Structure of Interface between Polymers and Non-solvents and Its Temperature Dependence

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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 the temperature effects on swelling behaviors for PMMA in water Deuterated PMMA (dPMMA) with number-average molecular weight of 296 k was used. A film of dPMMA was spincoated onto a quartz block from a toluene solution. The film thickness was about 70 nm. The film was annealed for 24 h at 423 K under vacuum. Figure 1 shows NR curves for the dPMMA film under air and water at 300, 330 K. For clarity, the data set under water is off-set by a decade, respectively. The NR curve for the dPMMA film in water showed two differences from that in air. The fringes were less visible in water than in air with increasing q value. This result means that the water/dPMMA interface is less sharp than that of air/dPMMA. Moreover, in water, the fringes at 330 K were unclear in comparison with those at 300 K. If the surface is infinitely flat, the reflectivity before reaching the critical q is identically unity. The reflectivity in the total reflection region in water at 330 K was lower than that at 300 K. In other words, to the extent that the surface became rougher increased with increasing temperature of water. These results obtained by in-situ measurements were consistent with our predictions which based on the previous study at C3-1-2:MINE.

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