

INDUCED MICELLIZATION BY INTERACTION OF DOUBLE HYDROPHILIC BLOCK COPOLYMERS WITH METAL COMPOUNDS

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Hybrid micelles of sodium (sulfamate-carboxylate)isoprene/ethylene oxide double hydrophilic diblock copolymer¹ and CdS nanoparticles (SCIEO-2/CdS) were prepared according to the following protocol: the SCIEO-2 was dissolved in water, acidified with a few drops of HCl. A weighted amount of cadmium acetate, Cd(Ac)₂, was added to the polymer solution under stirring for 24h. The amount of Cd(Ac)₂ was calculated according to the desired proportion of acidic groups (SO₃H and COOH), present on the polymer chain, to Cd²⁺ ions (molar ratios 1:1 and 2:1). The solution was subsequently heated to approximately 80°C and thioacetamide aqueous solution was slowly added drop wise. During heating, H₂S is formed by the thermal decomposition of thioacetamide and serves as a sulfur source (S/Cd molar ratio was kept at 2). The solution acquired a stable yellowish to orange colour, depending on the CdS content, in less than 2h. Then it was cooled at room temperature.

A number of characterization techniques, including fluorescence correlation spectroscopy (FCS), steady-state fluorescence spectroscopy, UV-vis spectroscopy (UV-vis), dynamic light scattering (DLS), atomic force microscopy (AFM) and transmission electron microscopy (TEM) were employed to characterize the prepared nanoparticles, both CdS and hybrid micelles. Upon addition of cadmium ions Cd²⁺ in the solution of the polymer in water, a solvent for both blocks, micelles are formed due to the complexation of Cd²⁺ with SO₃⁻ and COO⁻ from SCI units. The induced micelle core is composed of CSI/Cd²⁺ clusters, and the shell is composed of polyethylene oxide blocks. Therefore the precursor ions are confined in the micelles cores, resulting in a nanoreactor. Concomitantly with the introduction of sulfane, semiconductor CdS nanocrystals are formed. The resulting nanoparticles are stabilized by the interaction between SCI units with the surface of the CdS nanocrystals. UV-vis absorption spectra and TEM images show that larger CdS nanoparticles are produced at SO₃⁻, COO⁻/Cd²⁺ molar ratio 2:1.^{2,3} Hydrodynamic radii (R_H) of hybrid micelles were determined by DLS (90.2nm and 24.6nm) and FCS (57.4nm and 13.7nm) measurement at different SO₃⁻, COO⁻/Cd²⁺ molar ratios 1:1 and 2:1, respectively. Some differences in R_H were observed as expected, since the z-average and number-average diffusion coefficients were measured. The AFM images show primarily spherical particles with some secondary aggregation, towards worm-like structures, these agree with results achieved from DLS and TEM.

References

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