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Structural Properties of Micelles formed by Telechelic Pentablock Quaterpolymers with pH-responsive Midblocks and Thermo-responsive 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(nBuMA$_8$-*co*-TEGMA$_8$)-*b*-PDMAEMA$_{50}$-*b*-PEG$_{46}$-*b*-PDMAEMA$_{50}$-*b*-P(nBuMA$_8$-*co*-TEGMA$_8$) 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 nBuMA (*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 they are stabilized at low pH values. In summary, the micelles show complex responsive behavior in dependence on temperature and the pH value.

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