



ELSEVIER

Contents lists available at ScienceDirect

## European Polymer Journal

journal homepage: [www.elsevier.com/locate/europolj](http://www.elsevier.com/locate/europolj)

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

Alessandro Sepe<sup>a,1</sup>, Jianqi Zhang<sup>a,2</sup>, Jan Perlich<sup>b</sup>, Detlef-M. Smilgies<sup>c</sup>, Dorte Posselt<sup>d</sup>,  
Christine M. Papadakis<sup>a,\*</sup>

<sup>a</sup> Technische Universität München, Physik-Department, Fachgebiet Physik weicher Materie, James-Frank-Str. 1, 85748 Garching, Germany

<sup>b</sup> Deutsches Elektronen-Synchrotron DESY, Notkestr. 85, 22607 Hamburg, Germany

<sup>c</sup> Cornell High Energy Synchrotron Source (CHESS), Wilson Laboratory, Cornell University, Ithaca, NY 14853, USA

<sup>d</sup> IMFUFA, Department of Science, Roskilde University, P.O. Box 260, 4000 Roskilde, Denmark

## ARTICLE INFO

## Article history:

Received 20 October 2015

Received in revised form 16 December 2015

Accepted 18 December 2015

Available online xxx

## Keywords:

Nanostructured thin films

Solvent vapor annealing

Block copolymers

Grazing-incidence small-angle X-ray scattering

## 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 and to 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.

© 2015 Elsevier Ltd. All rights reserved.

## 1. 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, for instance, block copolymers [1], nanoparticle assemblies

\* Corresponding author.

E-mail address: [Papadakis@tum.de](mailto:Papadakis@tum.de) (C.M. Papadakis).

<sup>1</sup> Present address: Adolphe Merkle Institute, University of Fribourg, Chemin des Verdiers 4, CH-1700 Fribourg, Switzerland.

<sup>2</sup> Present address: National Center for Nanoscience and Technology, Beijing 100190, PR China.

[2] or small conjugated molecules [3]. In the present work, we focus on nanostructured block copolymer thin films, where SVA is a routine step, as reported in many studies (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 [12–14], 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 [1,4,10,19–23] and triblock [24–30] 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 [1,31–33].

Only few theoretical investigations have addressed the structural changes in block copolymer thin films during SVA so far [34–38], 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 [39–45]. 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 [23,47,48–50]. Using in-situ and real-time grazing-incidence small-angle X-ray scattering (GISAXS) [51–53], the improvement of lateral order [23] 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 solvent slightly selective for the PB block. 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 [41–43,45,54], we have identified the process accounting for the 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. To date, 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 reach in all cases 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 a structure different from the one in 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. 45,54. (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.

Download English Version:

<https://daneshyari.com/en/article/7804389>

Download Persian Version:

<https://daneshyari.com/article/7804389>

[Daneshyari.com](https://daneshyari.com)