

Surface and Bulk Ordering in Thin Films of a Symmetrical Diblock Copolymer

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ABSTRACT: Amphiphilic diblock copolymers have the ability to adapt their surface's molecular composition to the hydrophilicity of their environment. In the case of about equal volume fractions of the two polymer blocks, the bulk of these polymers is known to develop a laminar ordering. We report here our investigation of the relationship between bulk ordering and surface morphology/chemical composition in thin films of such an amphiphilic diblock copolymer. Upon annealing in vacuum, the expected lamella ordering in the bulk of the film is observed and we find the morphology of the film surface to be defined by the thickness of the as-deposited film: If the as-deposited thickness matches the height of a lamella stack, then the film exhibits a smooth surface. Otherwise, an incomplete lamella forms at the film surface. We show that the coverage

of this incomplete layer can be quantified by X-ray reflectivity. To establish the lamella ordering in the bulk, the film needs to be annealed above the glass temperature of the two blocks. Molecular segregation at the film surface, however, is already occurring at temperatures well below the glass temperature of the two blocks. This indicates that below the glass temperature of the blocks the bulk of the thin film is "frozen," whereas the polymer chains composing the surface lamella have an increased mobility. © 2013 Wiley Periodicals, Inc. *J. Polym. Sci., Part B: Polym. Phys.* 000: 000–000, 2013

KEYWORDS: block copolymers; diblock copolymers; films; surface reorganization; thin films; X-ray reflectometry

INTRODUCTION Diblock copolymers composed of two immiscible blocks have received great attention both in scientific and in technological applications owing to their tendency to segregate into two different phases.¹ This leads to the formation of nanoscale periodic patterns with potential applications, for example, in data storage, composite materials, and optical devices.^{2–4} One of their key properties is that size, volume fraction, and geometric shape (spheres, cylinders, and lamellae) of the autoassembled nanostructures is controlled by absolute and relative length of the chains of the two polymer blocks.⁵ Thin films of block copolymers are known to be able to possess different orderings, depending on surface energy, chemistry, and roughness.^{6–10} As a consequence, thermal and solvent vapor annealing techniques have been developed, allowing the manipulation of the interactions at the free surface and thus inducing large area ordering.^{8,11–14} Further, when solvent mixtures are used, it is possible to achieve a desired block copolymer morphology within the thin film.^{15–18}

Amphiphilic diblock copolymers are of particular interest owing to their ability of adapting the molecular composition of their surface reversibly to the hydrophilicity of their environment.¹⁹ When deposited as a thin film, the difference in hydrophilicity (surface energy) of the two blocks leads to preferential wetting of the surface/air interface by the hydrophobic block, whereas a hydrophilic substrate, such as SiO₂, will be wetted preferentially by the block with higher surface energy. This difference in hydrophilicity is also the driving force for the molecular segregation occurring within the bulk of the film, giving rise to the autoassembled nanostructuring.¹

Structural ordering phenomena in diblock copolymer films have been investigated intensively in the past, both experimentally^{2–5} and theoretically.¹ In the particular case of a symmetric diblock copolymer, that is, when the two blocks (A and B) have about equal volume fractions, the autoassembly will lead to the formation of a multilayer structure

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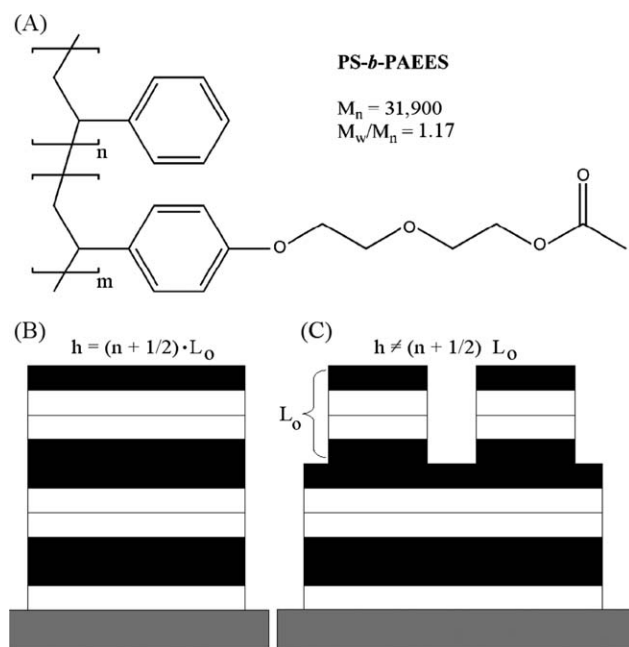


FIGURE 1 (A) Molecular structure of the amphiphilic block copolymer PS-*b*-PAEES.^{28,30} (B) Lamella ordering of the film leads to a smooth surface if the as-deposited film thickness matches the height of the lamella stack. (C) Otherwise, if too much or too less polymer material is deposited, lamella ordering leads to the formation of an incomplete surface lamella, that is, lamella islands on top or holes within the last surface lamella.

composed of lamellae of the individual blocks (...ABBAABBA...). In a thin film, this multilayer structure is oriented parallel to the substrate surface if one of the two blocks is preferentially wetting the polymer/substrate or/and polymer/surface interface.^{20,21} Otherwise, a perpendicular orientation of the lamellae can be observed.²² For example, Senshu et al.^{23,24} investigated the structural ordering under wet and dry conditions of poly(2-hydroxyethyl) methacrylate-*block*-polyisoprene and poly(2-hydroxyethyl) methacrylate-*block*-polystyrene interfaces by contact angle and transmission electron microscopy measurements. Morphology^{25–27} and chemical composition^{28,29} of the surface of thin amphiphilic diblock copolymer films have also been intensively studied in the past. Less is known, however, about the interplay between bulk order and surface properties and their respective influence on each other. We report here the results of our study on the influence of ordering in the film bulk on morphology and chemical composition of the film surface in the case of a symmetric amphiphilic diblock copolymer investigated by X-ray reflectivity.

EXPERIMENTAL

Materials

The symmetric diblock copolymer polystyrene-*block*-poly(4-(2-(2-(2-acetoxy)ethoxy)ethoxy)styrene) (PS-*b*-PAEES), shown in Figure 1(A), was synthesized by TEMPO-based controlled

radical polymerization.^{28,30} The number-average molecular weight (M_n) is 31,900 with a polydispersity of 1.17 and about equal volume fractions of the two blocks ($M_n[\text{PS}] = 19,600$ and $M_n[\text{PAEES}] = 12,300$).

Thin-Film Preparation

Thin films with thicknesses of 50–150 nm were prepared by spin coating from toluene solutions with polymer concentrations of 10–40 mg/mL. These were mixed at 30 °C for 12 h to completely dissolve the polymer. Prior to spin coating, the solution was passed through a filter of 0.2 μm pore size to remove any unsolved polymer and dust particles. In brief, 1.5-cm square pieces of commercial silicon wafers (SILTRONIX) were used as substrates. Prior to spin coating, these silicon wafers were cleaned by immersion in a ($\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O} = 1:1:5$) solution at 80 °C for 15 min, followed by extensive rinsing with distilled water (Milli-Q 18.2 M Ω ·cm) and drying in a stream of filtered nitrogen. To remove any residual solvent, the films were annealed after spin coating in vacuum at 150 °C for 12 h. At this temperature, which is well above the glass temperature of the two blocks ($T_g[\text{PAEES}] = -3$ °C) and $T_g[\text{PS}] = 100$ °C), the annealing is expected to lead to structural equilibration, that is, the lamella ordering is expected to occur. For equilibration in a hydrophilic environment, the film is immersed into 80 °C hot water for 8 h.

X-ray reflectivity measurements were performed at the Philips Panalytica X'Pert XRD reflectometer of the Institut des NanoSciences de Paris (INSP) using Cu-K α line radiation ($\lambda = 0.154$ nm). The electron gun of the X-ray tube was operated at 40 KeV and 30 mA. Scanning electron microscopy (SEM) images were obtained with the JMS-5510LV microscope of UPMC's microscopy platform operated at an electron energy of 5 KeV. A Veeco Dimension 3100 atomic force microscope was used to characterize the surface topography of the samples. Surface energy measurements were performed with a contact angle meter (Drop, Krüss, Germany).

RESULTS AND DISCUSSION

After annealing in vacuum, the films of the amphiphilic block copolymer PS-*b*-PAEES exhibit in general a rough surface. A smooth surface is found only for a few specific thickness values of the as-deposited film. As shown previously,³¹ we interpret this as indication for the presence of lamella ordering in the film. The underlying idea is shown in Figure 1 for the case of so-called antisymmetric wetting conditions, that is, the hydrophilic substrate (SiO_2) is wetted by the hydrophilic block (PAEES), whereas the hydrophobic block (PS) covers the polymer surface (air/vacuum interface). In this case, a smooth film surface is obtained whenever the as-deposited film thickness (h) equals $(n + 1/2) L_0$, with L_0 the thickness of a single lamella (ABBA). Otherwise, an incomplete surface lamella is formed, that is the lack (or excess) of polymer material giving rise to the formation of holes (and islands) as shown in Figure 1(C).

To verify that this model applies, we first recorded X-ray reflectivity on a series of films with increasing film thickness,

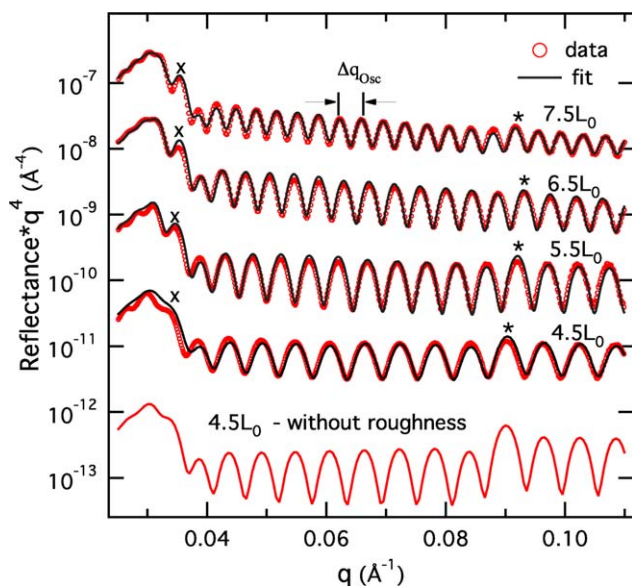


FIGURE 2 Reflectivity curves measured (open circles) on a series of PS-*b*-PAEES films exhibiting after vacuum equilibration a smooth film surface (for clarity, curves are offset and multiplied by q^4). A fit (solid lines) based on the presence of lamella ordering of the film as shown in Figure 1(B) is in excellent agreement with the data, and thus confirming the applicability of this model.

all exhibiting a smooth surface after thermal annealing (for deposition details, see Supporting Information Table S1). These reflectivity curves are plotted by the open circles in Figure 2, where the reflectance is multiplied by q^4 to facilitate their interpretation. In each case, one observes around $q = 0.09 \text{ \AA}^{-1}$ an oscillation (indicated by a star), which is slightly more intense than the neighboring ones. This behavior is related to the presence of a Bragg-like peak in the reflectivity curve, which is indicative for the existence of a multilayer structure in the film. The faint visibility of this peak is owing to significant surface and interface roughness in combination with the weak scattering contrast between different polymers for 8-keV X-rays.³²

For further evaluation, we fitted a model consisting of $(n + 1/2)$ lamella [Fig. 1 (B)] to these reflectivity curves using the *reflex*²⁸ software package developed by Gibaud.³³ These fits (solid lines in Figure 2, see Supporting Information Table S1 for details) reproduce well the experimental data and thus confirm the underlying model, that is, the presence of lamella ordering in the film as well as the assumed antisymmetric wetting of substrate and surface interface. As average lamella thickness, we obtained $L_0 = 21.7 \text{ nm}$ with a maximum variation of $\pm 0.3 \text{ nm}$. We note that this thickness is in line with estimates based on the molecular weight of the investigated block copolymer.³⁴ At the bottom of Figure 2, we reproduce the reflectivity curve calculated from the fit parameters obtained from the analysis of the film with a thickness of 4.5 lamellae, but under the assumption of abrupt, flat interfaces. The change

in amplitude of the reflectivity's oscillation with a periodicity corresponding to the number of lamella present in the film becomes clearly visible. Noteworthy, the comparison between data and model also identifies the peak around $q = 0.035 \text{ \AA}^{-1}$ (labeled by a cross, Fig. 2) as indicative for the presence of lamella ordering in the film.

To investigate the presence of lamella ordering also in the case of a rough film surface, we prepared a series of thin films with as-deposited thickness in between the ones of two successive smooth films (for deposition details, see Supporting Information Table S2). SEM images of the surface of these films, recorded after vacuum equilibration, are reproduced in Figure 3. These images indicate an evolution of the surface morphology, which is in-line with the model shown in Figure 1(C): Starting from a smooth film surface ("59.1 nm" thick as-deposited), a few islands appear ("62 nm," islands appear as dark dots in SEM), which number increases ("65.2 nm" and "68.6 nm"), until a continuous additional surface lamella with holes forms ("72.3 nm"). The number of holes decreases with increasing thickness of the as-deposited film ("74.7" and "76.3 nm"), until the amount of deposited polymer material corresponds again to the formation of a complete surface lamella ("79.3 nm").

To further, more directly verify the presence of lamella ordering in these films exhibiting a rough surface upon vacuum equilibration, we have recorded X-ray reflectivity curves, which are reproduced in Figure 4 (open circles). One notes that the form of these curves changes drastically with the thickness of the as-deposited film. The higher the island/

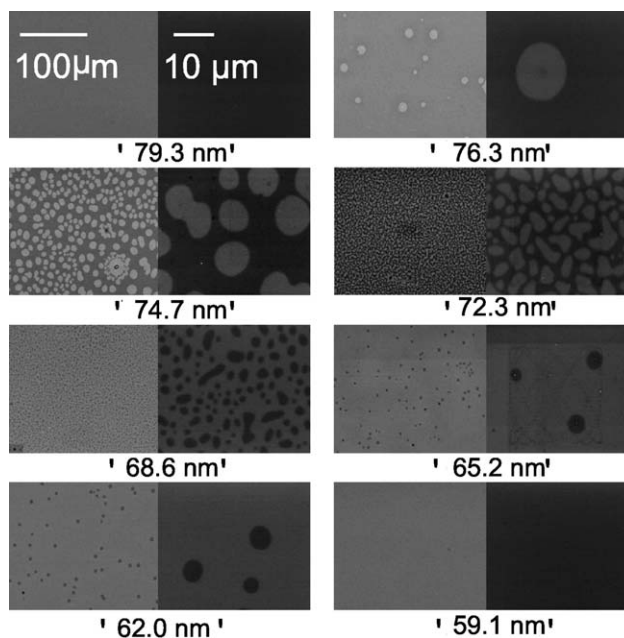


FIGURE 3 SEM images of the surface of a series of vacuum equilibrated PS-*b*-PAEES films. The film thickness of the as-deposited film, prior to vacuum equilibration, is indicated. The scale bars indicated in the upper left image of the smooth film with an initial film thickness of 79.3 nm apply to all images.

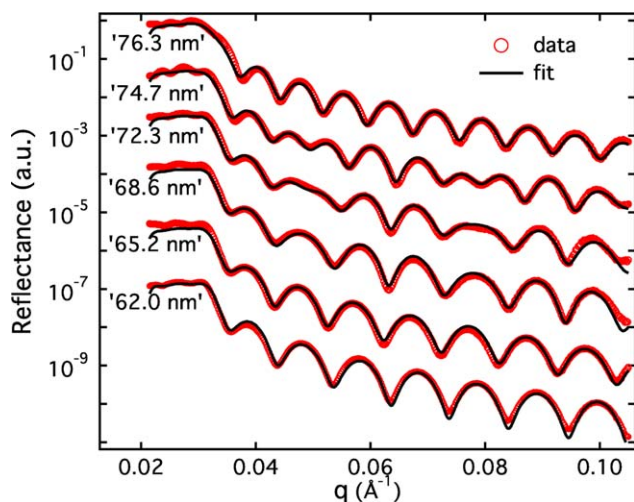


FIGURE 4 Reflectivity curves measured (open circles) on the same vacuum equilibrated PS-*b*-PAEES films shown in Figure 3. The indicated as-deposited thickness of the films is in-between the ones of two successive smooth films (for clarity, curves are offset). A fit (solid lines) based on the presence of a surface layer of lamella islands as shown in Figure 1(C) is in excellent agreement with the data, and thus confirming the applicability of this model.

hole density in the surface lamella is, the more the reflectivity curves deviate from the one of a smooth films; it becomes even difficult to identify the periodicity corresponding to the total film thickness.

This behavior is to be expected when a film contains regions of two different, distinct thicknesses, each giving rise to a reflectivity curve with a specific oscillation frequency. In the measurement, these two curves superpose, which yields the observed beating of the amplitude of the oscillations in the reflectivity curve. To quantitatively analyze these data, we use a model similar to the one applied before, but we scale the electron density of the blocks composing the incomplete surface lamella layer by a free fit parameter [Fig. 1 (C)]. The idea behind this approach is that owing to the applied

grazing incidence geometry, X-rays pass through a large number of islands and holes while penetrating the film.

The results of these fits, which are reproduced by the solid lines in Figure 4, are in excellent agreement with the experimental data. As an example, we show in Figure 5(A) the electron density profile obtained for the film with an as-deposited film thickness of 68.6 nm. However, owing to the presence of two distinct film thicknesses, the internal structure of the film cannot be verified directly; a fit using a homogenous film, that is without internal ordering, but with two different film thicknesses would equally well reproduce the data. We thus can only conclude from this fit that there are two distinct film thicknesses, obtain their respective height and the scaling factor of the electron density of the outermost lamella. This is a reasonable assumption as the formation of two distinct film thickness is driven by the internal phase separation. We note that this scaling factor corresponds directly to the fraction of islands in the outermost layer.

The graph in Figure 5(B) shows the island fraction of the surface lamella as deduced from the afore-mentioned analysis of the reflectivity curve (diamonds). As one would expect, the island fraction increases linearly (line fitted to the diamond data points) with the thickness of the as-deposited film, that is the amount of deposited polymer material. The fraction of island coverage can also be deduced from the SEM images by calculating their total surface area. These values (circles, Fig. 5) are in good general agreement with the values obtained from the analysis of the reflectivity curves. One notes, however, that the values derived from the image analysis, are consistently smaller, which we understand owing to principal limitations of image analysis. Objects smaller than the resolution limit cannot be taken into account and the presence of nonperpendicular walls is difficult to evaluate in these two-dimensional projections. Both these limitations do not affect the X-ray reflectivity data, which offer the additional advantage of averaging over a larger sample area, and thus providing a good statistical description of the sample.

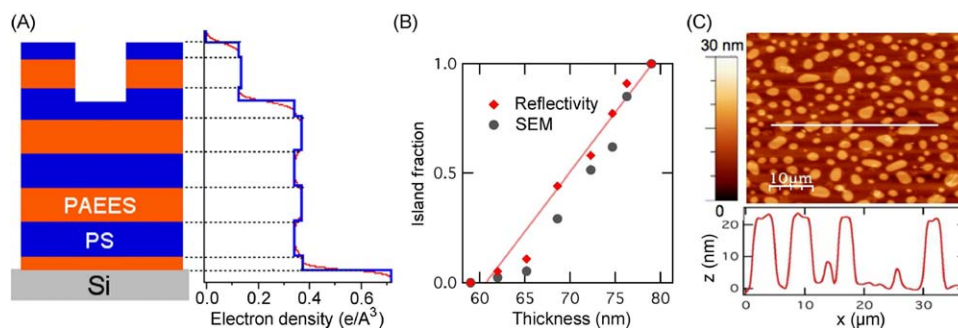


FIGURE 5 (A) Electron density profile derived by fitting the indicated model to the reflectivity curve of the vacuum equilibrated film with an as-deposited thickness of 68.6 nm (Fig. 4). (B) The island coverage of the surface as derived from the analysis of the reflectivity data (diamonds, representing the fitted scaling factor of the electron density of the outermost lamella) and the SEM images (circles, area of islands in images of Fig. 3). (C) AFM image and height profile of the surface topography of the vacuum equilibrated film with an as-deposited thickness of 68.6 nm, indicating a lamella thickness of about 22 nm.

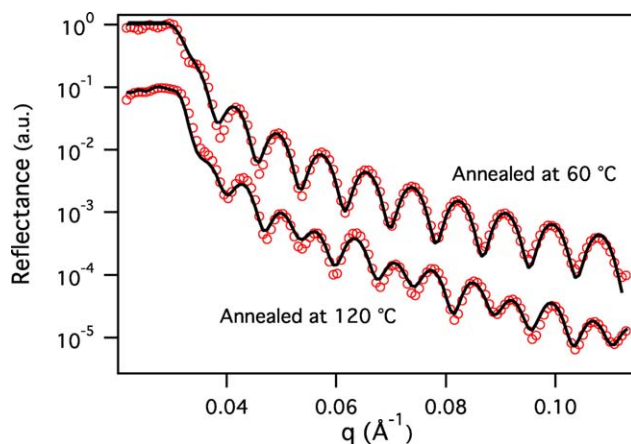


FIGURE 6 The reflectivity curve of a PS-*b*-PAEES film recorded after annealing in vacuum at 60 °C for 12 h (top) is well reproduced by a fit based on a single, homogeneous layer of 71 nm thickness. The reflectivity curve recorded after further annealing at 120 °C for 12 h (bottom, offset for clarity), on the other hand, clearly indicates the presence of two distinct film heights and is well reproduced by a fit based on the corresponding model [Fig. 5 (A)].

To further verify the model's assumption that the islands have the internal structure of a lamella (four polymer layers in the sequence ABBA), we have used atomic force microscopy (AFM) to measure the height of the islands on these films. As an example, we show in Figure 5(C) the surface topography of the film with an as-deposited thickness of 68.6 nm. From the profile cut along the indicated line, a mean island height of about 22 nm is obtained. The average value of the island height of all films is 22.1 nm with a maximum deviation of ± 1.2 nm. We note that these values are in excellent agreement with the lamella height of 21.7 nm obtained from the analysis of the reflectivity data, thus confirming the underlying model.

Previously, we have employed X-ray absorption spectroscopy to investigate the chemical composition of the surface of thin films of the block copolymer PS-*b*-PAEES and its evolution upon equilibration in a wet or dry environment.²⁸ Similar work has been done for a copolymer with PEGylated and fluoroalkyl side chains.³⁵ We showed that alternating equilibration leads to a reproducible, essentially complete exchange of the molecular blocks composing the surface layer of the film; from hydrophilic PAEES blocks after water equilibration to hydrophobic PS blocks after vacuum equilibration and *vice versa*. Interestingly, this exchange was found to take place already at temperatures well below the glass temperature of the PS block.

To reproduce this observation on the films studied here, we characterized the surface energy of films upon different annealing steps by measuring their contact angle with water. After water equilibration in 80 °C water for 8 h, we found a contact angle of 75°, which matches the contact angle measured on a thin film of the PAEES homopolymer. On the other

hand, after vacuum annealing at 120 °C for 12 h of the previously water-equilibrated film, a contact angle of 95° is observed, which is the very same angle we obtain on a PS film and also inline with the literature.³⁶ The occurrence of the molecular exchange well below the glass temperature of PS is also observed. A significant increase of the contact angle to 82° is already observed after vacuum annealing at 40 °C for 12 h. Annealing at 60 °C for 12 h yields a surface exhibiting the same contact angle of 95° as PS, without any further significant changes upon annealing at higher temperatures.

To relate these observations of the chemical composition of the film surface with the occurrence of ordering in the film bulk, we have recorded on these films X-ray reflectivity curves. In Figure 6 we compare the reflectivity curves recorded on a thin film after annealing for 12 h at 60 °C (top) and after subsequent annealing at 120 °C (bottom). For this film with an as-deposited thickness of 71 nm, the formation of lamella ordering is expected to give rise to an incomplete surface lamella. In line with this expectation, the reflectivity curve of the film annealed at 120 °C (lower curve, Fig. 6) exhibits the characteristic beating of the oscillation's amplitude. Furthermore, a fit (solid line) based on this model reproduces well the reflectivity curve.

The presence of a smooth film surface, without indications of lamella ordering in the film bulk, is indicated by the reflectivity curve recorded after annealing at 60 °C (upper curve, Fig. 6). Indeed, the experimental data can be well reproduced by the reflectivity calculated for a single, homogeneous 71-nm thick layer (surface roughness, 0.5 nm). We can thus conclude that ordering of the bulk in lamellae, composed of the two respective homopolymers, does not occur for temperatures significantly lower than the glass temperature of the two blocks.

CONCLUSIONS

We have investigated in an amphiphilic block copolymer with about equal volume fractions of the two blocks the relationship between surface morphology and occurrence of lamella ordering in the bulk of the film. We find that the hydrophilicity of the environment during equilibration determines the chemical composition of the film's surface. Detailed X-ray analysis was used a tool to study the thin films, allowing a simultaneous investigation of the film surface and the bulk. The morphology of the surface follows then from the ratio between the lamella height and the thickness of the as-deposited film. To achieve structural ordering of the bulk of the film, it is necessary to anneal the film at a temperature above the glass temperature of the two blocks. Molecular segregation at the film surface, however, is found to take place already at significantly lower temperatures. The presented X-ray methodology thus provides the possibility for an easy but thorough investigation of similar block copolymer thin-film behaviors, eventually allowing the utilization of the surface reorganization of amphiphilic block copolymer thin films in technological applications.

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