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Lattice Deformation of Hexagonally Packed Cylinders in Microphase Separated Structure of Block Copolymer Thin Film

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Introduction

Microphase separated structure of block copolymer hin films has been analyzed by means of grazing incidence small angle X-ray scattering (GISAXS). In a thin film of block copolymers, the various structures have been reported to appear according to the film thickness, which are not predicted in a bulk sample with the same volume fraction. And it has been revealed that the orientation of the structure also depended on the thickness.

We will report the thickness dependence on microphase separated structure of polystyrene-*b*-polyisoprene (SI) block copolymer which exhibits hexagonally packed cylindrical morphology in the bulk.

Experimental

Sample Preparation

SI block copolymer was synthesized by anionic polymerization. The molecular weight, its distribution, and the volume fraction of PS were 2.7×10^4, 1.04, and 34 vol%, respectively. The thick film (bulk sample) was prepared by a casting from toluene solution (5wt%) and annealed at 393K for a hour. SAXS measurement revealed a hexagonally packed cylindrical morphology of

$$q_z = k_0\left(\sin\alpha_i + \left\{\sin^2\alpha_{cp} + \left[\frac{m\lambda}{D_{out}} \pm \left(\sin^2\alpha_i - \sin^2\alpha_{cp}\right)^{1/2}\right]^2\right\}^{1/2}\right)$$

bulk film. Thin films of SI were prepared by spin casting of 20 wt% toluene solution at a rate of 3000 rpm on a silicon wafer and annealed. The film thickness was measured by ellipsometery. GISAXS measurement was conducted at BL9C station.

Result

Analysis of GISAXS using distorted wave Born approximation (DWBA)

The q_z-positions of the diffraction peaks appearing in addition to the specularly reflected beam peaks of the polymer film and the substrate are given by

Diffraction of the reflected beam and the direct diffraction process, which merges with the process where the diffracted beam is reflected from the substrate.

The two branches of this curve correspond to the Bragg. Figure 1 shows GISAXS pattern and diffraction peaks out

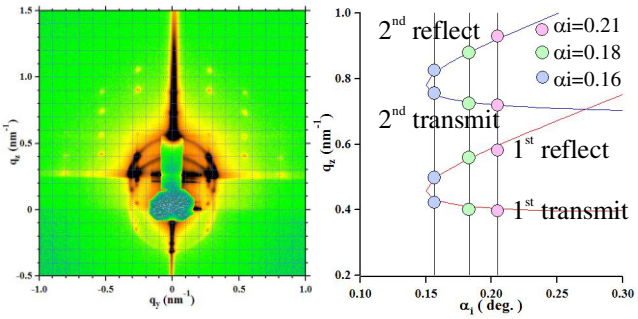

Figure 1. GISAXS pattern (left) and diffraction peaks (right) at different grazing angles of incident X-ray (thickness = 87 nm).

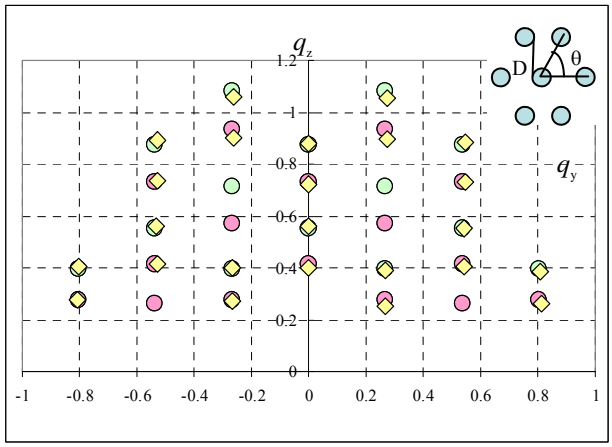

Figure 2 Experimental (diamonds) and simulated (circles) scattering positions from the cylindrical structure in thin film.

of plae direction at $q_y = 0$. The data were obtained at different grazing angles of incident X-ray. The lines were calculated using DWBA theory. The best fitting line was obtained when D_{out} = 19 nm and α_{cp} (critical angle of polymer surface) . Figure 2 shows all the diffraction spots of experimental and calculated ones with D_{out} and θ as fitting parameters. The lattice parameters were deformed.

Table 1: Structure Parameters Used for Analysis

thickness (nm)	83.7	136.0	bulk (∞)
D_{out}	19.0	19.0	20.3
θ	58.3	58.9	60.0

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