	Experiment title: Polymer 2D molds metallization induced by surface	**Experiment number**: **SC-3301**
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Report:

We developed an innovative method combining the self-assembled properties of organic amphiphilic molecules and the metal reduction to form nano-objects with adjustable functionalities [1,2]. Different shapes can be obtained by using organic structures as moulds which are covered by a metallic layer of nanometric thickness. In order to obtain more complex shape and elaborate mixed nanostructures we plan to enlarge the mould to polymers. Diblock copolymers “hydrophobic-hydrophilic” poly(styrene)-block-pol(acrylic acid) (PS-b-PAA) are then used as the organic material. These macromolecules present the advantages with respect to the classic surfactants, that their self-assembling properties are less sensitive to the physicochemical properties of the solution. However, we can easily adjust the shape and charge surface density of these molds by changing the copolymer architecture (blocks length) and/or its interactions with the solvent (pH, ionic strength).

The copolymer PS-b-PAA consists of a neutral hydrophobic block (PS) and a charged hydrophilic block (PAA). This last block is a weak polyelectrolyte containing a carboxylic group which’s pKa = 4,7. So, when the sub-phase pH’s is set at 2, the PAA is completely neutral. At basic pH=9, the PAA block is fully charged. Consequently, one expect to control the shape of the organic molds by simply adjusting the pH of the sub-phase. Surface pressure isotherms show that these molecules form very stable monolayer at the air-liquid and air-Ag+ ions solution interfaces, at basic pH (pH = 9) as well as acid pH (pH = 2). One expect that the hydrophilic chains can be aggregated to form collapsed surface micelles or they can split to form brush-like surface micelles. In the brush geometry, the thickness of the brush is governed not only by the sub-phase’s pH but also by the hydrophilic block length.

Therefore, we have studied the self-assembly of diblock copolymer PS-b-PAA at the air-liquid interface (pure water sub-phase at pH=2 and 9, and ionic (Ag^+) solution sub-phase at pH=9) by Grazing Incidence Small Angle X-ray Scattering (GISAXS). This measure led to an investigation of the polymer's monolayer in-plane structure according to the surface pressure. The obtained results were very unexpected. Indeed, GISAXS spectra exhibit a characteristic peak indicating a typical distance in the monolayer of the order of ~20nm at pH=9 and ~40nm at pH=2 (figure 2). These values are strongly larger than the ones corresponding to the copolymer's chain dimension (Rg~5nm at pH=9 and Rg~3nm at pH=2). Consequently, these results are a direct evidence that the copolymer chains do not form an homogeneous monolayer at the air-liquid interface, but self-assemble into micelles. Moreover, we have observed at pH=2, that this distance d* ($d^*=2\prod/q^*$) increases when the monolayer is compressed above 2mN/m, whereas it is not the case at pH=9 (figure 2). This surprising behavior is robust and reversible upon decompression. These results indicate that the monolayer diblock copolymers exhibit a complex surface behavior that cannot be accurately described by a usual model of polyelectrolyte brushes.

In addition, we have study at pH=9 the adsorption of silver ions at the organic mold neighborhood and their reduction by the irradiation of the x-ray beam (GISAXS). The concentration of silver atoms at the interface was followed by x-ray fluorescence (figure 3.a). Then, we have obtained a silver wire at the air-liquid interface resulting from the reduction of ions under footprint beam(figure 4.b).

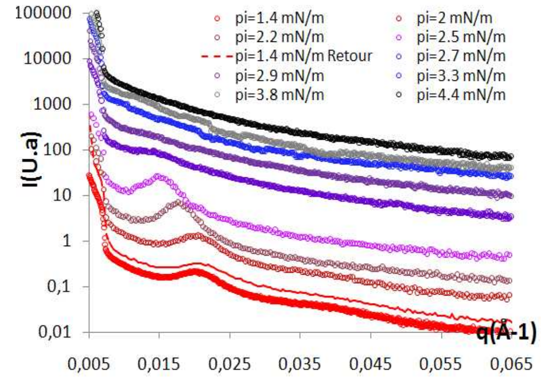

Figure1: GISAXS spectra at different pi and at pH=2.

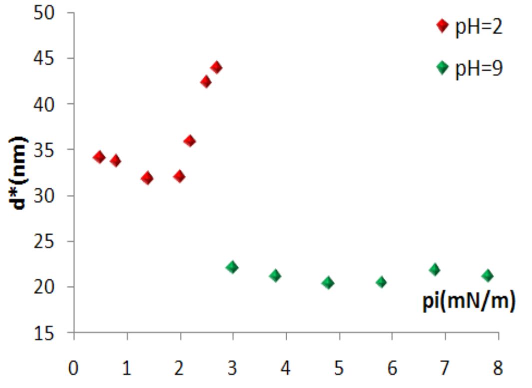

Figure2: In plane distance d* versus pi at pH=9 and 2.

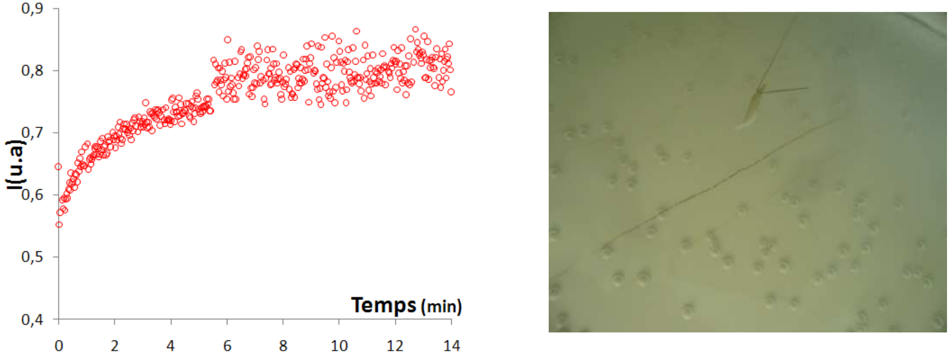

Figure3: (a) Intensity of silver fluorescence (at 3.1 Kev) as a function of time. **(b)** Photo of silver wire floating on the liquid interface after reduction of Ag^+ at pH=9

These results of GISAXS at the air liquid interface showed an unexpected and reversible behavior of the monolayer with respect to the surface pressure. It also evidenced a strong variation of the in-plane structure parameter with respect to the pH. We are currently developing models based on the formation of micelles copolymer on the surface, whose swelling and /or the aggregation number varies with pressure.