ESRF	**Experiment title:** **SAXS study of honeycomb films made of block copolymers**	**Experiment number**: SC-2899
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Films prepared from polystyrene-block-poly(4-vinylpyridine) diblock copolymers were observed by SAXS on ID02, the results from this experiment were used for the following publication:

P. Escale, L. Rubatat, C. Derail, M. Save, and L. Billon, "pH Sensitive Hierarchically Self-Organized Bioinspired Films," Macromolecular Rapid Communications **32** (14), 1072-1076 (2011).

Abstract:
In the present manuscript, we have demonstrated that hierarchically structured smart porous polymer films based on honeycomb-patterned surface can be elaborated from PS-b-P4VP pH- responsive block copolymer using the breath figure process. Despite the fast film formation by a bottom-up process, the copolymer nanostructuration was observed inside the walls of the honeycomb porous film. Atomic force microscopy (AFM), small angle X-ray and neutron scattering (SAXS and SANS) measurements were used to reveal both the hexagonal arrays formed by the pores at the micrometer length scale and the hexagonal copolymer self- assembly at the nanometer length scale.
Contact angle (CA) measurements were used to point out the reversible pH-responsive wettability character of the surface. The PS-b-P4VP honeycomb film shows a contact angle variation of 208 between pH 9 and pH 3. An increase of the roughness was obtained with the pincushions hexagonal array enhancing the pH responsiveness of the polymer film with a switching CA gap of 758 when pH tuned from pH 9 to pH 3. This work presents the first report on honeycomb porous and pincushion films exhibit- ing a reversible pH-responsive character.

Report:

The aim of this study was to investigate the morphology of hierarchically structured films made of block copolymers. The first level of structuring is a micrometer honeycomb (HC) morphology obtained by a controlled solvent evaporation method under humid atmosphere. The second level of structuring is achieved via the self-assembly of the diblock copolymers at the nanometer length-scale. We have monitored the time dependence of the morphologies under annealing procedures (thermal and solvent vapor) using SAXS combined with laser diffraction. Also, taking advantage of the small dimension of the X-ray beam we have performed a mapping of a sample to probe the spatial dependence of the structuration (sample dimension about 1cm×1cm).

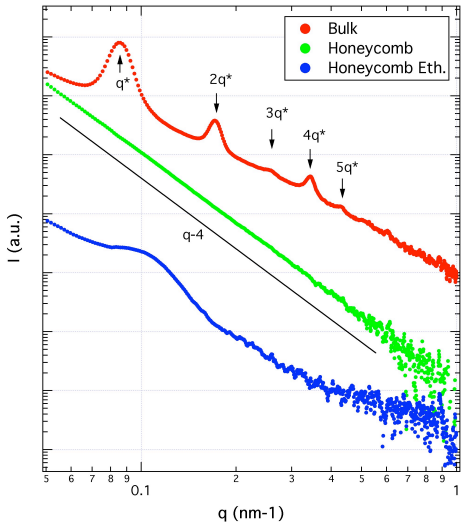

Figure 1. We have measured the scattering intensity on new synthesized copolymer series of PtBA-PS and PnBA-PS. Figure 1 presents an example of the spectra measured on the continuous film (red), and on the HC film in air (green) and ethanol (blue) prepared from PtBA-PS copolymer. After thermal annealing, the continuous film revealed a highly ordered lamellar structure. Whereas for the HC film in air the peaks disappeared under a q^{-4} slope. Our understanding of that phenomenon is that the pores (filled with air) are scattering more than the signal of the nanostructure. To confirm this hypothesis, we have performed the same experiment in ethanol to decrease the contrast between the pores and the polymer, doing so a broad peak appear on the spectra, associated to a liquid like ordering of PS domains within the PtBA matrix.

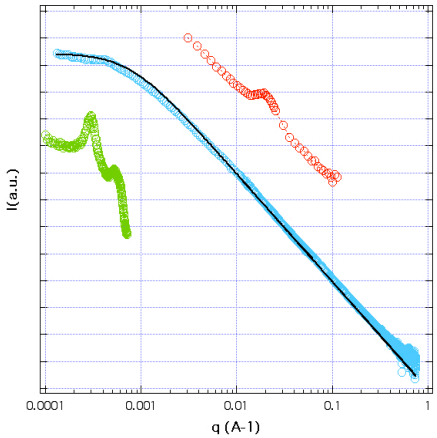

Figure 2. Presents the scattering curves measured by SANS (red), USAXS&SAXS (blue), and light scattering (green) on a HC film. The black line corresponds to the Debye-Bueche model with a characteristic dimension of 1.3µm. The Bragg distance obtained from the laser diffraction curve is about 2µm. Here again the SAXS in air presents a marked q^{-4} slope and no peak at the nanometer length scale, whereas SANS on the same sample presents a broad structural peak. The 3 complementary techniques reveal the hierarchical structure of the HC film made of diblock copolymers.

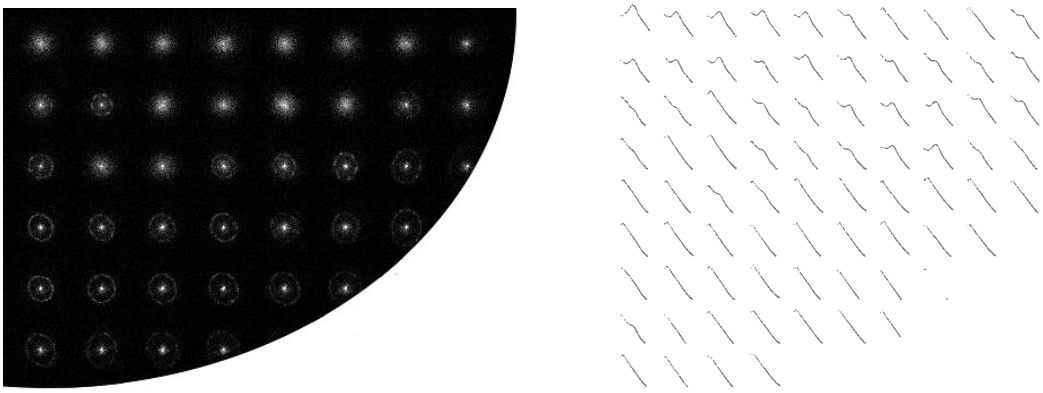

Figure 3. Laser diffraction (left) and SAXS (right) mapping on a quarter of the HC film (spatial reconstitution using ImageJ, about 5mm×5mm). The laser diffraction reveals a spatial inhomogeneity of the micrometer porosity, with local hexagonal orderings of the pores. The SAXS mapping reveals also an inhomogeneity of the morphology at the nanometer length scale. Note that the SAXS were performed in air, meaning that the q^{-4} slope may hide the structural peak of the copolymer self-assembly. This last point makes tricky to correlate the both mappings (an experiment in ethanol should be performed).