanopure water) for a few minutes, and then rapidly dried under a dry nitrogen flux. Samples were immediately scanned with AFM in air using Dimension 3100 and Multimode microscopes (Digital Instruments, Inc.). An in depth description of scanning parameters, AFM tip characterization, and force mapping procedures are detailed elsewhere.[9] For measurements in solvents, the AFM tip was brought very close (few mm) to the sample and using a micropipette, roughly 40 µL of solvent was placed on to the sample and held in place due to capillary forces between the tip and sample. The binary brush morphology was imaged under the above specified solvent conditions in contact and non-contact mode. Once the solvent was added, the binary brush was allowed to equilibrate with the solvent, which took less than five minutes based on contact angle and AFM analysis, but was allowed longer times to ensure minimal repulsion/attraction with the AFM tip. AFM scanning was very stable after an equilibration time of 20 minutes. Since toluene and acetone evaporate rapidly in air, it was necessary to keep adding solvent on the sample with a micropipette during this period until engagement of the sample with the AFM tip.

RESULTS AND DISCUSSION

AFM imaging revealed a wide range of morphologies and layer thicknesses under different solvents (Figure 1). Additionally, comparison was made between morphology in the wet state, compared with the analogous morphology after exposure to the same solvent with the dry brush. Results indicate that the dry state morphology is indeed associated to the solvated state with similar modes of chain segregation.

Micromapping of the surface elastic properties was carried out to gain an understanding of the vertical reordering in the mixed layer. Based on depth profiling of the elastic modulus, it was observed that vertical layering is greatly enhanced in selective solvent conditions, while a ripple morphology, in which both species are found at the top of the brush, is predominant in non-selective conditions.

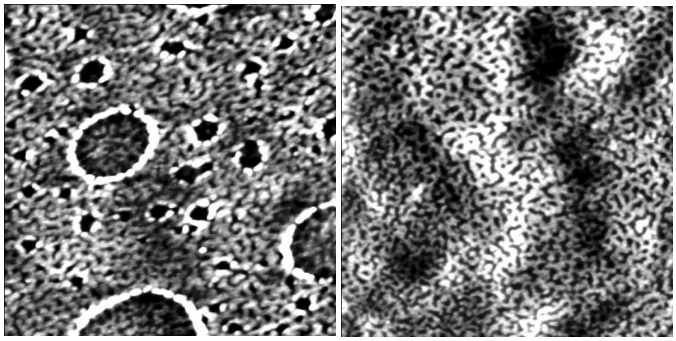

Figure 1. AFM topographical images of the mixed brush while scanning in water (left) and in ethyl acetate (right). Images are 2 x 2 µm, and z – scale is 20 nm.

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