Surface Structure of Thin Films of Multifunctional Ionizable Copolymers

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Phase segregation results in a rich variety of structures in co-polymers where interfacial forces often dominate the structure of thin films. Introduction of ionizable segments often drives the formation of compounded structures with multiple blocks residing at the interfaces. Here we probe thin films, 40-50nm, of an A-B-C-B-A co-polymer where C is a randomly sulfonated polystyrene with sulfonation fractions of 0, 26 and 52 mole %, B is poly (ethylene-r-propylene), and A is poly (t-butyl styrene) as the sulfonation level and temperature are varied using Neutron Reflectivity AFM, and surface tension measurements. As cast films form layers with both hydrophobic blocks dominating the solid and air interfaces and the ionizable block segregating to the center. Following annealing at 170°C, above Tg of styrene sulfonate, the films coarsen, with surface aggregation dominating the structure, though interfacial regions remain dominated by the hydrophobic segments. We show that in contrast to non-ionic co-polymers, formation of micelles dominated the structure of these ionic structured films.

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