Aggregation Structure and Relaxation Dynamics of Polymers at the Interface with Water: I. Analysis of Aggregation Structure by Neutron Reflectivity

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New tools for tailor-made diagnostics are generally made from polymers. In these applications, the polymer surface is in contact with a water phase. However, despite the importance of detailed knowledge of the fundamental interactions of polymer interfaces with liquids, such studies are very limited. We have hitherto studied aggregation structure of poly(methyl methacrylate) (PMMA) at the interfaces with non-solvents such as water, hexane and methanol by neutron reflectivity.[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 focus on alcohol with different alkyl lengths as non-solvents so that an impact of solubility parameter on the interfacial aggregation states can be discussed. A deuterated PMMA (dPMMA) with number-average molecular weight of 296k was used as a sample. A film of dPMMA was spin-coated onto a quartz block from a toluene solution. The film thickness was adjusted to be about 65 nm. The film was annealed for 24 h at 423 K under vacuum. Ethanol, 1-propanol, and 2-propanol were used as non-solvents.

Figure 1 (a) shows the NR profiles for the dPMMA films under air, ethanol, 1-propanol, and 2-propanol. The open symbols denote experimental data and solid lines show best-fitting curves calculated on the basis of the model scattering length density (b/V) profiles shown in the panel (b), where the abscissa was normalized with the initial thickness in air. While the dPMMA film was discernibly swollen under all alcohols, the extent was not the same among them. Interestingly, the segregation of alcohol molecules was observed at the substrate interface for all the cases. The overall contents of ethanol, 1-propanol and 2-propanol in the film were 13, 5.7 and 5.7 vol.%, respectively. The solubility parameters for ethanol, 1-propanol, 2-propanol and PMMA are, respectively, 26.0, 24.3, 23.5 and 22.7. Thus, to what extent alcohol molecules penetrate into the film can be hardly explained only in terms of the solubility parameter. The size of penetrants should be also taken into account.

References

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

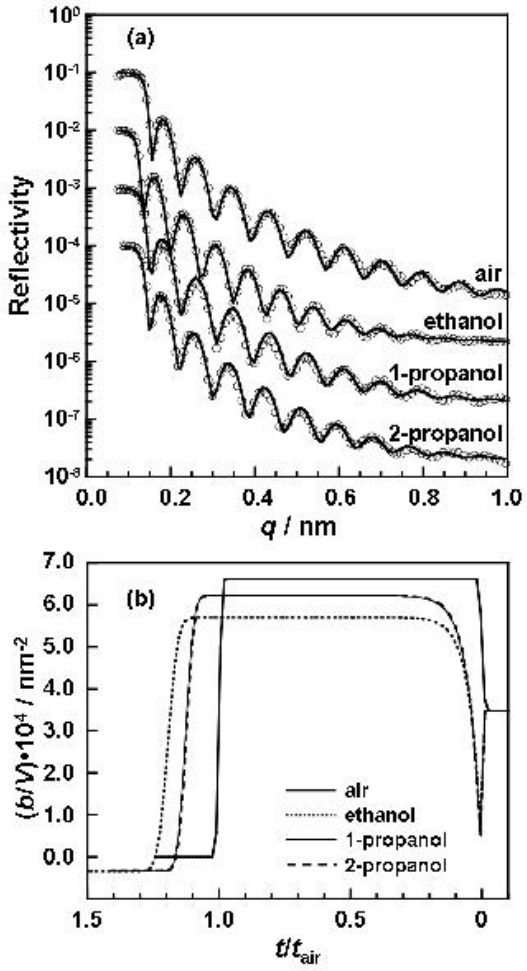

Fig. 1. (a) Neutron reflectivity for a dPMMA films under air, ethanol, 1-propanol, and 2-propanol. The scattering length density profiles are shown in (b). For clarify, each data is off-set by a decade.