

(※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。)

 MLF Experimental Report	提出日 Date of Report
課題番号 Project No. 2017A0197 実験課題名 Title of experiment Aggregation States of Rotaxaned Polymer Surface with Water and Its Effect on Bio-inertness Property 実験責任者名 Name of principal investigator Hisao Matsuno 所属 Affiliation Kyushu University	装置責任者 Name of responsible person Norifumi L. Yamada 装置名 Name of Instrument/(BL No.) SOFIA/BL16 実施日 Date of Experiment Apr. 30-May 2, 2017

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. 1. deuterated poly(methyl methacrylate) (dPMMA), (C ₅ D ₈ O ₂) _n 2. poly(methyl methacrylate- <i>ran</i> -methyl 2-hydroxy-3-azidepropylate) (PMAz), (CH ₂ CCH ₃ COOCH ₃ - <i>ran</i> -CH ₂ CCH ₃ COOCH ₂ CH(OH)CH ₂ N ₃) _n 3. α-ethynyl-ω-amine-poly(ethylene oxide), HCC-(CH ₂ CH ₂ O) _n -NH ₂ 4. (C ₆ H ₁₀ O ₅) ₆ 5. D ₂ O 6. H ₂ O
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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. As a foundation layer, a film of dPMMA was prepared onto a quartz block by a spin-coating method. Then, an ultrathin layer of poly(methyl methacrylate- <i>r</i> -methyl 2-hydroxy-3-azidopropylate) (PMAz) spread onto an ultrapure water surface was transferred onto the PMMA film by the Langmuir-Blodgett method. The film obtained was dried under vacuum for 24 h at room temperature. Hereafter, the resultant film is referred to as the PMAz film. Heterobifunctional poly(ethylene oxide) (PEO) chains were introduced onto a PMAz film by the Cu(I)-catalyzed click reaction. Subsequently, CuSO ₄ and sodium ascorbate were added into the PEO solution. The obtained film is referred to as a PEO-c film. α-CD molecules were threaded onto a PEO chain at the surface and trapped by capping the chain with 2,4,6-trinitrobenzenesulfonic acid. The PEO film was immersed into a CD solution and was then left undisturbed at 298 K for 12 h to complete the inclusion complexation. After 12 h, the film was washed with water and was then dried at room temperature for 24 h in a vacuum oven. The obtained films are referred to as a PEO/CD-c film.
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2. 実験方法及び結果(つづき) Experimental method and results (continued)

The density profiles of each film along the depth direction were examined by neutron reflectivity (NR) measurements. Here, dPMMA was used to enhance the contrast of the scattering length density (b/V) difference between each layer. A Teflon-made reservoir filled with D_2O was mounted on the film. Prior to the measurement, the films were measured in air, and then aged in H_2O or D_2O . A beam of neutrons with a wavelength ranging from 0.25 to 0.88 nm at a resolution of 3% was guided into the specimen from the quartz side.

The reflectivity was calculated on the basis of the (b/V) profile along the depth direction by means of Parratt32 software, a freeware program from the Hahn–Meitner Institute (HMI). The (b/V) values of dPMMA, SiO_2 , and D_2O used for the calculation were 7.02×10^{-4} , 3.48×10^{-4} , and $6.38 \times 10^{-4} \text{ nm}^{-4}$, respectively.

Panel (a) of Figure 1 shows q_z dependence of NR for each film in air. The solid curves were best fits to the experimental data on the basis of the model (b/V) profiles shown in panel (b) using the three-layer model. The data indicate that the PEO or PEO/CD-c layers formed in the outermost interfacial region of dPMMA film with the PMAz layer. While the thickness of PEO-c (*i.e.* PEO without α -CD molecules) was estimated to be 5.2 nm, it increased to 8.4 nm after complexation with α -CD molecules. These results mean that PEO chains immobilized on the foundation dPMMA layer elongated due to the formation of polyrotaxaned structure. In addition, we analyzed the NR data acquired in water, however, the best-fit curves are not obtained using the three-layer model at the moment, thus, we have to continue to fit the data using other models.

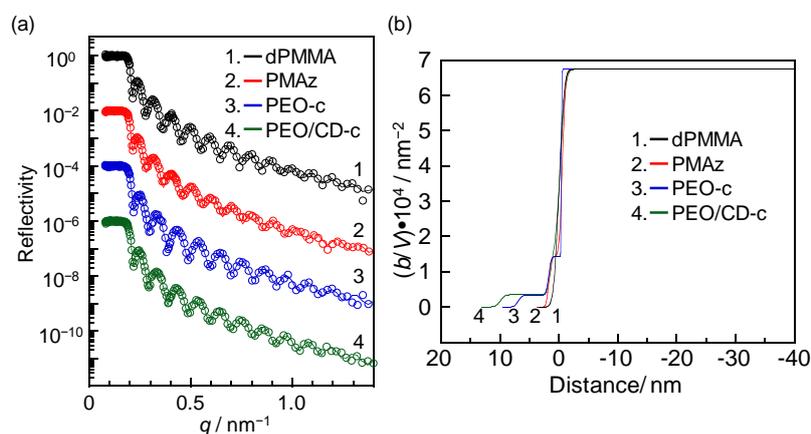


Figure. (a) NR curves for each film in air. Open symbols depict the experimental data, and solid lines are the reflectivity calculated on the basis of (b) the (b/V) profiles of the film in air.