Experimental report

01/03/2024

Proposal: 9-11-2089 **Council:** 10/2022

Title: Nanoscale domain evolution as a function of pressure in dual functional bactericidal and antifouling compositionally variant brush mixtures

Research area: Soft condensed matter

This proposal is a new proposal

Main proposer: Apostolos VAGIAS

Experimental team: Apostolos VAGIAS
Andreas BUCHNER
David KOSBAHN
Marcell WOLF

Local contacts: Philipp GUTFREUND
Leonardo CHIAPPISI
Lionel PORCAR

Samples: D2O
Si wafers
(-C9H8O2F8-)n (poly(2,2,3,3,4,4,5,5-(octafluoro) pentyl methacrylate)
(-C8H15NO2-)n (poly(2-(dimethylamino)ethyl methacrylate))
(-C5H8O2-)n (poly(methyl methacrylate))

Instrument	Requested days	Allocated days	From	To
D22	3	0		
FIGARO User-supplied	2	2	05/04/2023	07/04/2023

Abstract:

By means of Grazing Incidence Neutron Scattering (GISANS) and Time-of-flight Neutron Reflectometry (ToF-NR), we focus on lateral and transversal nanoscale morphologies respectively in a pressure (P) range from P = 1 bar to P = 1000 bar from two different grafted equimolar protonated immersed brush mixtures: (i) a strongly segregated Poly(2,2,3,3,4,4,5,5-(octafluoro) pentyl methacrylate) (POFPMA) / Poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) mixture and (ii) a weakly segregated Poly (methyl methacrylate) (PMMA) / Poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) brush homopolymer mixture. Heavy water (D2O) will be used as swelling and contrast agent, silicon wafer as the substrate. We are interested in correlating chemical composition to nanoscale segregation for these two immersed brush systems at different P-values at the solid-liquid interface. Lateral and vertical resolution of D22 and FIGARO will allow us to identify localization of nanoscale segregation and/or solvent domains and impact nanotribology and soft robotics for deep sea research.

Apostolos Vagias,[a,b*] Theodore Manouras,[c,d] Andreas Buchner,[a] Philipp Gutfreund,[b] Lionel Porcar,[b] Andrew Nelson,[e] Leonardo Chiappisi,[b] David P. Kosbahn,[f] Marcell Wolf,[a] Laura Guasco,[g,h] Maria Vamvakaki[c,d] and Peter Müller-Buschbaum[a,f]

a) Heinz Maier-Leibnitz Zentrum (MLZ), Technical University of Munich, Lichtenbergstr. 1, 85748 Garching, Germany

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

c) Institute of Electronic Structure and Laser, Foundation for Research and Technology—Hellas, 700 13 Heraklion, Greece

d) Department of Materials Science and Technology, University of Crete, 700 13 Heraklion, Greece

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

e) ANSTO, New Illawarra Road, Lucas Heights, NSW 2234, Australia

f) Technical University of Munich, TUM School of Natural Sciences, Department of Physics, Chair for Functional Materials, James-Franck-Str. 1, 85748 Garching, Germany

g) Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, D-70569 Stuttgart, Germany

h) Max Planck Society Outstation at the Heinz Maier-Leibnitz Zentrum (MLZ), D-85748 Garching, Germany

* Correspondence e-mail: vagias@ill.fr

During Proposal 9-11-2078, we have performed neutron reflectometry under pressure for the morphological characterization of the nanostructure in thin (<100 nm) soft matter films. A stainless steel-based pressure cell with sapphire windows is used as sample chamber and D_2O serves the role of both, hydrostatic pressure liquid and solvent (Kreuzer et al., 2011). By means of hand pump pressurization, a pressure (P) range from P = 1 bar up to P = 1 kbar is achievable. The neutron beam impinges at the solid (Si)-liquid (D_2O) interface. We demonstrate feasibility by investigating a mixture of strongly segregated PDMAEMA and POFPMA homopolymer brushes anchored on Si at T= 45 °C for two P-values, P = 1 bar (Fig. 1a) and P = 800 bar (Fig.1b).

Specular reflectivity. In order to comment on the vertical distribution of solvent across the brush thickness, we the specular reflectivity of this strongly segregated brush as a function of P on the instrument FIGARO at the ILL. We used a broad wavelength (λ) band of λ = 2–27 Å with a spectral resolution ($\Delta\lambda/\lambda$) of 7.5 % during the measurements. We carried out static ToF-NR experiments at two incident angles (αi) of αi = 0.7°and αi =3.0°, allowing to cover a broad q_Z-range up to q_Z = 0.3 $Å^{-1}$. By utilizing the Motofit software (Nelson, 2006), we model our reflectivity data by a six-layer model: backing (D_2O) / swollen polymer domain / less-swollen polymer domain / initiator /SiOx/ fronting (Si).

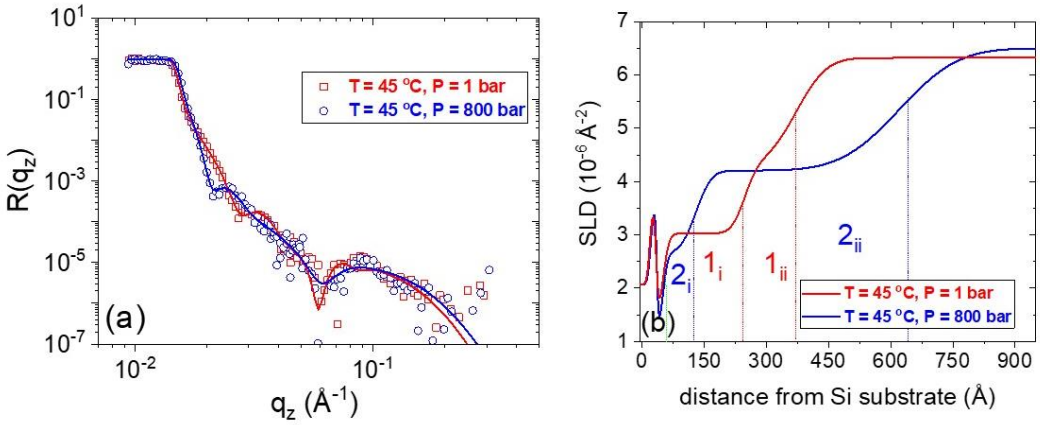

Fig.1. Static ToF-NR curves (panel (a)) and SLD profiles (panel (b)) along the sample's normal direction (z) for PDMAEMA/POFPMA homopolymer brush mixtures, a P t = 1 bar / T = 45 ℃ (red) and P = 800 bar / T = 45 ℃ (blue) obtained by model-fitting ToF-NR curves. The fits in panel (a) are shown by solid lines. In panel (b), the SLD profiles for P = 1 bar / T = 45 ℃ (red) and P = 800 bar / T = 45 ℃ (blue) by using a six-layer model: backing (D_2O) / swollen polymer domain / less-swollen polymer domain / initiator /SiOx/ fronting (Si). Along each SLD profile and at z > 0 Å, the different polymer-containing layers are identified by a number with a roman subscript for P = 1 bar (1i, 1ii) and P = 800 bar (2i, 2ii). Vertical dashed and dashed-dotted lines highlight the boundaries between the different polymeric slab layers, located at the inflection points of the SLD upturns. The profiles are aligned (z=0) at the Si substrate to show the changes in SLD occurring in the polymer film.

From the ToF-NR data presented in Fig.1a, a shift of the minima in the q_Z-axis to smaller q_Z-values with increasing P (red to blue) is shown. This suggests that the upturn in P induces an increase in brush thickness and/or increasing hydration of the swollen polymer domains of the brush (as shown by the cyan line in the SLD profiles (Fig. 1b)).

Off-specular scattering:

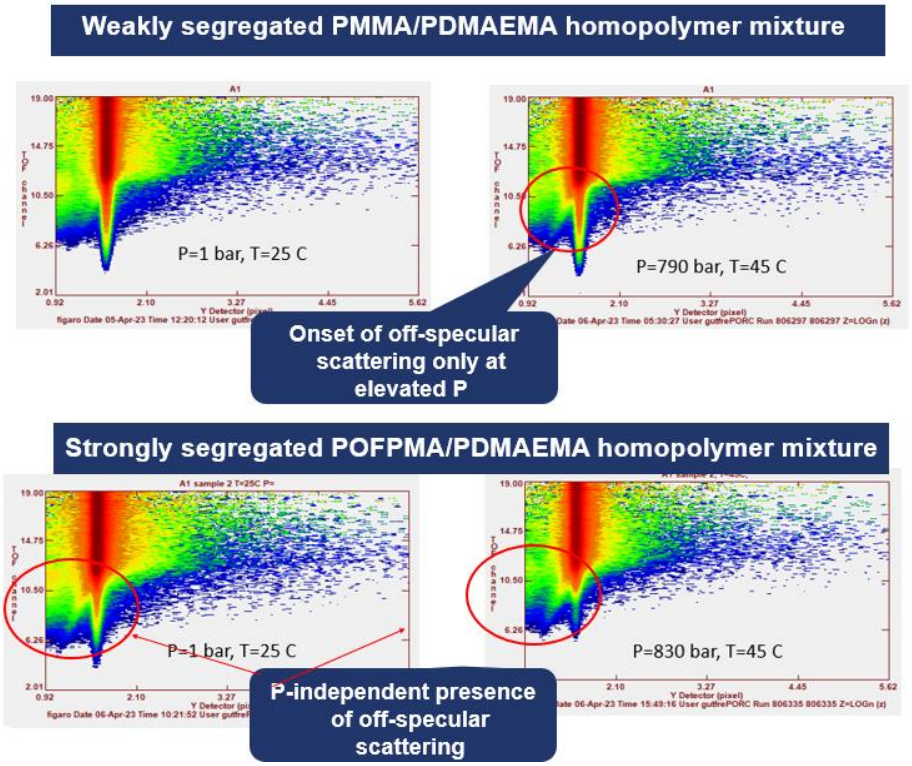

Fig.2. Summary of off-specular scattering plots, TOF channel vs. Y-pixel, obtained for (top row) weakly segregated PMMA/PDMAEMA homopolymer mixture and (lower row) strongly segregated POFPMA/PDMAEMA homopolymer mixture. Panels were recorded at different settings for each row: left (P = 1 bar, T =25 °C) and right (P = 830 bar, T = 45 °C). The red arrows with circled region indicate the presence of off-specular scattering in certain panels.

The off-specular scattering plots indicate composition and pressure-dependent alterations for each sample. Our reflectometry analysis is being supported by preliminary GISANS results (proposal EASY-1091), in order to obtain a broader understanding of water localization across and along the brush surface.

Concluding remarks: We demonstrate the feasibility of high- P GISANS studies for supported soft matter films. We present a case study of a strongly segregated polymer brush mixture where P-alteration has an effect on the lateral nanostructure of the brushes. As example, the supramolecular assembly of POFPMA chains embedded in a surrounding continuum matrix formed by solvophilic PDMAEMA polymer is resolved in terms of POFPMA domain sizes and distanced between neighboring domains. This methodology can be insightful in what concerns phase behavior of supported soft matter layers in soft condensed matter.

Bibliography

Nelson, A. (2006). *J Appl Crystallogr* **39**, 273–276.

Kreuzer, M. et al. (2011) *Rev. Sci. Instrum*. **82**, 023902 (2011)