MLF Experimental Report	提出日 Date of Report 2016/3/28
課題番号 Project No. 2015A0217 実験課題名 Title of experiment A neutron reflectometry study of polymer network structure at solid interface 実験責任者名 Name of principal investigator Manabu INUTSUKA 所属 Affiliation Kyushu university	装置責任者 Name of responsible person Norifumi L. YAMADA 装置名 Name of Instrument/（BL No.） SOFIA (BL-16) 実施日 Date of Experiment 2015/11/7 ~ 2015/11/10

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

In order to reveal the aggregation structure of polymer network near a solid interface, we have conducted neutron reflectivity to thin films of polyisoprene (PI, Figure 1) including photo-crosslink agents such as trimethylolpropane tris(3-mercaptopropionate). The films were prepared onto quartz substrates (60 mm × 60 mm × 8 mm) by a spin-coating technique and then irradiated with UV light to promote the cross-linking reactions. After rinsing the films with toluene to remove unreacted components, they were dried under vacuum at room temperature. The film thickness was evaluated to be 30 to 150 nm.

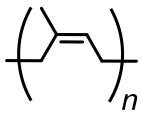

Figure 1. Chemical structure of PI.

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

Neutron reflectivity (NR) curves of the sample films were collected in air as well as deuterated hexane (*n*-hexane-d_{14}). The measurements in air were performed by introducing neutron beams from the air side. In the case of the experiments in *n*-hexane-d_{14}, the sample film was placed in contact with *n*-hexane-d_{14} in a cell. Then, neutron beams were conducted from the quartz side, as shown in Figure 2. Neutron beams with a wavelength from 0.2 nm to 0.88 nm were used, and the incident angles θ of 0.3, 0.75 and 1.8 deg. were chosen. The films contacted with *n*-hexane-d_{14} for at least 12 hours prior to the measurements so that the films could reach a quasi-equilibrium state. By combining the data sets acquired at different incident angles, NR curve in the q range from 0.08 to 2 nm^{-1} was obtained. The resolution of dq/q was about 0.03.

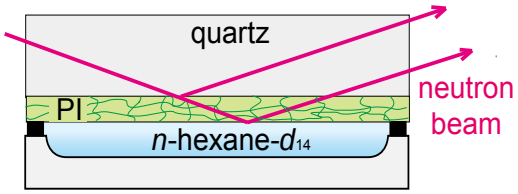

Figure 2. Schematic illustration of our sample cell for NR measurements in d_{14}-hexane.

2. 実験方法及び結果（つづき） Experimental method and results (continued)

Panel (a) in Figure 3 shows the NR curves for a PI thin film in air and *n*-hexane-d_{14}. The NR curve for a PI thin film in air exhibited Kiessig fringes corresponding to the total film thickness. On the other hand, the NR curve for the PI film in *n*-hexane-d_{14} exhibited a narrower fringe only in a low-q region. Also, in the region higher than 0.4 nm^{-1}, the fringes were not clear. These results make it clear that the film was swollen by *n*-hexane-d_{14} accompanied with the film thickening and the diffused interface. By fitting the NR curve by a layer model, we computed the depth profile of (b/V) for the PI film successfully, as shown in panel (b) of Figure 2. Both in air and *n*-hexane-d_{14}, the mass conservation of PI was hold: the total mass of PI in both profiles was exactly the same for each other. The film thickness was estimated to be 44.0 nm by fitting the data with a simple 1-box model with interfacial roughnesses. The value was consistent with that by X-ray reflectivity (XR) and ellipsometry measurements.

Then, we tried to fit the NR curve for the PI film in *n*-hexane-d_{14} using a 3-layer model. The best (b/V) model is shown in panel (b) of Figure 2. We also confirmed that there is no reasonable profile with 1- and 2-layers. The cross-linked PI film was swollen by *n*-hexane-d_{14}, and the total thickness increased from 44.0 to 71.4 nm. The (b/V) value of the film also increased due to the penetration of *n*-hexane-d_{14} into the network.

The swollen cross-linked PI film was divided into three layers: well-swollen bulk layer, less-swollen intermediate layer and not-swollen interfacial layer. The (b/V) value of the interfacial layer is almost the same as that in the neat PI, meaning that this layer could be hardly swollen even by a good solvent of PI, *n*-hexane-d_{14}. Moreover, the less-swollen intermediate layer was found between the interfacial and bulk layers. The average ϕ in this layer was calculated to be about 0.63. We believe that these two layers should correspond to "tightly" and "loosely" adsorbed layers historically discussed for the "bound rubber". Our results will be published as the first paper dealing with the detailed aggregation states of the polymer network near a solid interface.

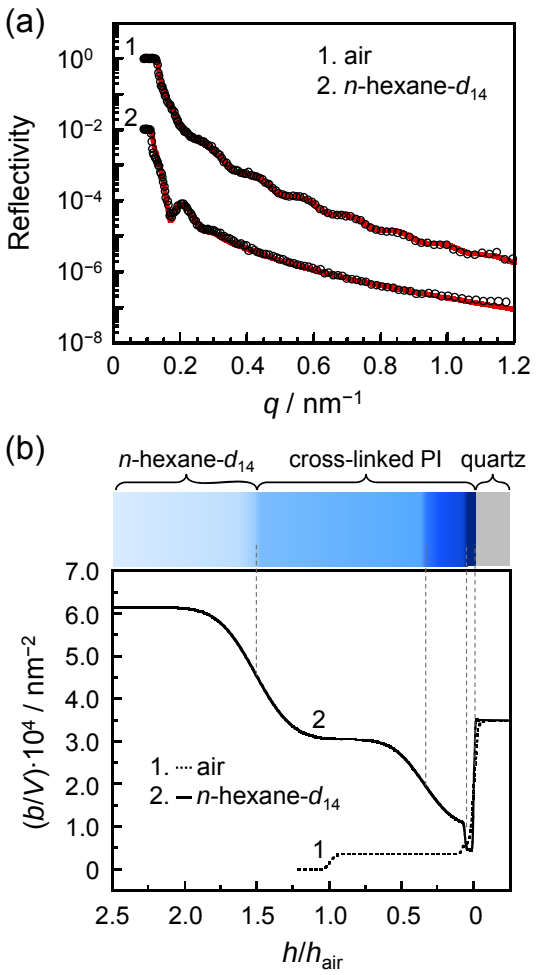

Figure 3. (a) Neutron reflectivity curves for a cross-linked PI film in air and *n*-hexane-d_{14}, respectively. Open symbols depict experimental data and solid and dotted lines represent reflectivity calculated on the basis of the scattering length density (b/V) profiles shown in (b).

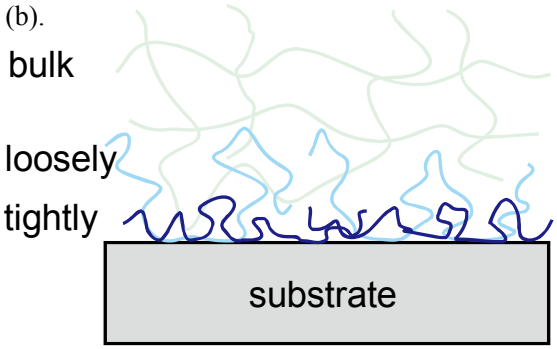

Figure 4. Schematic illustration of the interfacial structure with the adsorbed layers.