Self-Assembly of Multilayer Films of Spherical-Domain Diblock Copolymers

Gila E. Stein[1], Edward J. Kramer[1], Xuefa Li[2], and Jin Wang[2]

[1]*University of California, Santa Barbara, CA U.S.A.;* [2]*Argonne National Laboratory, Argonne, IL U.S.A.*

Introduction

It is well established that highly asymmetric block copolymers forming spherical microdomains pack in the body-centered cubic (BCC) lattice in bulk, but adopt a hexagonal (HEX) arrangement as a monolayer. The BCC symmetry in 3D and the HEX symmetry in 2D alleviate packing frustration by minimizing thickness variations in the majority domain, which must stretch to fill the interstitial space.[1,2] However, the transition from 2D to 3D is largely unexplored. The structure in thick films (>50 layers) of asymmetric block copolymers is consistent with stacking of BCC (110) planes.[3] The (110) plane of the BCC lattice is the closest-packed and this preferred orientation minimizes chain stretching along the free and substrate interfaces. In this paper, we present the first comprehensive study of the transition from HEX symmetry in 2D to BCC symmetry in 3D, using grazing-incidence small angle x-ray scattering (GISAXS) to measure the structure in films 1-23 layers thick. We find that the transition from HEX in 2D to BCC in 3D is in fact mediated by the formation of a structure similar to stacking of BCC (110) planes, but the symmetry changes continuously with increasing film thickness over the range of n=4-14 layers. In films thicker than 14 layers, the structure is consistent with stacking of BCC (110) planes.

Methods and Materials

Polymer System: Poly(styrene-*b*-2vinylpyridine) (PS-PVP) was synthesized via anionic polymerization. The polydispersity index is 1.04, the overall degree of polymerization is N=626, and the composition is 12% PVP by volume. The morphology is spherical domains of PVP in a PS matrix. At 220°C, the bulk morphology is BCC with a nearest-neighbor distance of 29nm.

Sample Preparation: Films of PS-PVP between 1 and 23 layers thick were prepared by spin-casting from toluene solutions (1-5wt%) onto 2in diameter, 5mm thick silicon substrates. Samples were annealed under high vacuum (10^{-7}*Torr*) according to three thermal profiles: (1) A short anneal at 240°C followed by an isothermal anneal at 220°C for 3 days; (2) An isothermal anneal at 220°C for 3 days; and (3) Slow cooling from the bulk ODT of 280°C followed by an isothermal anneal at 220°C for 3 days.

GISAXS: The GISAXS measurements were completed on two separate synchrotron X-ray beam lines at the Advanced Photon Source that operate at E = 12keV and 7.5keV. The incident angle was varied about the critical angle of the polymer $\alpha_{C,P}$, producing controlled penetration depths ranging from 20nm (top layer of spheres) up to the full film thickness. The diffracted intensity was recorded with a 2D MAR-CCD detector, where each point along the detector marks a diffraction angle $(2\Theta,\alpha_f)$. The peak positions in $(2\Theta,\alpha_f)$ coordinates are measured from the GISAXS patterns by performing line integrations at fixed α_f, subtracting the background, and fitting the maxima in intensity with Voigt functions. Within the small-angle approximation, the magnitude of the in-plane scattering vector is $q_{par} \approx k2\Theta$, where k is the wavevector modulus $2\pi/\lambda$.

Data Analysis: The lattice symmetry is calculated from the GISAXS measurements by fitting the positions of the in-plane diffraction peaks to a 2D model, defined by lattice vectors $a_1=\{a_1\cos\varphi,\ a_1\sin\varphi\}$ and $a_2=\{0,a_2\}$. This model describes the HEX lattice when $a_1/a_2=1$ and φ=30°, and the BCC (110) plane when $a_1/a_2=1.155$ and φ=35.3°. Analysis of the out-of-plane scattering is more complex, because effects such as refraction at the interfaces, multiple reflections from the substrate, and standing waves inside the film need to be considered. Rather than fit the out-of-plane data to a model, the position of stacked layers is determined by assuming a lattice basis, simulating the scattering, and comparing the simulations with the experimental data. Simulations are based on the distorted-wave Born approximation, (DWBA) which allows one to calculate the amplitudes of the reflected and transmitted waves from dynamic theory, but treats scattering from the spheres kinematically.[4,5] Three bases describing an FCC stacking (*ABC*), an HCP (*ABA*) stacking, and a BCC-like stacking of (110) planes (*ABA*) were evaluated to try to fit the data.

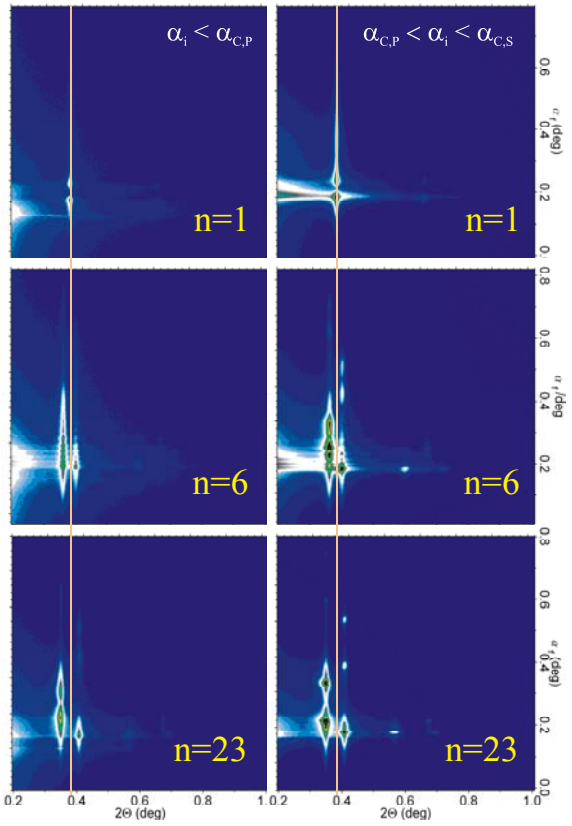

Figure 1. *GISAXS measurements (E=7.5keV) for films 1,6, and 23 layers thick. LEFT: Measurements collected below the critical angle of the polymer (top layer of spheres). RIGHT: Measurements collected above the critical angle of the polymer (full film thickness). Yellow lines mark the position of the (10) peak for the monolayer HEX symmetry*

Results

Measurements collected below and above the critical angle of the polymer for films 1, 6, and 23 layers thick are shown in Figure 1. The change in symmetry is evident from inspection of the peak positions. Figure 2 plots the in-plane symmetry, characterized by the ratio a_1/a_2 and lattice angle φ, as a function of the number of layers.

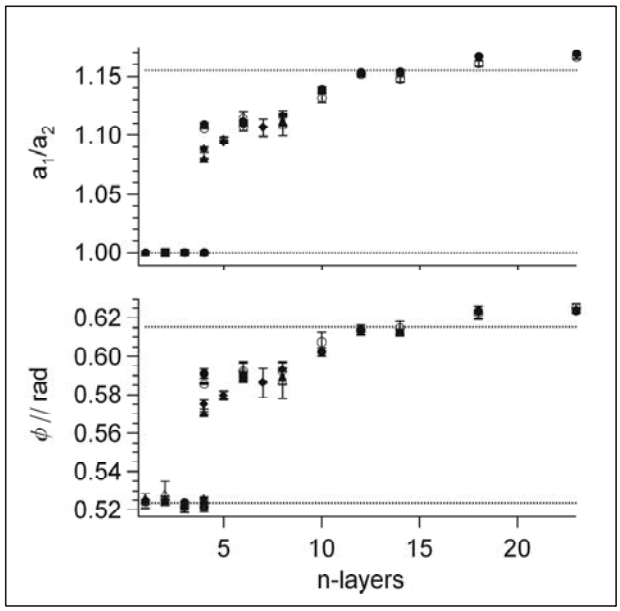

Figure 2. *The ratio a_1/a_2 and the lattice angle φ, calculated from fitting the experimental peak positions to a 2D model, are plotted as a function of the number of layers of spheres. Open/closed symbols denote measurements collected below/above the critical angle of the polymer, and circles/squares/triangles correspond to annealing profiles 1-3.*

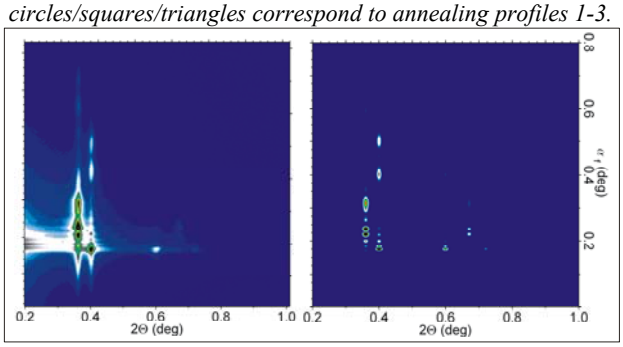

Figure 3. *LEFT: An experimental GISAXS pattern collected at an incident angle slightly larger than the critical angle of the polymer, for a 6-layer thick film. RIGHT: Simulated scattering based on the DWBA, using a lattice basis that describes stacking of BCC (110) planes. For this measurement and calculation, λ=0.1675nm.*

The hexagonal symmetry persists through films 3 layers thick. At 4 layers, an orthorhombic phase is first observed but coexists with regions of HEX. As the number of layers is increased from 4, the symmetry of the orthorhombic phase continuously stretches until it resembles the (110) plane of the BCC lattice. As a function of the number of layers of spheres the magnitude of the parameters a_1 and a_2 also change; the HEX lattice stretches slightly (1%) as the number of layers is increased from one to three but the nearest-neighbor distance for the orthorhombic phase remains constant over the range of n=4-23, and matches the bulk nearest-neighbor distance measured by SAXS. From simulations based on the DWBA, the stacking in films 3-layers thick was determined to be close-packed (ABA). The orthorhombic phase in films 4-23 layers thick was determined to be body-centered (ABA), with the (110) plane oriented parallel to the substrate (i.e., like stacking of BCC (110) planes). An example of the simulated scattering compared with a measurement for a 6-layer thick film is shown in Figure 3.

Discussion

From measurements below and above the critical angle of the polymer, we determined that the structure is uniform throughout the depth of the film. These results are highly reproducible and independent of annealing profile, which suggests that these are equilibrium phases. The interplay between the free energy $F_s(a_1/a_2)$ of the surface layers of the film, which has a minimum at $a_1/a_2 = 1$ and thus favors the HEX structure and that of one of the interior layers $F_i(a_1/a_2)$, which has a local minimum at $a_1/a_2 = 1$ (HEX) but a global minimum at $a_1/a_2 = 1.155$ (BCC), results in a Landau-like free energy [$F(n, a_1/a_2) = 2F_s(a_1/a_2) + F_i(a_1/a_2)(n-2)$ for $n > 2$] of the n-layer film as a whole if a_1/a_2 is constrained to be the same for both surface and interior layers. $F(n, a_1/a_2)$ has minima at both $a_1/a_2 = 1$ and $1 < a_1/a_2 < 1.155$, with the latter minima approaching 1.155 for large n. We believe that the minimum in F at $a_1/a_2 = 1$ is the global minimum until $n > 3$ while for n of 5 the minimum for $a_1/a_2 > 1$ is the global one, resulting in a first order transition at a thickness of n =4. Analysis of our GISAXS results reveal evidence of the coexistence of both HEX and orthorhombic structures at n = 4 so the free energy minima must be approximately the same depth at that thickness. Self-consistent field (SCF) simulations to check this qualitative picture are in progress.

Acknowledgements

We thank Alexander Hexemer and Vikram Khanna for assistance with GISAXS measurements, Rachel Segalman for synthesis of the block copolymer, Glenn Fredrickson, Eric Cochran and Kirill Katsov for valuable discussions on theory as well as SCF simulations. We had financial support from NSF DMR Polymers Program Award no. DMR0307233 and benefited from the use of the Central Facilities of the Materials Research Lab at UCSB supported by the NSF MRSEC Program under Award no. 0520415 and the Advanced Photon Source, which is supported by the U.S. Department of Energy under Contract No. W-31-109-ENG-38.

References

[1] E.L. Thomas, D. J. Kinning, D. B. Alward, C. S. Henkee, C Macromolecules **20**, 2934-2939 (1987)
[2] M. W. Matsen, J.Phys. Condens. Matter **14**, 21-47 (2002).
[3] H. Yokoyama, T. E. Mates, E. J. Kramer, Macromolecules **33**, 1888-1898 (2000).
[4] B. Lee, L. Park, J. Yoon, S. Park, J. Kim, K. Kim, T. Chang, M. Ree, Macromolecules **38**, 4311-4323 (2005).
[5] V. Holy, *High-Resolution X-ray Scattering from Thin Films and Multilayers*; Hohler, G. Ed.; Springer Tracts in Modern Physics **149**; Springer: New York, NY, 1999