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# 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.

| ESRF | **Experiment title:** Structure formation in thin films of symmetric diblock copolymers from solution: A time-resolved grazing-incidence small-angle X-ray scattering study | **Experiment number**: SC-984 |
|---|---|---|
| **Beamline**: ID10B | **Date of experiment**: from: May 7, 2002 to: May 14, 2002 | **Date of report**: February 28, 2003 |
| **Shifts:** 21 | **Local contact(s)**: Dr. Oleg Konovalov | *Received at ESRF:* |


**Names and affiliations of applicants** (* indicates experimentalists):

Dr. Christine M. Papadakis*, Peter Busch*
Faculty of Physics and Earth Sciences, University of Leipzig, Linnéstr. 5, D-04103 Leipzig, Germany

Dr. Detlef Smilgies*, Cornell High-Energy Synchrotron Source, Cornell University, Ithaca, NY 14853, USA

Dr. Dorthe Posselt*, IMFUFA, Roskilde University, P.O. Box 260, DK-4000 Roskilde, Denmark


**Report:**

**Aims of the experiment:** Thin films of lamellae-forming polystyrene-polybutadiene (PS-PB) form different structures on sub-micrometer length scale, depending on molar mass [1,2]. The aim of our experiments was to use time-resolved small-angle X-ray scattering under grazing incidence (GISAXS) for the following *in-situ* studies: **(i)** re-orientation of the lamellae, when dry spin-coated PS-PB films are exposed to toluene vapour, **(ii)** structure formation in thin PS-PB films during solvent casting from toluene solution. Additionally, the phase behaviour of thin films of binary blends of PS-PB diblock copolymers was investigated with static GISAXS **(iii)**.

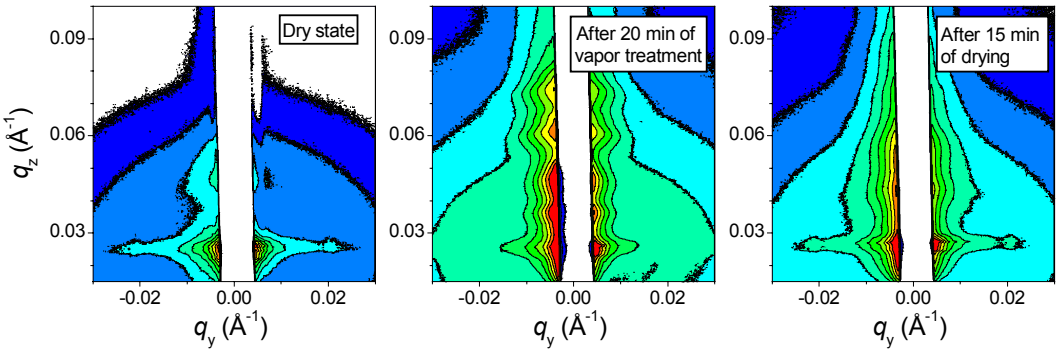
**Experimental:** We studied compositionally symmetric PS-PB diblock copolymers having molar masses of 13.9-183 kg/mol. In the bulk, lamellae with thicknesses $D_{lam}$ = 138-839 Å are formed [3]. Previously, we studied dry films of pure PS-PB using GISAXS [1]. The dry samples were characterised using ellipsometry (film thickness) and atomic force microscopy (surface structure). In contrast to earlier experiments, the samples were not $OsO_4$ stained. For the present experiment we used a similar set-up as previously [1], but with a better CCD camera from the Troika beamline. The ESRF spec control for the camera turned out to be very user-friendly. Reflectivity scans were performed after mounting each new sample, in order to select the incidence angle(s) for GISAXS – typically $0.20^o$, slightly above the critical angle of the film.
We used a flight tube that covered only part of the distance between sample and detector, which caused some problems with Kapton rings in the spectra. A dedicated flight tube would preferably have to be manufactured for similar experiments in the future. In general the experimental set-up performed well, but we lost one and a half-day of beamtime due to a major computer breakdown in the ESRF control room.

**Results:**

**i)** For time-resolved GISAXS studies of structural changes in thin films of PS-PB when swelled with toluene vapour, the sample was mounted in a custom built chamber. After measurements on the dry film, toluene was injected into a reservoir at the bottom of the chamber and GISAXS maps were recorded every 30s over a period of ~ 2 hours. Finally the lid of the chamber was removed and the subsequent drying of the sample was

followed in time. Every 60s a new spot on the sample was chosen. The data shown below are from a low molar mass sample (22.1 kg/mol) with a film thickness 10 times the bulk lamellar thickness of 189Å. The incident angle was 0.18° and the intensity scale is the same on all three figures. The film forms lamellae parallel to the substrate in the dry state, as can be deduced from the peak above the specularly reflected beam and the absence of out-of-plane Bragg rods (Fig.1a). Vapour treatment resulted in major changes in the scattering along $q_z$ (Fig. 1b), reflecting changes in the lamellar structure, while the overall lamellar orientation remained parallel. After drying, the film did not recover the initial structure (Fig. 1c). In conclusion, the measurements clearly show significant structural changes when the films are exposed to toluene vapour, but in order to elucidate the full nature of these changes, further measurements are needed, e.g. films should be exposed to repeated cycles of toluene exposure.

Fig.1a Fig.1b Fig.1c




**iii)** Three films with a long PS-PB diblock copolymer blended with a similar short copolymer in different proportions were investigated. The results are combined with data for four similar blends from experiments at CHESS [4]. For samples with small amounts of short copolymers, a one-phase state is found with perpendicular orientation of the lamellae relative to the substrate surface, in accordance with the structure of a thin film of pure long PS-PB, but with a smaller lamellar thickness. With increasing amount of short copolymers, coexistence of out-of-plane Bragg rods and intensity modulations in the scattering plane in the GISAXS maps, indicate macrophase-separation into perpendicular lamellae with predominantly long copolymers and parallel lamellae dominated by short copolymers. The Bragg rods are in some cases bent, indicating the presence of tilted lamellae. Our results show that the phase behaviour of thin PS-PB diblock copolymer films is similar to the phase behaviour of comparable blends in the bulk. Only for a composition close to the phase boundary between complete mixing and macrophase-separation is the phase behaviour significantly influenced by the thin film geometry compared to the bulk behaviour of similar blends. Our results show that the thin film geometry together with the lamellar thickness is crucial in determining the lamellar orientation.

**ii)** We wetted $Si/SiO_x$ wafers with toluene solutions of PS-PB diblock copolymer with varying block copolymer molar mass and concentration. The measurements presented a number of practical problems and have primarily served as pilot project for further measurements. One critical point is the relatively low contrast of PS-PB in combination with the low copolymer concentration in the drop. Another problem is the occurrence of 'ripples' in the surface of the drying drop. For future experiments, very long exposure times will be necessary, while the vapour pressure above the liquid sample should be controlled in order to avoid ripple formation.

**References:**

[1] C.M. Papadakis, P. Busch, F. Kremer, D. Smilgies, T.B. Bonné, D. Posselt, Experimental Reports of our beam times at ESRF, august 2000 (SC-696) and august 2001 (SC-823).
[2] D.-M. Smilgies, P. Busch, C.M. Papadakis and D. Posselt, *Synchrotron Radiation News* **15**, 35 (2002).
[3] C.M. Papadakis, K. Almdal, K. Mortensen, D. Posselt, *Europhys. Lett.* **36**, 289 (1996).
[4] P. Busch, D. Posselt, D.-M. Smilgies and C.M. Papadakis, in preparation.