Experimental report

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Proposal: 9-11-2199 **Council:** 4/2024

Title: Elucidation of the structure of single chain nanoparticles assembled at the air/water interface

Research area: Soft condensed matter

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Samples: P(NIPAM-co-AEMA)

Instrument	Requested days	Allocated days	From	To
FIGARO	2	2	21/05/2024	23/05/2024

Abstract:

Water-soluble amphiphilic copolymers containing 2-acetoacetoxyethyl methacrylate (AEMA) and N-isopropyl acrylamide (NIPAM) as monomers can self-fold into single-chain nanoparticles adopting a globular conformation displaying a hydrophobic core/hydrophilic shell morphology. We recently investigated in our lab that air/water interfaces can be used as platform for promoting the direct and spontaneous self-assembly of SCNPs based on P(NIPAM-co-AEMA). We also fine tuned the SCNPS ensemble by imposing interfacial flows and/or engineering the interfacial forces dictated by the hydrophobic/hydrophylic balance of the polymeric nanoparticles at the interface, by varying an environmental factor such as the temperature. To address the interfacial structure of P(NIPAM-co-AEMA) SCNPs, we will employ neutron reflectometry to investigate the out-of-plane density profile of SNCPS at air-water interfaces in-situ as a function of their lateral packing and temperature and compare these results with our previous findings involving atomic force microscopy in-plane characterization.

Experimental report of `Elucidation of the structure of single chain nanoparticles assembled at the air/water interface´.

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A neutron reflectometry (NR) study at the air-water interface of partially deuterated P(NIPAM$_{d10}$-co-AEMA) (PNIPA) block copolymer was performed on FIGARO. The aim of the experiment was to investigate the out-of-plane density profile of PNIPA SCNPs at the air-water interface using NR. By imposing interfacial flows through unilateral compression in a Langmuir trough and varying the temperature around the lower critical solution temperature (LCST) of PNIPA, we aimed to control the molecular structure of the SCNPs. A monolayer can induce lateral changes associated with nano/molecular level alterations of confined molecules in the perpendicular direction.

The experiment was carried out using a Langmuir trough with 47469 mm^2 of maximum area using D_2O and ACMW (air contrast-match water) as sub-phases. Measurements were performed at various surface pressures (15, 20, 25, and 28 mN/m) and temperatures (20°C and 40°C). These conditions were selected to investigate the structural behavior of SCNPs, taking into account the thermoresponsive properties of NIPAM. Notably, PNIPAM undergoes a transition to a hydrophobic state above 32°C.

The Langmuir trough was cleaned with chloroform prior to the experiment. Afterward, 170 mL of water was added to completely cover the trough. Once it was confirmed that the water was clean and the Langmuir setup was properly calibrated to accurately measure the interfacial pressure, 50 µL of SCNPs were added using a Hamilton syringe. A schematic representation of the experimental setup is illustrated in Fig. 1.

The initial results from the experiments (Fig. 2) are very promising, and the data obtained have been consistent with expectations. At room temperature (Fig. 2 A), higher surface pressures show a slower decrease in reflectivity compared to lower pressures, indicating the formation of a thicker layer as compression increases. However, when the temperature exceeds the LCST (Fig. 2 B) the data becomes more scattered, especially at lower pressures. Additionally, the

reflectivity drops more sharply, suggesting changes in the copolymer's structure or behavior at the interface under these conditions. However, due to the large number of measurements taken, we are still in the process of fully analyzing the results. This ongoing analysis aims to extract detailed information about the structure of the copolymer formed at the air-water interface, such as layer thickness, interfacial roughness, and the density of the copolymer layer.

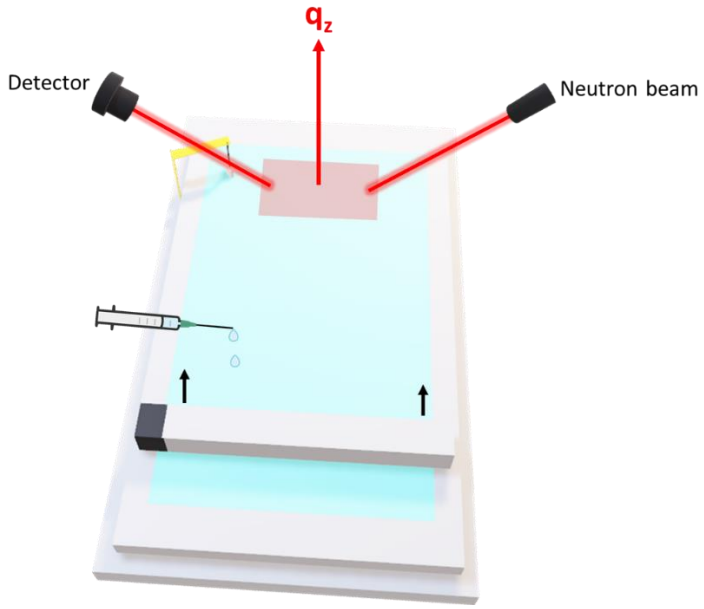

Figure 1. Diagram of the Langmuir balance setup for experiments at the air/water interface.

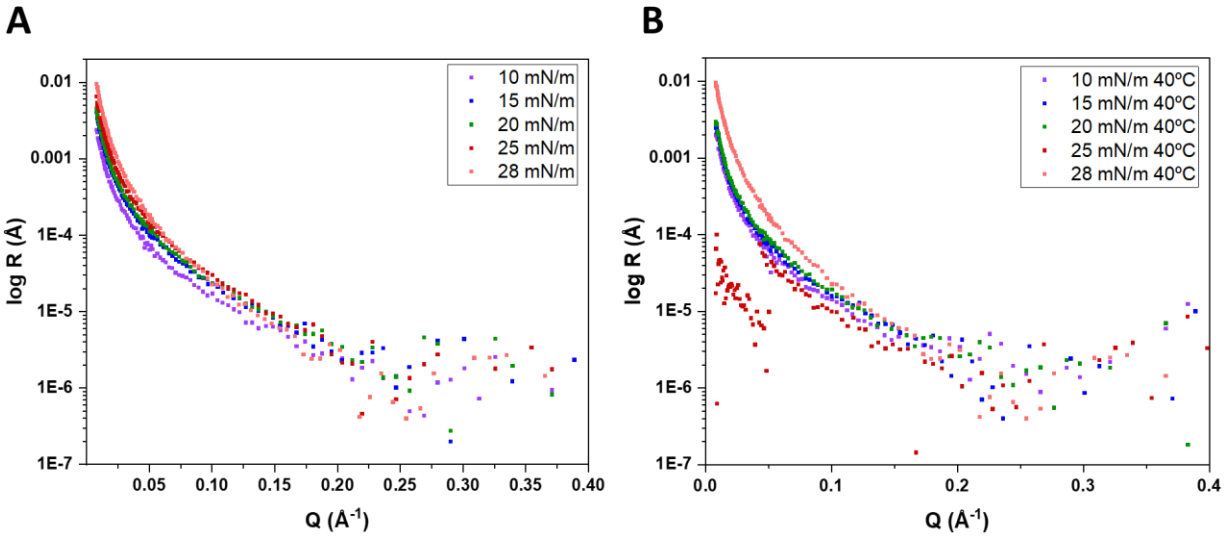

Figure 2. Some experimental data obtained from FIGARO. A) Reflectivity curves of the monolayer at different surface pressures at room temperature. B) Reflectivity curves of the monolayer at different surface pressures at 40°C.