

# Orientation behavior of lamellae forming blends of diblock copolymers with low molar mass additives

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Diblock copolymers represent a versatile class of materials because of the high flexibility to incorporate different material properties into the same material, simply by the covalently linkage of two chemically different polymers. Furthermore, mostly the two blocks are not miscible, and phase separation occurs. Due to the connectivity of the different blocks, this phase separation can only occur on a mesoscopic length scale and highly ordered structures like lamellae, cylinders or spheres are formed. The typical repeat period of these structures lies between 10 and 100 nm. The narrow polydispersity of this repeat period makes these materials suitable candidates for thin film technology, as they can be used as templates for lithography or nanopatterned surfaces.

The selective incorporation of low molecular weight additives into one of the two blocks opens not only the way to tune the length scale to a desired value or to change the morphology of the block copolymer. It has also been shown that they can be removed resulting in nanoporous materials which can be either used as membranes [1] or precursors for the fabrication of nanodots or nanowires [2]. For many of these applications it is required that the orientation of the cylinders or lamellae is perpendicular with respect to the film interfaces. However, usually they tend to align parallel, due to preferential absorption of one of the two blocks to the interfaces and major efforts have to be applied like creating neutral interfaces or applying electric fields [3, 4].

Recently it has been shown that in a thin film of a blend of Polystyrene-*b*-poly-4-vinylpyridine (PS-*b*-P4VP) diblock copolymer with 2-(4'-hydroxybenzene-azo)benzoic acid (HABA) the orientation of cylinders can be controlled by the exposure to different solvent vapors [2]. HABA is dissolved as an additive in the P4VP-block, which forms cylinders in a PS-matrix. If chloroform – which is a good solvent for both blocks – is used for the vapor exposure, the cylinders orient parallel to the film surface. If dioxane is used – which is a good solvent for the polystyrene-matrix, but a bad solvent for the P4VP-cylinders – a perpendicular orientation was observed. Even though the driving forces and the mechanism of the switching behavior have not been clarified in detail it could be shown that it is fully reversible. From the perpendicular oriented cylinders the HABA additive can be extracted by methanol, resulting in cylindrical pores, which can be loaded by metals [2].

In the present experiment we have extended this experiment to the case of lamella forming blends of PS-*b*-P4VP and HABA. Three films have been prepared under different conditions and have been investigated by grazing incidence small-angle x-ray scattering (GISAXS) at A2. The films have been illuminated by a well collimated incident beam (300  $\mu\text{m}$  height) under an incident angle  $\alpha_i = 0.99^\circ$ . The scattered intensity was recorded by a two-dimensional CCD-detector with a pixel array of  $2048 \times 2048$  and a pixel distance of 79  $\mu\text{m}$  at a distance of 960 mm from the sample. Most of the intensity is reflected specular and had to be covered by a beamstop. The off-specular intensity gives than information about the internal structure of the copolymer films [5].

The PS-*b*-P4VP block copolymer had the number average molar masses of 32.9 kg/mol for the PS-block and 8.08 kg/mol for the P4VP-block, respectively. The weight fraction of HABA was 31.2% with respect to the copolymer and the bulk lamellar thickness of the blend was 34 nm as

determined by SAXS. Thin films were prepared by dip coating from dioxane solution and had an initial film thickness of 40 nm. One film was investigated without further processing (A), one film was washed with methanol to remove the additive (B) and one film was exposed to chloroform vapor and afterwards washed with methanol (C). According to Ref. [2] it was expected, that the two films (A) and (B) show a perpendicular orientation of the lamellae, while film (C) should show a parallel orientation. Consequently, only for the first two films strong out of plane scattering was expected.

Fig. 1a shows horizontal cuts of the three films. For film (A) no out of plane scattering could be observed. In contrast, the two films, where the additive was extracted by methanol weak peaks point to a laterally order inside the films, pointing to perpendicular lamellae. In Fig. 1b the two-dimensional GISAXS-map for film (C) supports the weak out-of plane scattering. Thus, for lamellae forming blends of PS-*b*-P4VP and HABA the response to different solvents is differs significantly from cylinder forming blends.

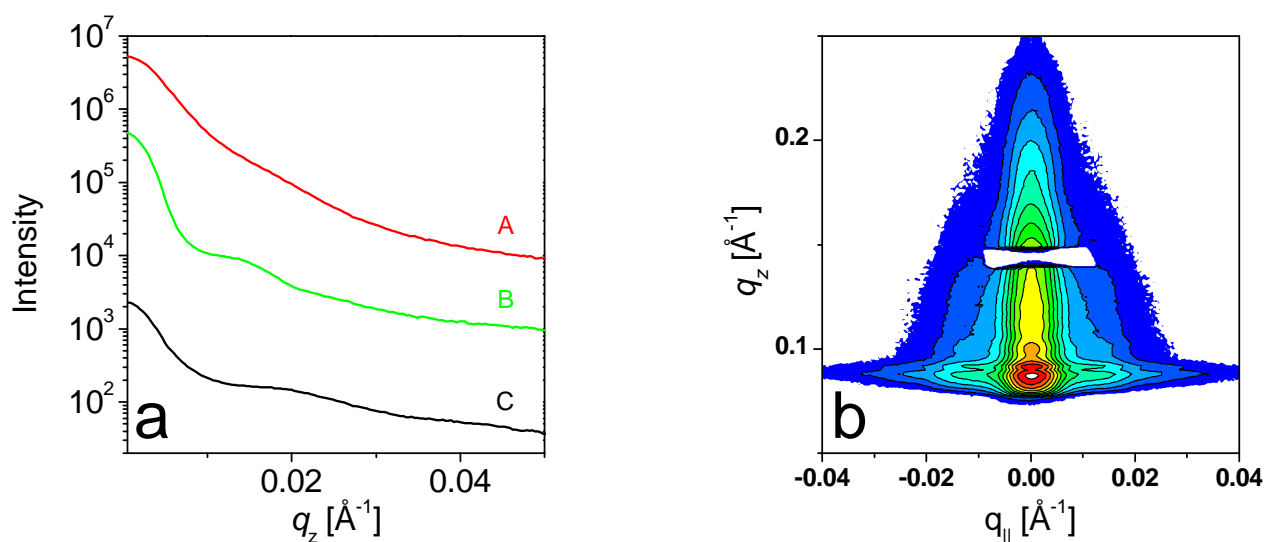


Figure 1: (a) Horizontal cuts of the films processed under different conditions. The curves are shifted for clarity. The processing conditions are given in the text. (b) Two-dimensional GISAXS-map of the film C, which was exposed to chloroform vapor and extracted with methanol.

## References

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