Aggregation Structure of Interface between Polymers and Mixed Non-solvents

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Polymer interfaces contacting with liquid play a pivotal role in many technological applications. The liquid does not solve the polymer, so-called non-solvent, however, it could change aggregation structure and dynamics of polymer chains at the interface, depending on the interaction between them. Thus, to design highly functionalized stable polymer interfaces with a liquid, it is important to study the aggregation structure of the polymer at the interface. Despite the importance of detailed knowledge of the interaction of polymer interfaces with liquid, such studies are limited. In this study, internal structure of poly(methyl methacrylate) (PMMA) in water-methanol mixture was examined.

As a material, deuterated PMMA (dPMMA) with a number-average molecular weight of 296k was used. Films of dPMMA were prepared from a toluene solution onto quartz blocks by a spin-coating method. As non-solvents for dPMMA, two kinds of mixtures, D2O and partially deuterated methanol (CH3OD), and H2O and partially deuterated methanol (CD3OH), with a volume fraction of water (fw) of 0.2 and 0.3 were used. Neutron beams were guided into the dPMMA film from the quartz side, and the reflected beam was detected under the specular condition. Figure 1(a) shows neutron reflectivity (NR, measured in FIGARO, France, 09/07/2012-11/07/2012) for dPMMA (CD3OH/H2O) mixtures. Open symbols denote experimental data and solid lines are reflectivity calculated on the basis of the scattering length density (b/V) profiles. Analysis of NR curves was repeated until self-consistency between the distribution of the solvent using CH3OD/D2O and CD3OH/H2O was satisfied. Figure 1(b) and (c) show model (b/V) profiles for dPMMA films in contact with water-methanol mixture with fw of 0.2 and 0.3. The volume fraction of liquid in the dPMMA films in contact with fw of 0.2 and 0.3 were 0.22 and 0.08, suggesting that the larger amount of liquid is adsorbed in the film in contact with the higher volume fraction of methanol. Moreover, Volume fraction of water in the film (Fw) for fw = 0.2 and 0.3 were 0.66 and 0.55. In both cases, In both cases the Fw values were larger than those of fw, indicating that water was segregated in the film.

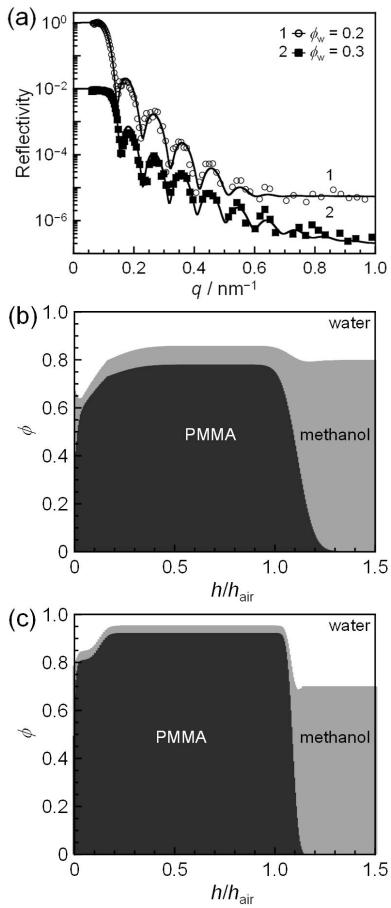

Fig. 1. (a) Neutron reflectivity for dPMMA films in contact with the mixtures of methanol and water. (b and c) Volume fraction profiles for dPMMA films determined from the (b/V) profiles. The liquids were methanol-water mixtures with (b) ϕ w = 0.2 and (c) 0.3.