Effect of Nanoscale Confinement on the Stability of Covalently-grafted, Polymeric Surface Coatings

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As the dimensions of channels in fluidic devices decrease, the importance of the surface properties of the channel walls increases. The progression of fluidic device dimensions from microscale to nanoscale dimensions has brought the fluidics and surface science communities together, and this intersection of disciplines provides opportunities for fundamental scientific insights and breakthrough technologies.

Within the polymer science community, the past two decades has seen the emergence of controlled radical polymerization schemes that enable the synthesis of surface-grafted macromolecules with relatively precise molecular weights and areal grafting densities. These so-called "polymer brushes" comprise polymeric films with nanoscale thicknesses using a variety of functional monomers grafted by one end of the polymer chains to a solid substrate. By extending away from the substrate into the third dimension, these systems achieve higher functional group density than monolayer coatings. Furthermore, the covalent grafting of the polymer chains results in a stable surface coating in liquid environments. However, for certain types of polymer chains in good solvents (e.g., polyelectrolytes in water), degrafting of the covalently grafted chains has been observed, with implications for their application in emerging and existing technologies.

In this presentation, I will provide an introduction to polymer brushes and the behavior of these grafted systems under nanoscale confinement. In doing so, I will introduce the concept of charge regulation in polyelectrolyte brushes, wherein the charge fraction (α) within the brush depends on the areal grafting density (σ) of the brush in addition to the pH of the surrounding fluid. Charge regulation plays an important role in the mechanism of degrafting of weak polyacid brushes in aqueous environments, and I will show that instability of the polyacid brushes increases with decreasing grafting density. I will close with strategies to mitigate degrafting of polymer brushes in case this phenomenon arises in your research.