



## Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.**

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

*<http://193.49.43.2:8080/smis/servlet/UserUtils?start>*

### ***Reports supporting requests for additional beam time***

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

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.



	<b>Experiment title:</b> Grazing Incidence Diffraction Studies of Tethered Diblock Copolymer Films	<b>Experiment number:</b> BM281888
<b>Beamline:</b> BM28	<b>Date of experiment:</b> from: 19/5/10 to: 25/5/10	<b>Date of report:</b> 11/6/10
<b>Shifts:</b> 18	<b>Local contact(s):</b> Oier Bikondoa	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): Benjamin O'Driscoll,* Maria Silvi,* and Ian Hamley Department of Chemistry, University of Reading, Whiteknights, Reading, RG6 6AD, UK		

## Report:

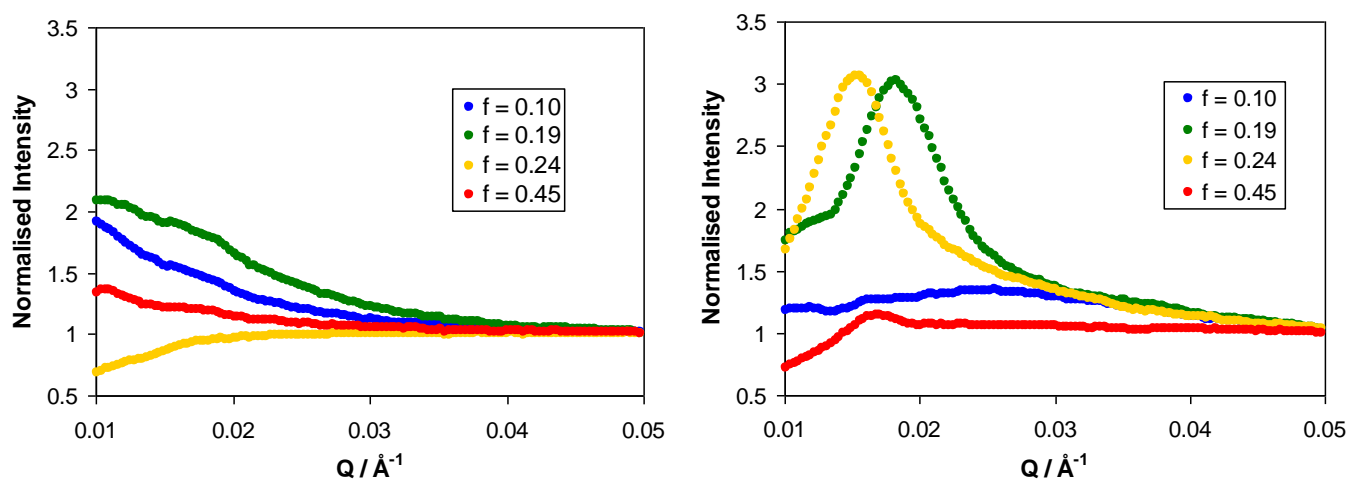
X-ray reflectometry (XR) and Grazing Incidence X-ray Diffraction (GIXD) measurements were performed on several sets of tethered diblock copolymer films in order to elucidate the nature of the phase separation in the films.

The films were prepared in the initial incidence by reacting various (deuterated)polystyrene-*block*-polymethylmethacrylate (dPS-PMMA) polymers with the oxide surface of silicon wafers to produce polymer brushes attached at the PMMA end. In total four polymers were used, with mol fractions of dPS ranging from 0.10 – 0.45, each comprising a set of which three were made. The first set of samples consisted of thermally annealed films; this procedure induces phase separation of the immiscible dPS and PMMA blocks.<sup>1</sup> The second and thirds sets of samples were treated via a solvent exchange process, where a good solvent for both blocks is replaced by a good solvent for only one block.<sup>2</sup> For the second set of samples the selective solvent was cyclohexane (selective for dPS), while for the third set the solvent was acetone (selective for PMMA).

All the films were measured in both their native state and after treatment with a staining procedure that is designed to increase the contrast between the polymer blocks.

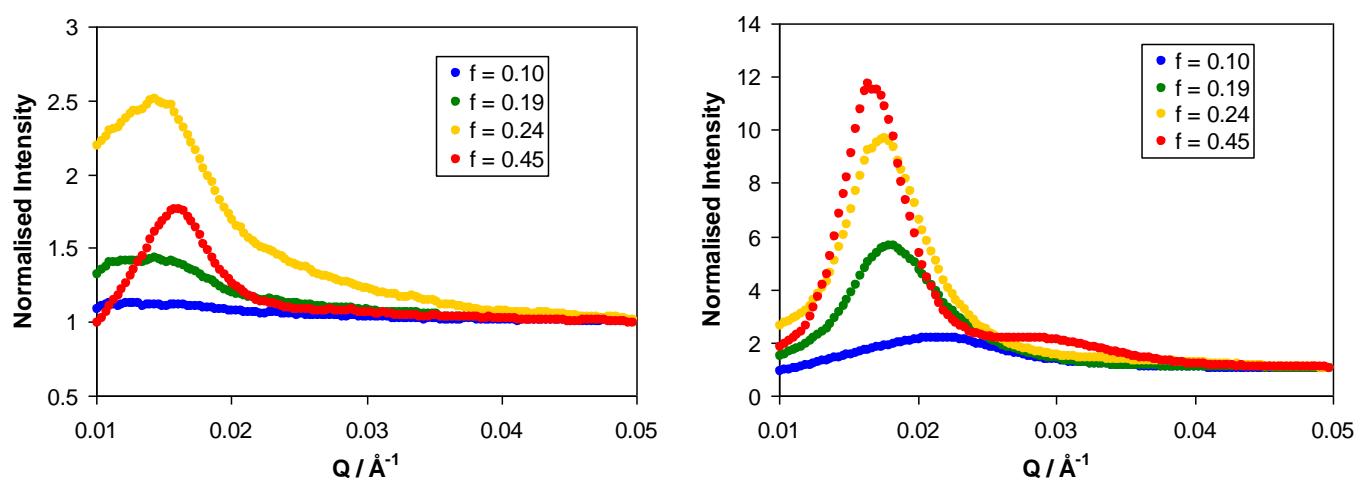
GIXD images were collected using a 2D Mar detector. The in-plane scattering was subsequently integrated to a line profile using the Fit2D programme. Scattering normal to the plane was not seen, in line with expectations, as phase separation in these films is psuedo two-dimensional.

For the thermally annealed films the stain significantly enhances the observed scattering (figure 1), with the position of the peaks being consistent with the values expected for these films. Equally the lack of structure in the  $f = 0.10$  film is consistent with this sample generating a 'uniform'-type structure.<sup>1</sup>



**Figure 1.** In-plane sector integrations of thermally annealed dPS-PMMA films in the native form (left) and treated with a staining procedure (right).

With the solvent exchanged films there was a noticeable difference between the two solvents. In the X-ray scattering of acetone treated films the intensity of the observed peak scales with the fraction of polystyrene in the film (figure 2). The position of the peak also changes with the polymer composition in line with atomic force microscopy (AFM) images taken of the same films. With the cyclohexane treatment process the correlations were not so strong, though prominent diffraction peaks were still observed in some of the samples (figure 2). Again this is consistent with preliminary AFM measurement performed on the film.



**Figure 2.** In-plane sector integrations of solvent exchanged dPS-PMMA films treated with cyclohexane (left) and acetone (right), and subsequently treated with a staining procedure.

XR data collected from the films are currently in the process of being modelled and it is hoped that they will give additional information on the structure of the films normal to the surface, particularly the specific location of the PS and PMMA blocks in the solvent exchanged films.

<sup>1</sup> Matsen, M. W.; Griffiths, G. H. *Eur. Phys. J. E* **2009**, *29* (2), 219-227

<sup>2</sup> Zhao, B.; Brittain, W. J.; Zhou, W.; Cheng, S. Z. D. *J. Am. Chem. Soc.* **2000**, *122* (10), 2407-2408.