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Self-Assembly of Monolayer and Multilayer Films of Spherical-Domain Diblock Copolymers¹ EDWARD J. KRAMER, University of California, Santa Barbara

Self-assembly of block copolymers in thin films can yield templates for nanolithographic patterning of substrates on very small length scales as well as ordered multilayer structures for membrane and electronic applications. On a fundamental level these thin block copolymer melts raise many interesting questions about self-assembly in 2D and how the transition from 2D to 3D occurs as the film is increased in thickness. To answer these, scattering techniques such as grazing incidence small angle X-ray scattering (GISAXS) can be a very useful complement to the normal imaging techniques of AFM, SEM and TEM, but in combination with self-consistent field theoretic (SCFT) simulations, these become even more powerful. I highlight one such set of questions, how the packing of spherical block copolymer domains confined to a thin film changes as the thickness of the film is increased layer by layer of spheres, as a concrete example of the usefulness to this combined approach and how the SCFT methods pioneered by Glenn Fredrickson and his colleagues have profoundly influenced experimental polymer physics. Using GISAXS we find hexagonal symmetry in films 1-4 layers thick. Stacking in films 1-4 layers thick is close-packed AB, ABA and ABAB. At 5 layers, the hexagonal symmetry breaks to form an orthorhombic phase, characterized by second/first nearest-neighbors a_1/a_2 and lattice angle φ . As the number of layers is increased, a_1 and φ increase continuously to approach that for BCC (110) planes. From measurements collected above and below the critical angle of the polymer, the structure is uniform throughout the depth of the film. SCFT calculations provide a semi-quantitative description of the transition and the insight that it is a consequence of competition between the optimal HEX packing at the film surfaces with the preferred BCC (110) inner layer packing in the bulk.

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