Surface Self-Assembly and Properties of Monolayers Formed by Reverse Poly(butylene oxide)-poly(ethylene oxide)-poly(butylene oxide) Triblock Copolymers with Lengthy Hydrophilic Blocks - DTU Orbit (09/11/2017)

Surface Self-Assembly and Properties of Monolayers Formed by Reverse Poly(butylene oxide)-poly(ethylene oxide)-poly(butylene oxide) Triblock Copolymers with Lengthy Hydrophilic Blocks

The surface behavior and properties of several reverse poly(butylene oxide)-poly(ethylene oxide)-poly(butylene oxide) block copolymers, $BO_8EO_{90}BO_8$, $BO_{12}EO_{227}BO_{12}$, $BO_{14}EO_{378}BO_{14}$, $BO_{20}EO_{411}BO_{20}$, and $BO_{21}EO_{385}BO_{21}$ at the air/water interface have been analyzed by drop tensiometry, Langmuir film balance, and atomic force microscopy (AFM). The kinetic adsorption process of block copolymer chains at the air/water interface is a diffusion-controlled process, at short times. Structural rearrangements of the copolymer backbones are progressively more important as the adsorption carries on. The adsorption layers formed at the interface display evident solid-like behavior in the whole range of frequencies analyzed even at the lowest frequencies used probably as a result of the interconnection between hydrophobic ends of polymeric chains. All the copolymer display adsorption isotherm profiles are composed of four different regions in which the different characteristic regimes ("pancake, mushroom", "brush", and collapsed conformations) are observed. The differences observed between copolymers come from the different block lengths and, hence, hydrophilic to hydrophobic (EO/BO) block ratios. In this regard, it is observed that the shortest copolymer, $BO_8EO_{90}BO_8$, having the lowest block ratio, displays the complete adsorption profile at much lower areas per molecule and within the narrowest range. Images of copolymer films transfer at solid substrates at determined transfer pressures enable having direct information about the structure and size of formed structures. In this manner, relevant differences were observed between copolymers with the shortest blocks ($BO_8EO_{90}BO_8$, $BO_{12}EO_{227}BO_{12}$) and those with the longest ones ($BO_{20}EO_{411}BO_{20}$ and $BO_{21}EO_{385}BO_{21}$). In this regard, surface circular micelles were observed for the former at low surface transfer pressures, evolving to continent-like structures first and then dewetted structures as the transfer pressure increases. Conversely, for $BO_{20}EO_{411}BO_{20}$ and $BO_{21}EO_{385}BO_{21}$ copolymers micelle formation is noted at lower transfer pressures than the shortest counterparts, and the formed micelles appear to be elongated, interconnected and with larger thickness. As the transfer pressure increases, attractive micellar interactions are enhanced and then-lead to formation of a dense network of interconnected micelles, first followed by an evolvement to continent-like and dewetted structures, as also observed for $BO_8EO_{90}BO_8$, $BO_{12}EO_{221}BO_{12}$ copolymers.

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