

POLYMER BRUSHES: SURFACE-IMMOBILIZED POLYMERS

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INTRODUCTION: Polymer brushes refer to an assembly of polymer chains that are tethered by one end to a surface or interface.[1] Tethering of the chains in close proximity to each other forces the chains to stretch away from the surface to avoid overlapping. Applications for polymer brushes include colloidal stabilization, tailored surface properties, chemical gates, stimuli-responsive surfaces and cell growth confinement.[2]

METHODS: We have synthesized multiblock polymer brushes using a “grafting-to” technique that first involves the surface immobilization of a polymerization initiator onto a silicate substrate. Most of our brushes have been synthesized using atom transfer radical polymerization (ATRP).[3] We generally use flat substrates for our studies to facilitate surface analytical techniques. We either used freshly cleaned silicon wafers or attenuated total reflectance (ATR) crystals for IR spectroscopy. ATRP is a living radical process that provides the opportunity to perform sequential monomer addition, and thus multiblock copolymer formation. Reactions are conducted under standard ATRP conditions, namely exclusion of oxygen and under inert atmosphere. Our samples have been characterized by X-ray reflectometry and ellipsometry to determine film thickness. Chemical composition at the surface was deduced by IR spectroscopy and X-ray photoelectron spectroscopy. In addition, we routinely used water contact angles to probe surface properties. Because we use free initiator in our polymerizations to maintain control of the polymerization, we generate free polymer in solution. The molecular weight of this free polymer often corresponds to the polymer brush, so we have used gel permeation chromatography to estimate polymer brush molecular weight.

RESULTS: We have synthesized a variety of stimuli-responsive diblock copolymer brushes. Rearrangement (Figure 1) of these diblock copolymer brushes can be induced by heat, block-selective solvents, pH, or ionic strength. A variety of divergent diblock copolymer systems were studied including a hydrophobic–hydrophilic diblock, a hydrocarbon–fluorocarbon diblock, and a hydrocarbon–polyelectrolyte diblock. The extent of rearrangement of these different diblock systems was primarily deduced using water contact angles. We

have found that grafting density and the interaction parameter between the two block segments plays a large role in the rearrangement. If the two blocks are too dissimilar (large interaction parameter), the rearrangement is retarded. We also studied the rearrangement of ABA triblock copolymers. For the Si/SiO₂//polystyrene-*b*-poly(methyl methacrylate), we observed an efficient rearrangement that was accompanied by a unique nanomorphology that we have attributed to pinned micelles.

We have generated metal nanoparticle–brush hybrid systems by making silver and palladium salts of a poly(acrylic acid) block followed by reduction with hydrogen gas. The silver nanoparticle hybrid has the potential to serve as an antimicrobial surface. Further applications may also include patterned reduction to create nanowires.

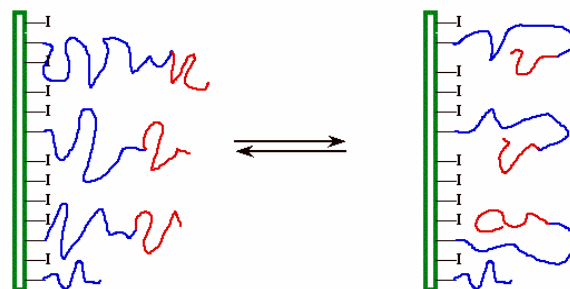


Fig. 1: Proposed rearrangement of diblock copolymer brushes in response to an external stimulus.

DISCUSSION & CONCLUSIONS: We have synthesized a variety of multiblock polymer brushes that show stimuli-responsive behavior. Key features that dictate the rearrangement include grafting density and the interaction parameter between blocks. We have also devised a synthetic route to metal nanoparticle–polymer brush hybrid systems.

REFERENCES: ¹B. Zhao, W. J. Brittain (2000) *Prog. Polym. Sci.* **25**: 677-710. ²J. R  he, *et al.* (1999) *J. Biomat. Sci. Polymer Edn.* **10**:859-74. ³K. Matyjaszewski, J. Xia (2001) *Chem. Rev.* **101**: 2921-90.

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