

# Aggregation Structure of Blood-compatible Polymer/Water Interfaces Based on a Simple Impregnation Method

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## 1. Introduction

We have examined the density profiles of a deuterated poly(methyl methacrylate) (dPMMA) thin film on a solid substrate in non-solvents such as methanol and water along the direction normal to the interface by neutron reflectivity (NR) measurement and found that the interface is quite diffused in comparison with the pristine surface probably due to the partial dissolution as well as swelling of segments into the water. In addition, the similar experiments were made for poly(2-methoxyethyl acrylate) (PMEA)/dPMMA blends. PMEA was preferentially segregated at the outermost region in the blend film in water. Furthermore, it has been revealed that the density profile in the blend films near the water interface was insensitive to its molecular weight, whereas the local dynamics became faster with decreasing molecular weight. However, more simple methods for surface coating with functional polymers compared to polymer blend technique are required in various industrial fields. In this study, we examined a simple impregnation method combined with non-solvent sorption for PMEA coating on various polymeric materials. Especially, the density profiles of the PMEA-impregnate films along the depth direction were examined by NR measurements.

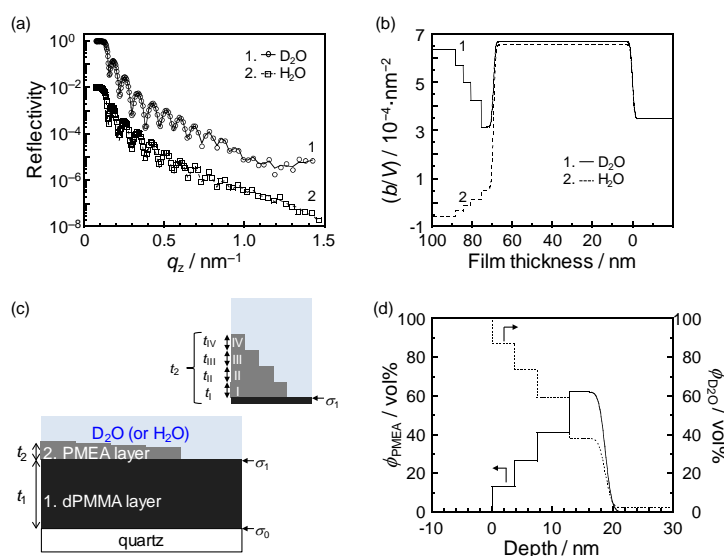
## 2. Experiment

As a model underlying substrate, dPMMA and deuterated polystyrene (dPS) films were prepared on a quartz block by a conventional spin-coating method from its toluene solution and they were dried in a vacuum oven at 298 K for 24 h. Then, the dPMMA films were immersed in 0.5 wt% solutions of PMEA in methanol at room temperature for 2 h in order to impregnate the PMMA films with PMEA. In the case of dPS films, mixture of methanol and 1-butanol (50/50 (vol./vol.)) was used as a non-solvent instead of methanol. After that, unfixed PMEA chains to underlying dPMMA or dPS layers were rinsed by methanol and then the films were dried in a vacuum oven at room temperature for 24 h. The density profiles of the PMEA-impregnate films along the depth direction were examined by neutron reflectivity (NR) measurements. Here, dPMMA or dPS was used to enhance the contrast of the scattering length density ( $b/V$ ) difference between the two components, that is, impregnated PMEA and underlying layer. A Teflon-made reservoir filled with H<sub>2</sub>O or D<sub>2</sub>O was mounted on the film. Prior to the measurement, the films were measured in air, and then aged in H<sub>2</sub>O or D<sub>2</sub>O. A beam of neutrons with a wavelength ranging from 0.25 to 0.88 nm at a resolution of 3% was guided into the specimen from the quartz side. The ( $b/V$ ) values of PMEA, PMMA, dPMMA, SiO<sub>2</sub>, H<sub>2</sub>O, and D<sub>2</sub>O used for the calculation were  $1.15 \times 10^{-4}$ ,  $1.04 \times 10^{-4}$ ,  $7.02 \times 10^{-4}$ ,  $3.48 \times 10^{-4}$ ,  $-0.56 \times 10^{-4}$ , and  $6.38 \times 10^{-4} \text{ nm}^{-4}$ , respectively.

## 3. Results

The upper trace in panel (a) of Figure 1 shows the scattering vector ( $q_z$ ) dependence of NR for the treated dPMMA film in contact with D<sub>2</sub>O and H<sub>2</sub>O. The data set acquired in H<sub>2</sub>O was offset by the two decades. Open symbols denote the experimental data and solid lines denote the calculated reflectivity on the basis of the model ( $b/V$ ) profile shown in Figure 1(b). First, to simplify the fitting model, the film was divided into ideal two layers with Gaussian roughnesses, unfortunately, however, the best fitting could not be attained on the basis of the bilayer model. Then, this lead to that the PMEA layer was further divided into sub-layers, as shown in Figure 1(c). Since the calculated NR curves were good accordance with the experimental data, it is most likely that the

$(b/V)$  profiles in Figure 1(b) closely reflect the composition profile in the film along the direction normal to the surface in  $H_2O$  as well as  $D_2O$ . The  $(b/V)_i$  values for all PMEAs sub-layers were greater in  $D_2O$  than in air. This means that  $D_2O$  with a higher  $(b/V)$  value infiltrated into these sub-layers. Also, once the film came in contact with  $D_2O$ , the PMEA layer ( $t_2$ ) became thicker from 16.6 nm to 18.7 nm. These observations make it clear that PMEA chains anchored onto the dPMMA film was definitely swollen by  $D_2O$ . The NR measurement for the treated dPMMA film in  $H_2O$  enables us to gain access the depth profile of the composition in the film. That is, assuming that the  $H_2O$  distribution in the treated dPMMA film was the same as the  $D_2O$  one in the film, the composition profiles of PMEA and water in the film were extracted. Figure 1(d) shows the depth dependence of volume fraction for PMEA ( $\phi_{PMEA}$ ) and  $D_2O$  ( $\phi_{D_2O}$ ) in the dPMMA film in close proximity to the  $D_2O$  interface. It was revealed that the PMEA layer which was well swollen with  $D_2O$  existed in the outermost region of the dPMMA film.



**Figure 1.** (a) NR curves for the PMEA-impregnated dPMMA films acquired in  $D_2O$  or  $H_2O$ . Open symbols depict the experimental data and lines are the reflectivity calculated on the basis of (b) the model  $(b/V)$  profiles of these films in  $D_2O$  or  $H_2O$ . For clarity, the NR data for the film in  $D_2O$  are off-set by two decades. (c) A schematic illustration of the model used for fitting. Here,  $t_i$  and  $\sigma_i$  represent the layer thickness and the Gaussian roughness, respectively. It is noted that the layer 2 (*i.e.* PMEA layer) was divided into four sublayers (layers I, II, III, and IV). (d) Depth dependence of the volume fraction of PMEA and  $D_2O$  in the film in the  $D_2O$  interfacial region. The x-axis denotes the depth from the  $D_2O$ /polymer interface.

Also, we have applied the same model described above for dPS film cases, however, unfortunately, good accordance between experimental data and fitting has not been obtained yet. We have to reconsider the model on the basis of further NR experiments and the surface morphology data acquired by atomic force microscopy and so on.

#### 4. Conclusion

NR measurements revealed that PMEA chains were anchored to the dPMMA surface and the thickness of PMEA layer was approximately 20 nm in water. Such the PMEA-impregnated PMMA film showed good suppression ability for protein adsorption and platelet adhesion. In the future, we will report the results for dPS film cases.