ELECTROSTATIC MICELLIZATION OF DOUBLE HYDROPHILIC BLOCK COPOLYMERS

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In the context of designing functional silica based mesoporous materials [1], the micellization of double hydrophilic block copolymers (DHBC) in the presence of an oppositely charged polyelectrolyte has been studied. So-called micellar interpolyelectrolyte complexes [2] or complex coacervate core micelles form upon electrostatic complexation in a narrow range of pH compatible with silica condensation. Polyion complex (PIC) micelles proved to be very versatile structuring agents that can be eluted by pH shift rather than calcined in order to reveal the porosity of the material. The copolymers are possibly recovered and reused in several synthesis cycles [1]. Moreover PIC micelles allow one pot preparation of drug-loaded porous materials [3]. Fine control of the structural characteristics of the porous materials and their functional properties calls for a better understanding of the physical chemistry of the interpolyelectrolyte complexes.

Series of poly(ethylene oxide)-*b*-poly(acrylic acid) (PEO-*b*-PAA) and poly(acrylamide)-*b*-poly(acrylic acid) (PAM-*b*-PAA) have been synthesized by controlled radical polymerization (atom transfer radical polymerization ATRP, and reversible addition-fragmentation chain transfer RAFT polymerization). These double hydrophilic block copolymers have been comicellized with polyamines such as oligochitosans (OC) or cationic antibiotics. PIC micelles have been characterized by light and X-ray scattering and consist of core-corona objects with typical size ranging from 10 to 50 nm. To infer on the composition of the core, the phase diagrams of mixtures of sodium PAA and oligochitosan have been established. Water contributes to 45 to 65% of the volume of the core and its activity is a parameter easily at hand to tune the porosity of the final silica material.

The electrostatic complexation has been monitored by conductimetry and potentiometry using specific electrodes.The release of the small ions upon ion pairing of the polyelectrolyte blocks is clearly observed which provide information on the kinetics of micellisation.

Finally, evidences have been obtained for comicellisation of both DHBC PEO-*b*-PAA and PAM-*b*-PAA with low polymerization degree. The degree of segregation of the neutral blocks PEO and PAM in the corona is currently studied by capillary electrophoresis and TEM after selective staining.

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