

Physico-Chemical nanomaterials science

A special self-assembly of block copolymers with chemically complementary components

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In the present paper, the results of long-term studies of micellization processes and micellar morphologies in dilute aqueous solutions of the double-hydrophilic A-*b*-B diblock and B-*b*-A-*b*-B triblock copolymers with asymmetric chemically complementary A and B blocks (such as (methoxy)poly(ethylene oxide)/polyacrylamide, (methoxy)poly(ethylene oxide)/poly(acrylic acid) and poly(acrylic acid)/polyacrylamide), which were carried out by static and dynamic light scattering, FTIR and TEM, are summarized.

Two kinds of self-assembly of these copolymers, which depended on the nature, the absolute and relative length of their blocks, are considered. The first one consists in the formation of intramolecular polycomplexes (IntraPCs) within separate copolymer macromolecules because of cooperative interactions (such as hydrogen bonds) between A and B blocks followed by segregation of hydrophobic bound parts of some IntraPCs at $C > CMC$. In the case of asymmetric diblock copolymers and triblock ones containing longer side blocks, such self-assembly results in appearance of the “cut” or “hairy”-type polymolecular micelles with complex “core” and short or developed “corona”, which is formed by surplus (unbound) segments of longer B blocks. Self-assembly process of asymmetric triblock copolymers with longer central blocks produces the “flower”-like micelles with similar complex “core” but alternative “corona” composed of the unbound “loops” of A blocks.

The second kind of a self-assembly consists in the intermolecular complex formation due to cooperative interactions between A and B blocks belonging to different copolymer macromolecules. It develops at $C > CMC$ and leads to emergence of special “needle”-like intermolecular aggregates. Such self-assembly takes place at the weakening A and B block binding.