Direct Visualisation of a Self-Organised Multilayer Film of Low T_g Diblock Copolymer Micelles

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Abstract

The first *in situ* proof of the presence of true micelle structure within alternating layers of a self-assembled cationic and anionic diblock copolymer micelle-micelle multilayer film on a silica substrate is presented using atomic force microscopy. Assembled at pH 9 in aqueous solution, the 'cationic corona' micelles used in the multilayer were 10% statistically quaternised poly(2-(dimethylamino)ethyl methacrylate)-*b*-poly(2-(diethylamino)ethyl methacrylate) (10qPDMA-*b*-PDEA) and the 'anionic corona' micelles used were poly(methacrylic acid)-*b*-poly(2-(diethylamino)ethyl methacrylate), (PMAA-*b*-PDEA).

The presence of micelles is unambiguously confirmed within each layer. Moreover, interaction force curves recorded normal to each layer indicate substantial adhesive forces between adjacent layers. The electrostatic nature of this interaction provides direct evidence for the electrostatic mode of self-assembly. Unlike in previous reports of micelle-micelle multilayers, the diblock copolymers used in this study have sub-ambient T_g values, thus the micelles are soft and may well undergo some exchange with unimers in bulk solution during the construction of the multilayer film. The high water content and stimulus-responsive nature of such multilayer films together with their mechanical resilience augur well for their future application.