| MLF Experimental Report | 提出日 Date of Report |
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| 課題番号 Project No.<br>2017B0034<br>実験課題名 Title of experiment<br>Interfacial structure and dynamics in stacked thin polymer films<br>実験責任者名 Name of principal investigator<br>Koji Fukao<br>所属 Affiliation<br>Ritsumeikan University | 装置責任者 Name of responsible person<br>Norifumi Yamada<br>装置名 Name of Instrument/（BL No.）<br>BL No.16<br>実施日 Date of Experiment<br>2017.12.14-2017.12.17 |

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-3: Mw=3.23x$10^5$, Mn=2.26x$10^5$ , 2) d-PMMA-5: Mw=7.63x$10^3$, Mn=7.00x$10^3$, 3) d-PMMA-6: Mw=2.63x$10^5$, Mn=2.29x$10^5$. All eight hydrogens are replaced by deutrons for d-PMMA-5 and d-PMMA-6. The scattering length densities (SLD) of h-PMMA and d-PMMA are 1.0865 and 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-3 and -4) are prepared as follows. **a) hd-PMMA-3:** A 35-nm-thick-film of blend of d-PMMA-6 and d-PMMA-5 with 4 different ratios of 1.0:0, 0.9:0.1, 0.8:0.2, and 0.6:0.4 is stacked on the glass substrate, and then a 36-nm-thick-film of h-PMMA-3 is stacked on the top of the d-PMMA layer. b) **hd-PMMA-4:** A thin film of d-PMMA-6 with various thicknesses of 14.5 nm, 25.6 nm, 39.2 nm, 47.9 nm is stacked on the glass substrate, and then a 35-nm-thick-film of h-PMMA-3 is stacked on the top of d-PMMA layer. For the two sets of two-layered thin films (hd-PMMA-3 and hd-PMMA-4), we made neutron reflectivity measurements during the isothermal annealing process at 409 K. From the neutron reflectivity as a function of scattering vector q, we evaluated the time evolution of the thicknesses of d-PMMA and h-PMMA layers, the roughness at the interface between d-PMMA and h-PMMA layers.

For hd-PMMA-3 samples, the glass transition temperature Tg of the d-PMMA layer decreases with increasing fraction of d-PMMA-5, because Tg of d-PMMA-5 is lower than Tg of d-PMMA-6.

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

Figure 1 shows the annealing time dependence of the thicknesses of d-PMMA and h-PMMA layers for four different ratios of d-PMMA-6 and d-PMMA-5. From this figure, we can see that the thickness of d-PMMA layer increases and the thickness of h-PMMA layer decreases with increasing annealing time for hd-PMMA-3 with the fraction of 1.0:0, while the thickness of d-PMMA layer decreases and the thickness of h-PMMA layer increases with increasing annealing time for hd-PMMA-3 with the fraction of 0.9:0.1, 0.8:0.2, and 0.6:0.4. This result suggests that the decrease in Tg of d-PMMA layer, by blending d-PMMA-6 with d-PMMA-5, can be monitored by the time evolution of the thicknesses of d-PMMA and h-PMMA layers.

Figure 2 shows the annealing time dependence of the thicknesses of d-PMMA and h-PMMA layers for four different thicknesses of d-PMMA layers from 13 nm to 49 nm. During the annealing process at 409 K, the thickness of d-PMMA layer increases with increasing annealing time for the 35nm-thick-d-pMMA layer and 49nm-thick-d-PMMA layer. For the 25nm-thick-d-PMMA layer, the thickness of d-PMMA layer decreases with increasing annealing time. Furthermore, the decreasing rate for th 13nm-thick-d-PMMA is much larger than that of the 25nm-thick-d-PMMA layer. Based on the observed results given in Figure 1, the observed dependence of the time evolution of the thickness of the d-PMMA layer on the initial thickness of the d-PMMA layer can be interpreted as follows. For 35nm- and 49nm-thick-d-PMMA layer, the glass transition temperature is almost equal to that of the bulk d-PMMA, which is by a few degree larger than that of the h-PMMA layer. As the initial thickness of the d-PMMA layer decreases from 35nm to 25nm and then 13nm, the Tg of the d-PMMA layer decreases and as a result, the Tg of d-PMMA layer is lower than that of the h-PMMA layer. If this interpretation is correct, the annealing time dependence of the thickness of the d-PMMA layer in the two layered thin films of d-PMMA and h-PMMA can be used for monitor to evaluate the glass transition temperature of the thin polymer layer.

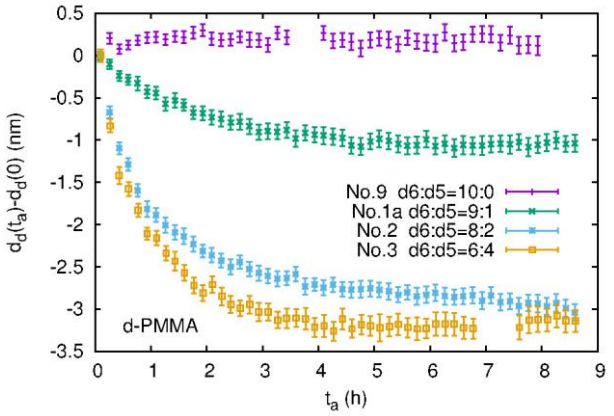


Fig.1 Annealing time dependence of thickness of d-PMMA layer for 2-layered films of hd-PMMA-3 with various blending fractions of d-PMMA-6 and d-PMMA-5.

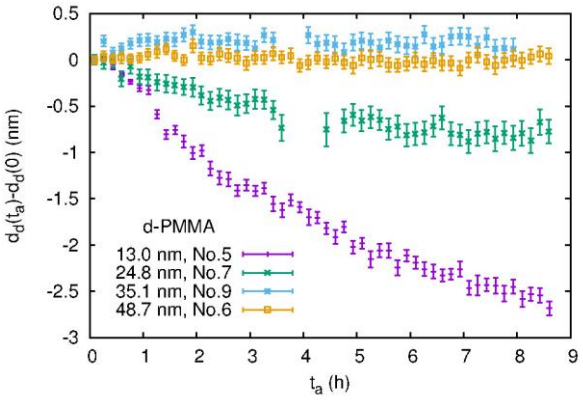


Fig.2 Annealing time dependence of thickness of d-PMMA layer for 2-layered films of hd-PMMA-4 with various initial thicknesses of d-PMMA-6.