Sorption behavior of a polymer thin film for gas separation membrane using neutron reflectivity

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Poly(dimethylsiloxane) (PDMS) has a high gas permeability, superior mechanical properties, and excellent thermal stability so that it is a promising material for large-scale CO_2 separation [1]. In the case of polymeric membranes, the gas permeability is generally explained in terms of the product of solubility and diffusivity of penetrant molecules in the polymer. Once the membrane becomes thinner, the interface-to-volume ratio for the membrane increases. In such a case, the solubility at the membrane surface becomes more important rather than the diffusivity inside a membrane. Aggregation states and molecular motion at the surface of a polymer thin film is generally different from those in the bulk. An effect of CO_2 sorption on those has been studied for films of a glassy polymer such as poly(methyl methacrylate) (PMMA) [2]. However, such a finding is limited to the PMMA surface. The objective of this study is to obtain a better understanding of the aggregation states at the surface of a PDMS film based on neutron reflectivity and sum-frequency generation (SFG) spectroscopy.

As a material, deuterated poly(dimethyl siloxane)(d-PDMS), was used. A film was prepared by a spin-coating method from a tetrahydrofuran solution onto a silicon wafer. The thickness was approximately 70 nm. Neutron reflectivity (NR) measurement was carried out under air and CO_2 at room temperature using the multilayer interferometer for neutrons (C3-1-2-2, MINE) at the Institute for Solid State Physics, the University of Tokyo. Incident neutrons have a wavelength of 0.88 nm and a resolution of 5%. The environment of the sample was controlled by a hand-made cell. The reflectivity was calculated on the basis of the scattering length density profile along the depth direction by using Motofit [3].

Figure 1 shows the NR curve for the PDMS film under air and CO_2, respectively. The solid curves denote the best-fit calculated reflectivity to the experimental data based on the model scattering length density (b/V) profiles, as shown in Figure 1(b). Since the calculated curves are in good agreement with the experimental data, it can be claimed that the model (b/V) profiles well reflect the density dsitribution in the film along normal to the surface. Once the film was exposed to CO_2, the thickness slightly decreased. This was contrary to the expectation. This result implies that CO_2 was interacted with d-PDMS film and changed the aggregation states. It will be more definite by an ongoing experiment of optical reflectivity measurements.

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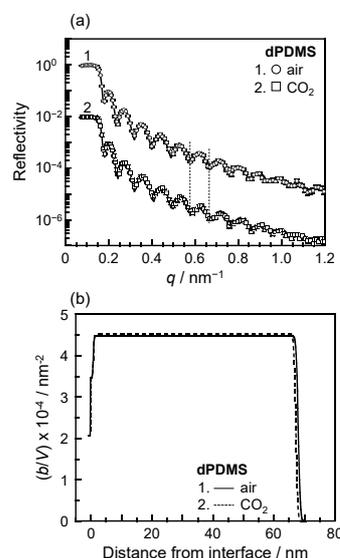
Fig. 1. (a) Neutron reflectivity curves for a d-PDMS film on silicon substrate under air and CO_2. Solid lines denote the depict the best-fit ones calculated from model scattering length density profiles shown in (b).