ESRF	**Self-assembly of block copolymers studied by in-situ GISAXS**	**Experiment number**: MA-1328
Beamline: BM02	**Date of experiment**: from: 26-10-2011 to: 31-10-2011	**Date of report**: 20-11-2012
Shifts: **15**	**Local contact(s)**: Mireille Maret	*Received at ESRF:*

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Report:

The GISAXS experiments were done on self-assembled PS-b-PMMA block copolymer (BCP) using a photon energy of 9.4keV and a beam spot size, 300µm wide and 100 µm tall. The samples were positioned at the center of a furnace set upon the goniometer stage. The GISAXS patterns were measured under an incidence angle of 0.14° (i.e. just above the critical angle of BCP), using a XPAD pixel detector mounted on the SAXS bench and located at a distance of 3.7m from samples. The BCP samples were spin-coated on top of brush PS-r-PMMA BCP prepared on both unpatterned Si wafers and prepatterned surfaces consisting of HSQ line grating generated by e-beam lithography and then rapidly annealed up to 240°C [1]. Such process leads to the formation of microdomain hexagonal arrays with perpendicularly oriented PMMA cylinders in a PS matrix. The BCP layer thicknesses were equal to 60nm and for a few ones 30nm. The size of the patterned area was 1x10mm^2. For the ex-situ measurements most of samples were recorded after removing PMMA by acid acetic treatment which leads to a strong increase of the truncation rod intensities stemming from the 2D hexagonal array, high order rods up to the 30 one could thus be measured. For the in-situ measurements, due to the presence of PMMA in the cylinders, only the appearance of the 10 spots exacerbated at the level of the Yoneda peaks could be monitored during self-assembly process.

Fig. 1a shows the GISAXS pattern of a self-assembled BCP on an unpatterned surface, characteristic of randomly oriented microdomains of hexagonal array of cylinders normal to the surface. The average distance between cylinders is equal to 35.6nm. The intensity along the 10 rod is modulated by the form factor of cylinders. Due to the restricted lateral coherence length of the photon beam it was not possible to determine precisely the ordered domain size. Fig.1b shows the GISAXS pattern obtained for the same BCP grafted on a line array (period =248nm, line height=50nm and line with=62nm), such as the direction of the photon beam is parallel to the HSQ lines. The absence of the 11 rod clearly indicates that the line grating guides the orientation of the 2D hexagonal array with its [10] direction parallel to the lines. The contribution of the line grating is very strong and can be decreased by misaligning the line grating of a few degrees with respect to the incident beam. However doing it, the rods coming from the hexagonal array of cylinders are not properly defined. From a detailed analysis of horizontal cuts through the 10 rod calculated at q_z=0.4nm^{-1}, two contributions can be separated: one narrow peak stemming from the 2D hexagonal array self-assembled between the trenches of the grating and a much broader peak located at slightly larger q_y values coming from the array formed on the top of lines. The q-shift between the two peaks is consistent with an increase of the distance between cylinders with the BCP thickness.

Several series of in-situ measurements were performed under N_2 pressure tuning the heating rate, annealing time and temperature. During self-assembling, a rapid radiation damage of PMMA starting especially above 200°C was observed, making necessary to move the sample with respect to the photon beam just before measuring it and to use short counting times (typically 10s).

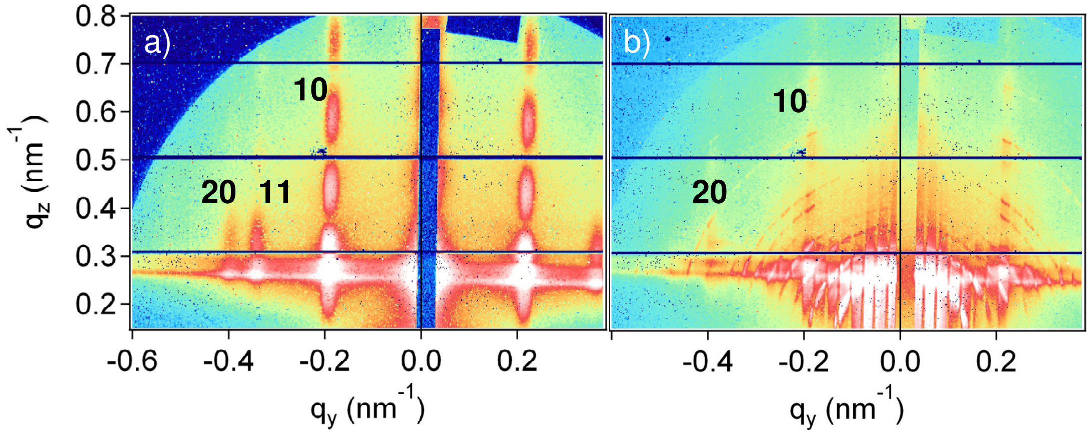

Fig. 1. GISAXS patterns of self-assembled diblock (PS-b-PMMA) copolymers after removing PMMA with acetic acid: a) on an unpatterned Si substrate; b) on a guiding pattern of HSQ e-beam line array.