European Polymer Journal 50 (2014) 87–96

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Macromolecular Nanotechnology

Creation of lateral structures in diblock copolymer thin films during vapor uptake and subsequent drying – Effect of film thickness

A. Sepe [a,1], P. Černoch [b], P. Štěpánek [b], E.T. Hoppe [a], C.M. Papadakis [a,*]

[a] Technische Universität München, Physik-Department, Physik weicher Materie, James-Franck-Str. 1, 85748 Garching, Germany
[b] Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 16206 Prague, Czech Republic

ARTICLE INFO

Article history:
Received 18 July 2013
Received in revised form 30 October 2013
Accepted 5 November 2013
Available online 13 November 2013

Keywords:
Polymer physics
Grazing-incidence small-angle X-ray scattering
In situ measurements
Atomic force microscopy

ABSTRACT

We have studied the structure formation in compositionally nearly symmetric poly(4-octylstyrene-*b*-butylmethacrylate) diblock copolymer films during exposure to saturated vapor of *n*-hexane (a poor solvent for both blocks) and subsequent drying using real-time, in situ grazing-incidence small-angle X-ray scattering (GISAXS). Previous bulk studies revealed a lamellar structure after thermo-annealing; and surface studies on hexane treated samples revealed a lateral surface structure (Černoch et al., 2007) [14]. We focus here on the effect of film thickness which is varied between 1.3 and 2.0 times the bulk lamellar thickness. We report on the lateral repeat distance as well as on the correlation length in the film plane. Complex, non-monotonous behavior is observed for both parameters. Upon drying, the lateral structure created during vapor treatment is stable only for the thick film, not for the intermediate and the thin film. The kinetics depends strongly on the film thickness; especially for the thinnest film, it is very slow. For all film thicknesses, we attempt to identify the most stable morphology, occurring when the inner film structure is close to the one in the bulk.

1. Introduction

Thin block copolymer films are promising candidates for a variety of applications, such as the preparation of nanoporous films, nanostructured templates, photonic crystals and biosensors [1,2]. Lateral structures are of special interest, e.g. for their use in organized inorganic substrates [3,4] and for the preparation of nanoporous membranes [5,6]. Solvent vapor induced annealing offers a simple and flexible method to create ordered structures with a potentially high degree of controllability through careful choice of solvent [7–16].

The thin film geometry allows detailed studies of the swelling and rearrangement during vapor treatment, because the structures may be oriented by the film surface and the film/substrate interface. Our previous investigations on lamellar poly(styrene-*b*-butadiene) thin films after spin-coating [17] and during vapor treatment and subsequent drying [15–19] or heat treatment [20] have shown that, using in situ, grazing-incidence small-angle X-ray scattering (GISAXS) with 2D detection, a wealth of information is accessible, such as the lamellar orientation and its distribution as well as the lamellar thickness, i.e. the repeat distance and the number of correlated lamellae. Moreover, information about the lamellar roughness and undulations of the lamellar interfaces can be gained. Combining in situ, real-time GISAXS with atomic force microscopy (AFM), which details the surface morphology, and X-ray reflectometry (XR), which reveals the film thickness as well as possible layered structures inside the film, detailed information on the processes during vapor treatment and drying can be gained giving information

---

[*] Corresponding author. Tel.: +49 89 289 12 447.
E-mail address: papadakis@tum.de (C.M. Papadakis).

[1] Present address: University of Cambridge, Department of Physics, Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK.

0014-3057/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.eurpolymj.2013.11.003

on their molecular origin. Knowledge of the mechanisms and the kinetics of the processes during solvent vapor annealing plays an important role in the preparation of long-range ordered and regularly oriented structures thus enabling their application.

In the present study, we have examined a poly(4-octylstyrene-*b*-butylmethacrylate) (P(OS-*b*-BMA)) diblock copolymer. It was investigated previously by two of us [14] and it was found that, in the bulk, it forms the lamellar structure after thermo-annealing. *n*-Hexane (HX) – the solvent used for vapor treatment in the present study – dissolves lower and swells higher molar mass fractions of both POS and PBMA homopolymers [14]. It is thus close to non-selective for both blocks, but not a good solvent. Moreover, it was found using AFM that a thin film which has a featureless surface after the preparation forms perpendicular (or standing) lamellae after swelling in HX vapor for a few minutes and subsequent drying [14]. In contrast, acetone vapor treatment resulted in a parallel lamellar orientation. Acetone is a non-solvent for POS and a good solvent for PBMA, thus very selective for PBMA. The quality and selectivity of the solvent for the two blocks thus seem to be key parameters for the final lamellar orientation.

In the present work, the structural changes during vapor treatment of spin-coated films having different film thicknesses were followed using in situ, real-time GISAXS. It was found that treatment with HX vapor results in the formation of lateral structures, as expected. The processes are complex, and the kinetics depends strongly on the film thickness.

2. Materials and methods

Materials: The synthesis and characterization of the poly(4-octylstyrene-*b*-butylmethacrylate) (P(OS-*b*-BMA)) diblock copolymer are described in Ref. [14]. The overall molar mass is 35 600 g/mol and the styrene content 62 wt.%. In bulk, it forms the lamellar morphology with a lamellar thickness $D_l^{bulk} = 260$ Å, as determined using SAXS on a thermo-annealed sample. The glass transition temperatures of the homopolymers are −40 °C for POS and 30 °C for PBMA [14].

Films of three different thicknesses were prepared by spin-coating a 1 wt.% toluene solution onto Si wafers at frequencies of 1000, 2000 and 3000 rpm. The wafers had previously been cleaned using an ammonium hydroxide/hydrogen peroxide/water mixture 1:1:1 at 68 °C for 1 h, then they were rinsed with millipore water and left overnight in water to stabilize the SiO_2 top layer. The day after, they were dried and coated with the polymer film.

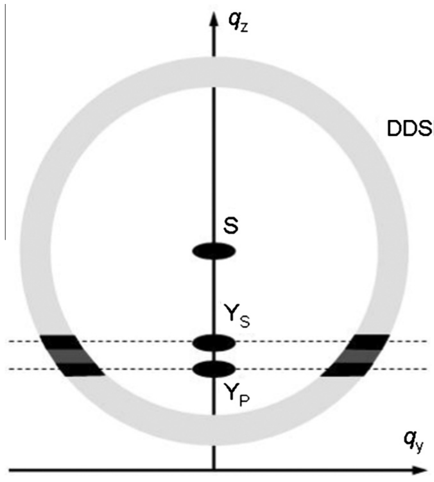
VIS interferometry: The film thicknesses of the as-prepared and post-treatment films were determined using a white-light interferometer (NanoCalc 2000, Ocean Optics).

Grazing-incidence small-angle X-ray scattering. GISAXS experiments were performed at HASYLAB beamline BW4 equipped with a MarCCD camera as an area detector [21]. The wavelength was 1.388 Å and the sample-to-detector distance 2.23 m. The beam was focused by Beryllium compound refractive lenses to a size of ~40 μm × 20 μm (horizontal × vertical) at the sample position. In the experiment, the incident angle, α_i, was chosen at 0.20°–0.25°, thus at values slightly above the critical angle of total external reflection of SiO_x which is $\alpha_{cS} = 0.19°$ at the wavelength used. In addition to a point-like beamstop shielding the detector from the specularly reflected beam, a rod-like beamstop from tantalum was used to block the intense diffuse scattering in the scattering plane. The pixel size of the detector was 79.1 μm × 79.1 μm. $q_{||} = \sqrt{q_x^2 + q_y^2}$ and q_z are the in-plane and the normal components of the scattering vector, respectively. For small incident angles and scattering angles, the coordinates of the 2D detector correspond approximately to q_y and to q_z. In all images, the specularly reflected beam as well as the Yoneda peaks are expected. The latter are intensity maxima at exit angles $\alpha_f = \alpha_{cS}$ or $\alpha_f = \alpha_{cP}$, α_{cP} being the critical angle of total external reflection of the polymer film.

For randomly oriented lamellae, rings of high intensity around the direct beam (diffuse Debye–Scherrer rings, DDSRs) and around the specularly reflected beam are expected as well (Scheme 1) [17]. In contrast to transmission scattering, the intensity along the DDSR is not homogeneously distributed, but is maximum near the Yoneda peaks appearing at the q_z values corresponding to the critical angles of the polymer film and the substrate (in the so-called Yoneda band) and decays towards high q_z [22]. The lamellar thickness, D_l, is calculated using Bragg's law:

$$D_l = \frac{2\pi}{q_{y,DDSR}}, \qquad (1)$$

where $q_{y,DDSR}$ is the radius of the DDSR centered at the specularly reflected beam. In the present case, the DDSRs are very weak and are only discernible from the background in the Yoneda band, thus their positions and radii cannot be read off at the q_z value of the specularly reflected beam. Instead, the intensity profiles along q_y were



Scheme 1. Schematic representation of the scattering from a randomly oriented lamellar thin film. *S*, Y_S and Y_P denote the specularly reflected beam and the Yoneda peaks of the substrate and the polymer film, respectively. DDSR denotes the first-order diffuse Debye–Scherrer ring. The darker the ring, the higher its intensity. The dashed lines mark the q_z positions of Y_S and Y_P. Not shown is the strong intensity decay of the ring below Y_P.