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Thickness Dependent Packing Symmetries of Spherical-Domain Block Copolymer Multilayers G.E. STEIN, E. COCHRAN, G.H. FREDRICKSON, E.J. KRAMER, UCSB, X. LI, J. WANG, ANL — The packing of spherical block copolymer domains confined to a thin film is investigated with grazing-incidence small angle x-ray scattering. Whereas the equilibrium structure of a monolayer is hexagonal (HEX), and that of the bulk is body-centered cubic (BCC), we find a remarkably complex transition from 2D to 3D packing as a function of film thickness. Films 1-3 layers of spheres thick have close-packed hexagonal symmetry. At four layers the hexagonal symmetry breaks to form an orthorhombic phase, characterized by a second-to-first nearest-neighbor distance ratio $a_1/a_2 = 1.08$ with an angle $\phi = 57^\circ$ between $\vec{a}_1$ and $\vec{a}_2$. As the number of layers is increased from 4 to 23, a_1/a_2 increases monotonically to 1.17, and ϕ decreases monotonically to 54.2°, a structure similar to the stacking of BCC (110) planes. From measurements above and below the polymer critical angle, we determine that all phases are uniform throughout the depth of the film. These results are interpreted in the context of a Landau-type theory, using SCFT calculations to demonstrate the competition between the packing preferred in the bulk with that at the interfaces.

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