Analysis of Adsorption Behavior for Proteins onto (Liquid/Polymer) Interface

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Recently, polymer films have been widely used in a wide variety of applications. In biomaterials and biosensors, the polymer surface is in contact with a water phase. Thus far, a density profile of a perdeuterated poly(methyl methacrylate) (dPMMA) film spin-coated on a substrate was examined in water along the direction normal to the interface by specular neutron reflectivity (NR).[1] The interface of dPMMA with the water was much more diffused than the pristine air/dPMMA interface. This was because segments at the outermost region of the film could be dissolved into the water phase. If the length of the segments can be controlled, adsorption behaviors of lipids and protein even onto PMMA in water might be controlled. Since the former will be realized by the technique of a precise synthesis in the near future, adsorption behavior of protein onto a PMMA film was studied as a first benchmark.

A film of dPMMA was prepared from a toluene solution, spin-coated onto a quartz block. The film thickness, evaluated by ellipsometry, was 60.4 nm. As protein and buffer solution, bovine serum albumin (BSA) and 0.1 mol/l phosphate buffer solution were used, respectively. The density profile of the dPMMA film along the direction normal to the surface was examined by the multilayer interferometer for neutrons (C3-1-2-2, MINE) at ISSP, the University of Tokyo. 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 a dPMMA film. For clarity, each data set for the dPMMA film in buffer and BSA buffer solution is off-set by a decade. Since just one film was used for all measurements, the NR curves can be directly compared. Solid and broken lines denote the best-fit calculated reflectivity, to the experimental data, on the basis of model scattering length density (b/V) profiles in the panel (b). The (b/V) values for quartz, dPMMA, buffer and BSA were 3.48x10-4, 6.62x10-4, -5.44x10-5 and 2.40x10-6 nm-2, respectively. Since the calculated curves are in good agreement with the experimental data, it can be claimed that the model (b/V) profiles used well reflect the density profiles of the dPMMA film along the direction normal to the interface. In buffer, the model (b/V) profile was almost the same as the one in water reported before.[1] And, as shown in the (b/V) profile, segments at the outermost region of the film were dissolved into the buffer phase. The interface of dPMMA with the BSA buffer solution became rougher than the one with buffer solution because of increasing interfacial roughness via the adsorption of BSA. This roughening was asymmetric to the interface; only the solution side became rougher. This interfacial roughening after the BSA adsorption was in excellent accord with the direct observation for the interface using atomic force microscopy. More conclusive study will be reported in the near future.

Reference

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

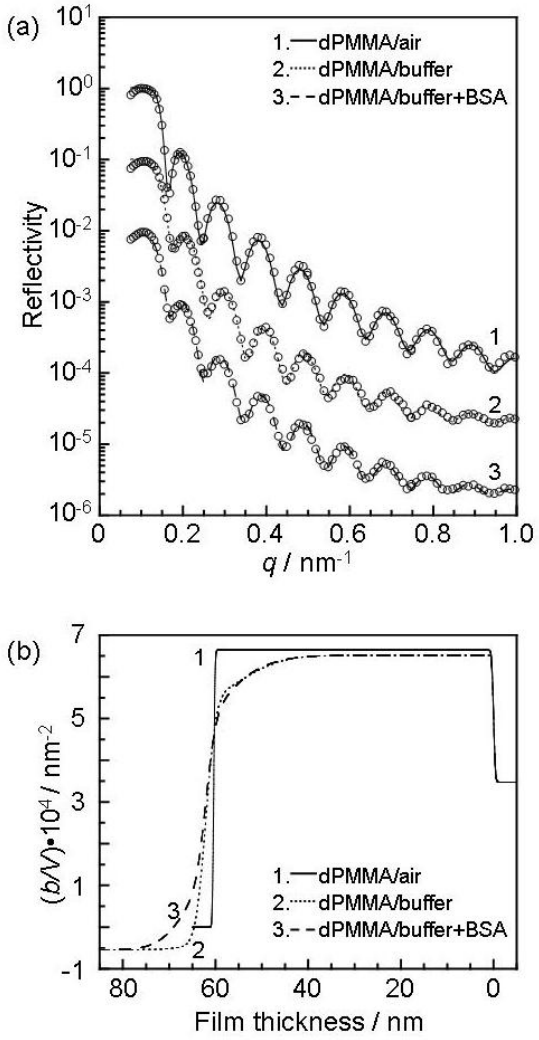

Fig. 1. (a) Neutron reflectivity for a dPMMA film in air, buffer and BSA buffer solution. Open symbols depict experimental data, and solid lines are reflectivity calculated on the basis of the scattering length density profiles shown in (b).