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Structural Properties of Micelles formed by Telechelic Pentablock Quaterpolymers with pH-responsive Midblocks and Thermoresponsive End Blocks in Aqueous Solution

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Stimuli-responsive polymers are of interest for applications in drug delivery or tissue engineering. Telechelic block copolymers, where a pH-responsive midblock is end-capped by thermo-responsive end blocks, have great potential due to their ability to form highly tunable micelles or hydrogels.

In the present work, micelles formed by the telechelic pentablock quaterpolymer $P(\text{BuMA8-co-TEGMA8})\text{-}b\text{-PDMAEMA50-}b\text{-PEG46-}b\text{-PDMAEMA50-}b\text{-P}(\text{BuMA8-co-TEGMA8})$ in dilute aqueous solution are investigated as a function of temperature and pH. The endblocks are statistical copolymers of the thermo-responsive TEGMA (triethylene glycol methyl ether methacrylate) and the hydrophobic BuMA (n -butyl methacrylate). The intermediate PDMAEMA poly(2-(dimethylamino)ethyl methacrylate) block is a weak cationic polyelectrolyte. The hydrophilic poly(ethylene glycol) (PEG) block ensures water-solubility. Using small-angle neutron scattering (SANS) at KWS-1, FRM II, we found that the micelles have a spherical core and a strongly swollen corona. Their aggregation number and size depend sensitively on the pH and temperature. At low temperatures, some polymers form dangling ends, especially at low pH values. With increasing temperature, dangling ends transform into loops at high pH values, while the dangling ends are more abundant at low pH values. In summary, the micelles show complex responsive behavior, including crosstalk between the stimuli.

Author: Mr JUNG, Florian A. (Technische Universität München)

Co-authors: Ms PANTELI, Panayiota A. (University of Cyprus); KO, Chia-Hsin (E13, Physik-Department, Technische Universität München.); KANG, Jia-Jhen (Technical University of Munich); BARNSLEY, Lester C. (Jülich Centre for Neutron Science); Prof. TSITSILIANIS, Constantinos (University of Patras); Prof. PATRICKIOS, Costas S. (University of Cyprus); PAPADAKIS, Christine M. (Technische Universität München, Physik-Department, Fachgebiet Physik weicher Materie)

Presenter: Mr JUNG, Florian A. (Technische Universität München)

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