

Title: The study of the association behaviour of the amphiphilic copolymers in solutions containing low molar compounds by means of computer simulations.

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Abstract

This doctoral thesis focuses on the study of electrostatic self- and co-assembly in complex polymer solutions containing polyelectrolyte (PE) block copolymers together with surfactants, neutral homopolymers, or oppositely charged PEs using the dissipative particle dynamics (DPD). It was shown that the electrostatic self-assembly depends not only on the cooperative interactions of oppositely charged PE chains, but also on the amphiphilicity of PE species or on the polymer block compatibility, among other properties. PEs with incompatible blocks create well-defined core-shell structures, while large ill-defined crew-cut aggregates form from PEs with compatible blocks

In non-stoichiometric mixtures of PEs with incompatible blocks, co-assembled nanoparticles are smaller than in stoichiometric mixtures and are charged. The destabilization of larger aggregates depends on how the PE charge surplus is introduced: the effect is strongest when the density of the surplus PE charge on the PE chains is increased and weakest when the PE chains with the surplus charge is elongated. In all cases, the surplus aggregate charge concentrates on the aggregate core-shell interface, where oppositely charged counterions partly offset the aggregate charge. The magnitude of the aggregate surplus charge is proportional to the surplus PE charge of the system.

It was also shown that the solubilisation of neutral chains into electrostatically co-assembled nanoparticles in non-stoichiometric systems may affect nanoparticle structure, especially in systems containing homopolyelectrolytes. If the solubilised chains are short, they can replace some of the homopolyelectrolytes and even reverse the aggregate surplus charge.

The DPD simulations reproduced the experimental results of the self-assembly of poly(N-isopropylacrylamide) (PNIPAm) modified by carboxyl and dodecyl terminal groups and its co-assembly with cationic surfactant dodecylpyridinium chloride for small amount of added surfactants. The discrepancies for large amount of added surfactant were explained as effects of specific interactions (i.e., redistribution of hydrogen bonds between PNIPAm units and water) that are not included in the DPD model.

Keywords: polyelectrolytes, block copolymers, electrostatic assembly, computer simulations, dissipative particle dynamics