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ESRF	**Experiment title:** Thin films of symmetric diblock copolymers and their blends: The inner structure of spin-coated films studied using grazing incidence small-angle X-ray scattering	**Experiment number**: SC-823
Beamline: ID 10 B	**Date of experiment**: from: 25.04.01 to: 02.05.01	**Date of report**: 31.08.01
Shifts: 18	**Local contact(s)**: Dr. Oleg Konovalov	*Received at ESRF:*

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Report:

Aims of the experiment: The aim of the experiment was to continue our investigation (SC-696) of the effect of a confining thin film geometry on the structure of lamellae-forming diblock copolymers. We had previously observed an unexpected molar-mass dependence of the lamellar orientation: parallel lamellae below 22.6 kg/mol and perpendicular above 91.9 kg/mol [1, 2]. In-between, coexisting regions of parallel, perpendicular and tilted lamellae were identified. In the present experiment, we have used small-angle X-ray scattering under grazing incidence (GISAXS) in combination with X-ray reflectometry (XR) in order to elucidate the inner film structures in dependence on preparation method. The surface texture of the films is known from our AFM studies.

Experimental: We studied compositionally symmetric polystyrene-polybutadiene (PS-PB) diblock copolymers having molar masses of 13.9-183 kg/mol. In bulk, they form lamellar structures with lamellar thicknesses D_{lam} = 138-839 Å [3]. For the XR and GISAXS experiments, most films were stained using OsO_4.

The GISAXS set-up was further optimized, based on experiences of the first experiments at Troika II and follow-up experiments at CHESS D-station, in which the use of a high dynamic range CCD camera was tested. In the present experiment, a CCD camera from the ESRF detector group was installed instead of the high-resolution set-up comprising asymmetric-cut crystals in combination with a 1D gas detector [1]. This allowed measurements of the entire 2D-GISAXS image on a timescale of minutes and for fine adjustment of the experimental conditions in order to obtain maximum sensitivity to the film structure. Compared to the Gruner CCD at CHESS, the ESRF camera had lower resolution and sensitivity, so that the overall quality of the data was somewhat better at CHESS. We thank John Morse for his invaluable help getting the ESRF CCD to work, and would like to encourage the Detector Group to look into the purchase of a higher performance CCD camera.

The XR measurements taken with the high-resolution set-up in our first run at ESRF left some open questions. Hence we redid these measurements with a conventional set-up (scintillation detector and slits); furthermore we also characterized a new set of samples. We found that the original data were of high quality, however, the dynamic range was limited in the XR set-up, and some structure at higher angles was not observed in the first run.

Results: We studied the molar-mass dependence of the structure of thin films prepared using spin-coating onto Si-wafers. In order to get detailed information about the electron density along the film normal, we performed XR measurements extending to higher angles than in our previous measurements. The XR curves of high molar mass samples (perpendicular lamellae) show Kiessig fringes related to the film thickness (Fig. 1a). In contrast, XR curves from low molar mass samples show modulated oscillations which points to density variations along the film normal (Fig. 1c). For some samples, shoulders or oscillations at high q-values are observed, indicating the presence of a very thin layer in the film (Fig. 1b). We are currently analyzing these data in terms of a box model.

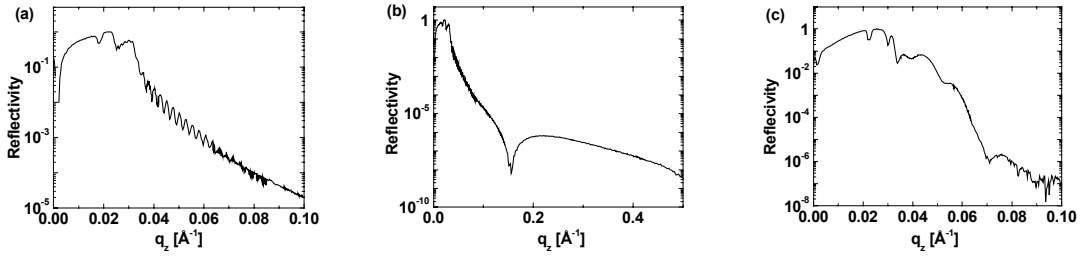

Fig. 1: XR curves of samples having (a, b) 148 kg/mol, D_{lam} = 752 Å and a film thickness D_{film} = 1990 Å and (c) 22.1 kg/mol, D_{lam} = 189 Å, D_{film} = 410 Å.

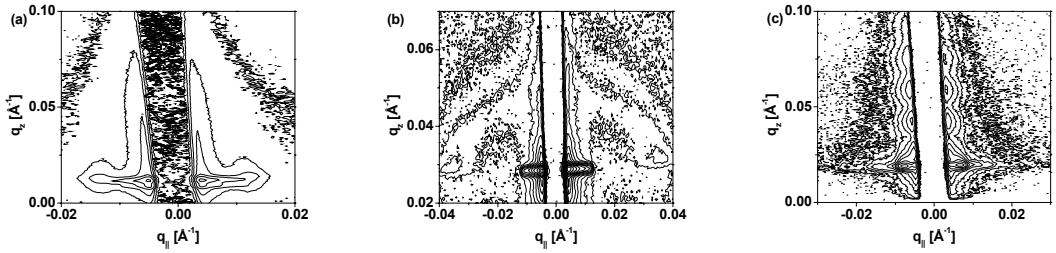

Fig. 2: 2D-GISAXS maps of spin-coated samples having (a) 91.9 kg/mol, D_{lam} = 528 Å and D_{film} = 1700 Å and (b) 18.3 kg/mol, D_{lam} = 160 Å and D_{film} = 1420 Å. (c) Vapor-treated film: 183 kg/mol, D_{lam} = 839 Å and D_{film} = 2420 Å.

GISAXS experiments provide information both in the scattering plane (q_z) and out of the scattering plane ($\mathbf{q}\|$) giving additional information about the correlated roughness oscillations between the interfaces if the lamellae are parallel to the film surface [1] and about the in-plane ordering of the films consisting of lamellae perpendicular to the film surface. We found straight out-of-plane Bragg-rods for high molar mass samples (Fig. 2a), indicating that the lamellae are perpendicular to the film surface. In contrast, for low molar mass samples, instead of Bragg-rods, a ring is observed (Fig. 2b). This is contrary to our previous observations where we did not observe scattering outside the scattering plane, also for even lower molar masses [1, 2], and might be related to the different film thicknesses studied. The ring indicates the presence of parallel and tilted lamellae.

We also performed measurements on a high molar mass sample treated by toluene vapor after spin-coating. Before vapor treatment, the GISAXS map displayed out-of-plane Bragg rods similar to the ones in Fig. 2a. During two days of vapor treatment, oscillations along the q_z-axis ($\mathbf{q}\| \cong 0$) develop (Fig. 2c). These oscillations are attributed to the correlated roughness of lamellar interfaces which are parallel to the film surface. Vapor treatment thus leads to substantial changes in the inner film structure, i.e. the initial perpendicular orientation is not the equilibrium structure.

[1] C.M. Papadakis, P. Busch, F. Kremer, D.-M. Smilgies, D. Posselt, Structure of thin films of symmetric diblock copolymers and of their binary blends, studied using grazing-incidence small-angle X-ray scattering, Experimental Report of our beam time SC-696 at ESRF, August 2000.

[2] P. Busch, D. Posselt, D.-M. Smilgies, C.M. Papadakis, submitted.

[3] C.M. Papadakis, K. Almdal, K. Mortensen, D. Posselt, *Europhys. Lett.* **36**, 289 (1996).