ESRF	**Experiment title:** Time-resolved SAXS/WAXS Studies on Morphologies in Self-assembled Oligosaccharide-containing Block Copolymer Systems for Photovoltaic and Nano-lithographic Applications	**Experiment number**: SC-4321
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Report:

1. Background and aim of the experiments

Over the past few decades, 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 melt, solid state, or solution. Although the self-assemblies of the BCPs made from petroleum have been well-explained according to the phase diagram, little is known on those from natural resource, in particular, poly-/oligosaccharides. Therefore, constructing poly-/oligosaccharide-containing 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 χ, enable reducing inter-domain size of nano-organized morphologies less than 20 nm. Indeed, we have prepared a variety of poly-/oligosaccharides-containing block copolymer (BCP) systems and created sub-10 nm scale patterned morphologies, which is much smaller the minimum domain feature (20 nm).

The objective of this project is the creation of sub-10 nm scale patterned morphologies (lamellae, cylinders, spheres, etc.), that fit perfectly within the exciton diffusion length between donor and acceptor domains for photovoltaic application and next-generation nano-lithography, by self-assemblies of oligosaccharide-containing "hybrid" block copolymers (BCPs). To achieve this goal, precise characterizations of the morphologies of the BCP bulk and films by combining scattering (SAXS/WAXS) and imaging techniques is mandatory. In this experiment, we aimed to study the effect of solvent vapor annealing for the self-organization and real-time morphological variation of newly synthesized hybrid BCP systems

containing conducting donor/acceptor polymers (poly(3-hexylthiophene): P3HT and/or PCBM-C60) designed for photovoltaic application, polystyrene: PS, polyisoprene: PI, and poly(ε-caprolactone) designed for next-generation nano-lithography through thermal annealing process by time-resolved SAXS/ WAXS analyses under step-by-step heating.

2. Experiments

The bulk samples of hybrid BCPs contatining PS (PS-*b*-maltoheptaose: PS-*b*-MH, PS-*b*-xyloglucan oligosaccharide: PS-*b*-XGO, PS-*b*-βcyclodextrin: PS-*b*-βCyD, PS-*b*-peracetylated maltoheptaose: PS-*b*-AcMH, PS-*b*-peracetylated xyloglucan oligosaccharide: PS-*b*-AcXGO, and PS-*b*-peracetylated βcyclodextrin: PS-*b*-AcβCyD), PI (PI-*b*-maltoheptaose: PI-*b*-MH and MH-*b*-PI-*b*-MH), PCL (PCL-*b*-(maltoheptaose)$_n$: PCL-*b*-(MH)$_n$), and P3HT (P3HT-*b*-maltoheptaose: P3HT-*b*-MH and P3HT-*b*-peracetylated maltoheptaose: P3HT-*b*-AcMH) with various molecular weights were put in glass capillaries. Some of the samples were annealed with solvent vapor before putting into the capillaries. The capillaries were set in sample holders equipped with an integrated heating system. The sample temperature was varied from 25 °C up to 200 °C by 5 °C step. Scattered intensities were recorded during 5-100 sec exposures at each temperature on a XPAD hybrid pixel detector (simultaneous SAXS-WAXS detector).

3. Rresult and duscussion

The SAXS profiles of MH-*b*-PI-*b*-MH without annealing and annealed with vapor from THF/H_2O = 1/1 (w/w) for 24 were shown in Figure 1a and 1b, respectively. The SAXS profile clearly varied through solvent vapor annealing which gives mobility of the BCP chains to self-organize into thermodinamically stable phase. The distinct primary scattering peak (q*) and the higher-order scattering peaks observed at $3^{1/2}q$*, $2q$*, $7^{1/2}q$*, and $3q$* positions in Figure 1b indicates that a hexagonally close-packed cylindrical phase of MH-*b*-PI-*b*-MH was self-organized after the solvent annealing process.

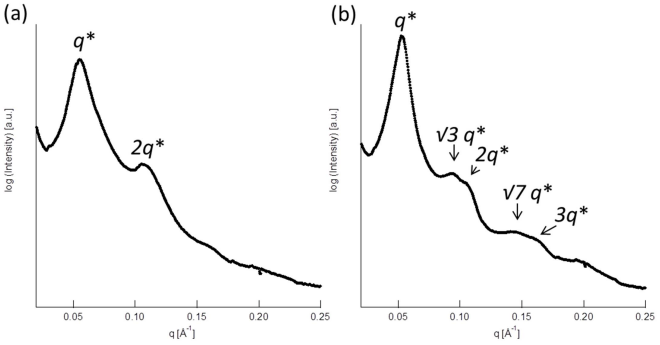

Figure 1. SAXS profiles of MH-*b*-PI-*b*-MH (a) without annealing and (b) annealed with vapor from THF/H2O = 1/1 (w/w) for 24h.

The SAXS profiles of PS-*b*-MH measured at different temperatures were shown in Figure 2. The SAXS profile was drastically changed through the heating process. The broaden SAXS profile without any clear scattering peak at 33 °C varied through heating process and the distinct primary scattering peak (q*) were observed above 150 °C, which is around the T_g of PS-*b*-MH. Higher-order scattering peaks were observed at 170 °C, *e.g.*, the peaks at $3^{1/2}q$* and $7^{1/2}q$* positions, indicating that PS-*b*-MH self-organized into a hexagonally close-packed cylinder phase.

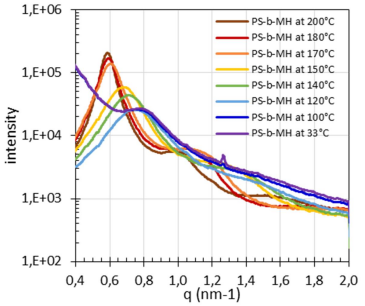

Figure 2. SAXS profiles of PS-*b*-MH at various temperatures.

4. Conclusion

From these experiments, we obtained whole picture of the effect of solvent vapor annealing and thermal annealing on the self-organization of the hybrid BCP systems. Based on the obtained results, self-organized BCP thin films having various patterned phases will be prepared. The morphology of such thin films will be investigated by forthcoming GISAXS experiments at BM02.