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Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

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Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

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All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** GISAXS study of sub-10 nm scale self-assembled oligosaccharide-containing block copolymer thin films	**Experiment number**: SC-4646
Beamline:	**Date of experiment**: from: 11/12/2017 to: 13/12/2017	**Date of report**: 24/02/2018
Shifts:	**Local contact(s)**: Nathalie Boudet (email: boudet@esrf.fr)	*Received at ESRF:*

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Report:

1. Background and aim of the experiments

Poly-/oligosaccharide-containing hybrid block copolymer BCP systems and their self-assembly properties represent a step forward towards new class of nanomaterials with sub-10 nm nanostructure sizes and with use of biobased carbohydrate sub-block for future advanced materials. Strong repulsions between natural saccharidic blocks and synthetic blocks, expressed by the Flory-Huggins parameter χ, enable reducing inter-domain size of nano-organized morphologies to less than 20 nm. A variety of poly-/oligosaccharides-containing BCP systems with *sub-10 nm* scale patterned morphologies (lamella, hexagonal cylinders, sphere), have been obtained and put to action in varies application from drug carrier nanoparticles to nanostructured thin films in transistor applications by the Borsali group. Targeted chemical modification to the interface between the BCP sub-blocks can trigger phase transitions with varying annealing (temperature, solvent vapor) conditions and enhance BCP self-assembly to obtain quasi-defect free nanostructures. These properties could be used in future materials for conducting BCP thin films with enhanced performance.

The objective of the GISAXS measurements done was to gain morphological information of the impressive library of carbohydrate based BCPs in hand for these experiments. Part of the material was designed with chemical modification (adding charge to the interface between BCP sub-blocks) possibly enabling the material to self-assemble in a long range manner on a surface. Part of the experiments were done to assess, the extent of order in BCP films modified with charge using two different methods, a) modifying the BCP with charge before film casting and b) after casting with reagent vapor. In addition, the GISAXS patterns obtained in our last GISAXS experiments shows the rang of q is so small that higher order peaks were not able to be observed, so we changed the distance between the camera and samples to get a larger *q* rang. During this experiment, we also performed in situ GISAXS measurement for carbohydrate-based BCP thin films at heating temperatures from room temperature up to 200 deg. C.

To confirm the hypothesis stated above, precise characterizations of the morphologies of the BCP thin films with GISAXS and imaging techniques is mandatory. In these GISAXS experiments, we aimed to study the effect of solvent vapor annealing, sub-block chemical modification and real-time morphological variation

of newly synthesized hybrid BCP systems containing varying carbohydrate sub-blocks and synthetic blocks of polyisoprene (PI) and polystyrene (PS). designed for next-generation advanced materials (targeting nano-lithography for example) through GISAXS analyses.

2. Experiments

GISAXS measurements were conducted for BCP thin films with varying molecular weights on Si wafer. All BCP materials used contained an oligosaccharide sub-block (maltoheptaose (MH), cyclodextrin (CD)) and a synthetic sub-block (PI, PS). Before GISAXS measurements, BCP thin films were prepared by spin coating BCPs on cleaned Si wafers. The samples were solvent annealed at ambiant temperature with varying solvent composition of THF and H_2O and time. GISAXS experiments used a photo energy of 16 keV. The distance between samples and camera was 1.9 m. GISAXS images were recorded at room temperature during 10-100 sec exposures on a CCD detector at incidence angles from 0.10° to 0.22°. For in situ GISAXS measurements, BCP thin films were placed on an integrated heating system. GISAXS images were recorded from room temperature up to 200 deg. C. with a step of 5 deg. C.

3. Result and discussion

The GISAXS 2D images and reflection peaks for Qx are shown in Figure 1. for ca. 25 nm thick pristine triblock MH-PI-MH and interface modified MH-(+)-PI-(+)-MH BCP thin films. They clearly demonstrate a drastic profile change as a result of BCP chemical modification with charge. The scattering peaks for MH-(+)-PI-(+)-MH thin film are very sharp and peak positions indicate lamella nanostructures with domain spacing as small as 8 nm for the MH-(+)-PI-(+)-MH BCP thin film. The long range order is clearly visualized in the AFM images with corresponding FFTs in Figure 1.

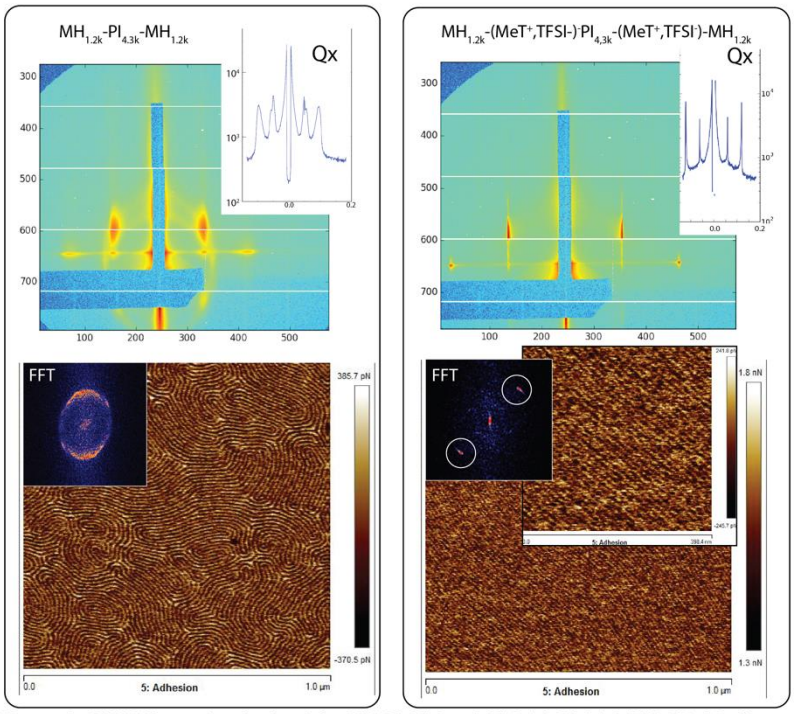

Figure 1. GISAXS results obtained for MH-PI-MH and MH-(+)-PI-(+)-MH BCP thin films (upper part) and AFM topography images of the films with corresponding FFTs as insets (down part).

4. Conclusion

GISAXS studies confirmed the hypothesis of gaining BCP thin films with long range order using MH-(+, MeTFSI)-PI-(+, MeTFSI)-MH were charge is put between the interface separating the BCP sub-blocks. Comparison between chemically modified thin films a) before film casting and b) after casting with reagent vapor hinted towards longer ranged order for premodified BCP film (a) compared to after casting modification (b). We are now concentrating on more conclusive data analysis to determine the extent of order gained in the thin film geometry and BCP conformation within the films. These results will be published as part study related to High χ Low N Carbohydrate-Elastomer BCP thin films with charge induced long range order.

In situ GISAXS measurements disclose the phase behavior of carbohydrate-based BCPs when the temperature was increased from room temperature to 200 deg. C. The self-assembly of MH-b-PS and CD-b-PS was not observed from their GISAXS images during the in situ GISAXS measurements. This implies that thermal annealing is not effective for MH-b-PS and CD-b-PS. For comparing different annealing methods, we also checked the MH-b-PS sample annealed by microwave method at the same incident angle. Hexagonally close-packed cylindrical lattice pattern was observed in its GISAXS image. This provides us an important clue to find the driving force of microwave annealing method. What more, we recheck some MH-b-PS samples with optimized parameters (a larger q rang) of GISAXS measurement. Higher ordered peaks were not found in the large q direction, which implies that the degree of ordering of MH-b-PS samples is limited after solvent vapor annealing even for 24 hours. These important results will be submitted soon to *Langmuir* as research article entitled “Self-assembly of maltoheptaose-block-polystyrene: Thin Film GISAXS results”.