	Experiment title: GISAXS study of sub-10 nm scale nano-organization in the thin films made form oligosaccharide-containing block copolymer system	**Experiment number**: **02-01-877**
Beamline:	**Date of experiment**: from: 16/11/2016 to: 18/11/2016	**Date of report**: 09/02/2017
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Report:

1. Background and aim of the experiments

Over the past few decades, block copolymers (BCPs) have received considerable attention as a promising platform for the synthesis of nanomaterials and fabrication of nanostructures due to their self-assembling nature into nanometer-scale periodic domains whether in the bulk or solution states. Preparing novel bio-based "hybrid" BCP systems and investigating their self-assembly properties represent a step forward towards new class of nanomaterials. Strong repulsions between natural saccharidic blocks and synthetic blocks, expressed by the Flory-Huggins parameter, enable reducing inter-domain size of nano-organized morphologies toward sub-10 nm scale. Indeed, we have reported the first nano-organized glyco thin film of the BCP (polystyrene-b-maltoheptaose: PS-b-MH) in sub-10 nm feature sizes, whose morphologies were precisely investigated by microscopy, SAXS and preliminary GISAXS using ESRF synchrotron beam line D2AM.

The aims of the experiments direct morphological characterization of the self-assembled thin films of oligosaccharide-based hybrid BCPs on silicon substrates by GISAXS technique. Generally, the morphologies of self-assembled BCPs (lamellae, gyroid, cylinder, sphere, etc.) have been characterized by combining scattering analysis (SAXS/WAXS) of the bulk polymers and microscopic analysis (AFM/TEM/SEM) of the thin films. However, the self-assembled morphologies of BCPs at the surfaces of the thin films are not same as those in bulk, i.e. the presence of two interfaces, air-film and film-substrate, could induce preferential order in the film, such as lateral and normal ordering to the surfaces. GISAXS technique can provide such a 3D ordered morphological information at the surface or inside of the thin film, which is very important when the BCP thin films are used for nanolithography.

2. Experiments

GISAXS experiments have been performed on thin films made from various BCPs investigating several key parameters leading to the nano-organization such as i) the nature of the blocks, ii) the solvent vapor annealing conditions, iii) the use of a new promising microwave assisted solvent annealing route and iv) the silicon surface energies after chemical functionalizations. Scattered intensities have been recorded at room temperature during 10-100 sec exposures on a CCD detector placed in some distance from the sample holder depending on the required q range, and for incidence angles between 0.10° and 0.22° with 0.02° steps.

3. Result and discussion

The AFM and GISAXS images of maltoheptaose-*b*-polystyrene (MH-*b*-PS) 40 nm thin films coated onto plasma treated silicon wafers and annealed with THF/H_2O (w/w) for 22h were shown in Figure 1. According to the GISAXS patterns, the nano-organization seems switch from horizontal cylinders ($C_{//}$) to vertical cylinders (C⊥) when the THF/H_2O ratio increases from 1/1 to 15/1, and then turn to spheres (S) for pure THF annealing.

For each samples, domain spacings between 10 and 12 nm have been extracted from the distinct primary scattering peak (q*) along the GISAXS q_y profile at the Yoneda peak and are in good agreement with the preliminary AFM and SAXS experiments. Higher-order scattering peaks can be observed, e.g. at $2q^*$ (Figure 1 e and g), but some are missing, especially at $2^{1/2}q^*$ and $3^{1/2}q^*$, which adds difficulties in the GISAXS data interpretations. Therefore the GISAXS pattern of what can be a mixture of $C_{//}$ and C⊥ (figure 1 f) appears quite close of the pattern of what we estimate to be S (figure 1 h). The GISAXS image for the THF/H_2O 15/1 annealing (figure 1 g) is also tricky to interpret and could be C⊥ as well as S in BCC arrangement. These states of uncertainty can be overcome by extra GISAXS measurements (e.g. recording at different rotation angles along the perpendicular axis to the sample) and maybe GISAXS simulations.

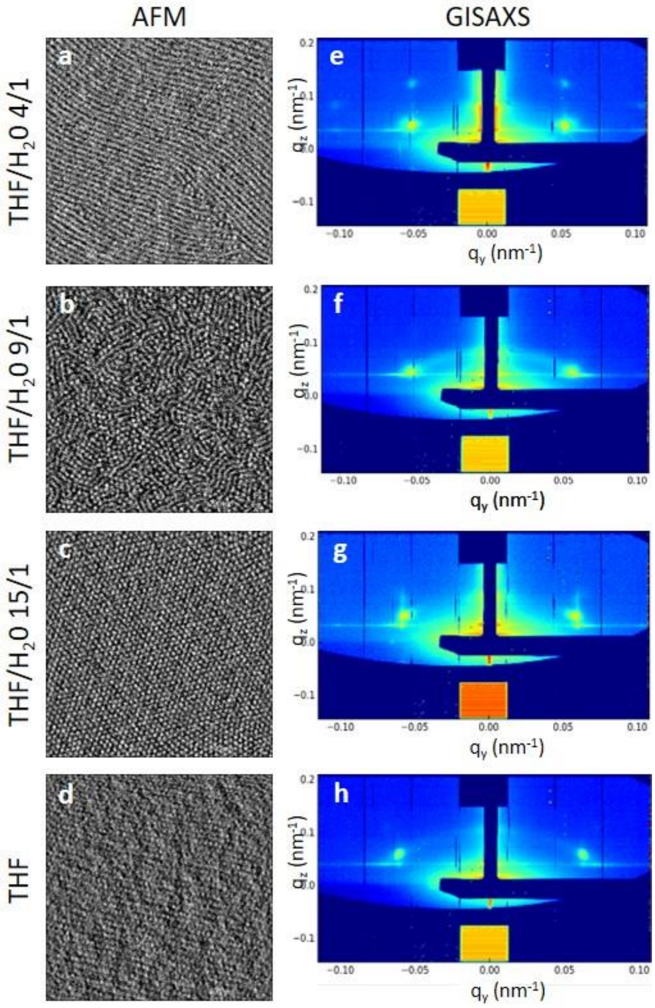

Figure 1: AFM phase (a-d) and GISAXS (e-f for an incidence angle of 0.14°) images of MH-b-PS according to the solvent vapor annealing conditions.

4. Conclusion

From these preliminary experiments, we obtained confirmation that GISAXS at BM02 is a powerful technics to study our systems. More experiments are needed to discriminate C⊥ of S and to go further in details, getting more information about the cylinders orientation all along the film cross-section and the effect of the substrate surface properties on these orientations. We also prospect for help in the data treatment and simulation.