Experimental report

06/06/2016

Proposal: 9-11-1679 **Council:** 4/2014

Title: Conformation of Hydrophilic Polymer Brushes under Confinement

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: silicon blocks
PEG lipids
phospholipids (DSPC)
deuterated PEG lipids

Instrument	Requested days	Allocated days	From	To
FIGARO	4	4	28/11/2014	02/12/2014

Abstract:

Soft interfaces constituted by molecular assemblies in interfacial geometries play important roles in a multitude of technological applications, for instance in the fields of liquid purification, separative chemistry, and lubrication. The term "soft interfaces" broadly covers flexible interfaces and interfaces composed of molecular groups with considerable conformational degrees of freedom. In contrast to the case of "rigid" interfaces, the interaction characteristics of soft interfaces depend on the conformation of their constituents. The interaction between polymer-decorated interfaces, for instance, will be crucially influenced by the ability of the polymer chains to mutually intercalate. With the planned experiment we aim at the structural characterization of hydrophilic PEG polymer brushes in an aqueous environment under confinement and while interacting with a second brush. This scenario is of great relevance in context with biological and technological soft interfaces, but so far largely unexplored. Sensitivity to the conformation of individual brushes will be achieved by the simultaneous use of hydrogenated and deuterated PEG brushes.

EXPERIMENTAL REPORT

EXPERIMENT N° **9-11-1679** INSTRUMENT FIGARO

DATES OF EXPERIMENT 28/11/2014 to 02/12/2014

TITLE Specific Adsorption of Backbone-Binding Antibodies to PEG Polymer Brushes

NOTE: "Conformation of Hydrophilic Polymer …" was performed instead on D17, **9-13-545**

EXPERIMENTAL TEAM
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Date of report 30/05/2016

Protein adsorption to material surfaces causes problems in numerous medical applications [1, 2], such as implanted biomedical devices (e.g., stents). A favored approach in order to prevent protein adsorption is to decorate surfaces with brushes of terminally anchored, neutral water soluble polymers (NWSP) [3, 4]. However, the interaction of proteins with these polymers is poorly understood. In particular, little is known about the mechanisms responsible for regularly observed "brush failure", where protein adsorption occurs despite polymer functionalization. During previous experiments on D17 we studied interactions between proteins and polymer brushes deposited at solid/liquid interfaces. We have fabricated PEG brushes of well-defined grafting layer chemistry, polymer length and polymer grafting density, and structurally investigated different modes of undesired protein adsorption using neutron reflectometry with contrast variation. Our results obtained after incubation with different types of proteins highlight the importance of the brush parameters [5] and the implications of PEG's reported but often neglected antigenicity, where we have worked with anti-PEG antibodies (Abs) specifically binding the end segment of PEG chains [6]. Brush failure induced by end-segment-specific antibodies may be prevented by non-antigenic end-modification of the PEG chains, but there are also other types of antibodies that bind to PEG segments along the chain.

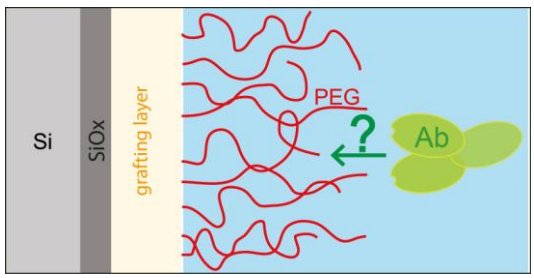

Figure 1: Schematic illustration of PEG functionalized surfaces exposed to solutions of backbone-specific Ab

During experiment 9-11-1679 we studied the adsorption of such "backbone-specific" (BB) Abs onto PEG brushes of defined polymerization degree ($N = 114$) and lateral density. The PEG grafting density was accurately adjusted by Langmuir-Schaefer transfer of water-insoluble DSPC lipid monolayers incorporating

defined fractions of lipid-anchored PEG onto silicon substrates hydrophobically functionalized with octadecyltrichlorosilane (OTS), see Fig. 1 for an illustration. Fig. 2 (left) shows exemplarily the reflectivity curves of a brush containing 2 mol% lipid-anchored PEG in D_2O-contrast before and after incubation with BB Ab solutions. Protein adsorption is seen to have a strong impact on the reflectivity curve at lower q_z (most pronounced at around 0.02 - 0.03 $Å^{-1}$). By simultaneously fitting 8 reflectivity curves (4 water contrasts, before and after incubation) with a global model, the volume fractions of all chemical components (Si, SiO2, hydrocarbon chains, lipid headgroups, PEG, Ab and water) were reconstructed. This is shown in Fig. 2 (right).

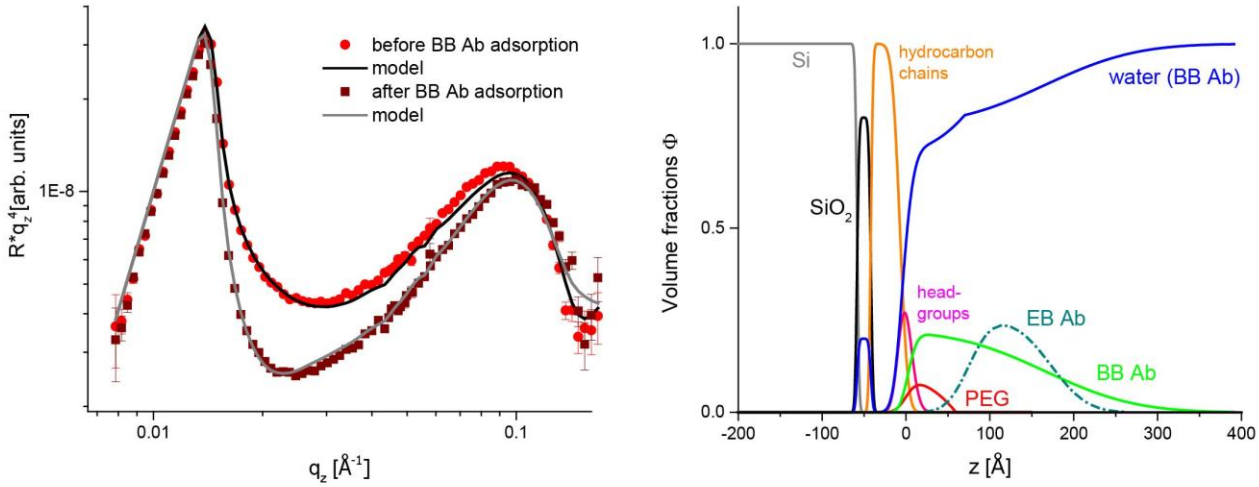

Figure 2:(left) Representative reflectivity curves in D_2O, before and after incubation with BB Ab solution. Solid lines indicate the best simultaneous fit to 8 reflectivity curves: before and after adsorption and in 4 water contrasts (shown: D_2O, not shown: 4-matched water, silicon-matched water and H_2O). (right) The corresponding volume fractions of silicon, silicon oxide, hydrocarbon chains (OTS + lipid tails), lipid head groups, PEG-chains, BB Abs and water fraction (for BB Ab case). The dashed line indicates the volume fraction of EB Abs determined under the same conditions in Ref. [6].

The profile of the BB Ab exhibits a widely distributed adsorption within the whole brush domain reaching as deep as the grafting surface. This behavior is consistent with adsorption along the PEG backbone and in clear contrast to the profile obtained for EB Abs in ref [6], where a dense Ab layer at the brush periphery was observed giving a clear indication of adsorption only to the terminal segments of the brush.

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[2] Hlady & Buijs, *J. Curr. Opin. Biotechnology* **7**, 72 (1996)

[3] Elbert & Hubbell, *Annu. Rev. Mater. Sci.* **26**, 365 (1996)

[4] Goddard & Hotchkiss, *Prog. Polym. Sci.* **32**, 698 (2007)

[5] Schneck, Schollier, Halperin, Moulin, Haertlein, Sferrazza, Fragneto, *Langmuir* **29**, 14178 (2013)

[6] Schneck, Berts, Halperin, Daillant, Fragneto, *Biomaterials* **46**, 95 (2015)