Stimuli-Responsive Magnetite Nanoparticle Monolayers: Hydration and Conformational Changes of the Copolymer Shell

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Interfacial properties of copolymer-capped iron oxide nanoparticles, recently developed and described as promising nanotools for biomedical applications, have been investigated at the air/water interface. These Fe₃O₄ NPs, capped with catechol-terminated random copolymer brushes of 2-(2-methoxyethoxy) ethyl methacrylate (MEO₂MA) and oligo(ethylene glycol) methacrylate (OEGMA), in different molar fractions, proved to be surface active. Their behaviour was studied at the air/water interface, below and above their lower critical solution temperature (LCST). The NP layers have been characterized in situ by compression–expansion isotherms, infrared reflection–absorption spectrometry, X-ray fluorescence and X-ray reflectivity, as well as by AFM and transmission electron microscopy after being transferred onto solid support. Only above the critical surface pressure (πc) the interfacial behaviour of the NPs is different: below the LCST (low dispersibility in the aqueous subphase) and above the LCST (lack of dispersibility in the subphase, high affinity for hydrophobic interactions, and agglomeration at the interface). Conformational transitions of the copolymer from pancake to brush and mushroom-like structures are the key factors of the stimuli-induced behaviour of the NPs at the air/water interface. These conformational changes of the copolymer shell are due to the ability of the ethylene oxide units to form hydrogen bonds with the water molecules of the subphase or being trapped inside the mushroom-like structure. The red shift of the C–O–C band accompanied by the blue shift of the CH₂ scissor band gives comparative information about the degree of hydration of the ethylene oxide groups for the different conformations.

Schematic representation of the interfacial behaviour of the Fe₃O₄ NPs dictated by the conformational changes of the copolymer: (A) Below the critical pressure: pancake-like conformation. Above the critical pressure: (B) Below the LCST: co-existence of pancake-like and brush conformation. (C) Above the LCST: mushroom-like structure.