Experimental report

03/09/2022

Proposal: **9-11-2057** **Council:** 4/2021

Title: Nanoscale domain evolution and solvent distribution during water vapor uptake by compositionally variantand bioinert polymer brush mixtures

Research area: Soft condensed matter

This proposal is a new proposal

Main proposer: **Apostolos VAGIAS**

Experimental team: Peixi WANG
Christina GEIGER
Julija REITENBACH
Apostolos VAGIAS

Local contacts: Philipp GUTFREUND

Samples: D2O
[-C2H4O-]nH2O (Polyethylene glycol)
Silicon wafer
[-N(COC2H5)CH2CH2-]n (Polyoxazoline)

Instrument	Requested days	Allocated days	From	To
D22	4	4	02/09/2021	06/09/2021
D17	0	1	06/09/2021	07/09/2021

Abstract:

By utilizing grazing incidence neutron scattering (GISANS), we aim at probing how polymer chain topology, expressed in graft copolymers vs. molecularly mixed homopolymers, affects D2O swelling kinetics and nanostructural hydration from Poly(ethylene glycol) (abbreviated as PEG) and Poly(2-alkyl-2-oxazoline) (abbreviated as PAOXA) protonated brushes grafted on silicon substrates. Our interest lies in quantifying how molecular mixing between PEG and PAOXA brushes affects nanoscale hydration at a single grafting density. The results can have profound impact on the optimization of such brush layers as nanotribological scaffolds. High contrast will be achieved by using heavy water (D2O) as contrast agent for these protonated polymer brushes. The lateral resolution of D22 instrument at ILL allows to probe the lateral D2O solvent localization in these polymer brushes of variable topology.

Nanoscale hydration effects in topologically variant grafted polyoxazoline brushes

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A. Vagias[1], P. Gutfreund[2], E. M. Benetti[3,4], C. Geiger[5], J. Reitenbach[5], L. P. Kreuzer[1,5],

P. Wang[5], L. Porcar[2], T. Saerbeck[2], R. Cubitt[2], P. Müller-Buschbaum[1,5]

1) Heinz Maier-Leibnitz Zentrum (MLZ), Technische Universität München, Lichtenbergstr. 1, 85748 Garching, Germany

2) Institut Laue Langevin (ILL), 71 Avenue des Martyrs, 38000 Grenoble, France

3) Department of Chemical Sciences, University of Padova, Via Marzolo 1, 35122 Padova, Italy

4) Laboratory for Surface Science and Technology, Department of Materials, ETH Zürich, Vladimir-Prelog-Weg 5, 8093 Zürich, Switzerland

5) Technische Universität München, Physik-Department, Lehrstuhl für Funktionelle Materialien, James-Franck-Str. 1, 85748 Garching, Germany

By mixing equimolar mixtures of poly(ethylene glycol) (PEG) and poly(2-ethyl-2-oxazoline) (PEOXA) homopolymers, significant turnover in the lubricious properties of such films can be achieved. [1] Although both are biocompatible, PEOXA exhibits stronger chemical resistance and stealth efficacy. When PEG and PEOXA are mixed together in a homopolymer mixture case, both lubrication and inertness against serum proteins are increased.[1]

Such brush mixtures have a pivotal role in the design of biosensors, coatings of improved immune response and cell-sensitive synthetic macromolecular scaffolds. [1] However, the role of topology variation for such grafted brushes upon exposure to solvent vapor has been scarcely experimentally investigated. The exact chemical composition of a brush formulation can translate to variable stealth efficacy and minimization of activation. [2] In addition, the swelling of such brush mixtures at the nanoscale under vapor atmosphere remains unclear, especially when considering a comparison between grafted PEG-*b*-PEOXA block copolymers ("BCP") and grafted mixture ("MIX") of PEG and PEOXA homopolymers.

Using grazing incidence neutron scattering (GISANS) at D22 and *in-situ* neutron reflectometry (NR) at the D17 instrument of ILL, we investigated the effect of topology into the lateral and transversal morphology in brush PEG/PEOXA homopolymer ("MIX") mixtures and PEG-b-PEOXA block copolymer brushes, both protonated systems having a PLL anchoring backbone to the TiO_2 substrate. The TiO_2 had been magnetron-sputtered onto cleaned Si substrates. The samples were inserted into our custom-made humidity chamber to realize solvent vapor uptake under controlled humidity conditions. D_2O was utilized as solvent vapor to generate the humid atmosphere and also to enhance neutron contrast. During the D_2O vapor injection in the sample chamber, the relative humidity (RH) was increased in one step from 5% to 100% RH, by enriching the dry N_2 carrier gas flow with a D_2O saturated vapor. The thermostat used to equilibrate the vapor generation and humidity chamber was set to 25 °C.

For ToF-NR at D17, we used time-of-flight (TOF) mode with a wavelength band of 2 to 30 Å. The sample-detector distance (SDD) was set to 3.4 m. To cover a large q_z range in static conditions (dry and fully swollen), reflectivity curves for the films in equilibrium were acquired at two different incident angles (α_i = 0.5° and α_i = 2.5°) with a total counting time of 45 min. We also monitored the kinetics of the solvent vapor uptake by the grafted brush layers, with reflectivity data recorded at a fixed incident angle (α_i= 1.0°) with a time resolution of 3 s. This high time resolution allowed the observation of the brush monolayer response during the D_2O hydration cycle. In order to avoid the oversaturation of the detector during SLD increase when D_2O was absorbed, the count rate was recorded for each kinetic run. If it exceeded the preset value of 15000 c/s, a change in the TOF angle was triggered (from α_i = 1.0° to α_i = 1.5°). The reverse of the TOF angle setting was triggered, if the count rate felt beneath a set value.

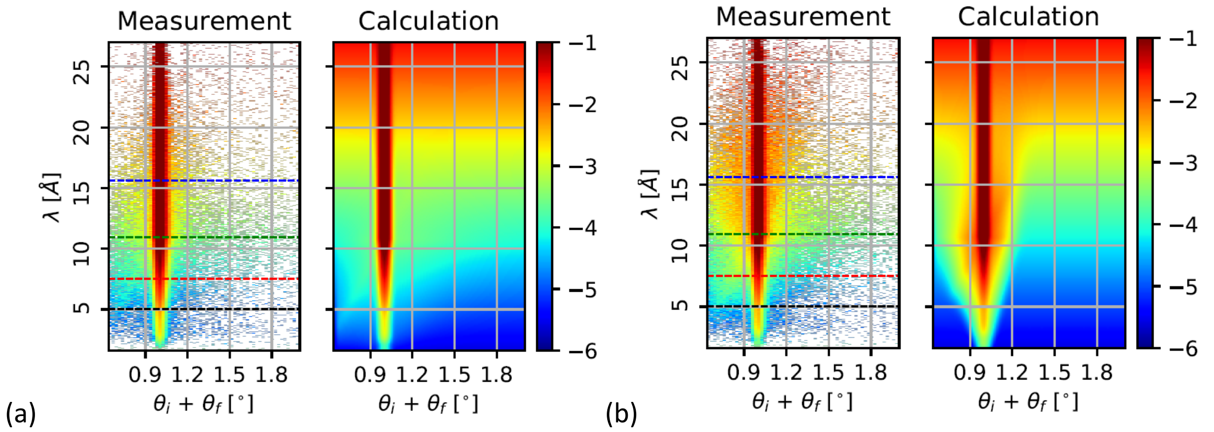

Figure 1. *2D ToF-NR plots of wavelength (λ) vs. exit angle ($\theta_i + \theta_f$) for the (a) PEG/PEOXA homopolymer brush mixture ("MIX") and (b) PEG-b-PEOXA BCP grafted brush layers in the swollen (RH = 95%* D_2O*) equilibrium state. The respective 2D simulations are shown next to each panel (a) and (b), showing the presence of off-specular scattering as a diagonal line.*

The specular reflectometry (NR) results were fitted by a block profile to describe the swollen polymer layer and the substrate contribution (not shown). The resulting out-of-plane structures (from specular reflectometry (NR), not shown) achieve 50% hydration at around 95% D_2O relative humidity (RH) and practically overlap for both systems examined. However, the in-plane structure (off-specular sacttering (OSS)), when in RH = 95% D_2O, suggested OSS for both "MIX" and BCP system (and not for the single component homopolymers), meaning that the water distribution is not homogeneous along the surface (in-plane) in both multicomponent systems.

However, the intensity of OSS was much larger for the BCP sample than for the "MIX" system, meaning that the size and/or the contrast of the inhomogeneities was larger for the BCP sample. Indeed, the BCP radius of $\sim$15 μm is 10 times larger than the analogous of the homopolymer mixture ($\sim$1.5 μm). The ongoing analysis aims at quantifying the amount of hydrated domains. So in essence concerning the in-plane structure, we identify a clear difference between the two multicomponent systems, with the block-copolymer ("BCP") showing domains completely phase separated from the water, whereas the homopolymer mixture ("MIX") shows just regions of slightly lower and slightly higher hydration with respect to the average hydration.

For GISANS at D22, we have measured at an SDD =17m and at 20m collimation, using an incident angle (α_i = 0.45°) and in monochromatic mode (λ = 6 Å) with $\delta\lambda/\lambda$ = 10%. Figure 2 shows the 1d $I(2\theta)$ GISANS horizontal line cuts, at the Yoneda peak position of the polymers, along the out-of-scattering-plane exit angle (2θ) in the swollen state *(RH =* 95% D_2O*)* for the MIX and BCP system. The two systems exhibit differences in the shape of their 1d line cuts between 2θ = 0.1° and 2θ = 0.5°.

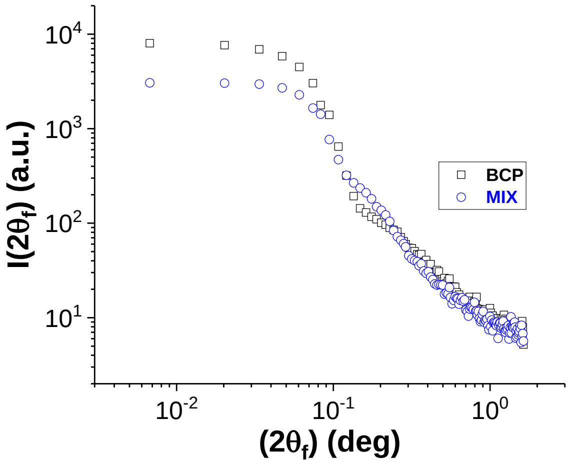

Figure 2. *Horizontal (out-of-scattering-plane) 1d line cuts from 2d GISANS images, shown as intensity vs. out-of-scattering-plane exit angle ($2\theta_f$). Black squares and blue circles denote the BCP and MIX system, respectively.*

The difference seems not drastic, but still significant. It has to be underlined that this has been a challenging experiment, on account of the ultra-low polymer thickness (brush monolayer) which pushed the investigation to the limits of GISANS technique. The current analysis focuses on the quantification of nanostructure sizes and spacing in the GISANS line cuts, for both dry and swollen state. For the GISANS modeling, cylindrical and/or spherical form factors using local monodisperse approximation [3-5] for the interference function are currently compared. The analysis will include comparison with the dry state of the same systems, as well as with dry and swollen state of the homopolymer, in order to proceed to publication of the results.

References

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