

Block Copolymer Self-Assembly Involving Different Length Scales

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1. INTRODUCTION

The presence of different length scales in block copolymer-based supramolecules and linear multiblock copolymers results in hierarchical structure formation. Due to the comblike molecular architecture of the supramolecules, obtained by hydrogen bonding short chain amphiphiles to one of the blocks of di- and triblock copolymers, the short-length-scale ordered domains usually orient perpendicularly with respect to the large-length-scale ordering.[1] Characteristic applications of such systems exploit the straightforward preparation of nanoporous templates by dissolving the amphiphiles after the self-assembly process. For two-length-scale linear multiblock copolymers, where one or two long end-blocks are attached to a multiblock consisting of relatively short diblocks, the relative orientation is usually parallel.[2]

2. RESULTS

During this presentation new experimental and theoretical developments concerning the self-assembly in the above mentioned classes of systems will be discussed. We show that in thin films of supramolecules consisting of diblock copolymers of polystyrene (PS) and poly(4-vinyl pyridine) (P4VP), with the latter block hydrogen-bonded to pentadecylphenol (PDP), PS-*b*-P4VP(PDP), hierarchical terrace formation is observed with the short-length-scale order being parallel to the large-length-scale due to the favorable interaction of PDP with substrate and free interface.[3] Although the PS-*b*-P4VP(PDP) supramolecules system, due to the presence of PDP, usually is in the intermediate segregation regime, the gyroid morphology with P4VP(PDP) forming the continuous networks has never been obtained despite considerable efforts. For template applications this morphology is most interesting since the relative orientation of the domains (e.g. cylinders) with respect to the film surface plays no role. This morphology was finally achieved by synthesizing PtBOS-*b*-PS-*b*-P4VP triblock copolymers, containing an additional poly(*tert*-butoxystyrene) (PtBOS) block. PtBOS-*b*-PS-*b*-P4VP(PDP) supramolecules with less than stoichiometric amounts of PDP (with respect to 4VP) self-assembled in the bicontinuous double gyroid morphology with P4VP(PDP) network channels.[4] Such systems are currently employed as templates to create nanoporous metal actuators. In two-length-scale linear multiblock copolymers lamellar-in-lamellar self-assembly with the different layers being oriented perpendicularly was recently observed by Bates and co-workers.[5] If time permits, a theoretical analysis of these kinds of systems addressing this and other aspects, e.g. the number of “thin” layers within a “thick” layer in relation to the number of blocks of the multiblock, will be presented.[6]

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