Preface

The spontaneous assembly of amphiphilic molecules in an aqueous environment represents a generic mechanism of self-organization on the supramolecular level exemplified by nature. In the living cell, the process of hierarchical assembly of bio(macro)molecules propagates from the nano- to the mesoscopic level and beyond, giving rise to highly organized structures, each perfectly adjusted for performing specific functions. This self-organization across multiple length scales occurs as an outcome of a delicate balance between a number of attractive and repulsive interactions: electrostatic, hydrophobic, hydrogen bonding, metal coordination, etc., each with its characteristic strength and range.

Recent advances in polymer chemistry, in particular, in controlled radical polymerization, have enabled the synthesis of complex macromolecular architectures with controlled topology, which comprise chemically different (functional) blocks of controlled length in well-defined positions. Block co- and terpolymers, molecular and colloidal polymer brushes, and star-like polymers present just a few typical examples. Furthermore, miktoarm stars, core-shell stars and molecular brushes, etc. exemplify structures where chemical and topological complexity are combined in one macromolecule.

Significant progress has been made in terms of understanding the self-assembly of amphiphilic diblock copolymers in selective solvents. In aqueous solutions, the assembly is typically driven by hydrophobic attraction between associating blocks and gives rise to diverse nanostructures (micelles, vesicles) and mesophases. Theory has established relationships between the macromolecular architectures of ionic/hydrophobic diblock copolymers and the equilibrium morphologies of the self-assembled aggregates. Unusual responsive properties of micelles with pH-sensitive coronas were predicted on the basis of the concept of coupling between ionization of the polyelectrolyte block and the aggregation state of the copolymer molecule and they have been recently observed in experiments. A multitude of experimental techniques, including radiation scattering, fluorescence spectroscopy, electron and atomic force microscopy, etc., have been used for structural and dynamic characterization of the block-copolymer self-assembly in solution and at liquid–solid and liquid–air interfaces.

Self-assembled structures of amphiphilic copolymers have been extensively explored in biomedicine as vectors for targeted delivery of drugs and biological molecules (enzymes, nucleic acids), in biomaterials engineering (antifouling surfaces), biosensors, etc. Further applications include food industry and agrochemistry, uptake and pre-concentration of toxic organic compounds and heavy metal ions in water treatment, molecular templates for nano-electronic devices. Many water-based industrial formulations include polymeric amphiphiles that aggregate and co-assemble with other macromolecules, nanoparticles and surfactants to form nano-aggregates, and different types of mesophases and structures at interfaces. An important requirement for the biomedical applications are pronounced stimuli-responsive properties of the polymeric nano-structures, that is ability of a triggered response to smoothly varied external conditions (e.g., tiny variations in temperature or pH) or recognition of weak specific stimuli (e.g., trace concentrations of biologically active or toxic compounds).

The electrostatic attraction between oppositely charged ionic macromolecules and (bio)nanocolloids is an appealing alternative mechanism for building up functional nano-assemblies in aqueous media. The association of linear polyelectrolytes in solutions or at charged interfaces leads to interpolyelectrolyte complexes or polyelectrolyte multilayers. The strength of attractive electrostatic interactions can be easily tuned by the pH or ionic strength of the solution. Hence, electrostatically assembled structures exhibit pronounced stimuli-responsive features. The enormous diversity of possible combinations of co-assembling components, including oppositely charged ionic polymers, nucleic acids and proteins, metal/ligand complexes, and inorganic nano-particles, opens a fascinating perspective of the possibility to use this mechanism to design novel functional materials based on supramolecular and supracolloidal assemblies.

Furthermore, such advanced applications as (bio)nanoreactors or molecular templates require progressing beyond the most elementary forms of self-organization and generic types of copolymer nanostructures. We need to explore routes of self- and co-assembly of macromolecules into non-centrosymmetric multi-compartment supramolecular nano-assemblies. For example, construction of nanoreactors for enzymatic (cascade) reactions requires immobilization of multiple proteins in close proximity to each other in well-segregated (protective) environments. Such enzyme cascades are very promising in biotechnological applications. The development of pathways for fabrication of well-defined multi-domain nano-structures via the spontaneous assembly of elementary macromolecular building blocks represents one of the future challenges in supra-macromolecular chemistry.

Co-assembly of amphiphilic and bis-hydrophilic block copolymers with oppositely charged polyelectrolyte blocks gives rise to sophisticated nanostructures with compartmentalized core or corona domains. The combination of nano-sized compartments that differ in polarity and composition within one colloidally stable polymeric nanostructure is promising in the development of novel, highly effective, multifunctional polymeric reagents for wastewater treatment (e.g., an one-stage removal of organic impurities and heavy metal ions from aqueous environment) as well as smart nano-containers capable of incorporation of various physiologically active compounds, e.g., proteins and nucleic acids. Co-assembly of two ionic-neutral block copolymers can lead to surface-compartmentalized polymer-based Janus nanoparticles ("Janus micelles") with two chemically different "faces" exposed to the surrounding environment. Janus micelles with coronas solvated in a common good solvent (e.g., water), but laterally segregated, are promising as they can selectively incorporate different enzymes or metal nano-particles possessing catalytic activity in segregated compartments, thus offering opportunities for (bio)catalytic cascades. Janus micelles are intrinsically highly surface active; their use may cut down the use of conventional surfactants with concomitant environmental impact.

Biomedical applications strongly require nanostructures based on the assembly of amphiphilic macromolecules comprising functional blocks of biological origin (peptides, oligo- or polynucleotides, polysaccharides) or their synthetic analogs. A novel class of biohybrid copolymers comprising a synthetic block conjugated to a polypeptide or polynucleotide block has attracted considerable attention. Their self-assembly gives rise to diverse ordered structures in aqueous media and at solid–liquid interfaces. The ability of biopolymer blocks to take part in specific interactions (e.g., ligand–receptor, DNA hybridization, etc.) with target molecules opens up a fascinating perspective for the design of novel generations of label-free diagnostic systems, or of smart vector systems that can deliver drugs or biologically active molecules on the basis of self-assembled bio-hybrid structures.

Based on these considerations, the European Union funded a Marie Curie Research Training Network "Self-Organized Nanostructures of Amphiphilic Copolymers (POLYAMPHI)." This network, consisting of 14 research teams from 7 European countries, worked successfully from 2004 to 2008. Some of the results obtained in these collaborations are presented in these two volumes, supplemented by chapters dealing with additional aspects of the topic. Thus, we present a comprehensive overview of the state of the art in experimental research and theory of self-organization via self- and co-assembly of amphiphilic or hydrophilic ionic (macro)molecules in aqueous solutions and at interfaces.

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