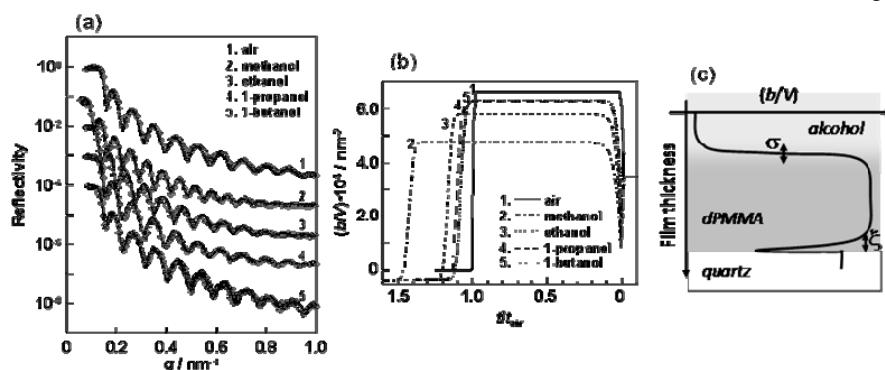


# Study on Structure and Dynamics of Polymers at Various Interfaces by Neutrons

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In the last two decades, it has been accepted that aggregation structures and physical properties of polymer materials at the air facing surface are different from those in the corresponding bulk. However, the surface will contact with a different phase if the polymer is used in applications such as biomaterials, nanocomposites, etc. Thus, the interfaces contacted with different phases should be studied structurally and dynamically as a next step. In this talk, we focus on the aggregation structure of perdeuterated poly(methyl methacrylate) (dPMMA) films in the presence of alcohol, which are all non-solvents for dPMMA, obtained by neutron reflectivity (NR).<sup>1-3)</sup> Monodisperse dPMMA with a number-average molecular weight ( $M_n$ ) of 296k was used. Methanol, ethanol, 1-propanol, and 1-butanol were used as typical non-solvents for PMMA. Films of dPMMA were prepared from a toluene solution onto quartz blocks by spin-coating. The thickness of the films measured by ellipsometry was in the range of 63 to 68 nm. The films were annealed for 24 hr at 423 K in vacuum to relax the film preparation history. Density profiles of the dPMMA films along the direction normal to the surface under the alcohols were examined by NR measurements. The neutron beam was guided into the dPMMA film from the quartz side and the reflected beam was detected under the specular condition. Reflectivity was acquired as a function of scattering vector ( $q$ ),  $q = (4\pi/\lambda)\sin\theta$ , where  $\lambda$  and  $\theta$  are the wavelength and the incident angle of the neutrons, respectively. The model to express a film structure was composed of three layers; alcohol, dPMMA and quartz. Two interfaces between alcohol and dPMMA and between dPMMA and the quartz substrate were, respectively, expressed by error and exponential decay functions. Thus, three parameters, the interfacial roughness between alcohol and dPMMA ( $\sigma$ ), the alcohol content in the internal part of the dPMMA film ( $\phi$ ) and the decay length of the excess amount of alcohol at the substrate interface ( $\xi$ ), were used to fit the experimental data. Since the alcohol molecules were not deuterated, the  $(b/V)$  value at a depth in the film decreased if they penetrated into the films. Also, at the same time, the film became thicker to conserve the mass of PMMA. The extent was in the order of methanol > ethanol > 1-propanol > 1-butanol. This order seems to be quite reasonable because methanol possesses the smallest size among them and also forms the highest number density of hydrogen bonds with side chains of dPMMA. The interfacial width of dPMMA with alcohol and the excess amount of alcohol at the substrate interface also varied in the same order as the extent of sorption.



**Figure 1** (a) Neutron reflectivity for dPMMA films in contact with air and non-solvents. Open symbols denote experimental data, and solid lines are reflectivity calculated on the basis of the scattering length density profiles shown in (b). (b) Scattering length density profiles for dPMMA films in contact with alcohols. The abscissa is normalized by the original thickness in air. (c) A model for a dPMMA film on quartz in an alcohol to fit the experimental reflectivity in panel (a). The model involves three fitting parameters: the width of the alcohol-dPMMA interface ( $\phi$ ), the alcohol content in the internal region of the film ( $\sigma$ ) and the decay length at the substrate interface ( $\xi$ ).

## References

1. *Langmuir* **24**(1), 296-301 (2008).
2. *Chem. Lett.* **39**(8), 810-811 (2010).
3. *J. Phys. Chem. Lett.* **1**(5), 881-885 (2010).