MLF Experimental Report

提出日 Date of Report

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実験課題名 Title of experiment

Neutron reflectivity study of inclusion complex formation of of cyclodextrin on poly(ethylene oxide) brush

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実施日 Date of Experiment
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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.

α-CD was purchased from Nihon Shokuhin Kako Co. Ltd. Poly(ethylene glycol) methyl ether thiol (mPEG SH) with a molecular weight of 5,500 (determined by GPC) was purchased from Shearwater. Poly(ethylene glycol) dithiol (PEG SH) with a molecular weight of 12,000 (determined by GPC) was purchased from Sigma–Aldrich Co. LLC. 6–Mercapto–1–hexanol was obtained from Tokyo Chemical Industry Co., Ltd. D2O was purchased from Wako Pure Chemical Indus–tries, Ltd. and Sigma–Aldrich Co. LLC. All reagents were used without further purification.

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.

PEG Brush

A 10–nm Au layer on a 3–nm Cr adhesive layer was fabricated on a quartz wafer. mPEG SH and 6–Mercapto–1–hexanol (MH) were dissolved in D2O. The Cr/Au–deposited wafer was immersed in the solution for 1 h to plant the PEG brush. Three types of PEG brushes with various densities were prepared from the mixed solution of mPEG SH and MH. The total concentration of mPEG SH and MH is 100 μmol/L. For IC formation, the PEG brushes on the wafers were washed with D2O and then exposed to either 5% or 10% α-CD solutions in D2O.

In–situ NR experiments were conducted with Soft Interface Analyzer (SOFIA) at the J–PARC, Ibaraki, Japan. The specular neutron reflectivity of the interface of the polymer brush on the substrate with pure D2O and with the α-CD solution was measured. After the polymer brush was exposed to the α-CD solution, time–resolved neutron reflectometry measurement was conducted by using remote–controlled stopped–flow cell.

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

The reflectivity curves were fitted with a multilayer model consisting of a quartz substrate, a Cr layer, a Au layer, a D2O-swollen brush layer or IC layer, and an ambient solution. The SLDs of PEG and α-CD were assumed to be 0.63 and 3.78 × 10−4/nm2, respectively. In order to calculate its SLD, α-CD was regarded as C36H42D18O30 because, in deuterium oxide solution, its OH groups are replaced by OD groups.
The NR measurements of the Cr/Au coated substrate, the PEG brush on the substrate and IC layer on the substrate were conducted sequentially so that the SLD profile of the substrate is fixed parameters when the brush profiles are to be fit.

We prepared the quartz substrates coated with Cr and Au and measured the scattering length density (SLD) profiles using NR. The substrates were subsequently immersed in the D2O solution of PEG with thiol functional group(s) to grow PEG brush and their interfacial structures were evaluated using NR. Fur-thermore, the PEG grafted quartz substrates were immersed in α-CD solution in D2O and monitored the growth of ICs as a function of time as shown in Figure 1.

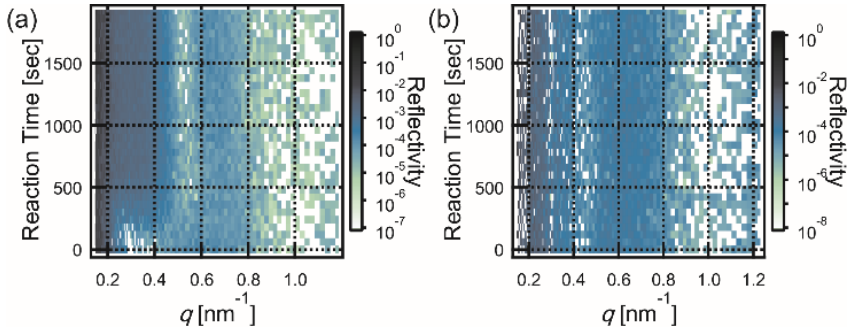

Figure 1: Time-resolved NR profiles of PEG brush 1 with 5% α-CD solution (a) and PEG brush 2 with 10% α-CD solution (b).

Figure 1 shows the time-resolved NR profiles of PEG brushes in 5% (a) and 10% (b) α-CD solutions. The NR profile of PEG brush in 5% α-CD solution exhibits a drastic change around 300-500 seconds after the exposure to the solution. In contrast, the similarly prepared PEG brush in 10 % α-CD solution shows no time dependence in the reflectivity profile. It should be noted that the reflectivity of 10% is different from the reflectivity of the PEG brush; therefore, it is suggested that IC formation takes more than 200-300 seconds in the 5% solution, but less than 10 seconds in the 10% solution, which is the shortest time scale accessible for the NR experiment. The only twofold difference in the concentration induced a much larger difference in the IC formation time. This significant difference is attributed to the kinetics of the IC formation. If the IC formation is simply governed by the hydrophobic interactions between PEG and the inner cavity of CD, the probability of the PEG chain end finding the CD is proportional to the concentration of CD. Thus, an order of difference in time scale cannot be explained solely by the hydrophobic interactions. We further discuss about the origin of IC formation later in this paper, but we focus only on the equilibrium structure of IC in this section.

We further analyze the results to extract the detailed structure of the complex and summarize it in an article or two.