Effects of Molecular Weight and Surface Density on Conformation of Poly(N-isopropylacrylamide) Brushes Immobilized Onto A Substrate

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In the future, the quantity of polymeric materials used for medical diagnosis and treatment will continue to increase. Poly(N-isopropylacrylamide) (PNIPAm) is well known to exhibit LCST-type phase behavior in water. This property has been cleverly utilized in number of biomedical application. In such an application, the polymer surface is in contact with a water phase and polymer is used in various temperatures. Previously, we studied interfacial structure of water/poly(methyl methacrylate), which was a simple model for water/PNIPAm. As a result, the water/PMMA interface was diffuse in comparison with the air/PMMA one due to the interfacial roughening and the partial dissolution of segments at the outermost region of the film. [1] In addition, the PMMA film was discernibly swollen even in water. Then, our interest is what happens with the aggregation structure of the PMMA film in water if the temperature increases.

A film of perdeuterated PMMA (dPMMA) was prepared from a toluene solution, spin-coated onto a quartz block. The film thickness, evaluated by ellipsometry, was 60.7 nm. The density profile of the dPMMA film along the direction normal to the surface was studied by the multilayer interferometer for neutrons (C3-1-2-2, MINE) at ISSP, the University of Tokyo. Prior to the measurement, the dPMMA film was aged in water at 360 K for 12 hr, which was enough to cause swelling. Incident neutrons with the wavelength of 0.88 nm and the resolution of 5.1 % were guided into the specimen from the quartz side, which was vertically mounted on a goniometer. The reflectivity was calculated on the basis of the scattering length density profile using Parratt32, which is a freeware from the Hahn-Meitner Institute.

Fig. 1(a) shows the scattering vector, q dependence of reflectivity for dPMMA film in water. Solid line denote the best-fit calculated reflectivity, to the experimental data, on the basis of model scattering length density (b/V) profile in the panel (b). Since the calculated curve is in good agreement with the experimental data, it can be claimed that the model (b/V) profile used well reflect the density profile of the dPMMA film along the direction normal to the interface. The water content in the interior region, namely constant density region, of the film was 4.0 vol%. Moreover, the overall water content of the entire film was 9.5 vol%, being much larger than the reported value of 3.4 vol% at room temperature.[1] Since the dPMMA film contained water molecules after being immersed in the water, it became much thicker than before, the thickness increasing from 60.7 to 66.5 nm. The increment of the film thickness was almost identical to the value calculated on the basis of the overall water content through the mass balance. In the case of the film aged in a hot water, the most striking feature is that water molecules were preferentially segregated at the substrate interface. Taking into account that the film sometimes peels off from the substrate during the aging process in the hot water, this result was quite reasonable. Such an interfacial segregation of water was not observed for the film aged in water at room temperature. A more conclusive discussion about an effect of temperature on the aggregation structure of the dPMMA film in water will be reported in

the future.

Reference

[1] K. Tanaka, Y. Fujii, H. Atarashi, M. Hino and T. Nagamura, Langmuir, 24, (2008) 296.

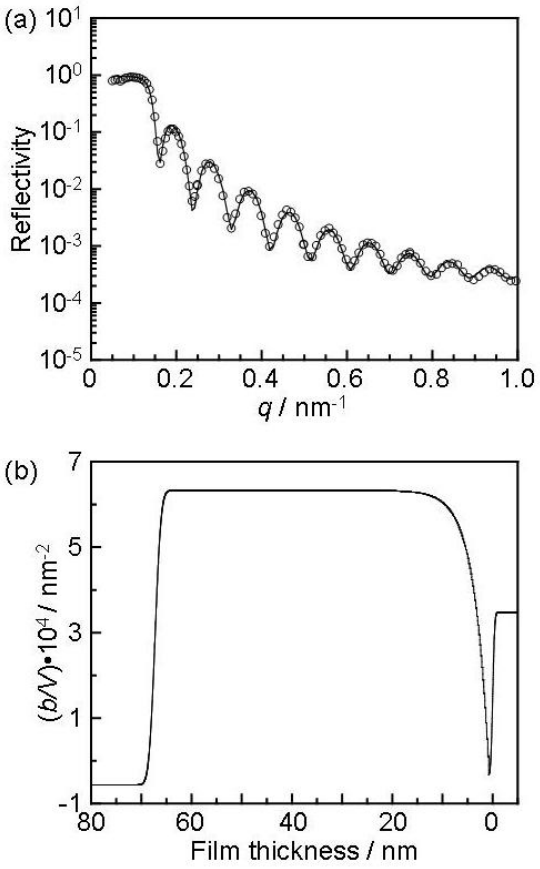

Fig. 1. (a) Neutron reflectivity for a dPMMA film in water. Open symbols depict experimental data, and solid line is reflectivity calculated on the basis of the scattering length density profile shown in (b).