Controlling Structure in Associating Polymer-Surfactant Mixtures

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Associating polymer-surfactant mixtures are used in a wide variety of contexts to induce phase separation, to enhance the viscosity of solutions and/or to general materials with crystalline or liquid crystalline structures. The latter materials include soft materials, based on organic polymers, but also hard materials where the polymer component is achieve by polymerization of, e.g., alkyl silicates. Through the latter route so-called mesoporous inorganic materials may be created. Associating polymer-surfactant pairs include oppositely charged species, but also nonionic couples, often involving surfactant molecules with ethylene-oxide based hydrophilic chains.

A striking and useful characteristic of surfactant systems is the rich variety of structural morphologies that surfactant molecules can produce by self-assembly. The self-assembled aggregates may be spherical, rod-like or sheet-like, and the aggregates may pack with or without long-range order. The resulting structures may be isotropic or anisotropic, compartmentalized or (bi)continuous, crystalline or disordered. All this has consequences for the optical and mechanical properties of the materials, and for the rate of molecular transport within them.

Associating polymer-surfactant systems, including mesoporous inorganic materials, have shown to give rise to the same types of structures as conventional non-ionic or ionic surfactant systems. However, we are only beginning to understand why and how the surfactant-binding polymer molecules affect these structures. This will be the topic of my talk, where I will try to identify molecular mechanisms that should be generally relevant in associating polymer-surfactant mixtures.

Many of the specific examples will be taken from our ongoing systematic studies of “complex salts” of ionic surfactants with polyions as counterions. Here, we have studied the effects of, *inter alia*:

- varying the polyion chain length and charge density
- gradually replacing the polyions with conventional simple counterions (which may be viewed as the reverse of a polymerization reaction)
- varying the surfactant chain length
- changing the surfactant aggregate morphology by introducing uncharged co-surfactants