

# Aggregation States of Poly(2-methoxyethylacrylate)/ Poly(methyl methacrylate) Blend Films at Water Interface

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## Introduction

Poly(2-methoxyethyl acrylate) (PMEA) has been regarded as one of promising blood-compatible polymers and used as a coating material for artificial organs. Nevertheless, the manifestation mechanism of such a surface functionality remains incompletely understood. Although the surface aggregation states of PMEA should be clarified as the first benchmark, such has not been realized yet. This is because a thin PMEA film supported on a solid substrate can be easily broken. In our previous study, we succeeded to prepare and characterize a stable surface covered with PMEA by mixing it with poly(methyl methacrylate) (PMMA) under an ambient condition. In this study, we have applied neutron reflectivity (NR) to a PMEA/deuterated PMMA (dPMMA) bilayer so that the aggregation states of PMEA at air and water interfaces can be discussed.

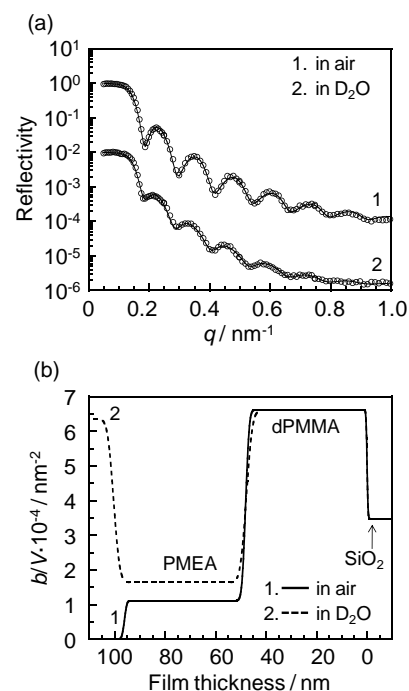
## Experimental

PMEA (number-average molecular weight ( $M_n$ ): 26k and molecular weight distribution ( $M_w/M_n$ ): 3.23) and monodisperse dPMMA ( $M_n$ : 296k and  $M_w/M_n$ : 1.06) were used. PMEA/dPMMA bilayer was prepared by a double spin-coating method. Firstly, dPMMA was spin-coated on a quartz substrate as a bottom layer and the obtained film was annealed at 423 K for 24 h. Then, PMEA was spin-coated on the dPMMA layer and the obtained bilayer film was again annealed at 403 K for 24 h. Aggregation states of the bilayer in air and D<sub>2</sub>O were investigated by NR measurement.

## Results and Discussion

Fig. 1(a) shows the scattering vector ( $q$ ) dependence of NR for the PMEA/dPMMA bilayer contacting air and D<sub>2</sub>O phases. The Kiessig fringes were less visible in water than those in air. In addition, the fringes shifted to a higher  $q$  side in D<sub>2</sub>O. These results make it clear that the bilayer became thicker in D<sub>2</sub>O than in air and that the D<sub>2</sub>O/PMEA interface became more diffuse compared to the air/PMEA one. Panel (b) of Fig. 1 shows the model scattering length density ( $b/V$ ) profiles used to obtain the best-fit reflectivity. The  $b/V$  value in the inter region of the PMEA layer in D<sub>2</sub>O was higher than that in air. This result indicates that D<sub>2</sub>O molecules are sorbed in the PMEA layer. In addition, the thickness of PMEA layer increased in D<sub>2</sub>O from 48.0 to 52.6 nm. This increment was striking compared to the homogeneous dPMMA film.<sup>1)</sup>

1) Tanaka et al, *Langmuir*, 2008, **24**, 296 – 301.



**Fig. 1** (a) NR for a PMEA/dPMMA bilayer in air and D<sub>2</sub>O. Circles are the experimental data, and solid curves denote the calculated reflectivity on the basis of the scattering length density profiles shown in (b). Solid and dotted curves denote the  $b/V$  profiles in air and D<sub>2</sub>O, respectively. For clarity, the data in D<sub>2</sub>O is off-set by two decades.