MLF Experimental Report

提出日 Date of Report	
課題番号 Project No. 2016B0276 実験課題名 Title of experiment Asymmetric mutual diffusion 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 2017.3.5-2017.3.8

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 used in the present measurements are atactic hydrogenated poly(methyl methacrylate) (h-PMMA) and deuterated poly(methyl methacrylate) (d-PMMA). 1) h-PMMA: Mw=323,000, Mn=225,500, Mw/Mn=1.4, 2) **d-PMMA-6:** Mw=307,000, Mn=220,000, Mw/Mn=1.4 and **d-PMMA-5:** Mw=7,630, Mn=7,000, Mw/Mn=1.09. Both d-PMMA-6 and d-PMMA-5 include 8 deuteriums instead of hydrogens within the monomeric unit. The scattering length densities of h-PMMA and d-PMMA in this case are 1.07 and 7.22, 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.

a) Sample preparation methods:

From the above d-PMMA and h-PMMA, we prepared alternately stacked thin films of d-PMMA and h-PMMA layers. First, we prepare a toluene solution of a mixture of d-PMMA-6 and d-PMMA-5 with different fractions, namely, 10:0 and 6:4. We utilized the blending of two d-PMMA with different molecular weights to control the overall glass transition temperature Tg of the d-PMMA layer. Using spin coating, thin films with thickness of about 25nm of d-PMMA and h-PMMA are made separately on the glass substrate. The thin films are once transferred onto the water surface to remove the residual stress induced by spin coating, and are moved onto the glass substrate (for d-PMMA) or the top of d-PMMA layer mounted on the glass substrate (for h-PMMA) . As a result, a stacked thin films of h-PMMA layer and d-PMMA layer are obtained on the glass substrate. The stacked thin films of h-PMMA and d-PMMA are mounted on the sample stage. The temperature of the sample stage was controlled to be 409 K, and the neutron reflectivity measurements at BL16 (Sofia) in MLF, J-Parc are performed during the isothermal annealing process at 409 K.

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

b) Experimental results:

Figure 1 shows the q-dependence of the logarithm of the neutron reflectivity , observed during annealing process at 409 K, for two different stacked thin films of h-PMMA and d-PMMA, where d-PMMA is a mixture of d-PMMA-6 and d-PMMA-5 with the fraction of 1) 1.0 : 0, and 2) 0.6:0.4. On the basis of data fitting using a model function including two layer thicknesses of d-PMMA layer (*d2*) and h-PMMA layer (*d1*), and two roughnesses between the h-PMMA layer and the air (*r1*) and between the d-PMMA layer and the h-PMMA layer (*r2*), we could reproduce the observed q-dependence of the neutron reflectivity for various annealing times, as shown by curves given in Figure 1. Figure 2 shows the annealing time dependence of the thicknesses of d-PMMA layer and h-PMMA layer for both cases. For stacked thin films of h-PMMA and d-PMMA(1.0:0), it is found that the thickness of the d-PMMA layer increases and that of h-PMMA layer decreases with increasing annealing time during the annealing process at 409 K. On the other hand, for stacked thin films of h-PMMA and d-PMMA layers, in which the d-PMMA layer is made from the blend of d-PMMA-6 and d-PMMA-5 (6:4), the thickness of d-PMMA layer decreases and that of h-PMMA layer increases with increasing annealing time. The annealing time dependence of the thickness of d- and h-PMMA layers is totally different between two different stacked thin films of d-PMMA and h-PMMA. The glass transition temperature of d-PMMA is higher than that of h-PMMA for the former stacked thin films, while the glass transition temperature of h-PMMA is higher than that of the d-PMMA for the latter stacked thin films. This suggests that asymmetrical character of the dynamics between d-PMMA and h-PMMA layers can play a crucial role for determining the interfacial interaction of the stacked thin films.

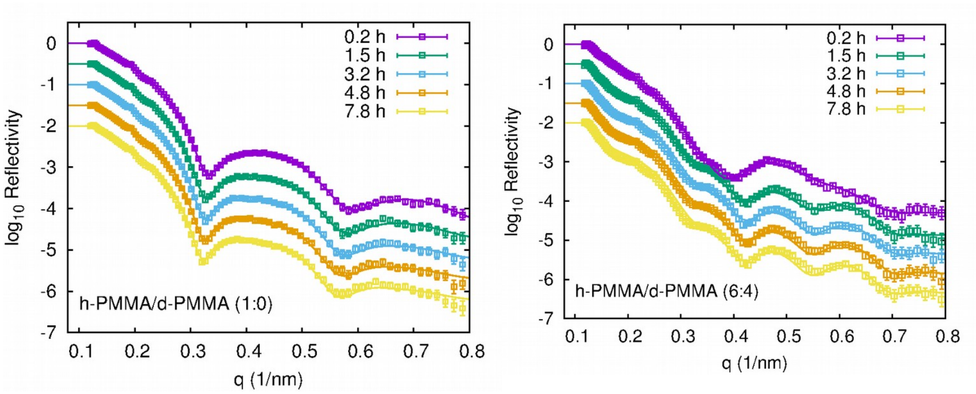

Fig.1 q-dependence of the neutron reflectivity for various annealing times for stacked thin films of h-PMMA/d-PMMA with two different fractions of d-PMMA-6 and d-PMMA-5, (a) 1.0:0 (b) 0.6:0.4.

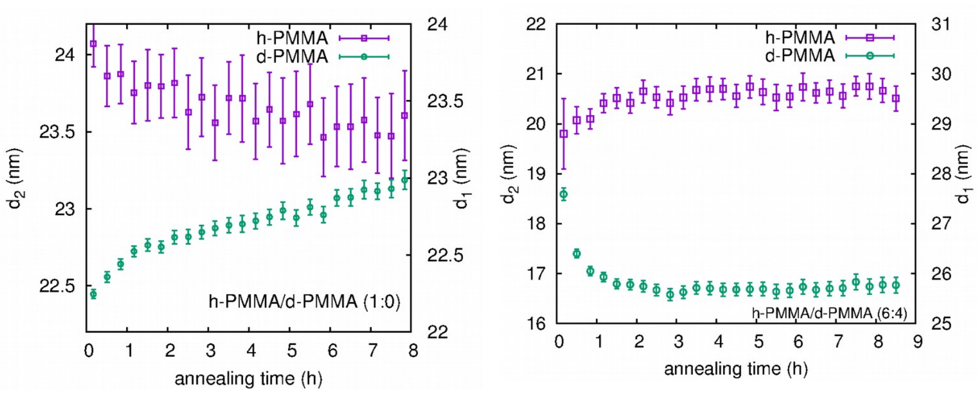

Fig.2 annealing time dependence of thicknesses of d-PMMA and h-PMMA layers for stacked thin films of h-PMMA/d-PMMA with two different fractions of d-PMMA-6 and d-PMMA-5, (a) 1.0:0 (b) 0.6:0.4.