MLF Experimental Report	提出日 Date of Report
課題番号 Project No. 2016A0025 実験課題名 Title of experiment Heterogeneous dynamics and interfacial structure in stacked thin polymer films 実験責任者名 Name of principal investigator Koji Fukao 所属 Affiliation Ritsumeikan University	装置責任者 Name of responsible person Norifumi Yamada 装置名 Name of Instrument/（BL No.） BL No.16 実施日 Date of Experiment 2016.6.4-2016.6.7

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.

The polymer samples used in our measurements are atactic hydorated poly(methyl methacrylate) (h-PMMA) and deuterated poly(methyl methacrylate) (d-PMMA) as follows: 1) h-PMMA-1: Mw=1.873x10^6, Mn=1.304x10^6, 2) h-PMMA-2: Mw=323,000, Mn=225,500, 3) d-PMMA-1: Mw=1.50x10^6, Mn=8.20x10^5, 4) d-PMMA-2: Mw=3.07x10^5, Mn=2.20x10^5, 5) d-PMMA-3: Mw=7.63x10^3, Mn=7.00x10^3. Five of eight hydrogen atoms of the monomeric unit are replaced by deutrons for d-PMMA-1, and all eight hydrogens are replaced by deutrons for d-PMMA-2 and d-PMMA-3. The scattering length densities (SLD) of h-PMMA and d-PMMA are 1.0865 and 4.9298 or 7.11, respectively.

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.

Two different types of 2-layered films of h-PMMA and d-PMMA (hd-PMMA-1 and -2) are prepared as follows. **a) hd-PMMA-1:** A 25-nm-thick-film of blend of d-PMMA-1 and d-PMMA-3 with the ratio of 0.7 : 0.3 is stacked on the glass substrate, and then a 25-nm-thick-film of h-PMMA-1 is stacked on the top of d-PMMA thin layer. b**) hd-PMMA-2:** A 25-nm-thick-film of d-PMMA-1 is stacked on the glass substrate, and then a 25-nm-thick-film of h-PMMA-1 is stacked on the top of d-PMMA thin layer. The glass transition temperature, Tg, of d-PMMA layer is higher than that of h-PMMA layer for hd-PMMA-2, while Tg of d-PMMA layer is lower than that of h-PMMA layer for hd-PMMA-1. Our previous neutron reflectivity measurements suggest the possibility that the difference in Tg between the d-PMMA and h-PMMA might induce the asymmetry of diffusion of polymer chains at the interface and hence the different time evolution of the thickness of the d-PMMA layer and h-PMMA layer in the 2-layered thin films of d-PMMA and h-PMMA during the isothermal annealing process.

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

For 2-layered thin films of d-PMMA and h-PMMA, we have performed neutron reflectivity measurements during the isothermal annealing process at 413 C in order to observe the change in the structure of the interfacial regions between two layeres. Using non-linear least square fit on the basis of the model functions with thickness and roughness of the two layers (d-PMMA and h-PMMA) in the framework of Motofit on Igor, we have successfully reproduced the observed reflectivity profile. The thicknesses of the two layers are obtained as a function of annealing time, as shown in Figs.1 and 2.

Figure 1 shows that **the thickness of d-PMMA layer increases** with increasing annealing time, while **the thickness of h-PMMA layer decreases** with increasing annealing time for 2-layered thin films, hd-PMMA-2. For hd-PMMA-2, Tg of d-PMMA layer is higher than that of h-PMMA layer. Hence, the dynamics of h-PMMA chains at the interface is faster than that of d-PMMA chains. This result is consistent with our previous one obtained by neutron reflectivity measurements.

On the other hands, Figure 2 shows that **the thickness of d-PMMA layer decreases** with increasing annealing time, while **the thickness of h-PMMA layer increases** with increasing annealing time during isothermal annealing process at 413 K for 2-layered thin films, hd-PMMA-1. For hd-PMMA-1, Tg of d-PMMA layer is controlled to be lower than that of h-PMMA layer by the blending of two d-PMMA with different molecular weight, that is, different Tgs. From Figures 1 and 2, it can be concluded that the annealing time dependence of thicknesses of d- and h-PMMA layers is strongly associated with the difference of Tg of the two layers. In other words, dynamical asymmetry causes the different annealing time dependence of thickness of d- and h-PMMA layers.

Blending d-PMMA-3 into d-PMMA-1 causes the decrease in Tg and as a result, the dynamical asymmetry between d- and h-PMMA layers could be inverted. Blending can induce a change in reflectivity profile in some complicated manner. The detailed effect should be analyzed and discussed further.

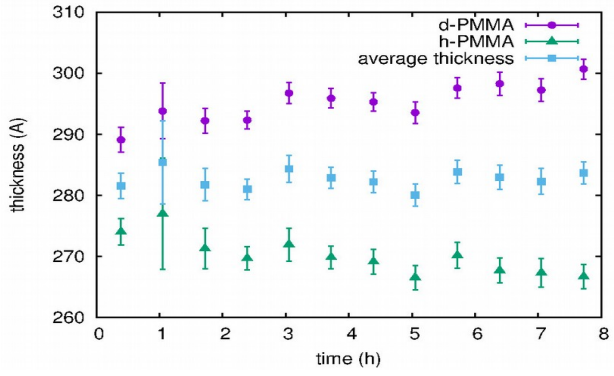

Fig.1 Annealing time dependence of thickness of d-PMMA and h-PMMA layers in addition to the averaged thickness for 2-layered films of hd-PMMA-2.

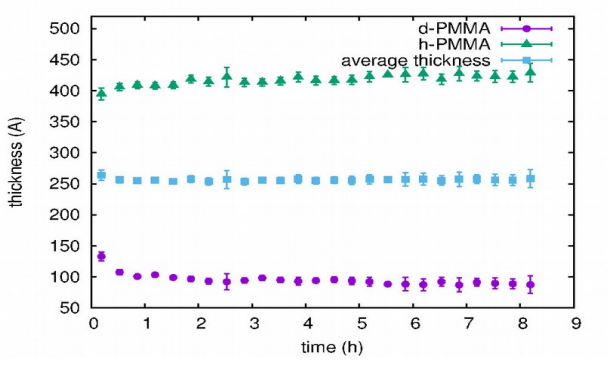

Fig.2 Annealing time dependence of thickness of d-PMMA and h-PMMA layers in addition to the averaged thickness for 2-layered films of hd-PMMA-1.