MLF Experimental Report	提出日 Date of Report 2015.2.6
課題番号 Project No. 2014B0073 実験課題名 Title of experiment Heterogeneous dynamics 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 2014.12.13-2014.12.16

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 hydrogenated poly(methyl methacrylate) (h-PMMA) and deuterated poly(methyl methacrylate) (d-PMMA). The weight-averaged molecular weight Mw and the number averaged molecular weight Mn are 1.826x10^6 and 1.304x10^6 for h-PMMA, and 1.558x10^6 and 8.20x10^5 for d-PMMA. The chemical structure is shown in Fig.1. Five of eight hydrogen atoms of the monomeric unit are replaced by deutrons. The scattering length densities of h-PMMA and d-PMMA are 1.0865 and 4.9298, respectively.

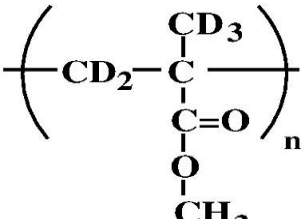

Fig.1: Chemical structure of d- PMMA..

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.

1) Stacked thin films:

Using the original polymeric material, different types of alternatively stacked thin films of h-PMMA and d-PMMA are prepared as follows. A 25-nm-thick-film of d-PMMA is stacked on the glass substrate, and then a 25nm-thick-film of h-PMMA is stacked on the top of d-PMMA thin layer stacked on the glass substrate. This is 2-layered thin films. Furthermore, 25nm-thick d-PMMA layer is stacked once more on the top of the 2-layered thin films, and then the 3-layered thin films are obtained. Stacking a 25nm-thick h-PMMA layer and a 25nm-thick d-PMMA layer are stacked on the top of the 3-layered thin films, we obtain the 5-layered thin films.

2) Results and Discussions:

For the above stacked thin films we have performed neutron reflectivity measurements during the isothermal annealing process at 413K in order to observe the change in the structure of the interfacial regions between two different layers of d-PMMA and h-PMMA.

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

Figure 1 shows the dependence of neutron reflectivity on the scattering vector q for the 2-layered thin films of h-PMMA and h-PMMA during the isothermal annealing process at 413 K. Colors of the symbols stand for the reflectivity profile at various annealing time from 0.33 h to 14.83 h. 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), we have successfully reproduced the observed reflectivity profile as shown by curves in Fig.2. The thickness and roughness of the two layers are obtained as shown in Figs.3 and 4.

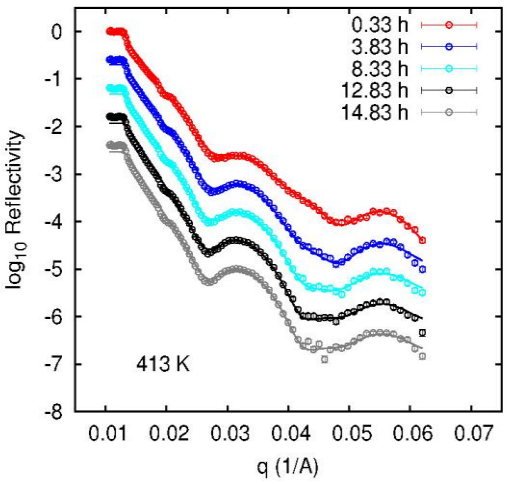

Fig.2: Reflectivity vs. scattering vector of 2 layered thin films.

Figure 3 shows that the roughness at the interface between h-PMMA and d-PMMA increases with increasing annealing time, while the roughness at the surface, that is, the interface between h-PMMA and air, remains almost unchanged. This suggests that the interdiffusion at the interface between d-PMMA and h-PMMA is activated during the isothermal annealing process. Figure 4 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. At the same time, the averaged thickness, or, the total thickness, remains almost constant during the annealing process. The glass transition temperature of d-PMMA used in this study is by about 10K higher than that of h-PMMA, which has been observed by using differential scanning calorimetry. The dynamics of h-PMMA is slower than those of d-PMMA at a given temperature. Therefore, we can conclude that the thickness of the slower component (d-PMMA) increases with annealing time, while that of the faster component (h-PMMA) decreases with time. The faster component enters the region of the slower component and then the molecular activity can swell the size of the slower component (d-PMMA layer) during the isothermal annealing process. The neutron reflectivity measurements of the 3- and 5-layered films of d-PMMA and h-PMMA layers can well support the present conclusions extracted from the results obtained for the 2-layered thin films.

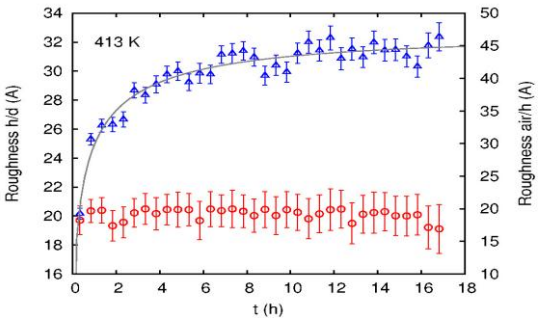

Fig.3: Roughness vs. annealing time.

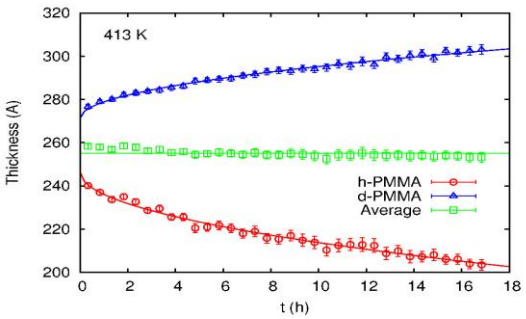

Fig.4: Thickness vs. annealing time of 2-layered thin films.