Spherical and planar neutral polymer brush layers formed by electrostatic co-assembly

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Complex Coacervate Core Micelles (C3M’s) are a novel type of aqueous polymeric micelles which are formed by co-assembly of oppositely charged water soluble blocks. The micellar core consists of a complex coacervate formed by oppositely charged polyelectrolytes and the corona of a layer of neutral brushes (Fig. 1a). The radius of the micelles is typically 20 and 30 nm, whereas the aggregation number ranges between 10 and 100. The micelles can be responsive to salt, pH, and temperature. At a critical ionic strength (between 0.1 and 2 M, depending on the system) the micelles fall apart. C3M’s have several potential applications such as carriers for enzymes, nanoreactors, (targeted) drug delivery, controlled release, antifouling, and contrast agents. The size of the core can be tuned by mixing the micelles with an additional amount of oppositely charged homopolyelectrolytes (C3M-microemulsions). By using two oppositely charged diblock copolymers with chemically different incompatible water soluble neutral blocks the corona is shown to segregate into two distinct hemispheres and so-called Janus micelles are formed. C3M’s are able to adsorb both on hydrophilic and hydrophobic surfaces. Upon adsorption the micelles (usually) attach with the complex coacervate core phase to the surface whereas the neutral coronas form a planar neutral brush layer (Fig. 1b). Depending on the nature of the polymers and the surfaces adsorption of proteins or adhesion of bacteria is (strongly) suppressed by these coatings.

(a) spherical brush
(b) planar brush

Fig. 1 Complex Coacervate Core Micelles (a) in solution and (b) at a surface

Similar layers but with tunable and high neutral brush densities can be obtained by a novel method. First, a charged brush layer is prepared. If we subsequently add a block copolymer with an oppositely charged block and a water soluble neutral block a stoichiometric amount of block copolymer is adsorbed and a neutral polymer brush layer is formed on top of the electrically neutral layer of complexed polyelectrolytes (Fig. 1b with the negative polymer fixed to the surface). The grafting density can be controlled by the length of the charged block and the number of charges in the polyelectrolyte brush. In this way very high brush densities, well over 1 nm$^{-2}$, are obtained. The diblock copolymer can be desorbed again by changing the solution conditions and therefore we call these systems ‘zipper brushes’.