Towards an equilibrium structure in lamellar diblock copolymer thin films using solvent vapor annealing – an *in-situ* time-resolved GISAXS study

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ABSTRACT. Solvent vapor annealing (SVA) is frequently used to improve the ordering in diblock copolymer thin films. An important question is which SVA protocol should be chosen to ensure thermodynamic equilibrium. Here, we investigate two thin films from a low molar-mass, lamellae-forming polystyrene-*block*-polybutadiene (PS-*b*-PB) diblock copolymer (28.0 kg/mol). The films are prepared by spin-coating Si wafers from toluene solutions and have film thicknesses of 215 nm and 332 nm. The as-prepared films have mainly the parallel lamellar orientation with a lamellar thickness $D_{lam,par}$ significantly lower than in the bulk. SVA cycles were carried out with cyclohexane, and the structural changes were followed in-situ using time-resolved grazing-incidence small-angle X-ray scattering (GISAXS). Before and after SVA, $D_{lam,par}$ is significantly lower than in the bulk, i.e. the equilibrium value of $D_{lam,par}$ in thin film geometry is different from the bulk value. Whereas the behavior of $D_{lam,par}$ is different for the two films in the early stages of the first swelling, it is very similar in the late stages of swelling and during drying. During the first drying, the lamellae deswell, initially slowly and later, when PS becomes glassy again, affinely. During the second SVA cycle on the thin film, the scaling behavior of the lamellar thickness is identical to the one during the first drying, as is the drying behavior of the thicker film. We conclude that one cycle of solvent vapor treatment with a degree of swelling of ca. 1.5 is sufficient to bring the PS-*b*-PB thin films studied into equilibrium and to create a nearly defect-free lamellar structure.

KEYWORDS. Nanostructured thin films, solvent vapor annealing, block copolymers, grazing-incidence small-angle X-ray scattering

Introduction

Solvent vapor annealing (SVA) has emerged as a promising and highly versatile method to improve ordering and morphology in a variety of nanostructured thin films comprising e.g. block copolymers,¹ nanoparticle assemblies² or small conjugated molecules.³ In the present work, we focus on nanostructured block copolymer thin films, where SVA is in many recent studies a routine step (examples are given in Ref. 1). Nanostructured block copolymer thin films find numerous applications, e.g. for creating nanoporous films and membranes^{4,5} as well as nanostructured templates for manufacturing,^{6,9} for potential use in future mass data storage,¹⁰ and as sensors.¹¹ Several reviews have compiled the fundamentals of block copolymer thin films and their applications,^{12,13,14} and defect-free structures are a common requirement. However, the self-assembly process of the block copolymer film during preparation – especially when using spin-coating – introduces defects and multi-domain structures. Post-preparation techniques, *e.g.*, thermal annealing above and below the glass transition temperature (T_g)^{15,16} and exposure to electrical fields^{17,18} have been used to remove defects. SVA has become increasingly popular to heal defects in diblock^{1,4,10,19,20,21,22,23} and triblock^{24,25,26,27,28,29,30} copolymer thin films prepared by spin-coating, since a thermal degradation of the polymer blocks can be avoided. It has been found that controlling the details of the SVA procedure is imperative to achieve the necessary structural control for applications, as reviewed recently.^{1,31,32,33}

Only few theoretical investigations have addressed the structural changes in block copolymer thin films during SVA so far,^{34,35,36,37,38} most of them focusing on the behavior of the thin film during solvent *evaporation* from the solvent-swollen state. The effect of the gradient of the solvent concentration during evaporation was found to be of importance for the microdomain orientation.^{34,35,37} The structural changes of lamellar thin films during *swelling* with non-selective

solvent in a saturated atmosphere were investigated by Rudov et al.³⁶ For the case of initially parallel lamellae formed by symmetric diblock copolymers, it was found that a drastic reorganization of the lamellar stack takes place with the creation of new and thinner lamellae, starting from the film surface, and that the solvent not only swells the two blocks but also accumulates at the lamellar interfaces shielding the repulsive interactions between the two blocks.³⁶ Perpendicular lamellae, in contrast, do not undergo such a drastic reorganization, but tilt sideways to accommodate a decreasing lamellar thickness. Hur et al. have studied lamellar block copolymers using Monte Carlo simulations and have observed that the morphology in the fully swollen state serves as a seed structure when the solvent is rapidly removed from the film, i.e. the final structure after drying is not necessarily in equilibrium.³⁸ This indicates that it is important to remove the defects already during the swelling to obtain a defect-free structure after drying.

Since the detailed conditions of SVA are crucial for the resulting structure, a number of protocols have been developed for in-situ investigations during swelling and drying of thin block copolymer films.^{39,40,41,42,43,44,45} Using bubblers enables continuous swelling and drying at controlled rates which allows detailed in-situ real-time structural investigations.^{23,46,47}

Only few experimental studies have so far characterized the structural changes during SVA.^{23,47,48,49,50} Using in-situ and real-time grazing-incidence small-angle X-ray scattering (GISAXS),^{51,52,53} the improvement of lateral order²³ and the possibility of erasing the processing history have been revealed.⁴⁷

In the present work, we investigate spin-coated thin films from symmetric, lamellae-forming polystyrene-*block*-polybutadiene (PS-*b*-PB) diblock copolymers and investigate the structural changes during two cycles of SVA with cyclohexane (CHX), a slightly PB selective solvent. In

the as-prepared film, the lamellae have mainly the parallel orientation with a certain fraction of randomly oriented lamellae. In our previous work on SVA of thin PS-*b*-PB films with different solvents,^{41,42,43,45,54} we have identified the process of restructuring in films featuring the parallel lamellar orientation in the as-prepared state: During swelling, the lamellae first swell uniaxially along the film normal; then, the lamellar interfaces start to undulate to increase the interfacial area per copolymer. The lamellae break up, and lens-like domains of one block in the other one are formed which merge to form additional lamellae. This latter process goes along with a decrease of the lamellar thickness and thus more Gaussian block conformations. So far, the subsequent drying process was only investigated in one case, where ethylacetate (EAC) was used for SVA.⁵⁴ Initially, the deswelling of the lamellae was found to be slower than expected for affine deswelling, which may be a consequence of increased non-favorable segmental interactions as the solvent is removed. Only in the late stages of drying – when the PS microdomains are glassy again – affine deswelling is found, i.e. the lamellar thickness is proportional to the film thickness.

Another peculiarity found in some of the spin-coated films was that the lamellar thickness of the parallel lamellae was significantly lower than the bulk value,^{41,43,54} and does not in all cases reach the bulk value after drying.⁵⁴ The question arises whether the lamellar thickness obtained after one SVA cycle is a remainder of the non-equilibrium state created by spin-coating or whether thermodynamics dictate that it is different from the bulk, e.g. whether due to the confinement of the thin film geometry and the interfacial interactions, a lower lamellar thickness than in the bulk constitutes the thin film equilibrium state.

To address these questions, we investigate here two thin films of the same low molar mass PS-*b*-PB diblock copolymer as in Refs. 45 and 54. (The two films are in the following referred to as

thin and thick, even though both are in the thin film regime.) Varying the film thickness, possible confinement effects should be detected. We chose CHX as a solvent to allow comparison with some of our previous results.^{43,45} Since the swelling behavior of the hitherto investigated films differed quantitatively, we repeated the entire swelling and drying process under identical conditions twice. Moreover, this procedure allows us to detect whether the structure after the first SVA cycle is in equilibrium. Our results not only give insight into the pathways of structural reorganization but also suggest a protocol to obtain a thin film of well-ordered parallel lamellae.

The paper is structured as follows: After a description of the materials and experimental methods, the results from the thin film are described. Then, we compare these to the ones from the thick film. Finally, we discuss the findings with respect to previous results on the PS-*b*-PB system and compare with theoretical predictions.

Materials and Methods

Materials

Polymer. The sample was a polystyrene-*block*-polybutadiene (PS-*b*-PB) diblock copolymer (*Polymer Source Inc., Canada*) having a molar mass of 28.0 kg/mol (15.0 kg/mol and 13.0 kg/mol for PS and PB, respectively), which, based on the PB monomer, corresponds to a degree of polymerization $N = 474$. Its polydispersity index is 1.05 and the PB volume fraction 0.51 ± 0.01 . At room temperature (RT), $\chi N \cong 25$,⁵⁵ the sample is thus in the intermediate segregation regime.⁵⁶ The bulk structure of the PS-*b*-PB diblock copolymer is lamellar with a lamellar thickness $D_{lam}^{bulk} = 220 \pm 4 \text{ \AA}$, and the lamellae are almost symmetric, as observed using transmission small-angle X-ray scattering.⁵⁴ The glass transition temperatures of the PS and the PB domains of a similar PS-*b*-PB diblock copolymer are 76 °C and -89 °C, respectively.⁵⁵ The

Hansen solubility parameters of PS, PB and CHX are $18.7 \times 10^{-3} \text{ (J/m}^3)^{1/2}$, $17.4 \times 10^{-3} \text{ (J/m}^3)^{1/2}$ and $16.8 \times 10^{-3} \text{ (J/m}^3)^{1/2}$.⁵⁷ Hence, CHX is a good solvent for PS-*b*-PB and slightly selective to PB.

Methods

Film preparation. The block copolymer was dissolved in toluene at a concentration of 40 mg mL⁻¹ or at 60 mg mL⁻¹ together with up to 2 % w/w (relative to polymer mass) antioxidant (Irganox 1010 from CIBA) to prevent crosslinking of the PB blocks during further treatment. Films were prepared by spin-coating Si(100) wafers (Silchem Handelsgesellschaft mbH) of size $4 \times 2 \text{ cm}^2$ at 3000 rpm for 30 s. The Si substrates were precleaned for 15 min at 35 °C in a dichloromethane bath and for 15 min at 80 °C in an acid bath consisting of 100 ml of 80% H₂SO₄, 35 mL of 30% H₂O₂, and 15 mL of deionized water, followed by rinsing in deionized water and drying with compressed oil-free nitrogen.⁵⁸ Then, the cleaned substrates were successively spin-dried with ethanol and acetone, resulting in a hydrophobic surface.⁵⁸ After spin-coating, the films were dried at RT in vacuum for one day.

Film thickness determination. A white-light interferometer (WLI, NanoCalc 2000, Ocean Optics) was used. For the as-prepared thin film, the film thickness was found to be $2150 \pm 20 \text{ Å}$, which was confirmed by X-ray reflectometry within 10% (not shown). The thickness of the as-prepared thick film was $3320 \pm 20 \text{ Å}$.

Grazing-incidence small-angle X-ray scattering (GISAXS). GISAXS experiments were performed at the wiggler beamline BW4, DORIS III at DESY in Hamburg, Germany.⁵⁹ The wavelength λ was 1.3808 Å with a bandwidth of 10^{-4} (Si(111) double-crystal monochromator), and the beam was focused to a size of $\sim 40 \text{ μm} \times 20 \text{ μm}$ (horizontal $\times$ vertical) at the sample position. The incident angle was $\alpha_i = 0.18^\circ$. At the chosen wavelength, the critical angles of the polymer film and of the substrate are $\alpha_{cp} = 0.13^\circ$ and $\alpha_{cs} = 0.19^\circ$, respectively. A disk-like

beamstop for the specularly reflected beam was used together with a tantalum rod with a diameter of 1.5 mm. The rod-like beamstop was used to protect the detector from the specularly reflected beam and the intense diffuse scattering appearing in the scattering plane, where sometimes streaks of very high intensity appear during the vapor treatment. Its use allows longer counting times and thus measuring of the out-of-plane sample scattering with improved statistics. As a detector, a MarCCD camera was used having a pixel size of $79.1 \mu\text{m} \times 79.1 \mu\text{m}$. The sample-detector distance was chosen to be 1.93 m or 2.52 m, resulting in nominal q resolutions of $\Delta q = 1.80 \times 10^{-4} \text{ \AA}^{-1}$ and $1.43 \times 10^{-4} \text{ \AA}^{-1}$ per pixel. q is the momentum transfer. q_y and q_z denote the in-plane and the normal components of the scattering vector, respectively. They are defined by $q_y = k_0(\sin\psi \cos\alpha_f)$ and $q_z = k_0(\sin\alpha_i + \sin\alpha_f)$ where $k_0 = 2\pi/\lambda$, and ψ and α_f are the in-plane scattering angle and the exit angle, respectively. The q -space calibration was performed using silver behenate.

Analysis of GISAXS maps. Schematic drawings of the GISAXS maps expected from different lamellar structures are shown in Figure 1. Alongside specific scattering features due to the lamellar morphology, the measured 2D GISAXS maps (see for instance Figure 2a) show the generally occurring features: (i) the specularly reflected beam (for $\alpha_i = 0.18^\circ$ at $q_z = 0.0293 \text{ \AA}^{-1}$), the center of which is blocked by the beamstop, and (ii) the Yoneda peaks of the PS-*b*-PB film and the Si substrate at $0.0257 \text{ \AA}^{-1}$ and $0.0297 \text{ \AA}^{-1}$, respectively. We refer to the high scattering intensity in this range of q_z values as the Yoneda band.⁶⁰

Figure 1. Schematic 2D maps from (a) parallel lamellae resulting in straight and narrow DBSs (m is indicated), (b) parallel lamellae with lens-like domains leading to DBSs which are broadened along q_z and bent, and (c) randomly oriented lamellae resulting in DDSRs centered around the direct and the specularly reflected beam. In (a,b), the even-order DBSs expected for asymmetric lamellae are shown as well. S denotes the specularly reflected beam, m the order of the DBSs, and M1, P1, M2, P2, M3 and P3 the minus and plus branch of the 1st, 2nd and 3rd order DBSs (Eq. 2). For clarity, only the first order ($m = 1$) is shown in (c).

For a thin film featuring parallel lamellae with plane interfaces, diffuse Bragg sheets (DBSs) are expected (Figure 1a). Using the distorted-wave Born approximation (DWBA), the lamellar thickness of parallel lamellae, D_{lam} , is deduced from the q_z position of the DBSs:⁶⁰

$$D_{lam} = \frac{2\pi m}{\sqrt{(q_z - k_{iz})^2 - k_{c,film}^2} \pm \sqrt{k_{iz}^2 - k_{c,film}^2}}. \quad (1)$$

$k_{iz} = k_0 \sin(\alpha_i)$ is the z -component of the wave vector of the incoming beam and $k_{c, film} = k_0 \sin(\alpha_{c, film})$ with $k_0 = 2\pi/\lambda$ and $\alpha_{c, film}$ the critical angle of total external reflection of PS-*b*-PB (including absorbed CHX). m is the order of the reflection. In case of symmetric lamellae with equally thick PS- and PB-rich parts, m takes only odd values. For each value of m , two diffuse Debye-Scherrer rings (DDSRs) denoted ‘minus branch (Mm)’ and ‘plus branch (Pm)’ are expected, which correspond to the DDSRs centered on the direct beam (Mm) and the beam reflected from the substrate (Pm), respectively. To determine the positions of the DBSs precisely, intensity profiles along q_z were created from the experimental 2D GISAXS maps by averaging over the q_y range $-0.0051 \text{ \AA}^{-1} < q_y < 0.0039 \text{ \AA}^{-1}$, i.e. centered at the maximum intensity along q_y , close to the beamstop (Figure S1a). For the thin film, the P1 peak was chosen for further analysis, because it is the most intense and does not overlap with the specularly reflected beam or the Yoneda region at any time. The profiles were found to be fitted well by the following empirical function, which is a combination of a decay following the Fresnel reflectivity and a Gaussian peak (Figure S1b):

$$I(q_z) = \frac{1}{(q_z - q_{zs})^4} \times \frac{A}{w_z \sqrt{\pi/2}} \times \exp\left[-2 \frac{(q_z - q_{z0})^2}{w_z^2}\right] + I_{bg} \quad (2)$$

q_{zs} is the q_z position of the specularly reflected beam, q_{z0} the q_z position of the DBS, A a prefactor, $w_z = 0.849 \times \text{FWHM}$ (full width at half maximum) and I_{bg} a constant background. The FWHM along q_z is related to the average number of correlated lamellae, N_{corr} . Neglecting the resolution of the setup, the number of correlated lamellae is estimated at:⁶¹

$$N_{\text{corr}} = 0.93 \times \frac{q_{z0}}{\text{FWHM}} \quad (3)$$

For rough lamellar interfaces, the DBSs become broad along q_y and, in case of mosaicity due to lens-like domains between the lamellae, they bend downwards (Figure 1b). To gain information

on the correlated roughness of the lamellar interfaces,⁶² intensity profiles along q_y were created from the experimental 2D GISAXS maps by averaging over a q_z range of width $0.015 \text{ \AA}^{-1}$ centered at the P1 peak (Figure S1a). Lorentzian functions were fitted to them to quantify the width w_y of the peak along q_y (Figure S1c):

$$I(q_y) = I^* / \left[1 + 4 \left(\frac{q_y - q_{y1}}{w_y} \right)^2 \right] \quad (4)$$

where q_{y1} is the peak position, w_y the FWHM along q_y and I^* the amplitude. The more long-ranged the lateral correlation of the lamellar interfaces, the narrower is the peak along q_y and the smaller w_y . Randomly oriented lamellae give rise to rings of high intensity (DDSRs) around the direct beam and around the specularly reflected beam (Figure 1c) which are enhanced in the Yoneda band.^{63,64} To gain information on those lamellae which are perpendicular, intensity profiles along q_y were created from the experimental 2D GISAXS maps by averaging over a q_z range of width $0.010 \text{ \AA}^{-1}$ centered at the Yoneda band (Figure S1a). Lorentzian functions were fitted to the peaks to quantify the position, $q_{y,perp}$, and width of the peak along q_y , $w_{y,perp}$ (Figure S1d):

$$I(q_y) = I_{perp} / \left[1 + 4 \left(\frac{q_y - q_{y,perp}}{w_{y,perp}} \right)^2 \right] \quad (5)$$

where I_{perp} is the amplitude.

The conversion of the 2D maps from pixels to q -values as well as the construction of 1D profiles and the peak fitting were carried out using a GISAXS Analysis Package, written by us within the Igor Pro development environment. The GISAXS maps of the thick film were analyzed in the same way with the only difference that the peak positions of the DBSs were

determined using the software used by us before to model the scattering from a stack of parallel lamellae.^{45,54,60}

Vapor treatment. The custom-made sample cell including the bubbler and the gas handling system as well as the protocol for SVA have been described in Ref. 54. Swelling of the films was accomplished by letting CHX vapor flow for 40-45 min at a rate of ~0.4 L/h into the sample cell using a bubbler. Drying of the films was performed by increasing the flow of dry N₂ gas directly into the cell stepwise from 0 to ~3 L/h over ca. 40 min while maintaining the flow of CHX vapor. Then, the flow of CHX vapor was stopped, and the direct N₂ gas flow was decreased to 0. For the thin and the thick film, two cycles respectively one cycle of swelling/drying were carried out. The film thickness was measured in-situ once per second using white-light interferometry. The polymer volume fraction was determined using

$$\phi = \frac{D_{film}^{dry}}{D_{film}(t)} \quad (6)$$

where D_{film}^{dry} is the film thickness in the as-prepared, unswollen state. GISAXS measurements were taken continuously with measuring times of 30 s and a technically required waiting time of 9 s. After each cycle, measurements of 300 s duration were taken. After each measurement, the sample was moved sideways by 0.05 mm to avoid beam damage. The thin film was this way scanned 4 times, the thick film only once.

Results

As-prepared thin film

The surface topography of the as-prepared thin film shows a random texture from which a clear lamellar orientation cannot be derived (Figure S2), similar to our previous observations on

similar thin films.⁵⁴ Detailed information regarding the lamellar orientation was obtained by GISAXS. The 2D GISAXS map of the as-prepared film (Figure 2a) shows one pair of DBSs (M1 and P1) near $q_y = 0$, *i.e.*, a significant fraction of the lamellae is parallel with respect to the Si substrate (Figure 1a). First-order DDSRs from randomly oriented lamellae (Figure 1c) are present as well, indicating a minor fraction of randomly oriented lamellae. The intensity of the DDSRs is enhanced in the Yoneda band, as expected. Second-order DBSs or DDSRs are not observed, presumably because the lamellae are symmetric or because of poor correlation along the film normal.

Figure 2. (a-c) 2D GISAXS maps of the as-prepared thin film (a) and after the first (b) and second (c) cycle of vapor treatment. Measuring times were 300 s. The regions of low intensity are due to the beamstops. (d) Corresponding 1D intensity profiles along q_z of (from below) the as-prepared film (black curve), after the first (green curve) and after the second SVA cycle (red curve). The intensity dip at $q_z \cong 0.03 \text{ \AA}^{-1}$ is due to the beamstop.

In order to characterize the parallel lamellae, Eq. 2 was fitted to the P1 peak in the intensity profile along q_z (Figure 2d), giving the lamellar thickness in the dry state, $D_{lam,par}^{dry} = 145 \pm 1 \text{ \AA}$ using Eq. 1. This value is the same as observed previously⁵⁴ and significantly lower than $D_{lam}^{bulk} = 220 \pm 4 \text{ \AA}$. The intensity oscillations in the Yoneda region indicate that the film thickness is homogeneous and that the film surface is smooth.⁶⁰ Dividing the film thickness of $2150 \text{ \AA}$ by $D_{lam,par}^{dry}$, the maximum number of stacked lamellae is estimated at $N_{lam} = 14.8 \pm 0.2$. From the FWHM of the P1 peak along q_z , a value $N_{corr} = 9.3 \pm 0.1$ is obtained using Eq. 3, which is significantly lower than N_{lam} , indicating that the lamellar stacking is not perfect. The relatively large value of N_{corr} confirms that the sample is indeed in the lamellar and not in the disordered state. Fitting Eq. 5 to the profile along q_y taken in the Yoneda region (Figure S1d) results in a lamellar thickness of the perpendicular lamellae of $D_{lam,perp}^{dry} = 227 \pm 2 \text{ \AA}$, much closer to D_{lam}^{bulk} than $D_{lam,par}^{dry}$. The same values of $D_{lam,par}^{dry}$ and $D_{lam,perp}^{dry}$ were found by us previously in a thicker, but otherwise similar PS-*b*-PB film ($D_{film} = 3260 \pm 10 \text{ \AA}$).⁵⁴ The findings on the as-prepared sample (together with the changes during vapor treatment discussed below) are summarized in Figure 3.

Figure 3. Schematic structure of the thin film: (a) as-prepared, (b) fully swollen after the first swelling and (c) after the first drying. PB and PS are depicted in yellow and blue, and the substrate in grey and hatched. The film thickness and the lamellar thickness are indicated. During the second cycle, the lamellar stack just swells and shrinks again without major rearrangements.

Time-resolved behavior of the thin film during SVA

The thin film was swollen twice in CHX vapor and then dried. During the first cycle, the film thickness increased linearly for 42 min from $2150 \pm 20 \text{ \AA}$ to $3135 \pm 20 \text{ \AA}$ with a rate of $25 \text{ \AA/min}$ (Figure 4a) and then decreased at a rate of $-26 \text{ \AA/min}$, reaching again its initial value after ~ 40 min. The film was left to dry for another ~ 64 min after which it reached $D_{\text{film}} = 2190 \pm 20 \text{ \AA}$. The polymer volume fraction, ϕ , decreased during swelling from 1.0 to 0.69 and went back to 1 during drying (Eq. 6). To assess the glass transition of the PS block, we use the glass transition temperatures, T_g , of PS/CHX mixtures given in Ref. 65, which were measured using calorimetry on bulk samples. T_g reaches room temperature at a polymer volume fraction $\phi_g = 0.78$. Assuming equal swelling of both blocks in spite of the slight selectivity of the solvent and neglecting possible accumulation of the solvent at the interfaces, the PS block crosses the glass transition at $\phi_g = 0.78$ after ~ 24 min of swelling and again after ~ 15 min of drying, i.e. it is in the mobile state for ~ 31 min.

Figure 4. Structural characteristics of the thin film during the first SVA cycle as a function of time. The grey region indicates swelling, the white region drying, respectively. (a) Film thickness D_{film} (left axis) and $D_{film} / D_{film}^{dry}$ (right axis). Missing film thickness data are interpolated (full line). The horizontal dash-dotted line indicates D_{film}^{dry} . The horizontal dashed line indicates the value where $\phi_g = 0.78$ is crossed, i.e. the glass transition of PS. (b) Lamellar thicknesses of the parallel (red closed circles) and perpendicular lamellae (green closed triangles), values reduced by, D_{lam}^{bulk} are given on the right axis. The horizontal dashed and dash-dotted lines indicate D_{lam}^{bulk} and $D_{lam,par}^{dry}$, respectively. (c) FWHMs of the P1 peak along q_z (red closed circles) and along q_y (blue open circles). (d) Number of correlated lamellae, N_{corr} (Eq. 3).

We first focus on the first SVA cycle of the thin film. At the end of the first cycle, the lamellar order has improved significantly (Figure 2b,d): The DDSR has vanished, i.e. the lamellar orientation is now purely parallel. Moreover, the GISAXS map shows not only the 1st order DBSs but also 2nd and 3rd order DBSs, thus, the correlation of lamellar interfaces has significantly improved. The sample thus seems to be already close to equilibrium during the first cycle of SVA. The kinetics was monitored in-situ using GISAXS. Representative 2D GISAXS maps measured during the first SVA cycle are shown in Figure 5. The corresponding movie comprising all maps is given in the SI (Movie S2) and the intensity profiles along q_z and q_y for the P1 peak (see Exp. Section) in Figure 6. During the first ~30 min of swelling, the DDSRs become weaker and finally vanish. The thickness of the perpendicular lamellae increases slightly, before they vanish altogether. Towards the end of the swelling, the DBSs M1 and P1 dominate, i.e. the randomly oriented lamellae vanish, and mainly parallel lamellae remain. The DBSs are relatively broad and bend downwards. This bending is indicative of the presence of a distribution of lamellar orientations around the parallel one. This could be on the level of entire domains, but, more probable, it is due to the formation of additional lens-like domains (Figure 1b) which later evolve into additional lamellae, i.e. a large scale reorganization of the lamellar structures takes place in the presence of solvent, as observed by us previously.^{41,43,45,54} The structural reorganization evident from the shape of the DBSs is accompanied by a streak of high intensity along q_z at $q_y \cong 0$ (Figure 6a) which points to large-scale roughness of the film surface. In the remaining time of the first swelling, the 1st order DBSs move again to higher q_z values, become straighter along q_y , i.e. the lamellae become thinner, and the lamellar interfaces become flat and smooth. Moreover, the DBSs become sharper along q_z . During the first drying, the DBSs rapidly narrow down along q_y , i.e. the lamellar interfaces become flat. They move upwards

again, as expected for decreasing lamellar thickness. Interestingly, 2nd and 3rd order DBSs appear during the drying cycle (Figure 6a), pointing to a transient state with asymmetric lamellae. These 2nd order DBSs vanish after ~15 min of drying, which is approximately when the PS domains become glassy again. Their presence points to an unequal degree of swelling of the PS and the PB domains, as observed by us previously with a thicker film of PS-*b*-PB in CHX vapor.⁴⁵ It is attributed to the slight selectivity of CHX to the PB domains. The structures during drying are different from the ones during swelling at the same degrees of swelling, which points to non-equilibrium states, possibly due to a concentration gradient during solvent evaporation for the structure formation.^{34,35,37} We note that solvent uptake has been found to proceed by, among others, rapid filling of existing voids by the solvent, i.e. a different pathway.^{66,67}

Figure 5. Representative 2D GISAXS maps of the thin film during the first SVA cycle. The times after the solvent vapor starts entering the cell are given in each map. Drying starts after 40 min. The measuring times were 30 s. For all maps, the color scale and the regions used to construct the intensity profiles are the same as in Figure 2a.

Figure 6. Intensity profiles during the first and second SVA cycle of the thin film (a) along q_z , centered at $q_y = -0.0006 \text{ \AA}^{-1}$. S, M1-P3 mark the positions of the specularly reflected beam (covered by the disk-like beamstop) and the minus and plus branches of the DBSs, respectively; (b) along q_y , centered at the q_z position of P1 and (c) along q_y , centered at the q_z position of the Yoneda band. In (a,b), the start of the first drying, second swelling and second drying are marked. The color scales are given next to the graphs.

The peak positions and the widths of the P1 DBS along the film normal, q_z , and in the film plane, i.e. along q_y , were determined using Eqs. 2, 4 and 5. They are related to the lamellar thicknesses as well as to the number of correlated lamellae along the film normal (Eq. 3) and to the roughness of the lamellar interfaces. The lamellar thickness of the parallel lamellae, $D_{\text{lam,par}}$, initially increases from $145 \pm 1 \text{ \AA}$ to $206 \text{ \AA}$ within 16 min (Figure 4b). After this time, it keeps increasing, but more slowly, and reaches a maximum of $221 \pm 1 \text{ \AA}$. After 16 min, the FWHM along q_z has a maximum (Figure 4c), which results in a sharp minimum of N_{corr} (obtained by combining $D_{\text{lam,par}}$ and the FWHM along q_z , Figure 4d), i.e. the lamellar stack breaks up and

reforms during the remaining swelling time. The FWHM along q_y is constant during the first ~ 10 min and increases afterwards (Figure 4c), which points to increasingly strong undulations of the lamellar interfaces which are possible due to the reduced interfacial tension between the PS and PB domains. Interestingly, a transient maximum is encountered after 24 min, the time when T_g of PS is crossed. This may be due to a local flattening which becomes possible when PS is not glassy any longer. $D_{lam,perp}$ increases from 228 ± 2 Å (a value similar to the bulk value) to 242 ± 2 Å within 18 min; then stays constant, until all perpendicular lamellae have vanished after 31 min, i.e. soon after the glass transition of PS is crossed (Figures 4b, 6c), i.e. the randomly oriented lamellae disappear and only the parallel orientation survives. Such a reorientation of domains is only possible when PS has crossed the glass transition. The structure in the fully swollen state is depicted in Figure 3b.

Upon drying, $D_{lam,par}$ decreases and reaches a value of 162 Å after 36 min of drying and afterwards stabilizes at 152 ± 1 Å. Interestingly, this value is still much lower than in the bulk (220 ± 1 Å), but slightly higher than the value in the as-prepared thin film (145 ± 1 Å). During the first 5 min of drying, the P1 DBS becomes rapidly narrower along q_y (Figure 4c), i.e. the lamellar interfaces smoothen quickly. We assign this decrease to the vanishing of lens-like domains. During the subsequent 55 min, the FWHM along q_y decreases more slowly before becoming constant. Thus, even when PS is glassy again (Figure 4a), the lamellar interfaces can become flatter by local improvements. The FWHM along q_z increases slightly and becomes constant at a lower value than initially. The corresponding N_{corr} (Eq. 3) is maximum after 10 min of drying, which we attribute to a further improvement of the correlation of the lamellar interfaces along the film normal. Afterwards, N_{corr} becomes constant at 14, i.e. at a value much

higher than the initial value ($N_{\text{corr}} = 9$), which shows that the lamellar stack is well correlated at the end of the first drying. The structure after the first SVA cycle is depicted in Figure 3c.

Figure 7. Representative GISAXS maps of the thin film during the second SVA cycle starting at 148 min. Same scale and notation as in Figure 5. Drying was started 189 min after the start of the first SVA cycle.

Figure 8. Structural characteristics during both SVA cycles of the thin film as a function of time. Same notations as in Figure 4. The black crosses in (d) denote $D_{\text{film}}/D_{\text{lam,par}}$. Missing data for 130-145 min and 165-169 min are due to a beam loss at the synchrotron.

We now turn to the second SVA cycle. The swelling and drying rates of 30 Å/min and -30 Å/min are nearly identical to the one of the first cycle, indicating very good reproducibility of our protocol. At the end, no qualitative changes are observed compared to the end of the first cycle (Figure 2b-d). We note that, at the beginning of the second cycle, the lamellae are already oriented parallel (no perpendicular lamellae are observed), and the lamellar interfaces are relatively flat; the starting state is thus better defined than in the beginning of the first cycle (upper part of Figure 6, Figures 7 and 8). Again, the DBSs move towards lower q_z , i.e the lamellae swell (Figure 8b). A slight broadening of the DBSs along q_z during swelling is

observed, pointing to a certain restructuring, which is, however, not as pronounced as during the first SVA cycle. The width of the DBSs along q_y also increases, but not as much as during the first swelling. This time, the 2nd and 3rd order DBSs are visible already during swelling, possibly because the high-intensity streak along q_z observed during the first swelling does not appear during the second swelling, so it does not overlap these DBSs. At the end of the second swelling, the DBSs are broadened and bent, similar to the end of the first swelling. During the second drying, the behavior is very similar to the one during the first drying. One difference is, though, that the width of the DBSs decreases more rapidly (within ~ 6 min), i.e. the lamellar interfaces flatten faster. This is related to the fact that the first SVA cycle has removed most defects from the film. N_{corr} only varies slightly during the second cycle with a weak maximum at the end of the swelling process (Figure 8d).

Since the lamellae are now purely parallel, we calculate the number of stacked lamellae by dividing the film thickness by the lamellar thickness (Figure 8d). The absolute values are around 14, i.e. similar to the ones of N_{corr} . A maximum is encountered at the end of the swelling, which is 14.6 and thus higher than the minimum of 13.6 (22 min after the start of the second swelling). This indicates that, on average, at most one additional lamella is formed once the PS microdomains are not glassy any longer. This behavior corresponds to previous predictions and observations.^{36,41,45,68} As the second drying process is started, the number of lamellae decreases again.

To conclude, after the first SVA cycle, the lamellar structure is closer to equilibrium, and the correlation of the lamellar interfaces along the film normal is better right from the beginning of the second cycle. The formation of – at most – one additional lamella and its subsequent

disappearance is observed during the second SVA cycle, as expected. The lamellae are slightly thicker than after spin-coating but still significantly thinner than in the bulk, which is surprising.

Scaling behavior of the lamellar thickness

We now focus on the behavior of $D_{\text{lam,par}}$ and $D_{\text{lam,perp}}$ in dependence on the polymer volume fraction, ϕ , for the thin film. Plotting the D_{lam} values vs. ϕ in a double-logarithmic representation reveals the scaling behavior and helps to identify the structural reorganization processes (Figure 9). $D_{\text{lam,perp}}$ is at first stable and slightly higher than the bulk value; later, it increases slightly, before the perpendicular lamellae vanish after ~30 min of swelling.

Meanwhile, $D_{\text{lam,par}}$ shows a more complex development during the vapor treatment. Two regimes are identified during the first swelling: In the high-concentration regime ($\phi < 0.88$), $D_{\text{lam,par}}$ increases as $D_{\text{lam,par}} \propto \phi^{-5.1 \pm 0.1}$, whereas the decrease for $\phi < 0.79$ is compatible with the prediction $D_{\text{lam,par}} \propto \phi^{1/6}$.⁴⁵ This increase and decrease of $D_{\text{lam,par}}$ during swelling have been observed by us previously^{41,43,45,54} and have been attributed to the initial swelling of the lamellae as long as PS is still in the glassy state with strong stretching of the PB blocks, and to the subsequent formation of lenses which become additional lamellae and allow for more interfacial area per chain and more Gaussian chain conformations in the swollen state.³⁶

During the subsequent drying and during the second SVA cycle, $D_{\text{lam,par}}$ first decreases smoothly and is later (after PS is glassy again) compatible with affine behavior, $D_{\text{lam,par}} \propto \phi^{-1}$, most of the time, i.e. the lamellar thickness scales with the film thickness.

Figure 9. Double-logarithmic representation of $D_{lam,par}$ and $D_{lam,perp}$ of the thin film as function of ϕ . $D_{lam,par}$: Red circles: first cycle, blue down triangles: second cycle. Closed symbols: swelling, open symbols: drying. $D_{lam,perp}$: Green up triangles. The error bars are smaller than the symbol size. For the first 17 min of the first swelling, the interpolated D_{film} values were used for the calculation of ϕ . The scaling laws corresponding to the lines are given in the graph. The arrow indicates the value of ϕ_g for PS.

Results from the thick film

Figure 10a shows the thickness of the thick film during SVA with CHX in dependence on time. The initial film thickness is 3320 ± 20 Å. The overall behavior is very similar to the one of the thin film: During swelling, the film thickness increases close to linearly until a degree of swelling of 1.58 is reached, corresponding to $\phi = 0.64$. The PS microdomains cross the glass transition after ca. 16 min. Initially, the orientation of the lamellar interfaces is mainly parallel with a certain fraction of randomly oriented lamellae (see 2D GISAXS maps in Figure 11). The

lamellae become asymmetric as evidenced by the 2nd order DBSs towards the end of the swelling process. Finally, only parallel lamellae survive. During drying, the lamellae stay parallel.

Figure 10. Structural characteristics of the thick film during the first SVA cycle as a function of time. (a) Film thickness D_{film} (left axis) and $D_{film} / D_{film}^{dry}$ (right axis). The horizontal dashed line indicates the value where $\phi_g = 0.78$ is crossed, i.e. the glass transition of PS. The grey region indicates swelling, the white region drying, respectively. (b) Double-logarithmic representation of $D_{lam, par}$ of the thin and the thick film as function of ϕ . Same symbols as in Fig. 9. $D_{lam, par}$ of the thick film: Black closed squares: first swelling, black open squares: first drying.

Figure 11. Representative GISAXS maps of the thick film during the first SVA cycle. The times after the solvent vapor starts entering the cell are given in each map. Drying starts after 40 min. The measuring times were 30 s. The color scale for all maps is given in the bottom.

The scaling behavior of $D_{lam,par}$ with ϕ is shown in Figure 10b in comparison with the data from the two SVA cycles on the thin film. Initially, the behavior during swelling is different from the one of the thin film. At $\log(\phi) < -0.15$ (i.e. $\phi < 0.71$), a behavior consistent with $D_{lam,par} \propto \phi^{1/6}$ is observed, as predicted.⁴⁵ The thick film is swollen to a slightly higher degree (i.e. down to slightly lower ϕ values) than the thin film. However, in the ϕ range where the data overlap, the drying behavior of the two films is indistinguishable, i.e. equilibrium has been achieved.

Discussion

Compared to our previous studies on lamellar PS-*b*-PB diblock copolymer thin films featuring parallel lamellae, the new aspects of the present studies are the following: (i) The thin film was

not only swollen, but also dried in a controlled way. (ii) Two SVA cycles were carried out, identifying different kinetics during the first swelling compared to the remaining swelling/drying cycles. (iii) Thin films from the same diblock copolymer but different initial film thickness were investigated and showed the same behavior during drying, while the first swelling behavior depended on differences in the structure of the as-prepared (non-equilibrium) film.

We also observe that, after spin-coating, the lamellar orientation is mixed and the lamellar thickness of the parallel lamellae is much lower than the bulk value, while the one of the perpendicular lamellae is slightly larger than the bulk value. We have previously observed such discrepancies and have attributed them to the forces present during spin-coating resulting in a non-equilibrium state.^{43,45,54} A similar observation was made by Gu et al. who observed that the repeat distance of lying cylinders was significantly lower than the bulk value.²³ However, the present study reveals that, in both films, the lamellar thickness does not relax to the bulk value after drying, but is only a little higher than before SVA. Thus, these low values do not seem to be a mere result of the fast spin-coating process and seem to be independent of the film thickness. Also in our previous study on a thin film from the same PS-*b*-PB diblock copolymer using SVA with EAC, the value of the lamellar thickness reached after drying (204 Å) was lower than the bulk value (220 Å), but higher than the one encountered in the present study using CHX (152 Å). We speculate that the reason is the difference in solvent quality and selectivity. EAC is a very good solvent for PS and a good solvent for PB, whereas CHX is a theta solvent for PS and a good solvent for PB. The phenomenon deserves further investigation.

We suggest that the final lamellar thickness reflects the balance of interfacial interactions and the degrees of swelling of the PS and the PB domains at the time when PS becomes glassy again. At this time, the area per chain at the lamellar interface is fixed and cannot change any longer.

The remaining solvent is removed from these lamellae which now can only change in a limited way. In the present study, the decrease of $D_{lam,par}$ during swelling sets in at $\phi \cong 0.71$ -0.78 for both, the thin and the thick film in CHX, i.e. $\log(\phi) = -0.11$ to -0.15 , similarly to the situation in toluene,⁴¹ whereas it occurs at $\phi = 0.90$, i.e. $\log(\phi) = -0.05$ in EAC.⁵⁴

The lamellar thicknesses in the thick and the thin film behave differently during the first swelling, but are very similar during the drying process. In analogy to results on cylindrical thin films,⁴⁷ the process history has thus been removed at this degree of swelling (1.46 for the thin film and 1.58 for the thick film).

The second question concerns the scaling exponent in the late stages of the first swelling. The general features during the first swelling observed before^{41,43,45,54} have been reproduced also in this study – undulations of the lamellar interfaces, formation of lenses and additional lamellae. This structural reorganization becomes possible when the PS domains are swollen by solvent to an extent that they are not glassy any longer. The scaling exponent in the present study is consistent with the predicted value $\beta = -1/6$.⁴⁵

The drying proceeds for both the thin and the thick film in the same way, namely affinely, after the PS domains have become glassy again. The same behavior was previously found in EAC.⁵⁴ Thus, once the PS domains are glassy, no more large-scale structural reorganizations are possible.

The present study shows that the (nearly defect-free) lamellar structure obtained after the first SVA cycle is stable during subsequent drying and a second SVA cycle. We argue that the structure which is present when the glass transition of the PS domains is crossed again during drying is preserved. Swelling the PS-*b*-PB thin films slowly with a good, slightly selective

solvent (CHX) up to a degree of swelling of 1.5-1.6 and subsequently drying them again slowly thus constitutes a protocol to obtain well-ordered lamellar thin films.

ASSOCIATED CONTENT

Supplementary Material. Details about the GISAXS data analysis, an AFM image and a movie of the time-resolved GISAXS measurements as described in the text.

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REFERENCES

- (1) Sinturel, C.; Vayer, M.; Morris, M.; Hillmyer, M.A. *Macromolecules* **2013**, *46*, 5399-5415.
- (2) Hanrath, T.; Choi, J.J.; Smilgies, D.-M. *ACS Nano* **2009**, *3*, 2975-2988.
- (3) Khan, H.U.; Li, R.; Ren, Y.; Chen, L.; Payne, M.M.; Bhansali, U.S.; Smilgies, D.-M.; Anthony, J.E.; Amassian, A. *ACS Appl. Mater. Interfaces* **2013**, *5*, 2325-2330.
- (4) Tokarev, I.; Krenek, R.; Burkov, Y.; Schmeisser, D.; Sidorenko, A.; Minko, S.; Stamm, M. *Macromolecules* **2005**, *38*, 507-516.
- (5) Nedelcu, M.; Lee, J.; Crossland, E.J.W.; Warren, S.C.; Orilall, M.C.; Guldin, S.; Hüttner, S.; Ducati, C.; Eder, D.; Wiesner, U.; Steiner, U.; Snaith, H.J. *Soft Matter* **2009**, *5*, 134-139.
- (6) Chang, S.-W.; Chuang, V.P.; Boles, S.T.; Ross, C.A.; Thompson, C.V. *Adv. Funct. Mater.* **2009**, *19*, 2495-2500.
- (7) Chao, C.-C.; Wang, T.-C.; Ho, R.-M.; Georgopoulos, P.; Avgeropoulos, A.; Thomas, E.L. *ACS Nano* **2010**, *4*, 2088-2094.

-
- (8) Chinthamanipeta, P.S.; Lou, Q.; Shipp, D.A. *ACS Nano* **2011**, *5*, 450-456.
- (9) Liu, Z.; Huang, H.; He, T. *Small* **2013**, *9*, 505-510.
- (10) Bang, J.; Jeong, U.; Ryu, D.Y.; Russell, T.P.; Hawker, C.J. *Adv. Mater.* **2009**, *21*, 4769–4792.
- (11) Jung, Y. S.; Jung, W.; Tuller, H. L.; Ross, C. A. *Nano Lett.* **2008**, *8*, 3776-3780.
- (12) Register, R.A. *Nature* **2003**, *424*, 378-379.
- (13) Segalman, R. A. *Mat. Sci. Engin.: R* **2005**, *48*, 191-226.
- (14) Hamley, I. W. *Progr. Polym. Sci.* **2009**, *34*, 1161-1210.
- (15) Albalak, R. J.; Thomas, E. L.; Capel, M. S. *Polymer* **1997**, *38*, 3819-3825.
- (16) Sepe, A.; Di, Z.; Posselt, D.; Smilgies, D.-M.; Papadakis, C. M. *J. Phys.: Cond. Matt.* **2011**, *23*, 254213.
- (17) Morkved, T. L.; Lu, M.; Urbas, A. M.; Ehrichs, E. E.; Jaeger, H. M.; Mansky, P.; Russell, T. P. *Science* **1996**, *273*, 931-933.
- (18) Olszowka, V.; Hund, M.; Kuntermann, V.; Scherdel, S.; Tsarkova, L.; Böker, A.; Krausch, G. *Soft Matter* **2006**, *2*, 1089-1094.
- (19) Xuan, Y.; Peng, J.; Cui, L.; Wang, H. F.; Li, B. Y.; Han, Y. C. *Macromolecules* **2004**, *37*, 7301-7307.

-
- (20) Kim, S. H.; Misner, M. J.; Xu, T.; Kimura, M.; Russell, T. P. *Adv. Mater.* **2004**, *16*, 226-231.
- (21) Peng, J.; Han, Y.; Knoll, W.; Kim, D. H. *Macromol. Rapid Commun.* **2007**, *28*, 1422-1428.
- (22) Bosworth, J.K.; Paik, M.Y.; Ruiz, R.; Schwartz, E.L.; Huang, J.Q.; Ko, A.W.; Smilgies, D.-M.; Black, C.T.; Ober, C.K. *ACS Nano* **2008**, *2*, 1396.
- (23) Gu, X.; Gunkel, I.; Hexemer, A.; Gu, W.; Russell, T.P. *Adv. Mater.* **2013**, *26*, 273-281.
- (24) Albalak, R. J.; Capel, M. S.; Thomas, E. L. *Polymer* **1998**, *39*, 1647-1656.
- (25) Fukunaga, K.; Hashimoto, T.; Elbs, H.; Krausch, G. *Macromolecules* **2002**, *35*, 4406-4413.
- (26) Ludwigs, S.; Schmidt, K.; Krausch, G. *Macromolecules* **2005**, *38*, 2376-2382.
- (27) Luo, C.; Huang, W.; Han, Y. *Macromol. Rapid Commun.* **2009**, *30*, 1917-1921.
- (28) Albert, J.N.; Bogart, T.D.; Lewis, R.L.; Beers, K.L.; Fasolka, M.J.; Hutchison, J.B.; Vogt, B.D.; Epps, T.H. *Nano Lett.* **2011**, *11*, 1351-1357.
- (29) Seppala, J.E.; Lewis, R.L.; Epps T.H. *ACS Nano* **2012**, *6*, 9855-9862.
- (30) Albert, J.N.; Young, W.S.; Lewis, R.L.; Bogart, T.D.; Smith, J.R.; Epps, T.H. *ACS Nano* **2012**, *6*, 459-466.

-
- (31) Lazzari, M.; De Rosa, C. In: Lazzari, M.; Liu, G.; Lecommandoux, S. (Eds) *Block Copolymers in Nanoscience*. Wiley-VCH Verlag GmbH & Co KGaA, Weinheim, Germany **2008**, 191-231.
- (32) Lazzari, M.; De Rosa, C. In: Geckeler, K.E.; Nishide, H. (Eds.) *Advanced Nanomaterials*, Wiley-VCH Verlag GmbH & Co KGaA, Weinheim, Germany, **2010**, 111-158.
- (33) Luo, M.; Epps III, T.H. *Macromolecules* **2013**, *46*, 7567-7579.
- (34) Tsige, M.; T.R. Mattson, G.S. Grest. *Macromolecules* **2004**, *37*, 9132-1938.
- (35) Phillip, W.A.; Hillmyer, M.A.; Cussler, E.L. *Macromolecules* **2010**, *43*, 7763-7770.
- (36) Rudov, A.A.; Patyukova, E.S.; Neratova, I.V.; Khalatur, P.G.; Posselt, D.; Papadakis. C.M.; Potemkin, I.I. *Macromolecules* **2013**, *46*, 5786-5795.
- (37) S.P. Paradiso, K.T. Delaney, C.J. Garcia-Cervera, H.D. Ceniceros, G.H. Fredrickson. *ACS Macro Lett.* **2014**, *3*, 16-20.
- (38) Hur, S.-M.; Khaira, G.S.; Ramírez-Hernández, A.; Müller. M.; Nealey, P.F.; de Pablo, J.J. *ACS Macro Lett.* **2015**, *4*, 11-15.
- (39) Elbs, H.; Fukunaga, K.; Stadler, R.; Sauer, G.; Magerle, R.; Krausch, G. *Macromolecules* **1999**, *32*, 1204-1211.
- (40) Smilgies, D.-M.; Busch, P.; Papadakis, C. M.; Posselt, D. *Synchr. Rad. News* **2002**, *15*, 35-42.
- (41) Papadakis, C. M.; Di, Z.; Posselt, D.; Smilgies, D.-M. *Langmuir* **2008**, *24*, 13815-13818.

-
- (42) Smilgies, D.-M.; Li, R.; Di, Z.; Darko, C.; Papadakis, C.M.; Posselt, D. *Mater. Res. Soc. Symp. Proc.* **2009**, *1147*, OO01-01.
- (43) Di, Z.; Posselt, D.; Smilgies-D.-M.; Papadakis, C.M. *Macromolecules* **2010**, *43*, 418-427.
- (44) Paik, M.Y.; Bosworth, J.K.; Smilgies, D.-M.; Schwartz, E.L.; Andre, X.; Ober, C.K. *Macromolecules* **2010**, *43*, 4253–4260.
- (45) Di, Z.; Posselt, D.; Smilgies, D.-M.; Li, R.; Rauscher, M.; Potemkin, I.I.; Papadakis, C.M. *Macromolecules* **2012**, *45*, 5185-5195.
- (46) Zhang, J.; Posselt, D.; Sepe, A.; Shen, X.; Perlich, J.; Smilgies, D.-M.; Papadakis, C.M. *Macromol. Rapid Commun.* **2013**, *34*, 1289-1295.
- (47) Gu, X.; Gunkel, I.; Hexemer, A.; Russell, T.P. *Colloid Polym. Sci.* **2014**, *292*, 1795-1802.
- (48) Sepe, A.; Černoch, P.; Štěpánek, P.; Hoppe, E.T.; Papadakis, C.M. *Eur. Polym. J.* **2014**, *50*, 87-96.
- (49) Gowd, E.B.; Böhme, M.; Stamm, M. *IOP Conf. Series: Mat. Sci. Eng.* **2010**, *14*, 012015.
- (50) Gowd, E.B.; Koga, T.; Endoh, K.M.; Kumar, K.; Stamm, M. *Soft Matter* **2014**, *10*, 7753-7761.
- (51) Müller-Buschbaum, P. *Lect. Notes Phys.* **2009**, *776*, 61-89.
- (52) Ree, M. *Macromol. Rapid Commun.* **2014**, *35*, 930-959.
- (53) A. Hexemer, P. Müller-Buschbaum. *IUCrJ* **2015**, *2*, 106-125.

-
- (54) Zhang, J.; Posselt, D.; Smilgies, D.-M.; Perlich, J.; Kyriakos, K.; Jaksch, S.; Papadakis, C.M. *Macromolecules* **2014**, *47*, 5711-5718.
- (55) Papadakis, C. M.; Almdal, K.; Mortensen, K.; Posselt, D. *J. Physique II* **1997**, *7*, 1829-1854.
- (56) Papadakis, C. M.; Almdal, K.; Mortensen, K.; Posselt, D. *Europhys. Lett.* **1996**, *36*, 289-294.
- (57) Burrell, H. in Barandrup, J.; Immergut, E.H. (Eds.): *Polymer Handbook*. 2nd ed. Wiley-Interscience, New York 1975.
- (58) Müller-Buschbaum, P; Hermsdorf, N.; Roth, S. V.; Wiedersich, J.; Cunis, S.; Gehrke, R. *Spectrochimica Acta Part B: Atomic Spectroscopy* **2004**, *59*, 1789-1797.
- (59) Roth, S.V.; Döhrmann, R.; Dommach, M.; Kuhlmann, M.; Kröger, I.; Gehrke, R.; Walter, H.; Schroer, C.; Lengeler, B.; Müller-Buschbaum, P. *Rev. Sci. Instrum.* **2006**, *77*, 085106.
- (60) Busch, P.; Rauscher, M.; Smilgies, D.-M.; Posselt, D.; Papadakis C.M. *J. Appl. Crystallogr.* **2006**, *39*, 433-442.
- (61) Smilgies, D.M. *J. Appl. Crystallogr.* **2009**, *42*, 1030-1034 and Erratum (vol. 46, p. 286).
- (62) Gutmann, J.S.; Müller-Buschbaum, P.; Schubert, D. W.; Striebeck, N.; Smilgies, D.-M.; Stamm, M. *Physica B* **2000**, *283*, 40-44.
- (63) Busch, P.; Posselt, D.; Smilgies, D.-M.; Rauscher, M.; Papadakis, C. M. *Macromolecules* **2007**, *40*, 630-640.

-
- (64) Busch, P.; Rauscher, M.; Moulin, J.-F.; Müller-Buschbaum, P. *J. Appl. Crystallogr.* **2011**, *44*, 370-379.
- (65) Bercea, M.; Wolf, B. A. *J. Chem. Phys.* **2006**, *124*, 174902.
- (66) Tang, Y.; Lu, J.R.; Lewis, A.J.; Vick, T.A.; Stratford, P.W. *Macromolecules* **2002**, *35*, 3955-3964.
- (67) Müller-Buschbaum, P.; Bauer, E.; Maurer, E.; Cubitt, R. *Physica B* **2006**, *385-386*, 703-705.
- (68) Potemkin, I. I.; *Macromolecules* **2004**, *37*, 3505-3509.

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Towards an equilibrium structure in lamellar diblock copolymer thin films using solvent vapor annealing – an *in-situ* time-resolved GISAXS study

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