

# SELF-ORGANIZED NANO-STRUCTURES OF AMPHIPHILIC IONIC COPOLYMERS: RECENT ADVANCES AND CURRENT CHALLENGES

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## ABSTRACT

Spontaneous assembly of amphiphilic molecules in aqueous environment is exemplified by nature as one of the basic ways for self-organization on macro- and super-molecular levels. In the realm of technology, self-assembly at nanometric length scales was explored too: self-organized nanostructures of amphiphilic block copolymers have found diverse applications ranging from biomedicine and agrochemistry to nano-electronics.

We present here an overview of theoretical principles of self-assembly of amphiphilic ionic/hydrophobic block copolymers in aqueous media and focus on selected experiments which demonstrate stimuli-responsive behavior of nano-structures formed by amphiphilic pH-sensitive block-gradient copolymers.

The main emphasis is made on theory of self-assembly of block copolymers containing hydrophobic and pH-sensitive ionic monomer units. We prove that even smooth variation in the pH or ionic strength of the solution may trigger an abrupt response of the system in terms of changing the aggregation state of the self-assembled polymer nano-structures. We demonstrate that variation in the ionic strength may induce different sequences of morphological transitions in self-assembled aggregates. These unusual responsive features are inherently related to the coupling between association of the copolymer molecules into nano-structures and ionization of the pH-sensitive polyelectrolyte blocks.

In experiment, ionic/hydrophobic diblock copolymers often make kinetically „frozen“ micelles. As an elegant way to enhance responsiveness of the aggregates, we suggested to introduce a fraction of pH-sensitive ionic monomer units into the associating hydrophobic block of the copolymers. The Nitroxide-mediated polymerization enabled us to synthesize copolymers, comprising one block of polyacrylic acid and either one or two terminal (associating) blocks with a gradient sequence of styrene and acrylic acid.

Because of presence of both hydrophobic styrene and pH-sensitive acrylic acid co-monomer units, the terminal gradient blocks in di- and triblock copolymers are capable of reversible pH-controlled association in aqueous solutions. The strength of the net cohesive interactions between the terminal gradient blocks depends on the ionization of the acrylic acid co-monomer units which is controlled by pH. In contrast to block copolymers with the same net composition which form “frozen” micelles, the block-gradient copolymers can form “dynamic” micelles capable of response to variation of pH and ionic strength by reversible changes in the aggregation state, as confirmed by DLS and SANS experiments. The pH-triggered association of the triblock copolymers in semi-dilute aqueous solutions gives rise to abrupt and reversible sol-to-gel transition, which is manifested in dramatic growth of zero-shear viscosity and characteristic change in visco-elastic properties of the solution.

## References:

<sup>1</sup>Zhulina, E. B.; Borisov, O.V. *Macromolecules (Perspectives Article)*. **2012**, *45*, 4429.

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