	Experiment title: SAXS and GISAXS for the directed self assembly of block copolymers	**Experiment number**: SC- 3862
Beamline: BM26	**Date of experiment**: from:14/03/2014 to: 17/03/2014	**Date of report**: 23/04/2015
Shifts: 9	**Local contact(s)**: Giuseppe Portale	*Received at ESRF:*

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Report:

The results obtained during this set of experiments led to the following publications:

- *Advanced Materials*, **2015**, *27*, 261-265 "Sub-10 nm Features Obtained from Directed Self-Assembly of Semicrystalline Polycarbosilane-Based Block Copolymer Thin Films" by Karim Aissou, Muhammad Mumtaz, Guillaume Fleury, Giuseppe Portale, Christophe Navarro, Eric Cloutet, Cyril Brochon, Caroline A. Ross and Georges Hadziioannou.

Abstract: Highly-ordered arrays with sub-10 nm features are produced with topographical-directed self-assembly of low-molecular-weight poly(1,1-dimethyl silacyclobutane)-block-poly(methyl methacrylate). This system turns out to be of high interest for lithographic applications since the domain orientation is solely controlled through the polymer layer thickness, while the promotion of the microphase separation is obtained by a short thermal annealing process under mild conditions.

- *Macromolecules*, **2014**, *47*, 6000-6008 "Thin Film Morphologies of Bulk-Gyroid Polystyrene-block-polydimethylsiloxane under Solvent Vapor Annealing" by Wubin Bai, Adam F. Hannon, Kevin W. Gotrik, Hong Kyoon Choi, Karim Aissou, George Liontos, Konstantinos Ntetsikas, Alfredo Alexander-Katz, Apostolos Avgeropoulos, and Caroline A. Ross.

Abstract: Thin film morphologies of a 75.5 kg/mol polystyrene-block-polydimethylsiloxane (PS-b-PDMS) diblock copolymer subject to solvent vapor annealing are described. The PS-b-PDMS has a double-gyroid

morphology in bulk, but as a thin film the morphology can form spheres, cylinders, perforated lamellae, or gyroids, depending on the film thickness, its commensurability with the microdomain period, and the ratio of toluene:heptane vapors used for the solvent annealing process. The morphologies are described by self-consistent field theory simulations. Thin film structures with excellent long-range order were produced, which are promising for nanopatterning applications.

Additional Comments:

Our research targets lithographic applications in which the self-assembly of block copolymers is exploited to obtain well-ordered structures with nanometer scale dimensions. The SC-3862 shifts on BM26B were used to probe the self-assembly of block copolymer systems with potential applications in nanolithographic applications through the use of directed self-assembly methodologies. Several systems of interest were probed during this session (poly(dimethylsilacyclobutane-b-methyl methacrylate), poly(dimethylsiloxane-b-D,L lactide), poly(styrene-b-polydimethylsiloxane)) in order to establich the segregation behavior both in bulk and in thin film configuration. We mainly focused our studies on the poly(dimethylsilacyclobutane-b-methyl methacrylate) system for which we have reported the production of highly-ordered patterns with sub-10 nm features (see *Advanced Materials*, **2015**, *27*, 261-265). These periodic structures consist of easily etchable PMMA domains separated by carbosilane-based chains and the carbosilane block could be transformed into a hard mask of SiC. By tayloring the block copolymer architecture (molecular weight and composition), SAXS charcterization allowed us to determine the phase diagramm of this partciluar systems exhibiting low periodicities, as shown in Figure 1 for hexagonnaly packed cylinders and lamellar morphologies.

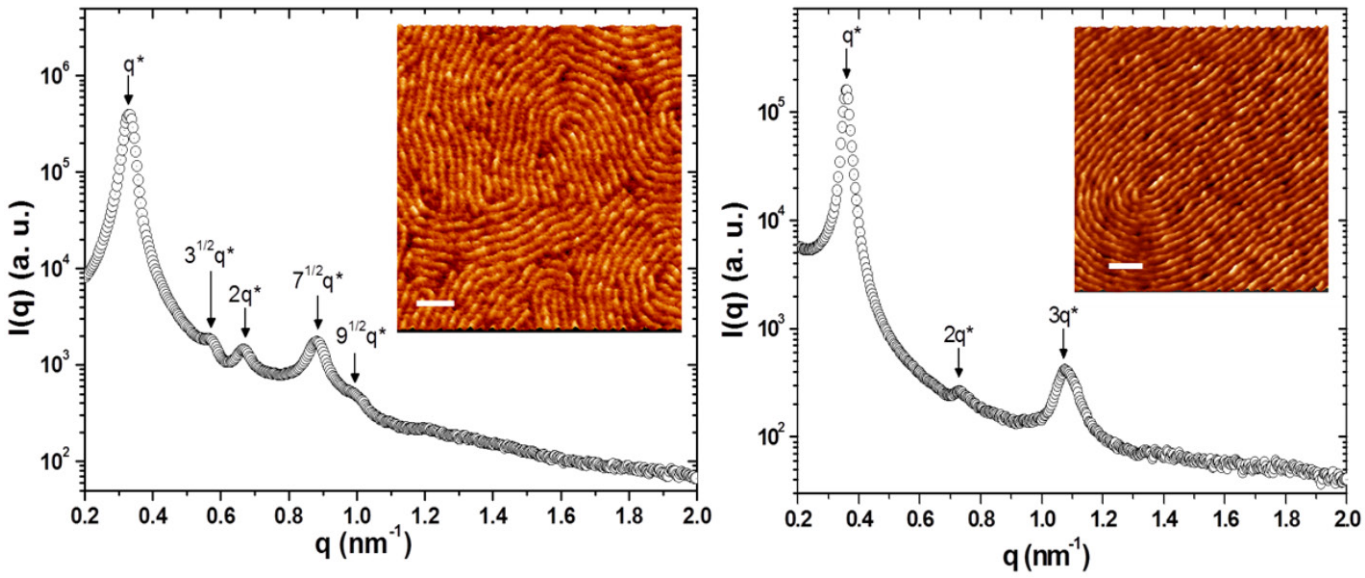

Figure 1: Synchrotron SAXS profiles of $PDMSB_{122}$-*b*-$PMMA_{43}$ (left) and $PDMSB_{47}$-b-$PMMA_{62}$ (right) obtained at room temperature. The SAXS patterns are indexed with the *p6mm* symmetry of the cylindrical morphology with a period of 21.7 nm and a lamellar morphology with a period of 20.3 nm, respectively. These results are in accordance with the morphologies and the pitchs observed in thin films as illustrated by the AFM phase images showed in the inset. Scale bar, 100 nm.

The mesostructures and periodicities determined by SAXS in bulk were in acordance with the AFM observtions obtained in thin film configuration.