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Surface Reorganization of Thin Poly(methyl methacrylate) Films Induced by Water

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Neutron reflectivity revealed that the surface aggregation states of poly(methyl methacrylate) film can be altered by water, which is a typical nonsolvent, in a relatively large scale.

In the future, the quantity of polymeric materials used for medical diagnosis and treatment will continue to increase.[1] New tools for tailor-made diagnostics, such as DNA arrays and tips for micro-total-analysis systems, are generally made from polymers.[2] Ultimately, we can expect that polymers will be buried in the human body as a part of organs and in situ diagnostic or treatment equipment.[3,4] In these applications, the polymer surface is in contact with a water phase. However, despite the importance of detailed knowledge of the fundamental interactions of polymer interfaces with liquids, such studies are very limited.

We have recently studied the density profiles of a deuterated poly(methyl methacrylate) (dPMMA) film spin-coated on a substrate in some nonsolvents along the direction normal to the interface by neutron reflectivity (NR).[5,6] NR measurement clarified that dPMMA film was swollen in water, which is a typical nonsolvent and that the interface with water was diffuse in comparison with the pristine surface, probably due to the partial dissolution of segments into the water. If this is the case, the surface aggregation states of dPMMA should be changed in a relatively large scale by water. However, such cannot be experimentally demonstrated without using a selective label at the surface. In this study, a dPMMA monolayer was mounted onto a poly(methyl methacrylate) (PMMA) film to confer contrast between the surface and internal regions, resulting in a dPMMA/PMMA bilayer film. NR was then applied to the bilayer films to demonstrate whether the surface reorganizes by water.

Monodisperse PMMA and dPMMA with number-average molecular weight of 300000 and 296000, respectively, were purchased from Polymer Source Inc. Monolayer preparation was carried out with a microprocessor-controlled film balance system (USI, Co., FSD-20). The surface pressure was measured by the Wilhelmy balance technique using a filter paper plate. A dPMMA monolayer was then transferred at $\pi = 3\,\mathrm{mN\,m^{-1}}$ onto a PMMA spin-coated film, which was preannealed under vacuum for 2 h at 423 K, resulting in a bilayer film. It was dried under vacuum for 1 h at room temperature. The top dPMMA layer possessed the root-mean-square roughness of ca. 0.15 nm and the thickness of approximately 1 nm. The density profile of the bilayer film along the direction normal to the surface was examined by NR measurement with an ARISA-II reflectometer at materials and life science experimental facility, J-PARC. Reflectivity was also calculated on the basis of a model scattering length density (b/V) profile using Parratt32 software, which is a freeware program from the Hahn-Meitner Institute.[7] The (b/V) values of SiO_2, Si, dPMMA, and PMMA used for the calculations were 4.15×10^{-4}, 2.07×10^{-4}, 6.62×10^{-4}, and $1.04 \times 10^{-4}\,\mathrm{nm^{-2}}$, respectively.

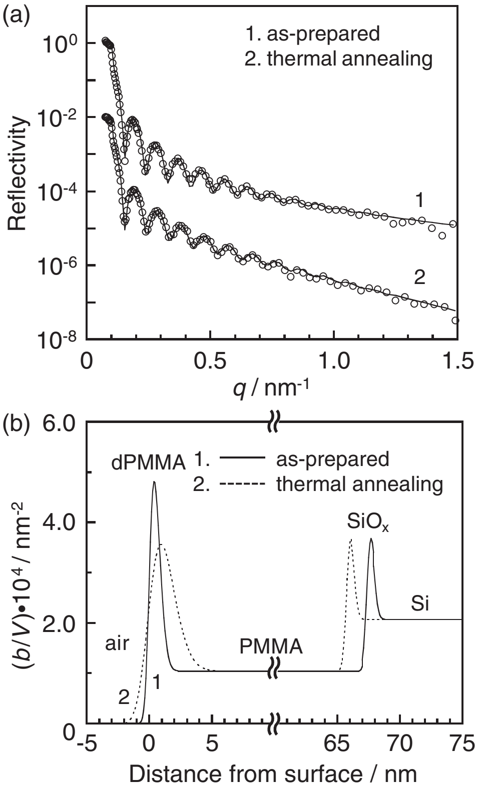

Figure 1. (a) NR for dPMMA/PMMA bilayer films before and after the annealing. Open symbols denote experimental data. Solid curves are calculated reflectivities based on model scattering length density (b/V) profiles shown in the panel (b).

Figure 1a shows the scattering vector ($q = (4\pi/\lambda) \cdot \sin\theta$, where λ and θ are the wavelength and the incident angle of the neutrons, respectively) dependence of NR for the bilayer films before and after annealing for 2 h at 423 K. Open symbols denote experimental data. Solid curves are calculated reflectivity based on model scattering length density (b/V) profiles shown in Figure 1b. The data after the annealing was offset by two decades for the sake of clarity. Table 1 shows the parameter values used for the fitting. The air/dPMMA and dPMMA/PMMA interfaces are simply expressed by Gaussian roughness of σ_1 and σ_2, respectively. It was judged on the basis of χ^2 whether the fitting was acceptable. Since the calculated reflectivities were in good agreement with the experimental data, it can be claimed that the model (b/V) profiles well reflect the density profiles of the bilayer along the direction normal to

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Table 1. Parameter used to fit obtained reflectivity curves

	σ_1/nm	σ_2/nm	χ^2
As-prepared	0.27	0.48	6.9×10^{-3}
Thermal annealing	0.79	1.32	5.4×10^{-3}
Water immersion	0.61	0.77	5.2×10^{-3}

the interface. In this study, two independent bilayer films were used as before and after annealing. The thickness of the top dPMMA layer prepared by Langmuir–Blodgett method was identical in the two samples. However, the bottom PMMA layer prepared by a spin-coating method was not the case. The bottom layer as after annealing was slightly thinner than that as before annealing, as shown in Figure 1b. However, this should not be crucial for our discussion because the top dPMMA layer was our interest. The annealing induced two clear structural changes for the bilayer; the (b/V) value decreased at the middle of the top dPMMA layer, and the interface between dPMMA and PMMA became broader. This means that dPMMA segments diffused toward the interior region. The current annealing conditions should be good enough to fully relax dPMMA chains and thus to delete the preparation history. Nevertheless, dPMMA segments still existed at the top of the bilayer. Although this may not be explained in terms of the bulk diffusion coefficient of PMMA chains, similar slow diffusion, along the direction normal to the surface, has been reported.[8,9]

To study to what extent the aggregation states of PMMA at the surface can be altered by water molecules, NR was applied to similar bilayer films. Figure 2 shows the q dependence of NR for the two bilayer films before and after water immersion for 2 h at room temperature. Open symbols and solid curves have the same meaning as before. The data after the water immersion was offset by two decades for clarity. The fitting parameters are also collected in Table 1. Surprisingly, the (b/V) profile shown in Figure 2b was discernibly changed after the water immersion. That is, the (b/V) value decreased at the middle of the top dPMMA layer, and the interface between dPMMA and PMMA became broader. Although the extent was not so striking in comparison with the previous thermal annealing, it is clear that dPMMA segments in the top layer diffused into the internal dPMMA phase. Taking into account that water has been regarded as a typical nonsolvent of PMMA, the results shown in Figure 2 are quite intriguing. This result is quite reasonable for our parallel experiment to examine interfacial relaxation of PMMA by lateral force microscopy,[10] showing that the segmental mobility of PMMA at the water interface was much faster than that at the sir-facing surface, and local conformation of PMMA at the water interface by sum-frequency generation spectroscopy.[11]

In conclusion, surface aggregation states of PMMA were altered by water, which is a typical nonsolvent. This is because water molecules could penetrate into the PMMA film. More conclusive study for the surface reorganization of PMMA by water will be reported shortly showing how fast it attains on the basis of in situ NR measurements.

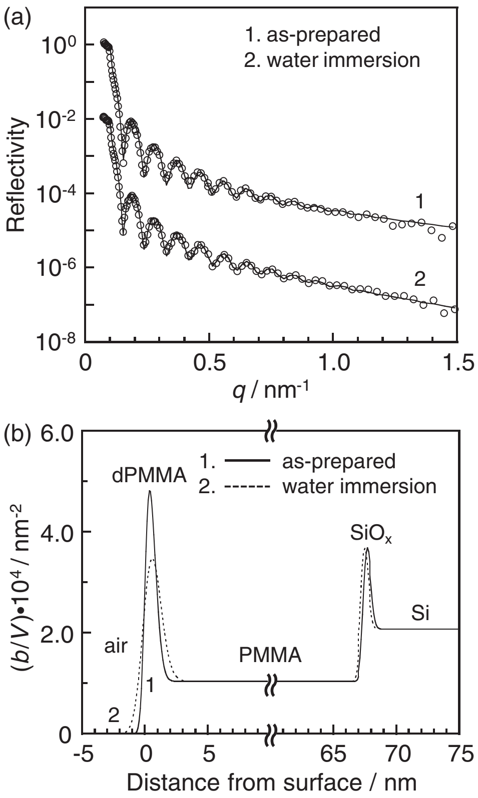

Figure 2. (a) NR for dPMMA/PMMA bilayer films before and after water immersion. Open symbols denote experimental data. Solid curves are calculated reflectivity based on model scattering length density (b/V) profiles shown in the panel (b).

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