（ ※本報告書は英語で記述してください。ただし、産業利用課題として採択されている方は日本語で記述していただいても結構です。 ）

J-PARC **MLF　Experimental Report**		提出日 Date of Report 23rd Jan. 2015
課題番号 Project No. 2014A0242		装置責任者　Name of responsible person Norifumi Yamada
実験課題名　Title of experiment Hydration and Ordering Behavior of Amphiphilic Polymer Thin Films in Contact with Bulk Water prior to Vesicle Formation		装置名 Name of Instrument/（BL No.） BL16 SOFIA
実験責任者名　Name of principal investigator Naoya Torikai		実施日 Date of Experiment 22nd Nov. 2014 – 24th Nov. 2014
所属　Affiliation Mie University		

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.

Materials.

The poly(ethylene oxide)-poly(butylene oxide) diblock copolymer $PEO_{115}PBO_{103}$ (M_w=12,500) with the volume fraction of PEO block of 0.37 was prepared by sequential anionic polymerization using high vacuum techniques. The molecular weight and PEO volume fraction were estimated by gel permeation chromatography and ^{13}C NMR, respectively.

Sample Preparation.

Silicon substrates with 3 inch diameter, 8 mm thickness were used for neutron reflectivity (NR) experiments. The surface of the silicon substrates was modified by two different ways: just oxygen plasma cleaning and chemical adsorption of polystyrene brush. The silicon substrates were cleaned by oxygen plasma prior to spin-coating with monocarboxy-terminated polystyrene (PS-COOH, M_w=13,000, Scientific Polymer Products, Inc.). A 5wt% PS-COOH solution in toluene was spin-cast onto the native oxide surface of the silicon substrates to obtain a hydrophobic surface. The substrates were then thermally annealed at 150 ˚C under vacuum conditions for 4 days. Ungrafted PS-COOH polymer was removed by washing the substrates with toluene several times. The thickness of the grafted PS layer on the substrates was less than 3 nm. Thin films of $PEO_{115}PBO_{103}$ were prepared by spin-coating a solution of the block copolymer in chloroform (1.6 wt%) at 3,000 rpm and 1,500 rpm onto the silicon substrates thus modified.

Table 1. The thin film specimens prepared for this study.

Sample No.	Spin coating speed [rpm]	Substrate
1	3000	Silicon
2	1500	Silicon
3	3000	PS modified silicon

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.

The purpose of this study was to understand the hydration behavior as well as structural changes of the amphiphilic block copolymer thin film in the direct water contact condition.

Experimental method.

In-situ NR measurements were performed during the hydration process just after the thin film samples were contacted with D_2O water using a solid-liquid contact cell (Figure 1) equipped on SOFIA.
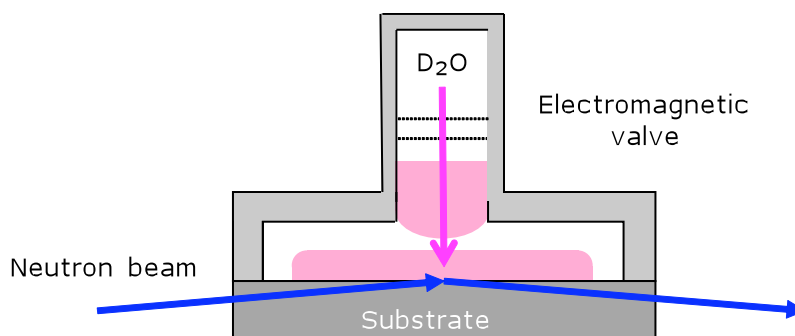

Figure 1. Schematic representation of the water contact chamber.

Results.

Figure 2 shows the *in-situ* NR profiles at different time after the thin film was contacted with D_2O. The profiles are sequentially arranged from bottom to top in each figure. All the thin films exhibited the changes in their NR profiles significantly and rapidly in the initial 180 sec. There is a broad peak at around 0.21 nm^{-1} in the bottommost profiles that were measured between 5 to 10 sec after D_2O contact. The broad peak shifted to the lower *q*-region with time, and their positions reached at around 0.19 nm^{-1} in the initial 180 sec. At the same time, the peak became sharp gradually. The initial broad peak might be arose from stacked lamellar structures with less preferential orientation. The lamellar thickness increased with absorbing water and the lamellar structures might change into loosely stacked bilayer sheets structures. After the initial rapid structural change, NR profiles changed their shape slightly and the peaks shifted to the higher *q*-region slightly. It seems that the samples remained on the substrate at least partly in this measurement conditions.

The peak in the profile after 180 sec in contact with D_2O shown in the figure b) was sharper than that in the figure a). The difference between the two lies on the film thickness, and the thin film shown in the figure b) (Sample No.2) was thicker than that in the figure a) (Sample No.1) though the other conditions for preparation were the same. And the thin film shown in the figure b) only shows the second peak at about 0.37 nm^{-1} in *q* after 600 sec. These differences may be caused by the different number of loosely stacked bilayer sheets formed in the thin films with different film thickness.

On the other hand, the peak observed in the profile after 180 sec in the figure c) was sharper than that in figure a). The block copolymer thin film for the figure c) (Sample No. 3) was prepared by spin-coating on the PS modified silicon substrate at the same rotation speed of a spin-coater as that on Si substrates for the figure a) . The bottommost sheet of the Sample No. 3 may be strongly contacted with the hydrophobic polystyrene surface. This may be attributed to the difference in NR profile.
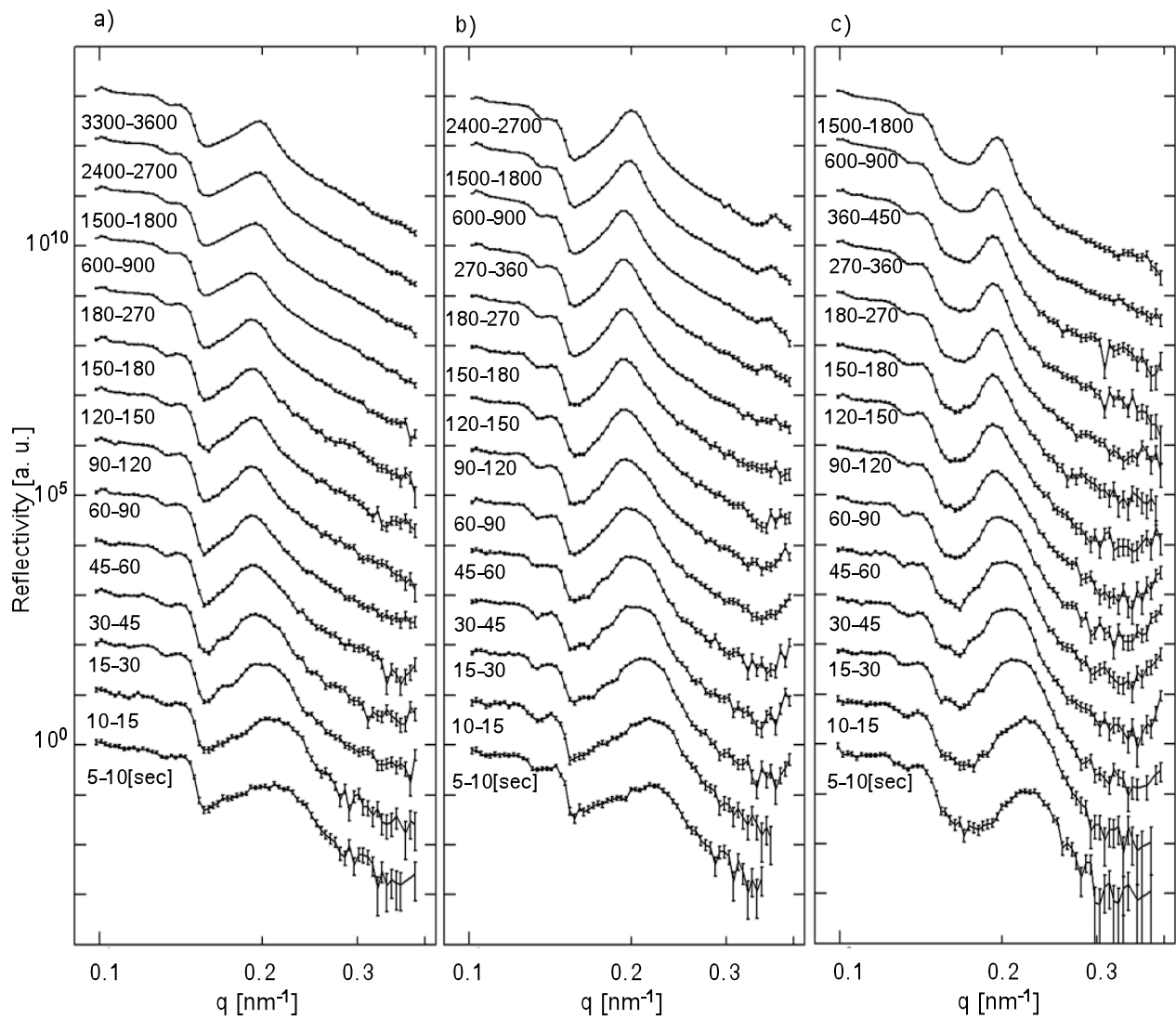
a)　　　　　　　　　　　b)　　　　　　　　　　　c)

Figure 2. In-situ neutron reflectivity measurements. a) Sample No.1 (Si, 3000 [rpm]). b) Sample No. 2 (Si, 1500 [rpm]). c) Sample No.3 (PS modified Si, 3000 [rpm]) .