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Effects of polymer block length asymmetry and temperature on the nanoscale morphology of thermoresponsive double hydrophilic block copolymers in aqueous solutions

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Nanoscale assemblies in water of novel thermoresponsive and double hydrophilic poly(N-isopropylacrylamide)-block-poly(oligo ethylene glycol methyl ether acrylate) (PNIPAM-b-POEGA) copolymers have been investigated by synergy of Fourier transform infrared (FTIR) spectroscopy and small angle neutron scattering (SANS) experiments. By focusing on the influence of temperature as external stimulus and block length asymmetry, differences in morphologies and molecular hydration characteristics of two PNIPAM-b-POEGA diblock copolymers were resolved. With increasing temperature, the macromolecular structures undergo block-length dependent transformations from hierarchical assemblies to more well-defined spherical morphologies as evidenced by SANS. Differences in the strength and/or amount of hydrogen bonding and hydrophobic interactions lead to distinct morphological transformations expressed by variations in cluster compactness and hydration. In these assemblies of PNIPAM-b-POEGA with the short PNIPAM block, the methyl side group hydration, as evidenced by FTIR, sensitively depends on the temperature increase at temperatures even beyond the nominal volume phase transition temperature. For both blocks, the evolution of the amide I band reflects that solvent-polymer interactions are still favorable even at the highest temperatures. The understanding of these assemblies provides ground for optimization of these scaffolds for drug encapsulation protocols.

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