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Micellization of pH-responsive Amphiphilic Diblock Copolymers in Aqueous Media and the Formation of Metal Nanocrystals¹

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External-stimuli responsive block copolymers, usually known as double-hydrophilic copolymers, respond to changes in their environment such as pH, temperature and salt concentration and undergo micellization in aqueous media. Micellization induced by controlling the solution pH is advantageous for certain applications in particular when fully hydrophobic cores are required. A category of such systems comprise a pH-sensitive (weak) basic or acidic block that forms the micelle core surrounded by a corona formed by a neutral hydrophilic block. In this work we investigate the micellization behavior and the metal-nanoparticle formation in poly(2-(diethylamino)ethyl methacrylate)-block-poly(hexa(ethylene glycol) methacrylate), PDEAEMA-b-PHEGMA, amphiphilic block copolymers in aqueous media. The hydrophobic PDEAEMA block is pH-sensitive: at low pH it can be protonated and it becomes partially or completely hydrophilic, leading to molecular solubility, whereas at higher pH micelles are formed; the behavior is studied by dynamic light scattering, ¹H-NMR and atomic force microscopy. The micelles consist of a PDEAEMA core and a PHEGMA corona, where the core can dissolve metal compounds due to coordination. In all these micellar nanoreactors, metal nanoparticles nucleate and grow upon reduction with sizes in the range of a few nanometers as observed by transmission electron microscopy whereas X-ray diffraction verifies their nanocrystalline structure. These particles exhibit significantly enhanced catalytic properties for hydrogenation and oxidation reactions.

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