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Experiment Report Form

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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

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The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

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.

Published papers

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:** Time-resolved SAXS Studies on Morphologies in Self-assembled Oligosaccharide-containing Block Copolymer Systems for Nano-lithographic Applications	**Experiment number**: 02-01 886
Beamline:	**Date of experiment**: from: 08/12/2017 to: 11/12/2017	**Date of report**: 24/02/2018
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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 drugg 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 SAXS measurements done was to gain morphological information of the guite impressive library of carbohydrate based BCPs in hand for these experiments. Part of the material was designed with chemical modification possibly enabling order-order phase transitions with varying temperature. The effect of the degree of polymerization (DP) of the carbohydrate sub-block on the microphase separation is another interesting issue. We though that microphase-separated structures of a BCP system consisting of maltotriose (DP = 3) should become even more ordered than those of BCPs consisted of maltoheptaose (DP = 7).

To confirme the hypothesis stated above, precise characterizations of the morphologies of the BCP bulk by combining scattering (SAXS/WAXS) and imaging techniques is mandatory. In these SAXS 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 , polystyrene: PS and poly(propylene oxide): PPO designed for next-generation advanced materials (targeting nano-lithography for example) through thermal annealing process by time-resolved SAXS/ WAXS analyses under step-by-step heating.

2. Experiments

SAXS measurements were conducted for bulk samples with varying molecular weights in glass capillaries. All BCP materials used contained an oligosaccaride sub-block maltoheptaose (MH)), xyloglugan oligosaccaride (XGO), cyclodextrin (CD) and maltotriose (MT) and an synthetic sub-block (PI, PS and PPO). BCP architechtural effects were considered measuring A-B and A-B-A BCP analoques. The capillaries were set in sample holders equipped with an integrated heating system. For a certain set of samples, the sample temperature was varied from 25 °C up to 200 °C by 5-10 °C steps. Scattered intensities were recorded during 5-100 sec exposures at each temperature on a XPAD hybrid pixel detector (simultaneous SAXS-WAXS detector).

3. Result and discussion

The SAXS profiles in Figure 1. a) and b) for interface modified MH-(+)-PI and MH-(+)-PI-(+)-MH BCPs, shown as an examble of succesful measurement, clearly demonstrate enhanced phase transition with stepwise heating from disordered to hexagonal cylinders and from lamella to hexagonal cylinders in bulk. The distinct primary scattering peak (q^*) and the higher-order scattering peaks observed at $\sqrt{3}q^*$, $2q^*$, $\sqrt{7}q^*$, $3q^*$, and $\sqrt{13}q^*$ positions in Figure 1. a) and b) indicate that a hexagonally close-packed cylindrical phase for both charge modified diblock MH-(+)-PI and triblock MH-(+)-PI-(+)-MH self-assembled after thermal annealing process. The scattering peaks for both samples got sharper with increased intensity as temperature rises and phase transition is permanent after cooling back to 25 °C. The domain spacing (centre to centre distance) for MH-(+, MeI)-PI hexagonally packed cylindrical structures was 13.6 nm and for the MH-(+, MeTFSI)-PI-(+, MeTFSI)-MH cylinders 12 nm. BCP conformation within these bulk nanostructures is under investication.

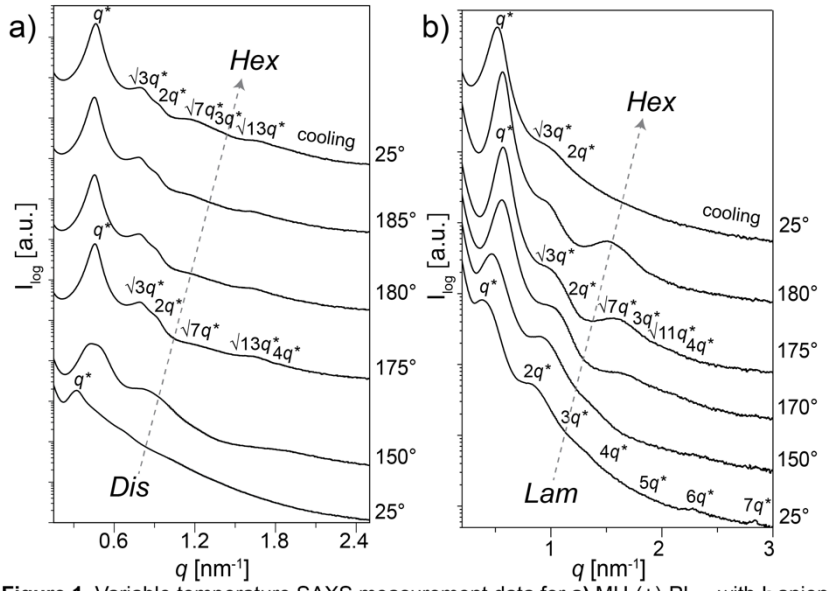

Figure 1. Variable temperature SAXS measurement data for **a)** MH-(+)-$PI_{3.6k}$ with I^- anion and **b)** MH-(+)-$PI_{4.3k}$-(+)-MH with $TFSI^-$ anion interacting with interface separating the BCP sub-blocks.

The time-resolved SAXS experiments were carried out on the PPO-*b*-MT and MT-*b*-PPO-*b*-MT bulk samples during the stepwise heating from 25 °C up to 200 °C (Figure 2). PPO-*b*-MT and MT-*b*-PPO-*b*-MT showed a scattering in the temperature range of 25 – 80 °C and 25 – 145 °C, respectively, suggesting the microphase-separated structure formation. Although the phase structure could not be assigned because of the absence of higher ordered scattering peak, the domain-spacing (d) for their microphase-separated structures was determined to be 8.6 nm for PPO-*b*-MT and 9.5 nm for MT-*b*-PPO-*b*-MT. Importantly, such d values are among the smallest feature sizes in carbohydrate-based BCPs. We also performed time-resolved SAXS measurement from 25 °C up to 200 °C for MH-*b*-PS, XGO-*b*-PS and CD-*b*-PS bulk samples. However, their SAXS profiles do not have any characteristic scatering peaks. Optimization of the annealing condition, such as solvent vapor annealing, will be needed to achive well-organized nanostructure formation in these BCP systems.

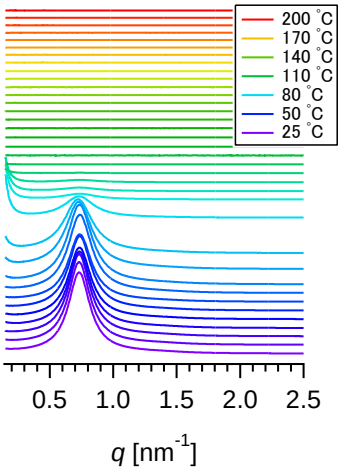

Figure 2. Time-resolved SAXS data for PPO-*b*-MT during the stepwise heating from 25 °C to 200 °C.

4. Conclusion

From the SAXS bulk studies at ESRF we could conclude the thermal annealing induced phase transition to hexagonally packed cylinders for MH-(+, MeI)-PI and MH-(+, MeTFSI)-PI-(+, MeTFSI)-MH BCP material. Also measurement from uncharged analoques gave valuable information of the effect of charge at the interphase between the sub-blocks. The effect of thermal treatment is crusial for studying the self-assembly in thin film geometry with coming GISAXS experiments at ESRF to realize the whole phase behavior for these materials under different annealing conditions. These results will be published as part study related to High χ Low N Carhohydrate-Elastomer BCP thin films with charge induced long range order. The time-resolved

SAXS experiments on the PPO/MT BCP system revealed their potential to form microphase-separated structures with a very small feature size. Further studies on this BCP system with SAXS and GISAXS is essential to obtaine well-organized nanostructure suitable for advanced material applications.