Experimental report

13/09/2024

Proposal:	**9-11-2198**	**Council:**	4/2024
Title:	Structure at the air-water interface of polyethylene oxide-polypropylene oxide-polyethylene oxide ¿ polydimethylsiloxane blends		
Research area:	Soft condensed matter		

This proposal is a resubmission of 9-11-2161

Main proposer:	**Sophie CANTIN**
Experimental team:	Pablo SANCHEZ PUGA ABDOUL AZIZ KA Sophie CANTIN ALAE EL HAITAMI Aurely ARAMINTHE
Local contacts:	Philipp GUTFREUND

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

Instrument	Requested days	Allocated days	From	To
FIGARO Langmuir trough	4	2	17/06/2024	19/06/2024

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: 9-11-2198	**Date(s) of experiment:** from 5/18/2024 to: 5/19/2024	**Beamline:** FIGARO

Local contact(s): Philipp Gutfreund	**Date of report:** 9/10/2024

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 the pure block copolymer polyethylene oxide-polypropylene oxide- polyethylene oxide (PEO_{11}-PPO_{35}-PEO_{11} called here P1) and pure polydimethylsiloxane (PDMS) Langmuir films and one blend P1/PDMS Langmuir film of PDMS volume fraction $\phi_{PDMS}=0.71$. This is a preliminary study of the mixing behavior of these two polymers at the air-water interface. The next objective is to complete this study by probing the vertical structure of other blends to understand the surface pressure vs. composition phase diagram previously established using compression isotherms. The studied surface pressures are indicated in **Figure 1A** by the red crosses for PDMS and the blue crosses for P1 while for the $\phi_{PDMS}=0.71$ blend only one surface pressure was studied indicated by the green cross. For both pure polymer films a common D_2O/H_2O mixture subphase was used of scattering length density SLD = 3.10^{-6} Å^{-2} in addition to a second subphase either matched to the PDMS in the case of the P1 film or pure D_2O in the case of the PDMS film. On the other hand, for the mixture, three subphases were used, namely pure D_2O and two D_2O/H_2O mixtures matched either to PDMS or the mixed film if it is homogeneous. This study provides essential information on the structure of pure polymer films that are necessary for understanding the blend properties of which only a single composition is now studied.

Results and conclusions of the study:

As an example, **Figure 1B** and **1C** respectively show the neutron reflectivity curves R(Q) obtained for both pure PDMS and pure P1 films as a function of surface pressure on two different subphases.

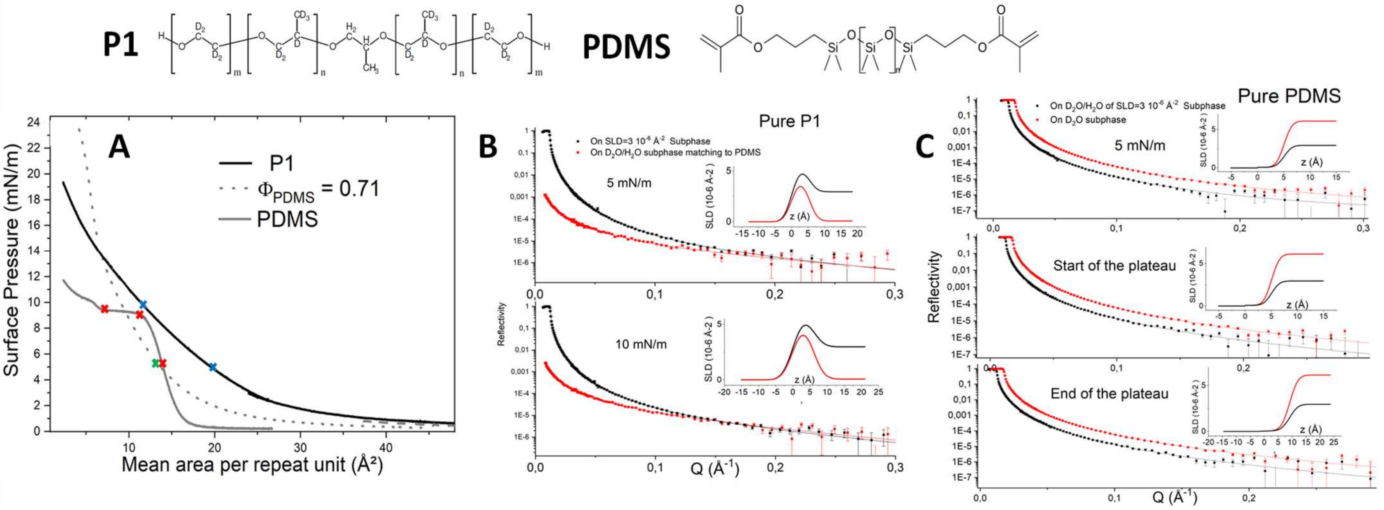

Figure 1: Chemical structure of the studied polymers. A) Compression isotherms of P1, PDMS and P1/PDMS $\phi_{PDMS}=0.71$ films at the air-water interface. Neutron reflectivity R(Q) of Pure P1 (deuterated P1) and pure PDMS films at the air-water interface over different subphases indicated in the graph and at different surface pressures indicated in Figure 1A. The SLD profile is also indicated for each case.

Motofit software has been used to simulate the NR data. For the P1 film studied at 5 and 10 mN/m, a single-layer model was sufficient to correctly fit both reflectivity curves simultaneously. Thus, the monolayer has a thickness of around 5 Å at both surface pressures but the hydration rate decreases from 37% at 5 mN/m 21% at 10 mN/m. The roughness at the interfaces is very low and negligible. For the PDMS film studied at 5 mN/m, at the beginning of the plateau and at the end of the plateau (isotherm presented in Figure 1A) the NR curves were correctly fitted simultaneously using a monolayer model. The film thickens with its compression and the following evolutions are noted: the thickness of 5 Å at 5 mN/mincreases to 8 Å and 9 Å at the beginning and at the end of the plateau at 9 mN/m, respectively. The layer remains unhydrated whatever the surface pressure and the roughness at the interfaces is negligible.

Figure 2 shows the reflectivity curves of the mixed film studied on three different subphases. In addition to the two classically used subphases that extinguish one of the two polymers, a new subphase is studied based on a D_2O/H_2O mixture whose SLD is equal to that of the mixed film if it is homogeneous, namely a sum of SLD of the two polymers weighted by their volume fractions.

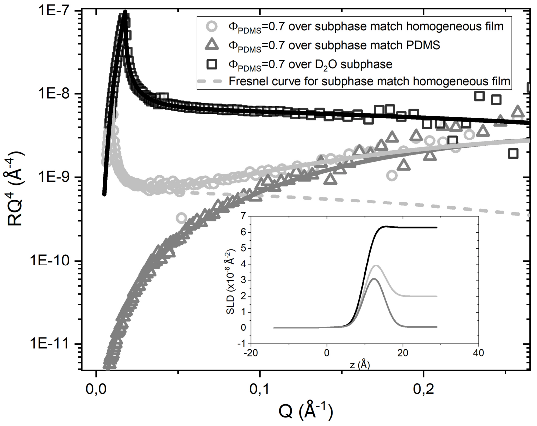

Figure 2: NR curves in RQ^4 representation as a function of wave vector transfer Q for P1/PDMS ϕ_{PDMS}=0.71 Langmuir film at 5 mN/m on the 3 studied subphases, accompanied by their fits and the Fresnel reflectivity of the subphase matched to the mixed film if homogeneous. The SLD profile is also indicated.

The deviation of the NR curve of the mixed film spread on the subphase matched to the homogeneous film from that of the subphase indicate the vertical inhomogeneity of the film. The simultaneous fit of the three NR reveals a vertical segregation with a bilayer structure and the fit was performed using a Python script in Jupyter lab format introducing a new constraint on the thickness of the top layer in the bilayer model so that the ratio of the excess surface between the two layers is an input. The bilayer obtained consists of a non-hydrated upper PDMS layer with a thickness of 10 Å, on top of a P1 layer with a thickness of 5 Å, hydrated at approximately 38%.

Such structure cannot be anticipated from preliminary isotherm and BAM characterizations which shows the advantage of NR to deeply analyze the structure of polymer blends in Langmuir films.

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.