

404e The Adsorption Mechanisms of Micelle-Forming Polyelectrolyte/Neutral Diblock Copolymers

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This talk will discuss the adsorption kinetics of poly(*t*-butyl styrene)-block-poly(sodium styrene sulfonate) copolymers at solid/liquid interface. Amphiphilic diblock copolymers comprising a polyelectrolyte block and a short hydrophobic tail have long been recognized as excellent anti-flocculation agents, for they can impart a combination of steric and charge stabilization to colloidal systems. Interestingly, self-assembled polyelectrolyte motifs may also realize their full potential in the growing field of microfluidics, where surface properties must be precisely controlled in many applications.

Ideally, in order for self-assembly to be successful, the amphiphilic block copolymer should be designed such that the polyelectrolyte block cannot itself adsorb. Nevertheless, such a condition is often difficult to meet in real situations and may not be dictated by any practical necessity. Moreover, the strong incompatibility between the hydrophobic and polyelectrolyte block often drives micelle formation. If micelles attach to the surface through the corona, the core must be sufficiently mobile to allow post-adsorption relaxation and layer reorganization. Development of the brush structure occurs when the surface density of the anchor blocks becomes sufficiently high to effectively displace adsorbed coronal blocks, leading to an end-tethered configuration.

The precise role that salt plays in governing the adsorption mechanisms of micelle-forming amphiphilic block copolymers, however, can be quite complex. In low salt environments, both micelle formation and surface adsorption are strongly inhibited for similar reasons. As salt is increased, micelles more easily form, however the adsorption of micellar structures leads to strong hysteresis effects in the adsorbing process.

The adsorption kinetics of amphiphilic poly(*t*-butyl styrene)-block-poly(sodium styrene sulfonate) copolymers have been monitored as a function of a monovalent 1:1 salt (sodium chloride) to hydrophobic octadecylsilane (OTS) surfaces and compared to the adsorption kinetics of poly(sodium sulfonate) homopolymer. At salt concentrations below 0.001M NaCl, the initial adsorption rates of the homopolymer and the block copolymer almost coincide. In this regime, the homopolymer reaches a definite plateau in the adsorbed amount in less than 24 hours; however, the block copolymer shows no sign of reaching saturation, even after 1 week of adsorption. Moreover, the block copolymer adsorbs with a trajectory that follows power-law behavior at long times, $\Gamma \sim t^{0.43}$. As the salt concentration is increased, the homopolymer adsorption proceeds more rapidly than the copolymer; at 1.0M NaCl, the homopolymer populates the surface nearly an order of magnitude more quickly than the block copolymer. The discrepancy can be attributed to micelle formation of the block copolymers. In this high salt regime, the block copolymer micelles adsorb logarithmically slow. Simple scaling relationships have been established to understand the qualitative differences between adsorption at low and high salt concentrations.