ESRF	**Experiment title:** SAXS and GISAXS for the directed self assembly of block copolymers	**Experiment number**: MA-2438
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Shifts: 9	**Local contact(s)**: Giuseppe Portale	*Received at ESRF:*

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Report:

With this project we aim to study the morphologies adopted by the self-assembly of block copolymers, both in bulk and thin film configurations. Our research targets lithographic applications in which the self-assembly of block copolymers is exploited to obtain well-ordered structures with nanometer scale dimensions. We are interested in correlating the macromolecular characteristics of the copolymers (i.e. molecular weight, composition, polydispersity) and the processing methodology (e.g. thermal or solvent annealing, control of the surface energy of the substrate) to the resulting mesostructure (i.e. the morphology as well as its orientation as regards to the substrate). The length scale of domains formed upon microphase separation are in the range of 5-60 nm, therefore, small angle x-ray scattering (SAXS) and grazing-incidence small angle x-ray scattering (GISAXS) experiments were indispensable for the characterization of our samples in bulk and thin film configurations, respectively.

For the SAXS study, we have focused our works on a newly developped block copolymer (BCP) system (poly(1,1-dimethyl silacyclobutane)-*block*-poly(methyl methacrylate) (PDMSB-b-PMMA)) which allow the definition of sub-20 nm periodic structures due to its high segregation strength.[1] We expected to map-out the phase diagram of this system keeping in mind the two potential structures of interest for DSA (PMMA cylinders in a PDMSB matrix and PDMSB/PMMA lamella). Consequently we explored the self-assembly behavior of PDMSB-*b*-PMMA melts in the PDMSB-rich region. Synchrotron SAXS powder patterns at 50°C are presented in Figure 1 for typical PDMSB-b-PMMA copolymers. By increasing the PMMA volume fraction from 0.09 to 0.53, the usual sequence of morphologies for diblock copolymers is retrieved. We subsequently aimed to determine the Flory-Huggins paramter of this system. The absolute intensity of the scattered X-rays, pre-calibrated against a low-density polyethylene standard, was plotted against the primary scattering vector q for a low molecular weight PDMSB-*b*-PMMA with atteignable order-disorder temperature (See Figure 2). SAXS profiles were collected over a range of temperatures relevant to thermal annealing processing. As the temperature increased, the intensity of the scattering maximum decreased because χ is inversely proportional to T. The value of χ has been extracted from these scattering profiles by fitting to Leibler's mean-field theory,[2] corrected for the effects of molecular weight dispersity and segmental volume asymmetry.

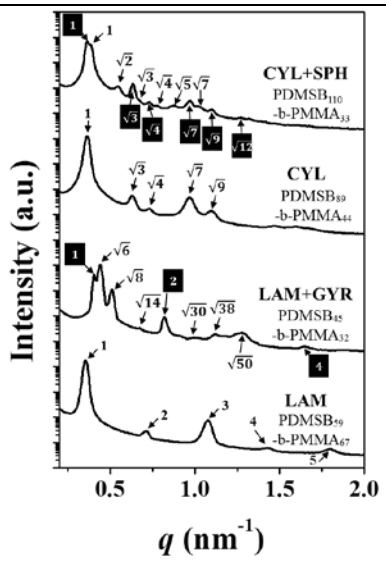

Figure 1: Representative synchrotron SAXS profiles acquired at 50°C for PDMSB-b-PMMA samples having different PMMA volume fraction. Coexistence of BCC (q/q* = 1, √2, √3, √4, √5,… are marked on black background where q* is the primary peak) and Hex phases (q/q* = 1, √3, √4, √7,… are marked on white background) identified with $PDMSB_{110}$-b-$PMMA_{33}$ (f_{PMMA} = 0.19). Hex phase (q/q* = 1, √3, √4, √7,…) identified with $PDMSB_{89}$-b-$PMMA_{44}$ (f_{PMMA} = 0.27). Coexistence of Lam (q/q* = 1, 2, .3, 4 are marked on black background) and Gyroid phases (q/q* = √6, √8, √14, √30, √38,… are marked on white background) identified with $PDMSB_{45}$-b-$PMMA_{32}$ (f_{PMMA} = 0.35). Lam (q/q* = 1, 2, 3, 4, 5) identified with $PDMSB_{59}$-b-$PMMA_{67}$ (f_{PMMA} = 0.47)

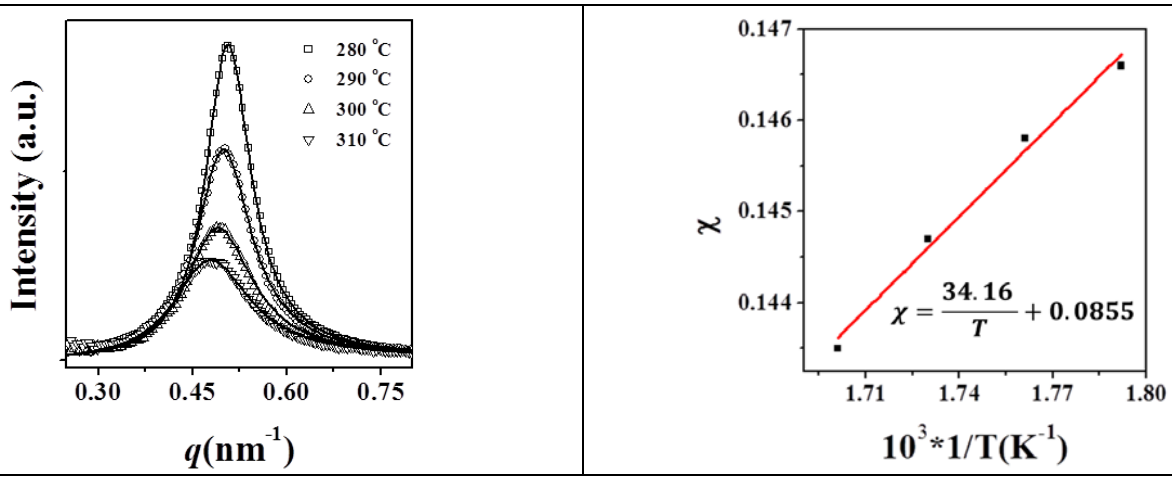

Figure 2: Best fitting scattering curves (black solid line) calculated by mean-field theory against experimental scattering data (symbol) at the region of the first order peak of $PDMSB_{45}$-b-$PMMA_{32}$, plot of Flory-Huggins parameter χ, evaluated by best fitting, plotted against inverse of absolute temperature 1/T. The red line is linear fit result.

We additionaaly performed GISAXS experiments on a symetric poly(D,L lactide-b-dimethylsiloxane-b-D,L lactide) (PLA-b-PDMS-b-PLA) triblock copolymer in order to evaluate the influence of a grafted polymer sublayer on the orientation of the block copolymer domains. Various poly(styrene-r-methyl methacrylate) (PS-r-PMMA) were grafted on Si wafers in order to control the surface energy of the substarte as regards to the block copolymer domains. This triblock copolymer exhibits in the bulk a hexagonaly close packed structure of PLA cylinders. Figure 3 shows the influence of the grafted layer on the domain orientation for two different PS-r-PMMA compositions which show that the control of the surface energy of the substrate allows us to tune the orientation of the BCP mesostructure for this particular system.

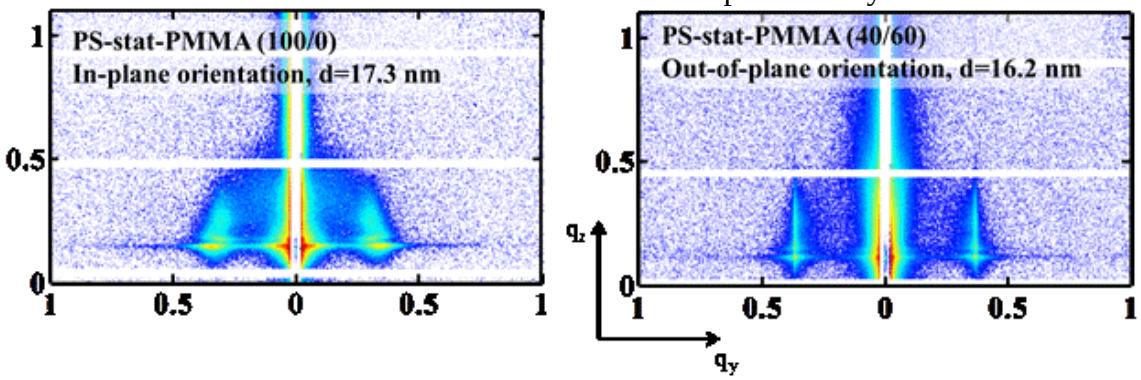

Figure 3: GISAXS pattern of PLA-b-PDMS-b-PLA thin films self-assembled by thermal annealing on grafting layers of different surface energies produced by the copolymerisation of PS and PMMA.