Experimental report

22/05/2026

Proposal: 9-11-2237 **Council:** 10/2024

Title: Structure at the air-water interface of (polyethylene oxide-polypropylene oxide-polyethylene oxide) ¿ poydimethylsiloxane blends

Research area: Soft condensed matter

This proposal is a continuation of 9-11-2198

Main proposer: Sophie CANTIN

Experimental team: Sophie CANTIN
Aurely ARAMINTHE
Fabrice COUSIN
ALAE EL HAITAMI

Local contacts: Pablo SANCHEZ PUGA

Samples: Polydimethylsiloxane
Deuterated Water
polyethylene oxide-polypropylene oxide-polyethylene oxide

Instrument	Requested days	Allocated days	From	To
FIGARO Langmuir trough	4	4	26/06/2025	30/06/2025

Abstract:

The proposed experiment aims to study by neutron reflectometry using the contrast variation method the structure of PEO-PPO-PEO/PDMS blends at the air-water interface at different positions of the surface pressure - PDMS volume fraction phase diagram. PEO11-PPO35-PEO11 called P1 and a di-methacrylate terminated PDMS (MW = 10000 g/mol) will be used. This study will provide insights on the 2D behavior of the mixed films depending on the composition and surface pressure.

Standard Project

Experimental Report

Proposal title: Structure at the air-water interface of polyethylene oxide-polypropylene oxide polyethylene oxide – polydimethylsiloxane blends		
Experiment number: 9-11-2237	**Date(s) of experiment:** from 26/06/2025 to: 30/06/2025	**Beamline:** FIGARO
Local contact(s): Philipp Gutfreund		**Date of report:** 20/05/2026

Objective & expected results:

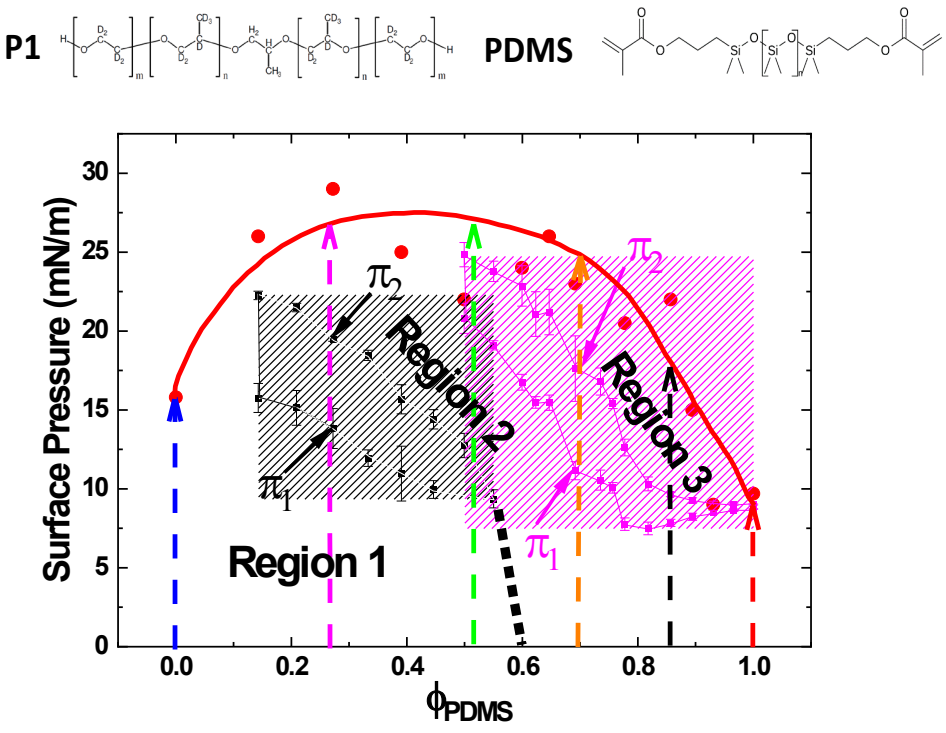
Structure at the air-water interface of polyethylene oxide-polypropylene oxide polyethylene oxide – polydimethylsiloxane blends

The proposed experiment aims to study by neutron reflectometry (NR) using the contrast variation method the vertical structure of block copolymer polyethylene oxide-polypropylene oxide- polyethylene oxide (PEO_{11}-PPO_{35}-PEO_{11} called here P1) / polydimethylsiloxane (PDMS) Langmuir films with various PDMS volume fraction: ϕ_{PDMS}=0.28; 0.51;0.70; 0.85. The 4 studied compositions were studied to probe the two phase transitions deduced from compressibility analysis and represented in the surface pressure vs. composition phase diagram shown in Figure 1A.

Methodology: We used either a deuterated P1, dP1, mixed with hydrogenated PDMS, or a hydrogenated P1 mixed with deuterated PDMS. To better assess the miscibility behavior, each polymer blend Langmuir film was first spread on a H_2O/D_2O subphase whose SLD was contrast-matched to that of the mixed film, if homogeneous. If the NR curve of the film matches that of the subphase, this would indicate that the film is homogeneous both laterally (from BAM) and vertically at length scales greater than a few microns. To further analyze the structure, we employed at least two additional H_2O/D_2O subphase contrasts for each blend and fitted all corresponding NR curves simultaneously. To guide the choice of the fitting model (single-layer versus multilayer), we primarily rely on measurements performed on the subphase contrast-matched to the homogeneous film.

The results have been published in Langmuir in 2026.

A



B

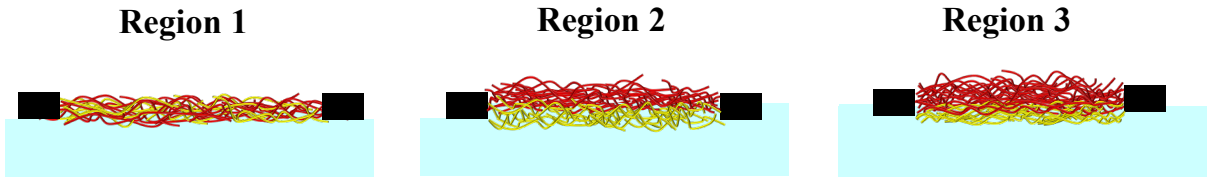


Figure 2. A- Surface pressure π - composition Φ_{PDMS} phase diagram of P1/PDMS blends at the air-water interface. The grey and pink hatched regions indicate the domains where two 1st-order phase transitions occur. Red points represent the film collapse pressures determined by BAM. The four arrows indicate the blend compositions selected for NR analyses: magenta for Φ_{PDMS} = 0.28, green for Φ_{PDMS} = 0.51, orange for Φ_{PDMS} = 0.70, and black for Φ_{PDMS} = 0.85. **B-** Schematics of the vertical film structure deduced from NR measurements in regions 1, 2 and 3. The red and yellow polymer chains represent PDMS and P1, respectively.

Results and conclusions of the study:

As an example, the results obtained for Φ_{PDMS}= 0.28 are presented. The NR curve measured for P1/dPDMS mixed film with Φ_{PDMS}= 0.28, spread on an H_2O/D_2O subphase contrast-matched to the film, was compared to the subphase reflectivity alone at 5 mN/m (Figure 2A) and 23 mN/m (Figure 2B). At low surface pressure (5 mN/m), the reflectivity curves for both blends closely match the subphase reflectivity. This suggests vertical homogeneity. However, above the phase transition, the NR curves deviate from the subphase reflectivity for both compositions, revealing the emergence of vertical inhomogeneity in the film structure.

To further investigate the structural organization of the films, the NR curves obtained for P1/PDMS films on four different H_2O/D_2O subphases were simultaneously fitted (Figure 2C and D). The fitting approach was based on the findings from the previous contrast-matching characterization: a single-layer model was used for homogeneous films, and a two-layer model served as a starting point for vertically inhomogeneous films, and revealed to be always sufficient to properly fit the data.

At surface pressure below the phase transition (5 mN/m): Figure 2C shows the NR curves measured at 5 mN/m for dP1/PDMS film. The vertical homogeneity is confirmed by the good agreement between the experimental curves and the single-layer model fits. The resulting SLD-depth profiles are shown in the insets of Figure 2C. The extracted thickness of the polymer blend layer is 4.9 Å and the film is weakly hydrated (< 20%). From these SLD-depth profiles, volume fraction depth profiles of P1 ($\Phi_{PEO_{11}\text{-}PPO_{35}\text{-}PEO_{11}}$), PDMS ($\Phi_{PDMS}$) and water ($\Phi_{water}$) were extracted and are presented in Figure 2E.

At surface pressure above the phase transition: the NR curves measured at 23 mN/m for the Φ_{PDMS}= 0.28 film are shown in Figure 2D. The previously observed vertical inhomogeneity prompted the use of a two-layer model for fitting the curves. This model provided a good fit, as shown in Figure 2D, and describes a bilayer structure composed of a 6.0 Å-thick top layer of pure PDMS, and a 20.7 Å-thick bottom layer of pure P1, as reflected in the SLD-depth profile shown in the inset of Figure 2D. As expected from the chemical nature of the polymers, the P1 layer in contact with water is hydrated (72% water), while the PDMS layer is not. The volume fractions-depth profiles presented in Figure 2F show that as expected, water is confined to the amphiphilic P1 layer, while the hydrophobic PDMS layer remains dry.

In conclusion, the 1st-order phase transition for P1-rich blends (grey hatched region in the phase diagram) corresponds to a structural transition from a homogeneous single-layer to a vertically segregated bilayer. This bilayer is characterized by a pure hydrophobic PDMS layer at the air interface and a hydrated amphiphilic PEO_{11}-PPO_{35}-PEO_{11} layer at the water interface.

Following similar analyses, we could determine the structure in the 3 regions of the phase diagram, as depicted in Figure 1B. For P1-rich blends, NR demonstrates a transition from a homogeneous monolayer to a vertically segregated bilayer as the surface pressure increases. A similar structural evolution — from homogeneous monolayer to bilayer — is also observed at low surface pressure when the PDMS content is increased from Φ_{PDMS} = 0.51 to 0.70. This indicates that, in the phase diagram shown in Figure 1A, the transition for P1-rich blends extends down to zero surface pressure at around $\Phi_{PDMS} \sim 0.6$. This is depicted in the Figure 1A as a black dotted line, which is only a guide to the eye. In PDMS-rich blends, a bilayer structure is present over the entire surface pressure range, with the 1st-order phase transition primarily associated with a thickening of the PDMS layer. This transition is similar in nature to that of pure PDMS, but its onset is influenced by interactions with the underlying P1 layer in contact with water.

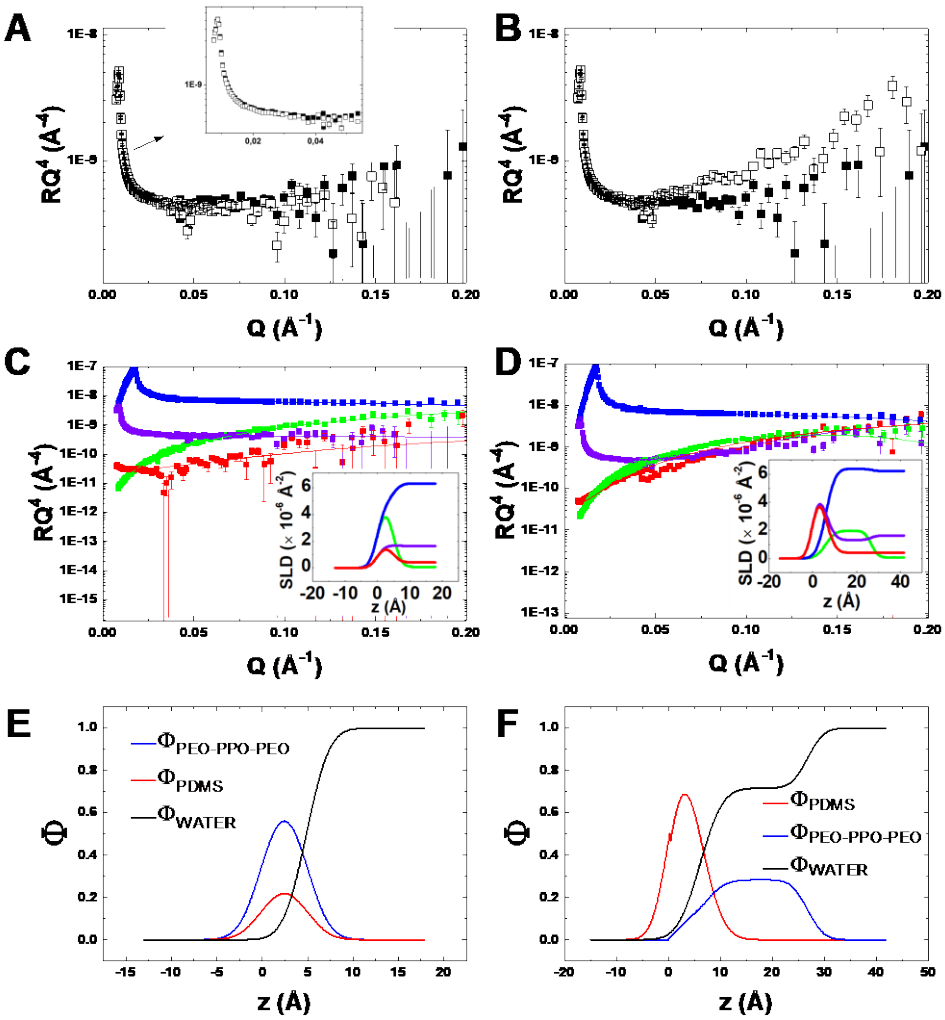


Figure 2. NR data for a P1/PDMS film with Φ_{PDMS}= 0.28 at **(A, C, E)** 5 mN/m and **(B, D, F)** 23 mN/m. **A and B-** NR curves in RQ^4 representation as a function of wave vector transfer Q ($Å^{-1}$) (open symbols) for P1/dPDMS film on a H_2O/D_2O subphase contrast-matched to the film if homogeneous (SLD = $1.69.10^{-6}$ $Å^{-2}$) compared to the reflectivity of the subphase alone (solid symbols). **C and D-** Fits of the RQ^4 =f(Q) NR curves obtained for dP1/PDMS film on two different H_2O/D_2O subphases: contrast-matched to PDMS (red), and to dP1 (blue), and for P1/dPDMS film on two subphases: matched to the mixed film if homogeneous (purple), and to P1 (green). Insets show the corresponding SLD profiles as a function of depth z. **E and F-** Volume fraction profiles of P1 (blue), PDMS (red), and water (black), denoted as $\Phi_{PEO_{11}\text{-}PPO_{35}\text{-}PEO_{11}}$, Φ_{PDMS} and Φ_{water}, respectively, as a function of depth.

Publication: "*Phase diagram of 2D poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) – polydimethylsiloxane blends: A combined neutron reflectometry and sum frequency generation study*"
A. Araminthe, A. El Haitami, B. Kővágó, F. Cousin, P. Sanchez-Puga, J. Webster, P. Gutfreund, E. Backus, S. Cantin. Langmuir **42**, 8548-8566 (2026).

Justification and comments about the use of beam time:

The FIGARO beamline is perfectly suitable to determine the vertical structure of very thin polymer Langmuir monolayers.