States of Poly(methyl methacrylate) Monolayers Supported on Substrates in Non-solvents

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Polymeric materials have been widely used for medical diagnosis and treatment in such applications as DNA arrays, tips for micro-total-analysis and scaffolds for artificial organs. When they are used in a human body, the surface is contact with liquid. In such cases, the interfacial structure and properties strongly affect the stability of the materials. We have hitherto studied aggregation structure of poly(methyl methacrylate) (PMMA) at the interfaces with liquids such as water, hexane and methanol by neutron reflectivity (NR) measurement.[1] As a result, the liquid/polymer interfaces were diffuse in comparison with the air/polymer interface, probably due to interfacial roughening and the partial dissolution of segments at the outermost region of the film. In this study, we focused on an ultrathin PMMA film with a larger surface to volume ratio so that the swollen structure at the outermost region of the film could be easily discussed. Deuterated PMMA (dPMMA) with number-average molecular weight of 296 k was used. A film of dPMMA was spin-coated onto a quartz block from a toluene solution. The film thickness was about 12 nm. The film was annealed for 24 h at 423 K under vacuum.

Figure 1 (a) shows NR curves for the dPMMA film under air and methanol. For clarity, the data set under methanol is offset by a decade. The open symbols show experimental data and solid lines are best-fitting curves calculated on the basis of the model scattering length density (b/V) profiles shown in the panel (b). The dPMMA film was swollen under methanol by a factor of 1.65. Interestingly, it was higher than that for the 70 nm-thick film, 1.39. [1] Also, the overall content of methanol for the 12 nm-thick dPMMA film was larger than that for the 70 nm-thick film.

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

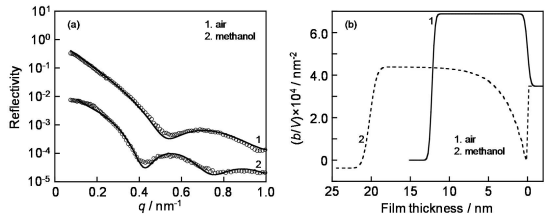

Fig. 1. Figure 1 (a) Neutron reflectivity for a dPMMA film under air and methanol. The scattering length density profiles are shown in (b). For clarity, the data under methanol is off-set by decade.