Structural analysis for a poly(methyl methacrylate) ultrathin film in water by neutron reflectivity

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Abstract. Density profiles of a perdeuterated poly(methyl methacrylate) (dPMMA) film spin-coated on a substrate in water (H2O) and deuterated water (D2O) were examined along the direction normal to the interface by specular neutron reflectivity (NR). Although H2O and D2O were typical non-solvents for dPMMA, their interfaces were more diffuse than the air/dPMMA interface due to the swelling caused by the sorption of H2O and D2O molecules. An isotopic effect on aggregation structure of the dPMMA film in water was also discussed.

1. Introduction
Surface structure and dynamics in polymer materials have been extensively explored for the last two decades, both experimentally and theoretically, with respect to associated functional properties such as blood compatibility, lubricant, wetting, permeability, and so on. [1-3] However, when the materials are used for the aforementioned applications, the surface is generally supposed to be contacted with other phases; that is, the surface serves as the interface. Thus, after an understanding of the polymer surface has been attained, [4-6] further inquiries should focus on the structure and dynamics at polymer interfaces as the next step.

Poly(methyl methacrylate) (PMMA), which is a typical glassy polymer, has been widely used in a variety of technological applications on account of excellent mechanical, optical and surface properties. Above all, biomedical applications are intriguing. In ophthalmology, for instance, PMMA is an important component in artificial lenses. [7,8] Nevertheless, it seems to us that fundamental science of PMMA at the water interface has been still open. In this study, we examine density profiles of PMMA at water interface by specular neutron reflectivity (NR).

2. Experimental Section
As a material, monodisperse and perdeuterated PMMA (dPMMA) with number-average molecular weight (Mn) of 296k was used. Purified water (H2O) and deuterated water (D2O) were used. A film of dPMMA was prepared from a toluene solution onto a quartz block with the size of 60 x 60 x 8 mm by a spin-coating method, and was annealed under vacuum for 24 hr at 423 K. The film thickness evaluated by ellipsometry was 67.7±0.5 nm. Density profiles normal to the surface in dPMMA contacted with water were examined by NR using the multilayer interferometer for neutrons (C3-1-2-2, MINE) [9] installed at Japan Research Reactor-3M (JRR-3M) in Japan Atomic Energy Agency
A Teflon reservoir filled with water was mounted onto the film. Incident neutrons with the wavelength ($\lambda$) of 0.88 nm and the resolution of 5.1 % were guided into the specimen from the quartz side, which was vertically set onto a goniometer. The reflectivity was calculated on the basis of the scattering length density ($b/V$) profile along the depth direction using Parratt32, which was a freeware from the Hahn-Meitner Institute (HMI). [10] The ($b/V$) values of dPMMA, SiO$_2$, H$_2$O and D$_2$O for the calculation were 6.62 x 10$^{-4}$, 3.48 x 10$^{-4}$, -0.561 x 10$^{-4}$ and 6.37 x 10$^{-4}$ nm$^{-2}$, respectively.

3. Results and Discussion

The panel (a) of Figure 1 shows the scattering vector, $q$ =$(4\pi/\lambda)\sin \theta$, dependence of NR for a dPMMA film contacting H$_2$O and D$_2$O. Prior to the measurement, the dPMMA film was aged in the water for 2 hr, which was sufficiently enough to reach a quasi-equilibrium state. [11] For comparison, the NR curve for the dPMMA in air is also presented. Each data set for the dPMMA film in water is offset by a decade for clarity. As a general trend, once the $q$ went beyond the critical value, the reflectivity started to decrease. Then, it periodically increased and decreased with increasing $q$ because of the interference between reflected and refracted beams at water (or air)/dPMMA and dPMMA/quartz interfaces. This undulation of the reflectivity is so-called Kiessig fringe, and is mainly due to the film thickness.

The NR curve for the dPMMA film in water showed two differences in comparison with that in air. In the $q$ region higher than 0.5, the fringes were less visible in water than in air. This means that the water/dPMMA interfaces are not as sharp as the air/dPMMA one. In addition, in water, the Kiessig fringes shifted to the higher $q$, implying that the dPMMA film became thicker, probably due to the swelling caused by the sorption of water molecules. However, the fringe positions were recovered at $q$>0.75 nm$^{-1}$. If the dPMMA film had been homogeneously swollen along the direction normal to the interface, the Kiessig fringes should have simply shifted to higher $q$ values. Hence, it is plausible that the internal swollen structure of the dPMMA film was not so simple.

![Figure 1](image_url)  
**Figure 1** (a) Neutron reflectivity for a dPMMA film in air, H$_2$O and D$_2$O. Open symbols depict experimental data, and solid lines are calculated reflectivity on the basis of scattering length density profiles shown in (b). For clarity, each data set in water is off-set by a decade.

To discuss the density profiles normal to the interface in quantitative terms, the experimental NR data were fitted on the basis of a layer model illustrated in Figure 2. Solid curves drawn in the panel (a) of Figure 1 were so obtained. The model ($b/V$) profiles to obtain the best-fit reflectivity and the fitting parameters are, respectively, shown in Figure 1(b) and Table 1. Here, $\sigma_1$, $\sigma_2$ and $\sigma_3$ are the
standard deviation in Gaussian roughness for the water (air)/dPMMA interface, the density depletion layer and the quartz/dPMMA interface, respectively, as shown in Figure 2. Also, \(t\) denotes the total thickness of the film. Since the calculated curves were in good accordance with the experimental ones, it can be claimed that the model \((b/V)\) profiles in Figure 1(b) well reflect the real composition changes along the direction normal to the interface.

![Diagram](image)

**Figure 2** Schematic illustration of the model for a dPMMA film in water to be used for NR fitting.

### Table 1 Parameters to fit reflectivity curves experimentally obtained.

| environment | \(t\) / nm | \(\sigma_1\) / nm | \(\sigma_2\) / nm | \(\sigma_3\) / nm | \(\chi^2\) | \(t/t_{air,NR}\) |
|-------------|-----------|------------------|------------------|------------------|--------|------------------|
| air         | 67.8      | 0.210            | -                | 0.312            | 1.2 \times 10^{-2} | 1.00             |
| H\(_2\)O    | 69.7      | 1.66             | 6.95             | 0.312            | 2.1 \times 10^{-2} | 1.03             |
| D\(_2\)O    | 71.6      | 2.15             | 9.42             | 0.312            | 3.0 \times 10^{-2} | 1.06             |

The interface between dPMMA and H\(_2\)O was diffuse in comparison with that between dPMMA and air, as shown in the panel (b), and the \(\sigma_1\) value was 1.66 nm. Also, it is noteworthy that there exists a density depletion layer with the \(\sigma_2\) of 6.95 nm beneath the interface. This seems to infer that the formation of a swollen layer in the vicinity of the interface is induced by the sorption of H\(_2\)O molecules. Also, it is interesting that the \((b/V)\) value in the interior region of the film was lower than that of the bulk dPMMA, 6.62 x 10\(^{-4}\) nm\(^{-2}\). When we increased the H\(_2\)O content in the interior region of the film during the fitting process, the calculated reflectivity became larger and smaller than the experimental data at the middle and higher \(q\) regions, respectively. If the film is swollen by water molecules, the thickness must be increased to conserve the mass of dPMMA. This was actually what was observed, as shown in Table 1, and was confirmed by atomic force microscopy operated in water. On the contrary, in the (dPMMA/D\(_2\)O) system, the \(\sigma_1\) and \(\sigma_2\) were 2.15 and 9.42 nm, respectively. Moreover, the total film thickness was 71.6 nm which was larger than that of the dPMMA film in H\(_2\)O. These results indicate that the dPMMA film in D\(_2\)O was much more swollen than in H\(_2\)O. In other words, a deuterated polymer prefers deuterated species.

### 4. Conclusions

It was demonstrated that NR was a powerful tool to examine aggregation structure of an ultrathin polymer film in liquids. The interface between dPMMA and water was more diffuse than that between dPMMA and air, and the swollen layer was formed beneath the water/dPMMA interface. These clearly showed that water molecules penetrated into the dPMMA film although water was a typical non-solvent for dPMMA. Interestingly, to what extent water was sorbed into the film was more striking in D\(_2\)O than H\(_2\)O. This may be interpreted by a notion that a deuterated polymer prefers deuterated species.

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