

Probing the Self-Organization Kinetics in Block Copolymer Films

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ABSTRACT

Solvent annealing [1-3] has recently emerged as a powerful alternative to thermal annealing of block copolymer (BCP) thin films and nanocomposites. Taking a more general point of view, solvent treatment procedures, employing the selectivity of the solvents towards the different blocks, can produce new structures [4], and provide fascinating insights into the swelling kinetics and instabilities in such self-assembled and oriented thin films [5]. Taking a lamellar polystyrene-polybutadiene (PS-*b*-PB) film right from the spin coater into an in-situ vapor cell provided an intriguing trip through configuration space, with various lamellar re-orientations encountered during swelling.

INTRODUCTION

The standard preparation of BCP thin films is spin coating from solution and then careful thermal annealing above the glass temperature in an oxygen-free environment. This

procedure yields highly oriented block copolymer films, e.g. parallel or perpendicular lamellae [6-8], standing or lying cylinders[3, 4, 9, 10], or monolayers of spheres [10]. However, laterally the BCP film microstructure often only features short-range order. The groups of Krausch and Russell have recently shown that the lateral order in BCP thin films can be significantly improved by exposing the film to the vapor of a non-selective solvent [1-3].

Solvent annealing avoids the danger of the polymer decomposing or crosslinking when at elevated temperature, and thus appears as a much gentler procedure than a thermal anneal. Moreover, a large variety of solvents is available for most polymers, in order to dial up just the right kinetics for the annealing process. However, swelling in vapor is a much more complex process than thermal annealing from the melt, due to the interaction of the solvent with each block which changes block volumes as well as rescales the effective interaction parameter.

In fact, not all polymer films simply feature solvent annealing, in particular when the swollen state is incompatible with the dry state. For instance, if the scaling of the film thickness with solvent uptake is incompatible with the scaling of the lamellar period with solvent content, the film may reorganize to form extra lamellae [5]. If the solvent is somewhat selective, the change in volume ratio in the swollen film may induce a BCP phase transition in the swollen state [4]. Hence in the following we will speak more generally of “solvent treatment”.

EXPERIMENTAL DETAILS

The block copolymer material was synthesized by living anionic polymerization by Polymer Source, Montreal, Canada. The molecular weights of the polystyrene and polybutadiene blocks were determined by size exclusion chromatography (SEC) and proton NMR as 15 kg/mol and 13 kg/mol, respectively, with a polydispersity index of 1.05. The resulting 28 kg/mol polymer PS-*b*-PB has a volume ratio close to 0.5, and

features symmetric lamellae after microphase separation. A 150 nm thick film was deposited on a clean silicon wafer via spin coating.

We have developed an in-situ vapor chamber with Kapton windows for the incoming and outgoing x-ray beams as well as with a built-in film thickness monitor. Liquid solvent can be injected in-situ through a long Teflon capillary. The injected 1-2 mL of toluene builds up the equilibrium vapor pressure characteristic of ambient conditions which corresponds to 3.79 kPa at 20°C for toluene. For thin film characterization we used grazing-incidence small-angle x-ray scattering (GISAXS), which is compatible with in-situ and real-time measurements [11], and provides simultaneous information on both the lateral and the perpendicular morphology of the film [12].

GISAXS experiments were performed at CHESS D1 station, featuring a high-flux multilayer monochromator providing 10^{12} photons/sec/mm². at 10 keV photon energy and 1.5% bandwidth. The sample chamber was mounted on a goniometer comprising crossed arcs to control the incident angle and the sideways tilt as well as vertical and horizontal translations to line-up the sample in the 0.5mm (H) × 0.1mm (V) x-ray beam. A movable rod-like beamstop blocked the intense reflected beam as well as the intense diffuse scattering in the incident plane. An ion chamber was used to position the sample precisely in the beam, and also produced low-resolution x-ray reflectivity data for a first characterization of the films. GISAXS images were recorded with a CCD-type x-ray area detector.

The film was lined up and pre-characterized with GISAXS before vapor exposure, using a spot close to the edge of the sample. The light beam of the thickness monitor impinged on the sample at the other edge. Between these two sample areas we defined the active part of the sample for the in-situ measurements. In order to reduce radiation damage to a minimum, the sample was moved laterally perpendicular to the beam after each image, in order to expose a fresh spot of material to the beam. Between images the upstream x-ray shutter controlling the x-ray exposure of sample and detector was kept closed.

DISCUSSION

In our experiments we wanted to explore what happens, if we forego the usual initial thermal annealing step altogether, and expose a freshly spun film to solvent vapor. Fig. 1 displays the film swelling as a function of vapor exposure. The film swelling was defined as $(d-d_0)/d_0$ where d and $d_0=150$ nm refer to the swollen and initial film thicknesses, respectively. At 100% swelling the film has doubled its thickness. Overlaid are GISAXS images of the film, as obtained in individual 5 sec exposures during swelling. In the images, the horizontal and vertical directions correspond to the parallel and perpendicular directions with respect to the polymer film.

The first order lamellar scattering of the as-spun film revealed a relatively disordered film with only a faint and broad powder ring. The powder ring showed a weak texture, with intensity maxima in the lateral direction indicating a tendency towards forming perpendicular lamellae. This was a surprise, since thermally annealed films of this molecular weight display the parallel orientation with the lamellar planes parallel to the substrate [6-8].

As soon as toluene was injected into the cell, the film rapidly started swelling. At about 20%-30% swelling the powder ring associated with the first-order lamellar Bragg reflection became sharper and more intense, indicative of improved lamellar order. The lamellar orientation changed towards forming parallel lamellae, giving rise to intense scattering close to the beam stop. At 40% swelling the radial width and the lateral width became the narrowest, i.e. the best ordering was reached and the lamellae were solidly parallel to the substrate.

As the film continued swelling, the lamellae slowly started to disorder and reorient again, until beyond 100% swelling the film structure looked very similar to the initial morphology after spin-coating: Again the powder ring was broad with regard to both radial and azimuthal width, with a slight preference towards formation of perpendicular

lamellae. This indicates that the structure of the film as spun corresponded to quenching the structure of a highly swollen state by rapid drying.

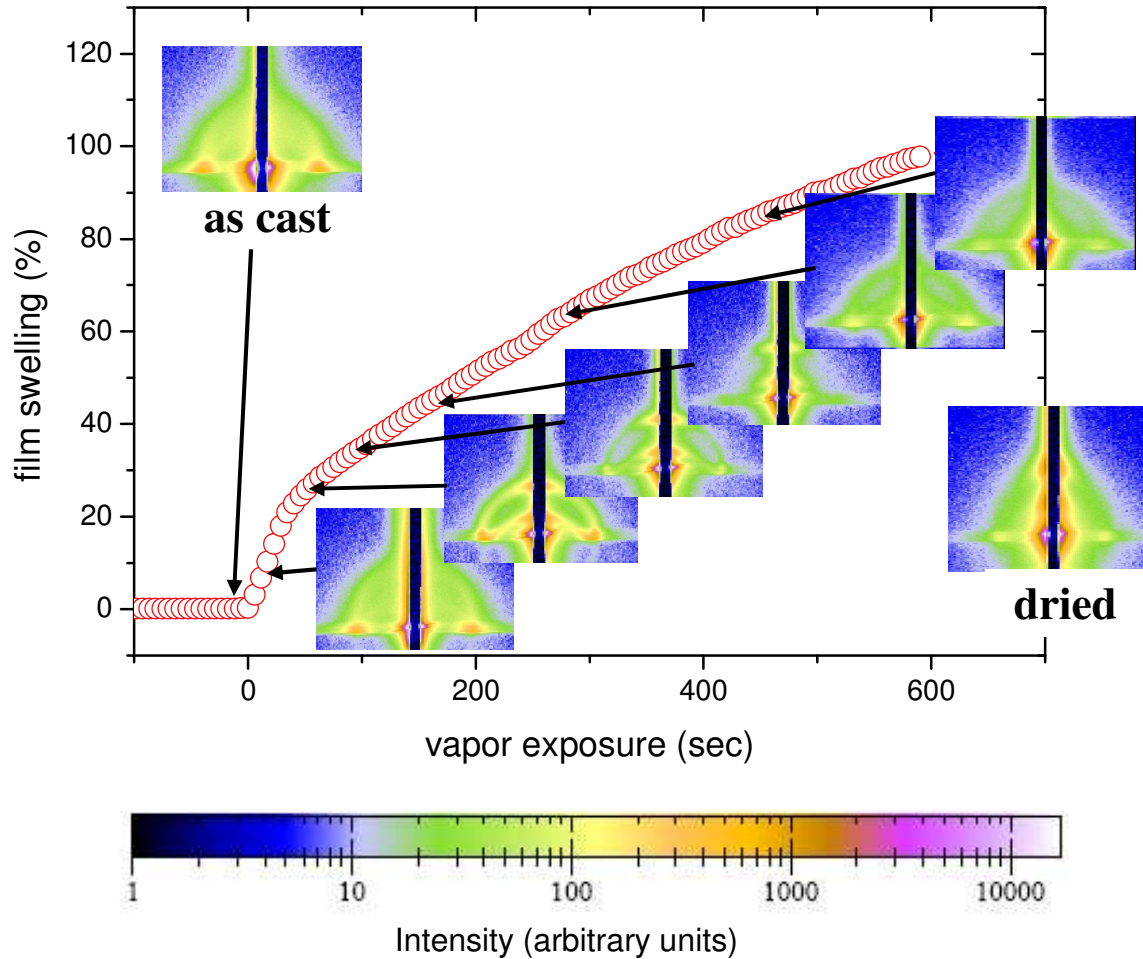


Figure 1. Swelling of a 150 nm PS-*b*-PB block copolymer film in toluene vapor under ambient conditions. Superimposed to the film thickness monitor signal are GISAXS images acquired at the vapor exposure indicated by the arrows. Images are plotted on a logarithmic intensity scale provided below the graph. The first-order reflection are at 0.285 nm^{-1} corresponding to a lamellar period of 22 nm. For further discussion see text.

By removing the lid of the vapor chamber, the swollen film could be dried. By the time the x-ray beam was available again, a couple of minutes after removing the lid, the film behaved static, i.e. the deswelling had already finished within this time period. A film thickness measurement after removal of the remaining toluene liquid in the cell showed that the film had deswollen close to its original thickness.

The scattering image of the dried film was again different from earlier images: The film had regained the equilibrium parallel lamellar orientation [8]. The overall scattering intensity was stronger than during the vapor treatment, however, the radial width of the lamellar signal remained broad, as opposed to the much sharper peak width obtained for this lamellar orientation at low swelling ratio. The appearance of the scattering from the dried film was indeed very similar to that of a thermally annealed film [7]. Thus the film appeared to be better ordered at the early stage of swelling, albeit yielding an overall smaller scattering intensity indicative of remaining disorder.

In successive experiments we exerted more control over the vapor pressure and we could show that, apart from initial states with quenched disorder acquired during spin coating, the various states of ordering and orientation encountered seemed to be reversible and only dependent on the swelling ratio. So far we have not succeeded in preserving the acquired order of the 40% swollen film for the dried film. This may be related to the removal of the vapor in the cell being too slow at low swelling ratios. Recently Bosworth et al. reported that for ordering in a selective solvent occurring close to saturation vapor pressure, the ordered BCC phase of the swollen film could be quenched by fast drying, albeit with a uniaxial compression of the dried film of 40% along the surface normal [4].

CONCLUSION

Solvent treatment of BCP thin films in combination with time-resolved in-situ GISAXS opens a new window into the study of polymer kinetics and phase transitions, and facilitates the study of polymers “under the influence”.

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