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Internal Structure Characterization of Nanoholes and Densely Branched Morphology Thin Films

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Abstract

The internal structures of thin films, having Nanoholes and densely branched morphologies and prepared from a long chain polystyrene-b-poly (ethylene oxide) (PS-b-PEO) diblock copolymer, were characterized. Using grazing-incidence small- and wide-angle X-ray scattering (GISAXS & GIWAXS), the thickness of the lamellar mesophase repeat unit and the orientation of the PEO crystalline chain stems within the thin film were determined. The dimensions of the internal structures and their orientations were linked to the surface morphologies measured by atomic force microscopy. For the Nanoholes morphology, the film thicknesses were found to deviate from an integer multiple of the diblock copolymer lamellar units (~70 nm) promoting the hole textures. Dewetted architectures were obtained by annealing freshly prepared films under toluene/water vapor environment at an elevated temperature. After that, some PEO chains were able to crystallize within the Dewetted large holes resulting in a densely branched morphology (DBM). The crystalline chain stems of the crystalline lamellar, within the Dewetted large holes, were found to be roughly perpendicular to the film substrate with thicknesses of about 10nm. This is in agreement with the diffusion-limited aggregated model.

Keywords: Nanoholes; Densely Branched Morphology; Diblock Copolymer Thin Films; Crystalline Diblock Copolymer; X-ray scattering

Abbreviations: DBM: Densely Branched Morphology; GISAXS: Grazing-Incidence Small-Angle X-ray Scattering; GIWAXS: Grazing-Incidence Wide-Angle X-ray Scattering; DLA: Diffusion Limited Aggregation; PEO: Poly (Ethylene Oxide); LP: Lorentz and polarization; ODF: Orientational Distribution Function.

Introduction

Fabrication of Nano thin films has been an essential process in the field of Nanotechnology and several Nano templates have been created for many applications [1-5]. Diblock copolymers have been employed in the creation of the thin film Nano templates because of their unique self-assembly properties [6-11] and they have been applied in the Nano sciences assisting in the fabrication of quantum dots [12,13], Nanowires [14,15], magnetic data storage [16], and bio sensing devices [17]. The self-assembly properties of Diblock copolymers that allow structuring of the thin films into Nano and micro-phase structures (hexagonal, lamellar, gyroid etc.) are controlled by the volume fractions and the Florry-Huggins interaction parameter [18-21] of the polymers involved. The orientation of these Nano and micro-phase structures can be tuned to generate unique surface templates and morphologies that can be controlled by substrate surface treatment [22,23], film thickness [24], the presence of an
Nanoholes formation in thin films of diblock copolymers was observed for thin films having a thickness (h) deviating from an integer multiple of the lamellar copolymer period, L [26]. It was noted that Nano templates having whole textured surfaces were formed whenever there is a mismatch between the film thickness and the lamellar period of a symmetric diblock copolymer parallel to the substrate. Such formation of holes requires the interface to deform and stretch (increase area) causing an increase in the surface energy [27]. Also, such formation of holes leads to the relaxation of internal strains that decreases the total energy. Crystallization of polymers is an important topic treated as one of the most practical and experimental problems in polymer science [28]. Polymer crystals are generally not in thermal equilibrium since their formations are hindered by the connectivity of the segments [29]. Consequently, polymer crystals represent metastable states with a significant degree of disorder, mainly characterized by the degree of chain folding. The process of annealing at elevated temperatures, but below the melting temperature (Tm), enhances chain mobility thereby improving the crystalline order. Thus, imperfect crystals are thermodynamically driven towards states of a higher degree of order [30,31].

The crystal formation is a kinetic control process. The processes are; the incorporation of chains where molecules are attached to crystals at the interface between the crystals and melt phases (interface growth kinetics), the molecular diffusion where chains diffuse from the melt phase to the interface and lastly, the diffusion process of latent heat at the interface [32]. Hence, Nano templated patterns such as snowflakes or spherulites, dendrites, seaweed or densely branched morphology (DBM), etc., from crystalline diblock copolymers are considered to be controlled by molecular self-assembly which is cooperative movements of a large number of connected monomers [33-38]. For a crystalline diblock copolymer, the resulting patterns promoted by molecular organizations or reorganizations are affected by the problems of chain folding, lamellar thickening or chain diffusion. The mechanisms can be linked to the diffusion-limited aggregation processes (DLA) [39,40]. The DLA promote the production of a finger-like branched pattern caused by the competition between material transport at the surface of the crystalline finger and the attachment to the crystal in quasi-two-dimensional (2D) geometry.

Crystallization of Poly (ethylene oxide) (PEO) chains have been used to induce different surface patterns because of the PEO chain folding and the diffusion process mechanisms involved [41-44]. It was noted that substrate adsorption effects impose limitations on the chain folding but water assisted the diffusion of the chains (i.e. PEO aggregates under humid chamber) and enabled chains to diffuse towards the crystal front to form crystalline lamellar [41]. It was explained that the transition from fractal-like patterns to DBM structures was due to the limited availability of polymer chains in the diffusion field and that higher humidity conditions lowered the crystal lamellae growth. Also, Meyer et al. [45] observed the crystallization of PEO chains in Dewetted ultrathin films and obtained highly branched lamellar morphology because of the DLA processes. Besides, Zhai X, et al. [46] observed different patterns like dendrite, seaweed, compact structure, and square single crystals by crystallizing PEO chains at different crystallization temperatures (Tc) in ultrathin films. Under such investigations, it was noted that at a particular set Tc, the chain folding could be explained by the DLA process.

The main question in all the above studies is how the chains are aligned within the thin films. Revealing the chain fold and the mesophase repeat unit orientations within the thin films as well as the quantification of the repeat lamellar units will contribute to the understanding of the complex polymer crystallization processes. This study focuses on the internal thin films characterization of the Nanoholes and densely branched morphology from a long chain poly (styrene-b-ethylene oxide) (PS-b-PEO) crystalline diblock. The lamellar repeat unit and the crystalline orientations were analyzed and compared to the surface morphologies.

**Experimental**

The P(S-b-PEO) diblock copolymer was purchased from PSS, Mainz. The blocks have molar masses of 109kg/mol each with a polydispersity index of 1.09. The volume fraction for PEO, fPEO, is 0.46 leading to lamellar structure. The melting temperature, Tm, of PEO was found to be 62°C while the glass transition temperature (Tg) of PS is 98°C by Differential Scanning Calorimetry.

For the formation of Nanoholes, three thin films were prepared by spin coating toluene solutions at 20, 25 and 30mg/ml concentrations onto UV/ozone cleaned Silicon wafers resulting in film thicknesses of 110, 170 and 220nm, respectively. The film thicknesses were determined by ellipsometry. After spin coating, the films were annealed at Tc of 40°C, for an hour, in a humid atmosphere (i.e. 90% relative humidity) using a heating plate from Instec, USA. The heating plate was placed in a vacuum oven chamber with inner dimensions of 30cm x 30cm x 40cm. After annealing, the samples were dried overnight by quenching the temperature of the oven, at a rate of 0.5°C/min, to room temperature under vacuum with a vacuum pressure of 10-3 mbar. The films were later kept at room temperature (i.e. at 20-27°C). It was confirmed that the water vapor did not influence the surface morphology formed (see supplementary data). It may have assisted small internal PEO chain mobility because of the...
hygroscopic nature of PEO [41], while the PS chain remains partially glassy. Thus, there was no further microphase separation.

A freshly prepared sample having a film thickness of 170nm was Dewetted by following the same procedure and condition (i.e. 90% relative humidity) above but placed under toluene/water vapor environment. Toluene is a selective solvent for PS [47], but can dissolve both the PS and the PEO, hence used in the preparation of the PS-b-PEO solution before spin coating. The surface morphologies were investigated using an optical microscope with differential interference contrast (Axio Imager from Carl Zeiss, Jena, Germany) and an Axio-Cam video camera. Detailed images of the surface texture were obtained by tapping mode AFM using a JSPM-5200 (Jeol, Eching, Germany) scanning probe microscope with scan rates between 2.8 and 9.3Hz. Silicon cantilevers (NSC35/ABS) having a force constant of 3.5N/m and a resonance frequency of ~135 kHz were used.

To determine the internal lamellar mesophase domain, L, Grazing-Incidence Small-angle X-ray scattering (GISAXS) experiments were performed by beamline BW4, HASYLAB [48]. Sample-to-detector distances were selected between 1.08m and 2m. The wavelength of the X-ray beam was \( \lambda = 1.388 \text{Å} \) or 1.381Å. The incident angle, \( \alpha_i \), was varied between 0.15 and 0.5°, thus above the critical angle of the polymer film (\( \alpha_{cp} = 0.14° \) for \( \lambda = 1.388 \text{Å} \)). The latter is calculated from the X-ray scattering length densities (SLDs) of PS and PEO using the relation \( \alpha_{cp} = (\text{SLD}/\pi)^{1/2} \) where \( \lambda \) is the X-ray wavelength [49]. \( \alpha_{cp} = 0.135° \) for the amorphous state of PEO using the relation \( \alpha_{cp} = (\text{SLD}/\pi)^{1/2} \) where \( \lambda \) is the X-ray wavelength [49]. \( \alpha_{cp} = 0.135° \) for the crystalline state of PEO [47], but can dissolve both the PS and the PEO, hence used in the preparation of the PS-b-PEO solution before spin coating. The surface morphologies were investigated using an optical microscope with differential interference contrast (Axio Imager from Carl Zeiss, Jena, Germany) and an Axio-Cam video camera. Detailed images of the surface texture were obtained by tapping mode AFM using a JSPM-5200 (Jeol, Eching, Germany) scanning probe microscope with scan rates between 2.8 and 9.3Hz. Silicon cantilevers (NSC35/ABS) having a force constant of 3.5N/m and a resonance frequency of ~135 kHz were used.

Measurements were carried out at room temperature. Rod-like beam-stops were used to protect the detector from the specular peak and strong diffuse scattering in the plane of incidence. 2D images were given as a function of \( q_y \) and \( q_z \), the lateral and the normal components of the scattering vector, respectively. The measuring times were between 8 and 1200s. Parallel lamellar resulted in diffuse Bragg sheets (DBS) along \( q_z \)-axis. To analyze their positions as a function of \( \alpha_i \), intensity profiles along \( q_z \) were created by integrating over the region \( q_y = -0.009 \) to +0.009°. The peaks observed in these intensity profiles along \( q_z \) were analyzed using a model for lamellar structures in the distorted wave Born approximation (DWBA) [50]. In this model, the peak positions, \( q_z \), of the DBS were found to depend on \( L \), and the incident angle by:

\[
q_z = \frac{2\pi}{\lambda} \left[ \sin \alpha_i \pm \frac{m\lambda}{L} \pm \sqrt{\sin^2 \alpha_i - \sin^2 \alpha_p} \right]^2 \tag{1}
\]

where \( m \) denotes the order of reflection. In this way, refraction at the air-polymer interface as well as reflections at the polymer/substrate interface was taken into account.

The orientation of the crystalline PEO chains within the films was also investigated. Grazing-Incidence Wide-angle X-ray scattering (GIWAXS) experiments were performed at Risø National Laboratory, Roskilde, Denmark. A Rigaku rotating anode with \( \text{KCu} \), \( k_\alpha = 1.542\text{Å} \) was used together with a Fuji film image plate having pixel sizes of 50µm × 50µm. The scattering geometry described by Apitz D, et al. [51], with a sample-detector distance of 124mm and a \( \alpha_i \) of 0.18° was used for all samples. Measurements were done at room temperature under vacuum, and the images were interpolated to reciprocal space units (\( q_{xy}, q_z \)). A region near the \( q_z \) axis in reciprocal space is not available when using a fixed incidence angle.

The GIWAXS data were analyzed (including indexing) by comparing them with simulated results using Sim Diffraction software [52-54]. It incorporates the unit cell of PEO that include atomic positions, the geometrical Lorentz and polarization (LP) corrections, and is specifically designed to model samples with varying degree of anisotropy and preferred orientation. The PEO block crystallizes in a monoclinic crystalline lattice defined by the following parameters: \( a = 8.05\text{Å}, b = 13.04\text{Å}, c = 19.48\text{Å} \) and \( \beta = 125.4° \) [55]. The conformation of PEO is a (7/2) helix which means that seven monomeric units turn two times per fibre period. In the classical uniaxial distribution models (e.g. Kratky O, et al. [56]; Breiby DW, et al. [52,53], the director of a crystallite (in polymers often the chain axis) orients at an angle \( \chi \) with respect to the sample normal, with an orientation distribution function (ODF), \( f(\chi) \). On average, all crystallites orienting with a certain \( \chi \) assume all possible rotational angles about the director. Note that this model assumes no in-plane orientation of the crystallites, often referred to as “2D powder” or cylindrical symmetry. Thus, in the simulations, the c-axis orientation (“director”) of the PEO crystal unit cell with respect to the film normal was varied systematically according to an ODF with a given width, and the crystallites were rotated about the director while maintaining in-plane isotropy [54]. The “rods in soft matrix” model of Kratky O, et al. [56] was found to describe the observed scattering well for the samples with a low degree of preferred orientation. In the Kratky O, et al. [56] model, the crystallites are considered stiff rods in an affine matrix, and when the matrix is stretched by an elongation ratio \( \lambda K \), the rods obtain an ODF of:

\[
f(\chi) = \frac{1}{4\pi} \frac{\lambda K^3}{\left(\lambda K^3 - (\lambda K^3 - 1) \cos^2 \chi \right)^{3/2}} \tag{2}
\]
actual scattering geometry, such as $\alpha_i$, the $\lambda$ and the sample to detector distance.

**Results and Discussion**

**Nanoholes**

Observations of large and tiny Nanoholes were made on the freshly prepared films but with a very rough texture. The observed Nanoholes within a freshly prepared film were attributed to flow instability within the solvent-rich long PS-b-PEO chain films created by the Marangoni instabilities [57] and the fast evaporation of the volatile toluene solvent. Moreover, it was observed that slow evaporation provides enough solvent leveling time that hinders the Marangoni instabilities and promotes smooth surfaces [58]. In this work, the fully extended PEO chain length of molar mass 109,000g/mol is: $\kappa = \ell_u N \sim 689$nm (where $\ell_u = 0.2783$ nm is the monomer length and the degree of polymerization $N = 2477$) [55]. The fully extended PS chain length of molar mass 109,000g/mol is: $\kappa = \ell_u N \sim 160$nm (where $\ell_u = 0.154$nm is the monomer length and the degree of polymerization, $N = 1038$). The long PS and PEO chains might have influenced the Marangoni effect by delaying the solvent leveling.

After annealing the films at $T_c = 40^\circ C$ under water vapor environment, very smooth hole textures were obtained (Figures 1a-1c). The AFM images revealed large rounded Nano-holes ranging from 480.0±10 to 550±10nm and tiny holes of less than ~5nm diameter lengths. The cross-sections of the large Nanoholes (Figures 1d-1f) revealed whole depths of 35±5 nm, 56±5nm and 75±5nm for 110, 170 and 220nm thin films, respectively.

![Figure 1a-1f: AFM topography images of the Nanoholes films. The images represent micrographs having film thicknesses of 110 (a), 170 (b) and 220 (c) nm. (d), (e) & (f) represent cross-sectional cuts of (a), (b) and (c), respectively.](image)

The 2D GISAXS image (Figure 2a) enabled the evaluation of the internal diblock copolymer repeat unit, $L$. It is worth to mention that the films were not annealed above the order-to-disorder transition temperature to properly structure the mesophase repeat layers. Hence, weak DBS resulted from the weak contrast between the crystalline and the amorphous layers (see supplementary GISAXS data). Figure 2a shows weak intensity maxima only along the $q_z$ axis; no maxima were observed at finite $q_y$. The peak maxima were indicated by the (black) arrows. The weak intensity maxima were attributed to the DBS’s from the crystalline PEO lamellae in the films having their interfaces parallel to the substrate, separated by amorphous PS layers. Fitting the $q_z$ positions of the DBS’s (Figure 2b) measured at several incident angles, the repeat distance, $L$, was determined to be 70±7nm (Figure 2c).

Combining the GISAXS and the AFM results, a distinct relationship between the whole depth and the repeat distances were noted. The lamellar repeat units of 70±7nm can be said to be twice the hole depth (i.e. 35±5nm) found on the 110nm film. For the 170nm film, the whole depth of 56±5nm is found to be about 0.8 multiples of $L$ while the 220nm whole depth is close to the repeating units.
Figures 2a-2c: (a): 2D GISAXS image of the 170 nm thin film measured at $\alpha_i = 0.2^\circ$. The grey rectangle and oval shapes indicate the beam stops for the direct beam and the intense secularly reflected peak, respectively. The arrows show the position of the DBS. (b): Intensity profiles along $q_z$ obtained from the 2D image. The area marked ↓ represents the area of the oval beam stop and the peaks marked ▼ show the positions of the DBS's. (c): Peak positions $q_z$ from the intensity profiles in (b) as a function of incident angle. Note: Peak positions from images measured at different incident angles were included. Squares: secularly reflected beam, circles: DBS's. Lines: fits of Equation 1. Fitting was made using $L = 70\pm7$nm.

Densely Branched Morphology

The introduction of toluene/water vapor allowed partial Dewetting of the Nanoholes at the surface of the freshly prepared 170nm film. Quasi-Dewetted large, irregular, micro-sized holes were observed as shown in Figure 3a. It is worth to mention that the Nanoholes were not completely Dewetted and this can be attributed to the mixture of toluene and the water vapor present during the dewetting process. The dewetting process was initiated by the presence of toluene vapor only. As stated earlier, it was suggested that the presence of water vapor assisted the PEO chain mobility during crystallization [41] and might be attributed to the hygroscopic nature of PEO. It is believed that under such conditions, the toluene/water molecules may have diffuse through the PS-PEO film surface into the polymer-silicon interface because of the total equilibrium moisture absorption constant [59], destroying the block copolymer microphase structure at some portions of the film. It is worth to mention that the total equilibrium moisture absorption constant varies with the film thicknesses [59], but this was not the focus of the study.

Figures 3a-3e: Optical and Atomic force micrographs of 170nm film annealed at $T_c =40^\circ$C under toluene/water vapour environment. (a) Optical micrograph of the quasi-Dewetted film. (b) Atomic force micrograph showing DBM within the Dewetted hole, (c) a phase image of (b), (d) detailed atomic force micrograph showing features of the dendritic structures, and (e) cross-sectional graph of the line shown in (d) representing the height of the dendrites.

Thus, there were the crystallization of some free PEO chains and chain folding initiated from the inner whole periphery towards the center resulting in a finger-like DBM (Figures 3b-3d). The DBMs observed have a characteristic finger
height of 10.0±0.5nm representing the height of the PEO crystal lamellae with an average width (i.e. correlation width) of ~0.3µm. The observed DBM is consistent with similar investigations having comparable length scales [60]. In that study, extensive computer simulations based on the DLA were found to agree with the experimental results having the crystalline chain stem orienting perpendicularly to the crystal front (Figure 3e).

Comparing the two experimental patterns with the simulated result, it was clear that both films have the 120, 101, 032 and 122 reflections but the DBM film exhibited additional Bragg reflections of 024 and -124. These additional peaks suggest a larger size of PEO crystals that gives sharper and intense peaks, mostly with perpendicular orientations (Figure 4b). Different simulated orientations can be seen in the supplementary data. The results suggest that the chain stems within the DBM show perpendicular oriented PEO crystal lamellae.

Conclusion

In summary, the lamellar mesophase repeat unit of the diblock copolymer was calculated and the PEO crystalline chain orientations were determined. The dimensions of the internal structures and their orientations were linked to the formed Nanoholes and DBM templates formed. After the films were freshly prepared, and because of the characteristics of the long-chain of the selected PS-PEO diblock, it was noted that several factors contributed to the hole templated Nano textures.

First, it was evaluated that there was a mismatch between the lamellar repeat unit (70±7 nm) and the film thicknesses. Secondly, it was believed that fast evaporation plus flow instability within the solvent-rich long PS-b-PEO chain films created by the Marangoni instabilities occurred. Lastly, the mismatch between the lamellar repeat unit and the film thicknesses might have created strong surface tension that influenced the interaction between the block copolymer chains and substrate [62-65]. As observed before (27), under such conditions it requires the interface to deform and stretch (increase area) causing an increase in the surface energy that promoted the hole formation. In this Nanoholes textured films, the PEO chains were not oriented but the hole depths were found to be 0.5L, 0.8L and 1.1L for the 110, 170, 220nm films, respectively.

The large Dewetted hole obtained after the dewetting processes of annealing films under toluene/water vapor...
assisted in freeing some of the PEO chains. The free PEO chains were able to crystallize within the quasi-Dewetted holes, with a crystalline lamellae thickness of ~10nm, forming an overall DBM texture. The mechanisms surrounding the formation of the DBM texture is in complete agreement with the DLA model where the crystal chains are said to diffuse and attach perpendicular to the crystal lamellae front. The internal PEO chain stem was analyzed to orient perpendicular the film substrate.

The results contribute to the understanding of crystalline chain folding processes that are complex in nature and also promote the visualization of the resulting morphology. It suggests that the repeat lamellar units and the chain folds within Nano thin films can be linked to the surface architectures.

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