Conformation of Single Homopolymer Chain in Micro-Phase Separated Block Copolymer Monolayer Studied by Scanning Near-Field Optical Microscopy

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Supporting Information

1. Surface morphology after overcoating

As described in the paper, the monolayer was overcoated by PVA thin film to prevent quenching. In this Supporting Information, we confirm that the surface morphology of the monolayer was not altered by the overcoating of PVA.

We performed AFM measurement of the monolayer before and after overcoating. Figure 1 shows AFM images of a monolayer before and after overcoating (not the same scanning area). The domain structures for them appears the same, and the FFT analysis showed that the domain width was not altered by the overcoating. The height difference between the PiBMA and PODMA

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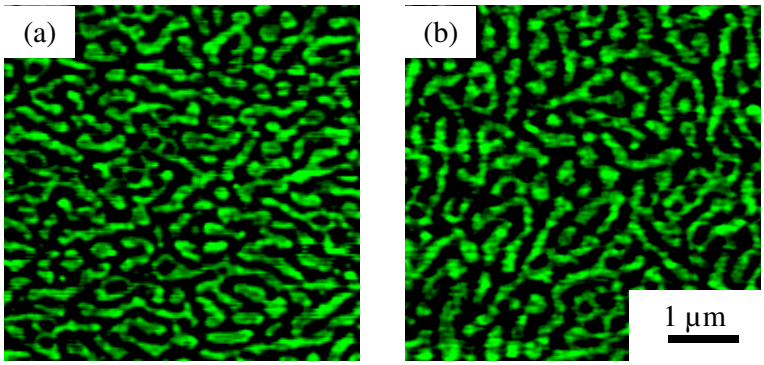

Figure 1: Surface topography of the (a) before and (b) after overcoating.

domains in Figure 1b was about 2 nm as well as Figure 1a. These results indicate that the overcoating by PVA does not affect the micro-phase separation structure of PiBMA-*b*-PODMA.

To confirm that the bright part in Figure 1b corresponds to the PODMA domain, we prepared a dye-labeled symmetric PiBMA-*b*-PODMA (PiBMA-*b*-PODMA:Pe), in which the whole contour of the PODMA sub-chain was labeled by perylene dye. When the PiBMA-*b*-PODMA forms a phase separated structure, the PODMA domain can be identified from the perylene fluorescence in the FL image. The PVA-protected PiBMA-*b*-PODMA:Pe monolayer was prepared in the same procedure as mentioned in the Experimental section. A 438 nm laser was used as the light source to excite the perylene dyes inside the film. All the SNOM experiments were performed in the same conditions as those for the PiBMA-*b*-PODMA / PiBMA system.

Figure 2 shows a set of SNOM images obtained simultaneously from an area of 5 μm $\times$ 5 μm.

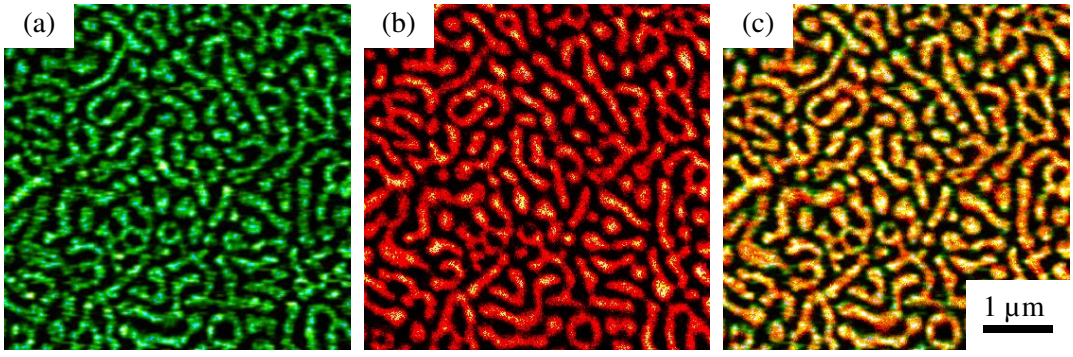

Figure 2: SNOM images of PiBMA-*b*-PODMA:Pe monolayer (a) surface topography (b) fluorescence image, and (c) superimposition of the panels a and b. The bright areas in (b) correspond to the perylene-labeled PODMA domain.

The bright domain in the FL image of Figure 2b indicates the PODMA domain. Figure 2a and Figure 2b shows almost the same structure. For the quantitative comparison of these images, we superimposed the TP and FL images (Figure 2c). For the superimposition of these images, the FL image was shifted 110 nm according to the X-axis and 14 nm to the Y-axis. The reason of the image shift is the different positions of the topographic and optical probes, which correspond a physical protrusion and an aperture at the tip end, respectively. The superimposed image shows that the TP and FL images are completely overlapped. This indicates that the bright part in the topographic image of Figure 2a corresponds to the PODMA domain. Thus, the monolayer was expected to be not affected by the overcoating method.

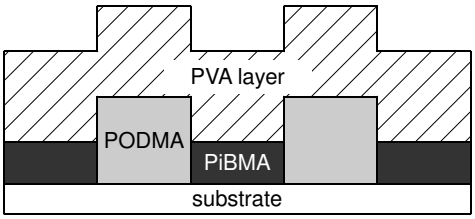

Figure 3: Schematic image of the PVA-protected monolayer

2. Distribution of the homo-PMMA chain in a three-dimensional micro-phase separated structure of PS-*b*-PMMA lamella

In our previous work, Yang *et al*. reported that the homo-PMMA chains embedded in the PS-*b*-PMMA were distributed through the PMMA domain (Figure 4).[1] We also analyzed the data for the three-dimensional system with eq.5 in the text. The solid line in Figure 4 indicate the fitting result. The full width at half maximum (FWHM) is estimated to be 44 nm. Because of the domain width (D) of 82 nm, FWHM/D was evaluated to be 0.56.

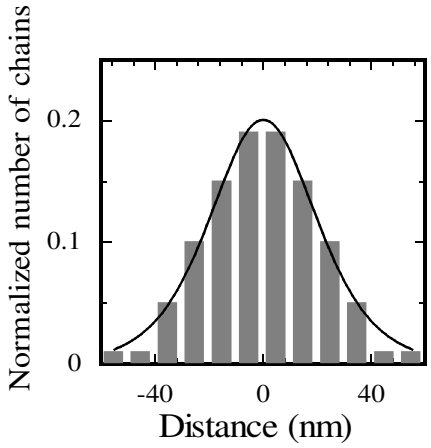

Figure 4: Histogram of the distribution of the homo-PMMA chain in the PS-*b*-PMMA lamellar domain. The normalized population of the homo-PMMA chains is plotted against the distance between the CM of a homo-PMMA chain and the center of the PMMA domain. The interface correspond to ± 41 nm in the distance coordinate. The solid line indicate the fitting result. The figure was reproduced from the data in the literature: Yang *et al*. *Macromolecules*, **2007**, *40*, 7573-7580.

3. Distributions of the orientation of PMMA in a three-dimensional micro-phase separated structure of PS-*b*-PMMA lamella

In our previous work, Yang *et al*. reported that the homo-PMMA chains embedded in the PS-*b*-PMMA lamella were oriented themselves depending on their locations in the PMMA domain in three dimensional bulk.[1] Figure 5 shows the distribution of the orientational angle, ϕ, of the homo-PMMA chains located at the domain center and near the interface, respectively. Orientational angle of the PMMA chain located near the interface are randomly distributed from 0° in 50°, while most of the chains located near the interface showed the orientational angle of $< 30^\circ$ in two-dimensional system (Figure 5b). This weak tendency for three-dimensional system is attributed to the increase of the conformational freedom. Since the polymer chain in three-dimensional system is allowed to entangle with other chains, the polymer chains can more freely rotate than in two-dimensional system.

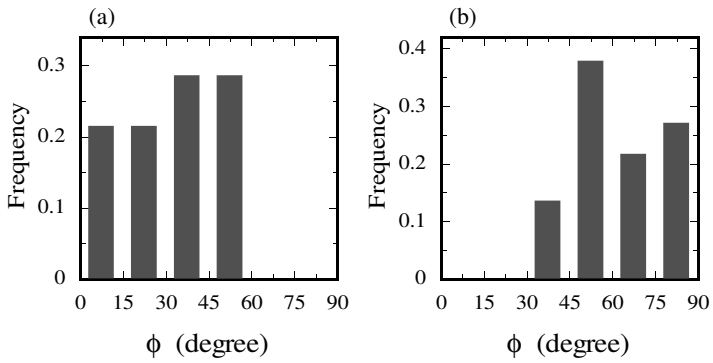

Figure 5: Histograms of the orientational angle, ϕ, of the homo-PMMA located near the interface (a) and at the domain center (b), respectively. The figure was reproduced from the data in the literature: Yang *et al*. *Macromolecules*, **2007**, *40*, 7573-7580.

References

(1) Yang, J.; Sekine, R.; Aoki, H.; Ito, S. *Macromolecules* **2007**, *40*, 7573–7580.