Structural changes in a lamellar block copolymer thin film during vapor treatment

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Vapor treatment has recently emerged as a powerful alternative to thermal annealing of block copolymer (BCP) thin films to remove the defects inherent to self-organization [1]. Despite the extensive application of vapor treatment, the mechanisms of the structural changes observed and the underlying processes are still not well understood. We have carried out in-situ, real-time grazing-incidence small-angle x-ray scattering (GISAXS) measurements during vapor treatment. A time resolution of 30 sec could be achieved which allowed us to investigate the structural changes of lamellar diblock copolymer thin films with great detail.

Symmetric poly(styrene-b-butadiene) (P(S-b-B)) having a molar mass of 28 kg/mol with a volume fraction of PB of 0.51 was used. A film having a thickness of 347 nm was prepared by spin-coating from a 60 mg/ml toluene solution onto an acid cleaned Si wafer. The sample was annealed at 60°C for 24 h. The GISAXS measurements were carried out at beamline BW4 at HASYLAB with a wave length of 0.138 nm and a sample-detector distance of ~2 m. For GISAXS measurements during vapor treatment, the sample was mounted in a custom-made closed cell (Fig. 1). GISAXS images were taken every 30 s. Simultaneously, the film thickness was monitored using a white light interferometer. Saturated vapor pressure was installed by means of a flow of N₂ gas through a toluene reservoir. Toluene is a good and non-selective solvent for both blocks.

Scheme 1. Sample cell used for in-situ GISAXS during vapor treatment.

The GISAXS image of the as-prepared film shows three orders of diffuse Bragg sheets (DBSs) (Fig. 2, each order has two branches, Ref. 2). The lamellar interfaces are thus parallel to the substrate with a high degree of order. Vapor treatment with toluene resulted in drastic changes (Fig. 2): 10 min after the start of bubbling N₂ gas through the toluene reservoir (the time required for the vapor to reach the cell, as evidenced from the constant film thickness during the first 10 min), the DBSs elongate along qₚ and bend downwards (12.9 min). Moreover, a side maximum is present after 12.9 min, which indicates the formation of a regular lateral structure. The DBSs become more narrow again after 15 min and eventually weaken and broaden until no more scattering due to the lamellar structure is observed.
These observations are in accordance with our previous study on a similar P(S-b-B) film in saturated toluene vapor which was achieved by injecting liquid toluene directly into the sample cell [3]. The changes of the shape of the DBSs have been attributed to the increased spatial demand of the block copolymers which is due to a tendency to coiling when solvent is present [4]. This is accommodated first by undulations of the lamellar interfaces, and, at later stages, by the creation of new domains which fuse to form additional lamellae. At last, the film is disordered due to the high content of toluene which screens the interaction between the two blocks.

References