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Experiment Report Form

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- 1st March for experiments carried out up until June of the previous year;
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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.
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- bear in mind that the report will be reduced to 71% of its original size. A type-face such as "Times", 14 points, with a 1.5 line spacing between lines for the text, produces a report which can be read easily.

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ESRF	**Experiment title:** Structure of thin films of symmetric diblock coplymers and of their binary blends, studied using grazing incidence small-angle X-ray-scattering	**Experiment number**: SC-696
Beamline: ID 10 B	**Date of experiment**: from: 26.04.00 to: 02.05.00	**Date of report**: 29.08.00
Shifts: 18	**Local contact(s)**: Dr. Detlef Smilgies	*Received at ESRF:*

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Report:

Aims of the experiment

The aim of the experiment was to study the internal film structure of spin-coated films of compositionally symmetric polystyrene-polybutadiene (PS-PB) diblock copolymers by means of grazing-incidence small-angle X-ray scattering (GISAXS). At room temperature, the samples have a lamellar structure in the bulk. Using atomic force microscopy (AFM) to study the surface structure of thin films, we had observed lamellae (i) parallel to the film surface for molar masses below 22.6 kg/mol, (ii) perpendicular above 148 kg/mol and (iii) coexisting domains in-between. Using GISAXS it is possible to study whether in case (ii) the lamellae are perpendicular only at the surface or down to the substrate and to obtain information on the lamellar orientation *in* the films in case (i) and (iii).

Experimental

The samples were prepared by spin-coating on Si wafers, the film thicknesses were measured using ellipsometry and the surface topography was obtained by AFM. In order to increase the X-ray contrast the samples where stained with OsO_4, which binds selectively to the PB-blocks. Reflectivity and GISAXS experiments both in (q_z) and out of the scattering plane (q_{xy}) were performed to get information about the (i) electron density profile along the film normal, (ii) correlated roughness oscillations between the interfaces if the lamellae are parallel to the film surface [1] and (iii) in-plane ordering of the films consisting of lamellae perpendicular to the film surface. These three methods allow us to get a full description of the inner film structure which complement the AFM results. The samples investigated are listed in Table 1.

Table 1: Parameters of the samples investigated: M_N number averaged molar mass, D_{film} film thickness obtained by ellipsometry, D_{lam} bulk lamellar thickness obtained by SAXS.

Sample	M_N [kg/mol]	D_{film} [Å]	D_{lam} [Å]
SB 183/30	183.0	2320	838
SB 183/10	183.0	500	838
SB 148/30	148.0	1990	749
SB 70/30	69.9	1840	462
SB 70/10	69.9	430	462
SB 22/10	22.1	410	189
SB 18/10	18.3	360	159

Results

For high molar mass PS-PB (148–183 kg/mol) a lamellar surface texture was observed using AFM (Fig. 1a). Using GISAXS, we found an out-of-plane Bragg-rod (Fig. 1b), indicating that the lamellae are perpendicular to the film surface. In the reflectivity curves, only Kiessig fringes related to the film thickness are observed, and no Bragg-peaks related to possible horizontal lamellae. In contrast, for a low molar mass sample (22.1 kg/mol) no Bragg-rods were observed in GISAXS (Fig. 1c), but in this case we found oscillations in $I(q_z)$ (for $q_y \cong 0$) with a spacing Δq_z resulting in $d_{corr} = 2\pi/\Delta q_z = 110 \pm 20$ Å which corresponds to half the bulk lamellar thickness. We thus attribute them to vertical roughness correlations [1] between the lamellar interfaces. The lamellae are thus indeed parallel to the film surface, which is confirmed by Bragg-peaks in the reflectivity curves. Note that for high molar masses, no correlated roughness oscillations were observed as expected. The GISAXS results thus show that the lamellae are perpendicular to the film surface down to the substrate for high molar mass samples and parallel for low molar masses. The experiment is an important demonstration that GISAXS is possible for low-density materials and on the length scale of ~1000 Å.

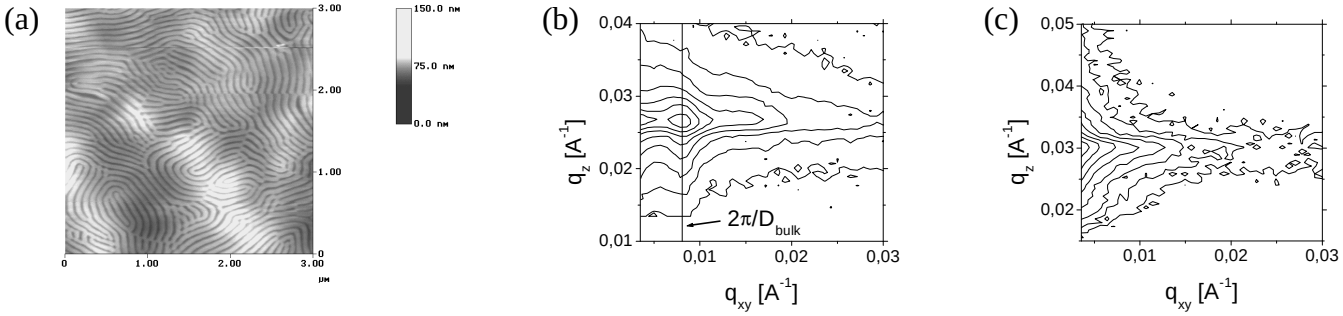

Fig. 1: 3x3 μm AFM height image (a) and GISAXS off-specular intensity (b) from sample SB 183/30. (c) GISAXS off-specular intensity from sample SB 22/10.

For intermediate chain lengths (54.5–69.9 kg/mol) coexistence of domains with no material contrast and domains with laterally structured patterns was seen in AFM (Fig. 2a). The spacing is ~50 % larger than the bulk value [2]. In GISAXS, bent Bragg-rods are seen (Fig. 2b), indicating the presence of tilted lamellae as well. However, also the parallel orientation is present, as is evident from the correlated roughness oscillations which again is equal to half the lamellar thickness for SB 70/30 ($d_{corr} = 225 \pm 20$ Å). By means of GISAXS we can thus obtain quantitative information on the structure of spin-coated diblock copolymer films as a function of molar mass and film thickness.

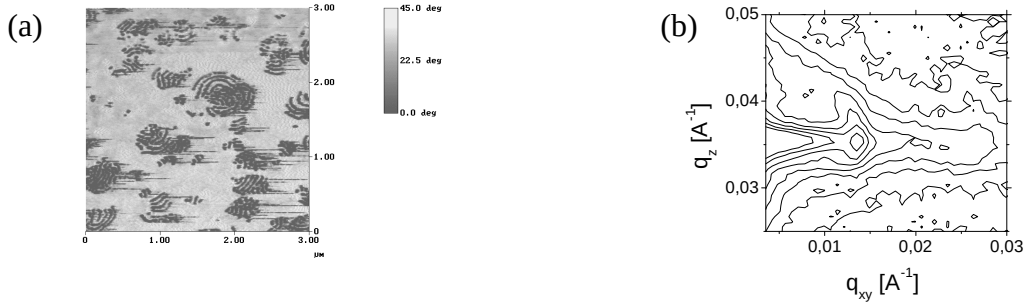

Fig. 2: (a) 3x3 μm AFM phase image of a sample having 54.5 kg/mol, $D_{lam} = 413$ Å, and $D_{film} = 2400$ Å. (b) GISAXS off-specular intensity from sample SB 70/30.

We also performed a first test experiment on a binary diblock copolymer blend which in the bulk is macrophase-separated into domains consisting of thin and thick lamellae. A Bragg-rod from the domains consisting of thick lamellae is observed, i.e. these lamellae are perpendicular to the film surface. The reflectivity shows modulations which in conjunction with AFM indicates that thin lamellae lie on top of the vertical thick lamellae. The structure of such blends will be the task of future GISAXS investigations.

[1] P. Müller-Buschbaum and M. Stamm, *Macromolecules,* **31** (1998) 3686.
[2] C.M. Papadakis, K. Almdal and D. Posselt, *Europhys. Lett.* **36** (1996) 289.