Stimuli-responsive multicompartment micelles from amphiphilic ABC block terpolymers

Eva Betthausen,1,* Felix Schacher,2 and Axel H. E. Müller1

1Macromolecular Chemistry II, University of Bayreuth, D-95440 Bayreuth, Germany
2Group of Inorganic, Macromolecular and Materials Chemistry, School of Chemistry, University of Bristol, Bristol BS8 1TS, United Kingdom
*e-mail: eva.betthausen@uni-bayreuth.de

Multicompartment micelles are self-assembled structures with the ability to combine several properties or functionalities in close proximity. We recently investigated the formation of such structures in aqueous solution [1]. Here, we present stimuli-responsive multicompartment micelles prepared from polybutadiene-block-poly(tert-butyl methacrylate)-block-poly(N,N-dimethylaminoethyl methacrylate) (PB-b-PtBMA-b-PDMAEMA) triblock terpolymers. In aqueous media, the solubility of the micelles can be triggered by two external stimuli, pH and temperature, due to the responsive PDMAEMA corona. The response of the micellar aggregates to these stimuli was investigated via both dynamic light scattering (DLS) and cryogenic transmission electron microscopy (cryo-TEM).

These materials can be further modified by hydrolysis of the PtBMA block to poly(methacrylic acid) (PMAA). The resulting ampholytic terpolymers form micellar aggregates, where both size and architecture can be tuned by variation of the pH. A cryo-TEM micrograph of these micelles in aqueous solution at pH 5 is shown in Figure 1A. Subsequent quaternization of PDMAEMA renders core-shell-corona micelles with a positively charged corona. At high pH values, the shell consists of an intramicellar interpolyelectrolyte complex (IPEC) between quaternized PDMAEMA and PMAA. These micelles were employed as precursors for the complexation with different anionic polyelectrolytes and the results are compared to earlier studies on corresponding systems containing negatively charged micelles and cationic polyelectrolytes [2]. IPEC formation with double hydrophilic diblock copolymers like poly(acrylic acid)-block-poly(N-isopropylacrylamide) (PAA-b-PNIPAAm) allowed the preparation of complex micellar aggregates (see Figure 1B) which exhibit temperature responsive behavior.

Figure 1: Cryo-TEM micrographs of multicompartment micelles from PB-b-PMAA-b-PDMAEMA terpolymers in aqueous solution (A) and IPEC particles obtained by complexation with PAA-b-PNIPAAm (B).