BL-6A/2018G027

# Regular Ordering of Spherical Microdomains in a Dewetted Monolayer Film by Thermal Annealing of a Superthin Film of a Triblock Copolymer

Rasha Ahmed Hanafy BAYOMI[1,2], Takashi AOKI[1], Sono SASAKI[1], and Shinichi SAKURAI[1,*]

[1] Department of Biobased Materials Science, Graduate School of Science and Technology, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan
[2] Department of Apparel Design and Technology, Faculty of Applied Arts, Helwan University, Orman, Giza 12111, Egypt

## 1 Introduction

In the block copolymer system, it is well known that the dewetting takes place when the film tends to satisfy the commensurability between the film thickness and the alternating period of the microdomains. Dewetting phenomena of the block copolymers have been widely studied for the cylindrical and lamellar systems, but few studies have focused on the spherical system. In this presentation, we investigated the dewetting phenomena of a monolayer film of the block copolymer forming spherical microdomains. Especially, we focused on the packing manner of the spherical microdomains. Fundamentally, it has been reported that the spherical microdomains order on a hexagonal (hcp) lattice for the thickness of the layer up to three or four times larger than the alternating period of the microdomains [1, 2]. Interestingly, we have found that the ordering manner in the dewetted monolayer film varies from hcp to deformed hexagonal. Furthermore, the number of grains in the dewetted film has been examined as a function of the size of the dewetted film. We investigated the ordering regularity of spherical microdomains of block copolymers in confined spaces (in a dewetted specimen on a Si wafer).

## 2 Experiment

We used a polymethylmethacrylate-block-poly(n-butylacrylate)-block-polymethylmethacrylate (PMMA-PnBA-PMMA; MAM) triblock copolymer, in which PMMA spherical microdomains are formed in a PnBA matrix. The volume fraction of PMMA in this specimen was 0.20. An ultrathin film was prepared by spin coating. Before annealing, the film exhibits a homogeneous state with a full coverage on the Si wafer (the film thickness ~ 15 nm). In order to measure the film thickness before annealing, we engraved a line in the film using a stationery cutter, then we conducted the contact-mode atomic force microscopy (AFM).

The SAXS (small-angle X-ray scattering) measurements were conducted at the BL–6A beamline of PF, using X-ray with $\lambda$= 0.150nm. The sample-to-detector distance was 2.184m, which was calibrated using a chicken tendon collagen having a d-spacing of 65.3nm. The beam size was measured at the detector position as 0.245mm (an FWHM value) in the vertical direction and 0.498mm (an FWHM value) in the horizontal direction. A PILATUS3-1M (DECTRIS Ltd., Baden, Switzerland) was used as a two-dimensional detector.

## 3 Results and Discussion

The 1 d-SAXS profile for the MAM specimen, which was annealed for 5 h at 180 °C under a nitrogen atmosphere. Many lattice peaks are observed. The relative peak positions can be assigned as 1: $\sqrt{2}$: $\sqrt{4}$: $\sqrt{5}$: $\sqrt{6}$: $\sqrt{7}$, exhibiting the bcc lattice. It is striking to observe the $\sqrt{7}$ lattice peak for the direct confirmation of the bcc symmetry because the $\sqrt{7}$ lattice peak should not appear for the simple cubic system. Furthermore, the lack of the $\sqrt{3}$ reflection peak is remarkable, which is ascribed to the fact that its peak position completely matches with the position of the destructive interference of the particle scattering. From this relationship, we can evaluate the radius of the spherical microdomains by modeling the particle scattering function for the sphere, because it only depends on its radius ($R$). The particle scattering function with $R$ = 8.9 ± 1.25 nm can meet the extinction condition of the $\sqrt{3}$ reflection peak.

After five hours thermal annealing at 180°C, the dewetting took place, forming islands with a height ~22 nm. AFM revealed many spherical microdomains regularly ordered in the island. The Fourier transform (FT) pattern clearly displays the six spots. In order to discuss the ordering manner of the spherical microdomains in the dewetted islands, the FT patterns of many islands were examined in details. The packing manner of the spheres is examined in terms of the island shape (degree of circularity of the island). The islands having a higher circularity (mostly complete round shape) exhibit a well-ordered arrangement of the spherical microdomains mainly ordering on a symmetric hexagonal lattice. According to Black et al., over time the defects in the islands diffuse towards the island's perimeter and vanish, resulting in a well-ordered structure, which attests to the validity of our results. On the contrary, the islands having less circularity exhibiting a deformed hexagonal lattice, forming more than one grain (polygrain state) inside of one island (not showing the result in this abstract). The polygrain state could be a result of the islands coalescence.

* shin@kit.ac.jp