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Confined Block Copolymer Thin Films

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ABSTRACT: Thin films of nearly symmetric diblock copolymers of poly(ethylenepropylene)–poly(ethylethylene) (PEP–PEE) were investigated in confinement between two hard walls. The domain thickness was found to be a function of the film thickness. Mechanically stable films with an integral number of domains were found with the ordering parallel to the hard walls at all degrees of frustration. The PEE block was found to preferentially segregate to both the confining surfaces. A discontinuous first-order-like transition occurred in the number of domains. These results provide a new approach toward probing the influence of chain stretching (or dilation) on the stability of block copolymer structures.

Introduction

Diblock copolymers are known to self-assemble into two- and three-dimensional morphologies in the bulk state.[1] The process of self-assembly is driven by total free energy minimization, with enthalpic and entropic contributions. In block copolymer *thin* films, the copolymer experiences restraints due to proximity to *two* surfaces (the term *thin* here refers to film thicknesses that are a few to several tens of the bulk domain thickness). There are additional contributions to the overall free energy from surface and interfacial energies of the two blocks and the substrate. Nevertheless, diblock copolymers have also been observed to assemble into two- and three-dimensional morphologies in thin films.[2–7] The self-assembling process in thin films can be completely described by characterizing three different, but closely related, phenomena: morphology, surface wetting, and surface topology.

In a *symmetric* film, the same block wets both the air and substrate interfaces, while in an *asymmetric* film different blocks wet the air and substrate interfaces.[6] If the total film thickness is different from nD in a symmetric film, or $(n + 1/2)D$ in an asymmetric film, "islands" or "holes" are formed on the surface, where D is the domain thickness in the film and n is an integer. The height (or depth) of the islands (or holes) is equal to D. Figure 1a is a schematic of island formation in a symmetric film. The formation of islands or holes can be spontaneous (spinodal like), or they can nucleate and grow.[8–11] This process, nonetheless, is associated with material transport. It is readily apparent that the transport must occur in both the vertical and horizontal directions, as illustrated by arrows in Figure 1a. Such a rearrangement is a direct consequence of the incompressibility of polymer melts which dictates that the total volume remain constant. Hence, the average film thickness is invariant provided there is no macroscopic lateral contraction or expansion. Furthermore, formation of islands and holes requires the interface to deform and stretch (increase area), as indicated in Figure 1a. Here, the interface is between air and the wetting block of the diblock copolymer. This air interface, which is easily deformable, is termed a "soft wall", while the substrate, silicon for example, which is not easily deformable, is called a "hard wall". Most prior research with block copolymer thin films has dealt with the interfacial behavior in "pseudoconfinement", i.e. between hard and soft walls. The twin words in the term "pseudoconfinement" are to be interpreted in light of the deformable interface and the obvious reduced size effects of the copolymer. In pseudoconfinement, the surface topology of the film is the *consequence* of energetics that govern the morphology and the surface wetting. This cause–effect can be reversed if the film is confined between two hard walls so that the formation of surface structures is suppressed. In this report, we examine how surface topology, or lack of it, influences the morphology and the surface wetting of diblock copolymer films confined between two hard walls.

Distortion of morphology of diblock copolymers has been observed before in pseudoconfined thin films.[12,13] In a symmetric diblock copolymer of PS–PMMA, the width of the individual domains of PS and PMMA and the interfacial width between PS and PMMA was found to vary with the film thickness.[12] Russell *et al.*[12] also note that in higher molecular weight systems, it is more favorable to distort the copolymer morphology than form a surface structure of islands (or holes). In off-symmetric diblock copolymers of PEP–PEE, Karim *et al.*[13] report distortion in the inplane hexagonal packing of the smaller block. They attribute this to the film thickness restraints and the strong tendency of the PEE block to wet the surfaces.

In an independent experimental research effort, Russell and co-workers have recently studied model PS–PMMA symmetric diblock copolymers constrained between hard walls of silicon oxide.[14] Here, we report effects of contraining on a different copolymer system that exhibits a different type of wetting. Although our experimental methods of confinement differ, the conclusions from both studies are generally consistent.

Experimental Section

The diblock copolymer chosen for this study was a poly(ethylenepropylene)–poly(ethylethylene) (PEP–PEE) with molecular weight $M_n = 106\,000$ and PEP volume fraction of $f = 0.54$. This polymer has been well characterized in bulk[15] and in (pseudoconfined) thin films.[5] The PEP–PEE copolymer

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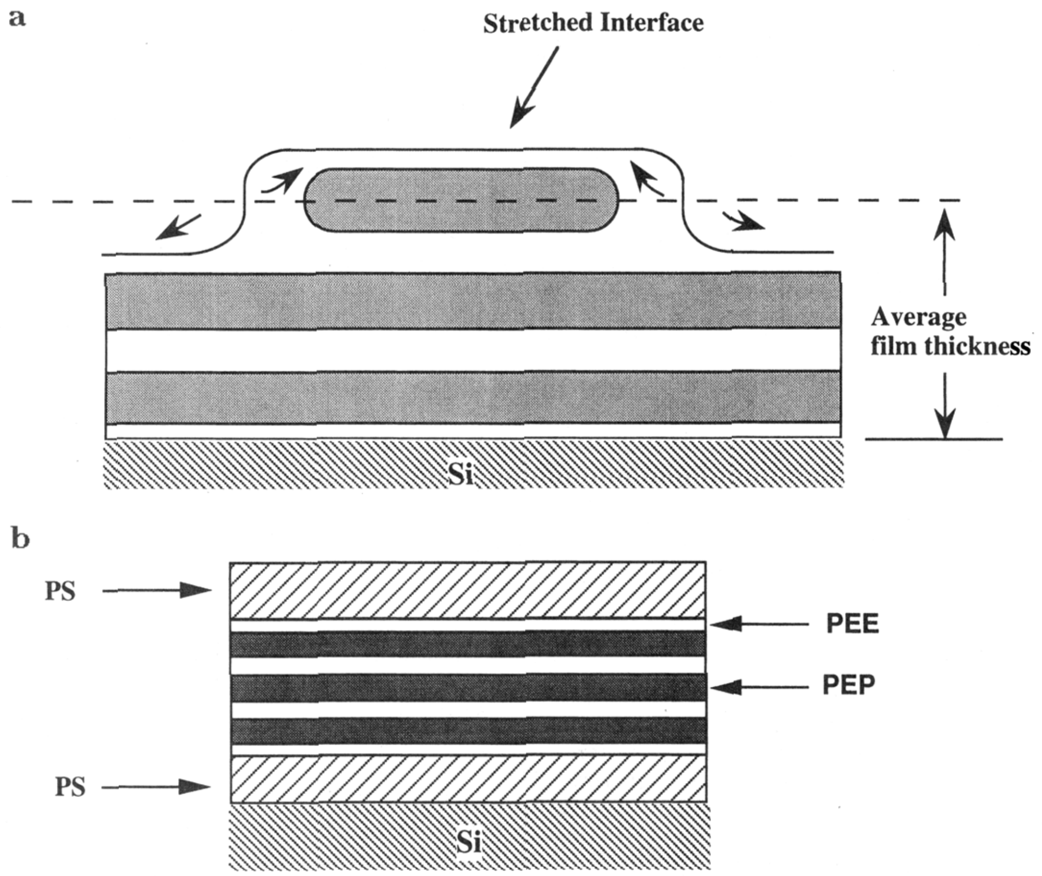

Figure 1. (a) Schematic of island formation in a diblock copolymer film at equilibrium. The arrows indicate material movement that should have occurred at the surface for the island to form from an as-cast film. The height of the island is equal to the equilibrium domain thickness D^*. (b) Schematic of PEP−PEE copolymer confined between two similar hard walls poly(styrene).

was confined between two similar hard walls of poly(styrene) and between two dissimilar hard walls of poly(styrene) (PS) and silicon. Chemically pure PS of molecular weight ~100 000 was synthesized by anionic polymerization.[16] The glass transition of PS occurs at ~100 °C.[17] Thin film samples for reflection experiments were prepared in a class 10 clean room. Silicon wafers of 10 cm diameter and 0.476 cm thickness, having (111) orientation, were used in this study. The wafers were cleaned in a 30%−70% mixture of hydrogen peroxide and sulfuric acid, respectively, at 115−120 °C for 5 min. After thorough rinsing, the wafers were etched in a 10% HF aqueous bath for 90 s to remove any native oxide. After subsequent rinsing, the wafers were cleaned with high-purity nitrogen and immediately spin coated. About 4−5 mL of the solution that had been filtered with a 0.2 μm filter was placed on the wafer and the substrate was spun at speeds ranging from 1200 to 3500 RPM. The concentration of the copolymer in solution (2−4 wt %) and the speeds were appropriately changed to obtain films of different thicknesses.

In confinement between two *similar hard walls*, the PS film was coated first from a solution of methyl ethyl ketone (MEK).[18] The film was allowed to dry under ambient conditions and the film thickness measured by ellipsometry. Subsequently, a film of PEP−PEE was spin coated on top of the PS film from a solution of heptane. Heptane is a nonsolvent for PS and spin coating PEP−PEE does not affect the PS film. The film was dried, and the thickness measured by ellipsometry. Finally, a PS film was spin coated on top of the PEP−PEE film from a solution of MEK, a nonsolvent for PEP−PEE, and the total thickness measured again. Confinement between two similar hard walls is illustrated in Figure 1b. For confinement between two *dissimilar hard walls*, the PEP−PEE film was spin coated on a silicon wafer from a solution of heptane; and the PS film was deposited on top of the PEP−PEE from a solution of MEK.

We assessed the possibility of solvent-induced distortion within the PEP−PEE films in the following way. A uniform film of PEP−PEE was made from a solution of heptane, by spin coating on a silicon wafer. A few drops of pure MEK (1−2 mL) was placed away from the center of the PEP−PEE film. The wafer was spun and then examined under the microscope. There was no significant difference between regions that were wetted by MEK and the regions that were not. On any choice of optical filter in the microscope, the colors of the two regions were indistinguishable; difference in color is a definite indication of variation in the thickness. In addition, thickness measurements were performed by ellipsometry on regions that were wetted by MEK and the regions that were not. Within the resolution of the instrument (±25 Å), the film was uniform. This clearly demonstrates the feasibility of using this pair of solvents with the polymers selected for this study.

A check for spontaneous island−hole formation was done on two PEP−PEE films (M_n = 106 000). The as-cast films were flat (no surface topology) and showed no evidence of islands or holes formation up to 2 weeks from the time each film was cast. Both the films, however, did form islands and holes upon annealing at 90 °C for 12 h. This confirms that the PEP−PEE films (M_n = 106 000) develop no surface structure in the as-cast state in the time frame (few minutes) it takes to spin coat a PS film on top of PEP−PEE.

The thickness of the spin-coated PS films were in the range 700−1100 Å and that of the PEP−PEE films varied from 1600 to 2300 Å, corresponding to ~3 to 4 domains. Poly(styrene), which is glassy at room temperature, is effectively a hard wall that suppresses islands and holes formation. Neutron reflectivity experiments were performed on the cold neutron reflectometer at the National Institute of Standards and Technology (NIST), Gaithersburg, MD.[19] Reflectivity measurements were conducted on all the samples before and after annealing (70 °C, 6−8 h in a vacuum).

Theoretical

Phase behavior of symmetric diblock copolymer melts confined between parallel hard walls has been studied by simulations[20] and theoretically.[21,22] Kikuchi and

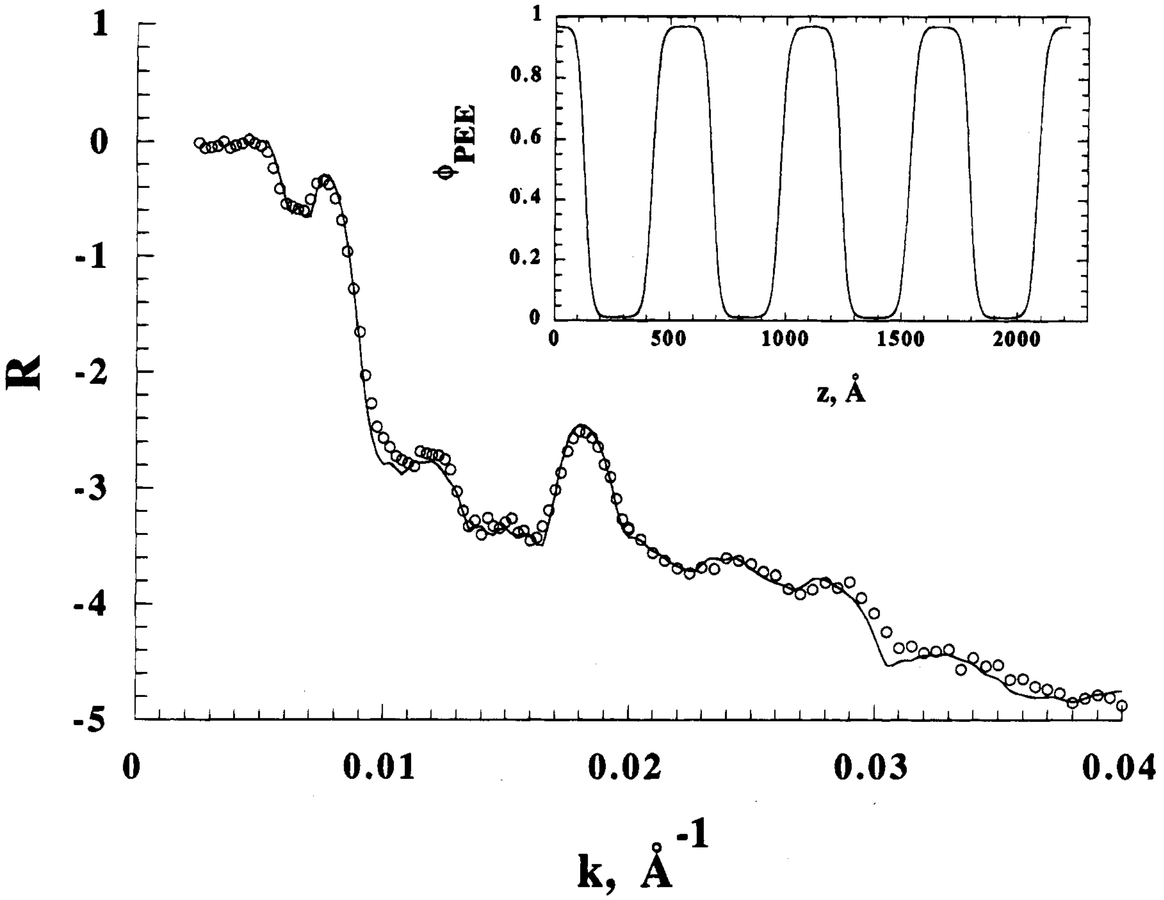

Figure 2. Reflectivity data (open symbols) from a PEP–PEE film on a 1023 Å PS film shown along with the best fit (solid line). The composition profile of the PEP–PEE film (volume fraction of PEE block) is shown in the inset.

Binder[20] employed Monte Carlo methods to obtain order parameter profiles normal to the surface, when one of the blocks experiences a repulsive potential with the surface. They find that ordering of a copolymer parallel to the surface is suppressed, when the two fundamental length scales, viz. the domain thickness and the film thickness, strongly "conflict" with each other. Based on a self-consistent mean-field analysis, Shull[21] predicts that the domain thickness adjusts so as to accommodate changes in the film thickness. Turner[22] has proposed a simple and lucid theory that describes the equilibrium behavior of symmetric diblock copolymer confined between two hard walls. Analytical expressions are obtained from free energy considerations in the strong segregation limit. This theory predicts a discontinuous transition in the number of domains (integral or half-integral) as the film thickness is varied; the accessibility of integral or half-integral number of domains depends on the relative difference of interfacial tensions between the blocks, and the blocks with the confining surfaces. Ordering of the copolymer parallel to the surface is implicitly assumed in the theoretical treatise of Shull[21] and Turner[22] while in the simulations of Kikuchi and Binder[20] ordering of lamellae normal to the surface is also seen.

Results and Discussion

Shown in Figure 2 are the reflectivity data plotted against the momentum vector normal to the surface k, ($\equiv 2\pi(\sin\theta)/\lambda$, where θ is the angle of incidence parallel to the surface and λ is the wavelength) for a PEP–PEE film on a 1023 Å PS film (pseudoconfinement), that was annealed at 70 °C in vacuum for 7 h. The presence of multiple order reflections indicate order in the film parallel to the surface. The solid line in Figure 2 is the calculated reflectivity from an assumed composition profile in the PEP–PEE film that is shown in the inset. The domain spacing from the fit was calculated to be 555 ± 3 Å. It is also evident from the composition profile that PEE blocks are located at both the air and the PS interface. The interface width calculated as defined in ref 23 was 60 ± 3 Å. Foster *et al.*[5] report the domain thickness to be 566 ± 5 Å and an interface width of 63 ± 3 Å for the same copolymer. These measurements, conducted on different instruments, are in good agreement with those obtained here. $D^* = 555$ Å is used as the equilibrium domain thickness in all further calculations.

The reflectivity data from PEP–PEE copolymer confined between two similar (PS–PS) and dissimilar (PS–Si) hard walls are presented in Figure 3. These figures show reflectivity profiles obtained for different reduced film thicknesses of copolymer, L/D^*, where L is the overall PEP–PEE film thickness. For reasons of clarity, the profiles are progressively offset by a decade on the ordinate. L has been estimated from model fits to the data; for reflectivity data where fitting was not performed, values from ellipsometric measurements are used. The discrepancy in thickness between the two is no larger than 80 Å for any film. First and third Bragg reflections dominate in all the profiles shown in Figure 3 and the position of these peaks provides a direct measure of the domain thickness. Domain thickness was calculated from the fits of the reflectivity data with an error of ±3 Å. For data from the samples where fitting was not performed the domain spacing was calculated from the position of the Bragg reflections with an estimated error of ±7 Å.

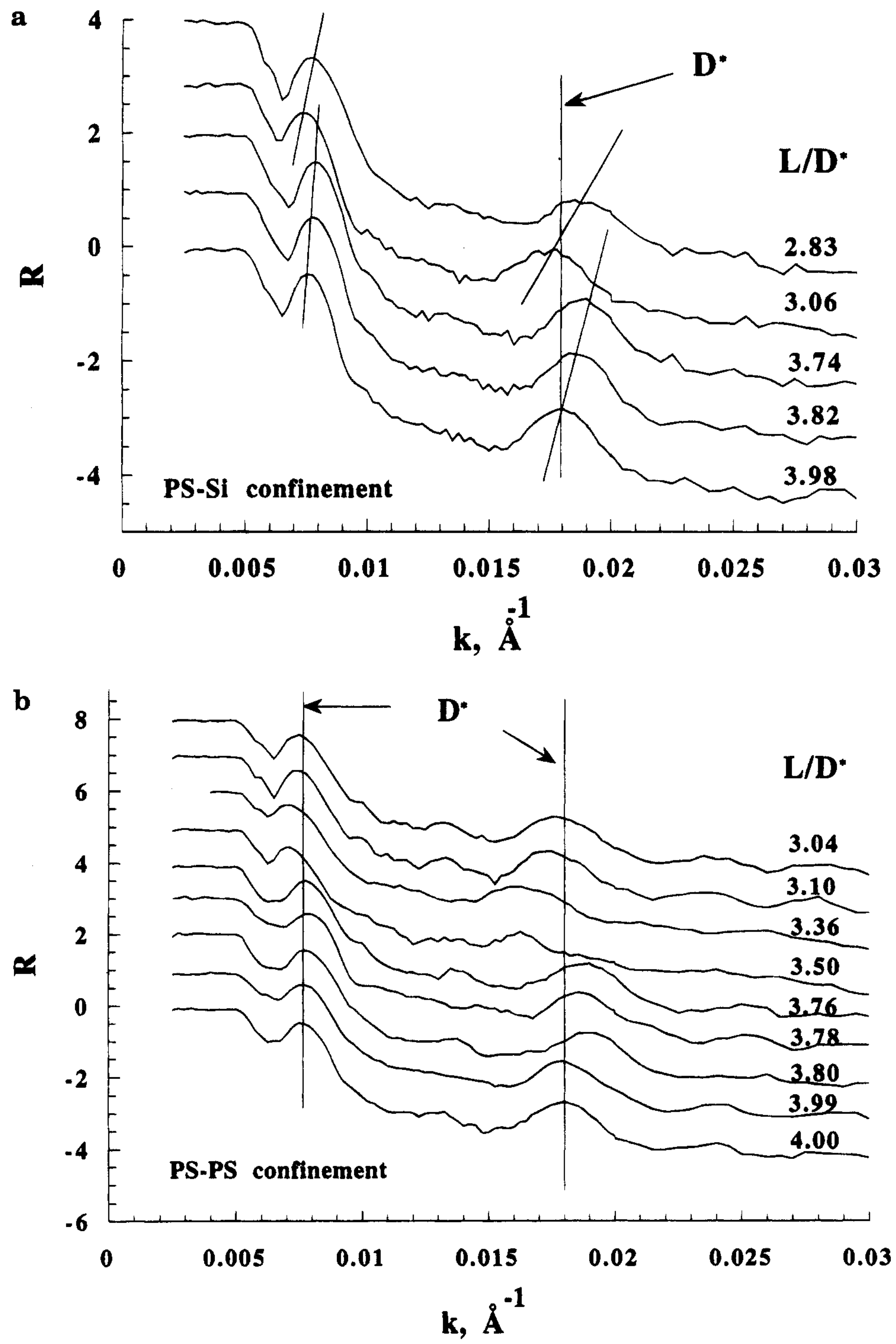

Figure 3. Reflectivity profiles from PEP−PEE diblock copolymer confined between two dissimilar hard walls of PS and silicon (a) and confined between two similar hard walls of PS (b) plotted for different reduced film thicknesses (L/D^*). The profiles are offset by a decade on the ordinate axis. The slanted lines in (a) are to guide the eye.

For films in confinement between two *dissimilar hard walls* (PS−Si) the PEP−PEE film thickness was varied in multiples of D^* from 2.83 to 3.98 (Figure 3a). All the reflectivity profiles shown were obtained from annealed samples. The slanted lines in the figure are guides for the eye and the vertical line corresponds to the peak position associated with D^*. As is evident from Figure 3a, the domain thickness decreases as L/D^* is decreased from 3.98 to 3.74, as inferred from a shift of the first and third Bragg reflections to higher k. This decrease precisely compensates for the nonstoichiometric amount of confined polymer, leading to exactly 4 domains. In other words, samples with $L/D^* = 3.98$, 3.82, and 3.72 form 4 contracted domains in confinement. Furthermore, the sample with $L/D^* = 3.06$ forms 3 expanded domains while the sample with $L/D^* = 2.83$ forms 3 contracted domains. A similar plot is constructed for PEP−PEE confined between two *similar hard walls* (PS−PS), as shown in Figure 3b. The reflectivity data shown for samples with $L/D^* = 3.36$ and 3.50 are from as-cast samples, while the other profiles shown are from annealed samples. As L/D^* is decreased from 4.00 to 3.76, the domains become progressively contracted; it appears that there is a discontinuous, first-order-like transition from contracted to expanded domains for $3.50 < L/D^* < 3.76$. The equilibrium domain thickness (D^*) is recovered as the reduced thickness is further decreased from 3.36 to 3.04.

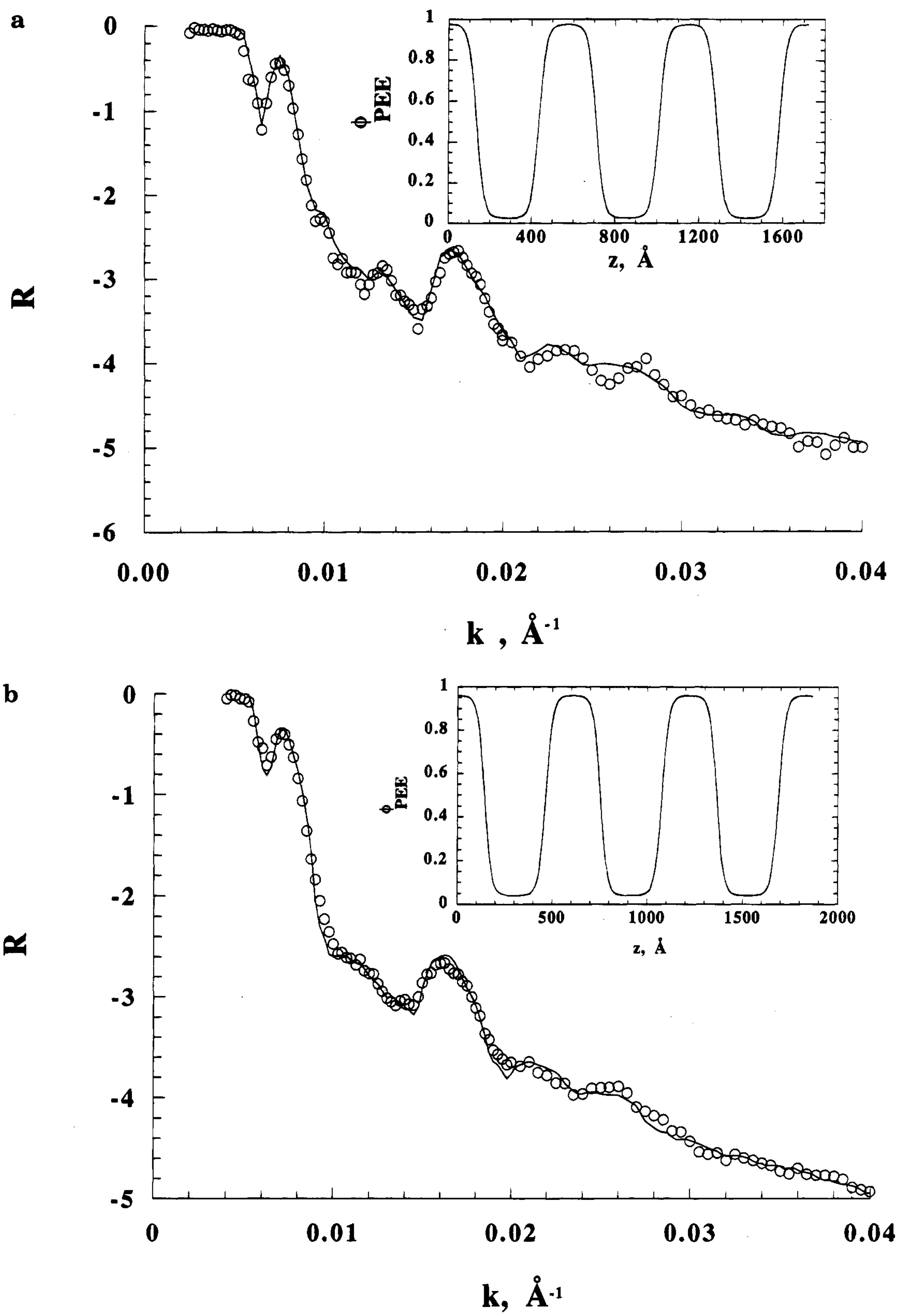

Figure 4. Fits of reflectivity data for the sample $L/D^* = 3.10$ (a) and $L/D^* = 3.36$ (b) confined between two similar hard walls of PS. The composition profile of the PEP–PEE film (volume fraction of PEE block) is shown in the inset. The PS film thicknesses for the sample with $L/D^* = 3.10$ are 855 Å (adjacent to air) and 720 Å (adjacent to Si) and for the sample with $L/D^* = 3.36$ are 1100 Å (adjacent to air) and 800 Å (adjacent to Si).

Fits of reflectivity data from representative samples with $L/D^* = 3.10$, 3.36, 3.78, and 3.99 are shown in Figures 4 and 5. A hyperbolic tangent composition profile that describes the interface in the PEP–PEE copolymer was employed in fitting the data; the composition profile of the PEP–PEE copolymer for the fits obtained are shown in the insets. As evident from the composition profiles from Figures 4 and 5, samples with $L/D^* = 3.10$ and 3.36 form 3 expanded domains while the samples with $L/D^* = 3.78$ and 3.99 form 4 contracted domains in confinement. Furthermore, the composition profile from fitting the reflectivity data also reveals a single domain period (monodomain) in all the films in confinement, suggesting that thickness re-

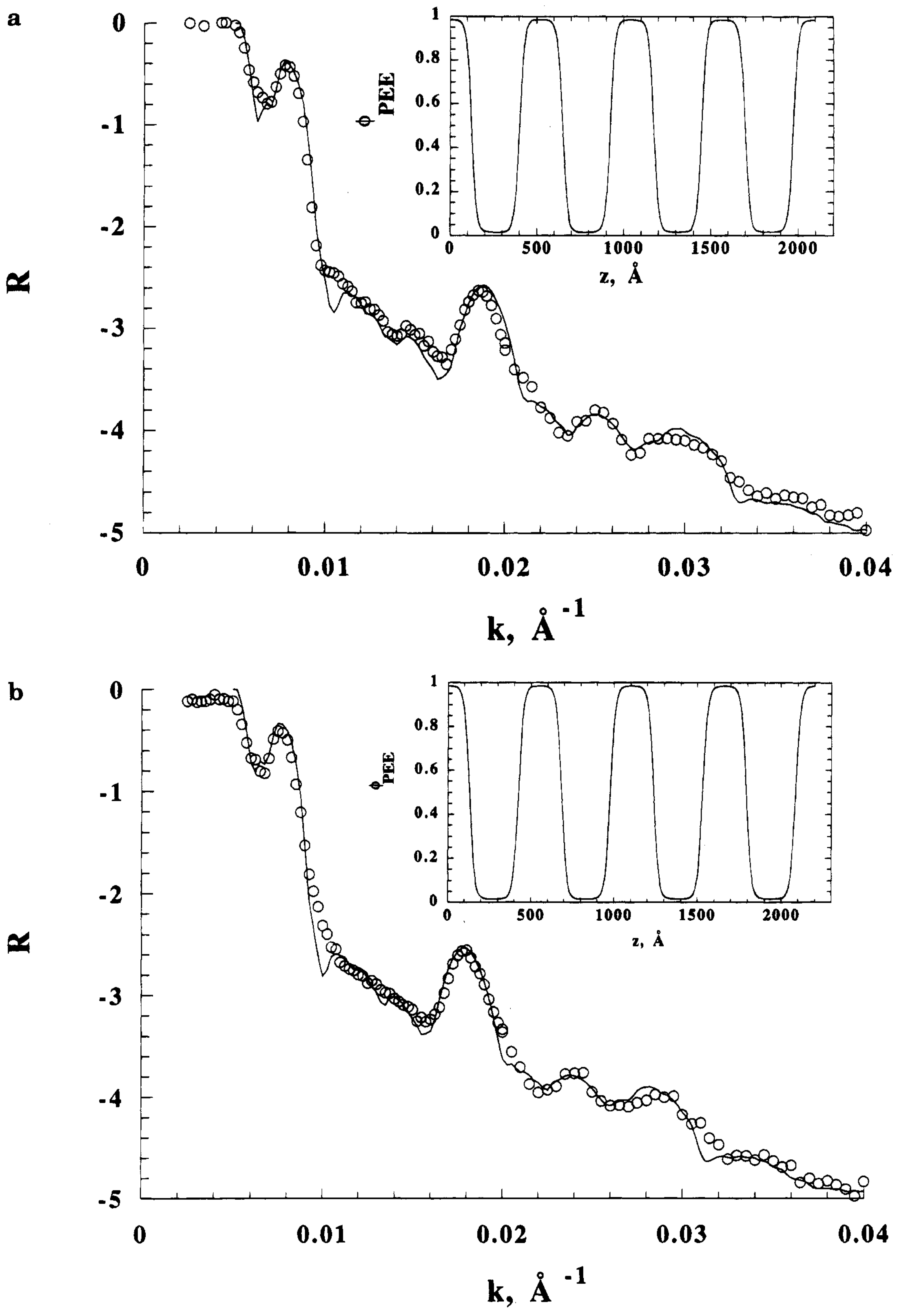

Figure 5. Fits of reflectivity data for the sample $L/D^* = 3.78$ (a) and $L/D^* = 3.99$ (b) confined between two similar hard walls of PS. The composition profile of the PEP–PEE film (volume fraction of PEE block) is shown in the inset. The PS film thicknesses for the sample with $L/D^* = 3.78$ are 1023 Å (adjacent to air) and 900 Å (adjacent to Si) and for the sample with $L/D^* = 3.99$ are 1050 Å (adjacent to air) and 908 Å (adjacent to Si).

straints due to confinement are relieved equally between all the domains in the film. The interfacial widths between the PEP and the PEE blocks were found to be between 58 ± 3 and 72 ± 3 Å and showed no consistent trend as the degree of frustration in the film varied. The width of the PEP microdomain was between 52.2% and 53.0% of the overall domain period for eight samples whose fits were obtained, consistent with the composition $f = 0.54$.

In all the samples, confined between *similar* (PS–PS) and *dissimilar* (PS–Si) hard walls, the films formed an *integral* number of domains (3 or 4). The formation of a half-integral number of domains was not observed in this study, indicating that such a morphology is

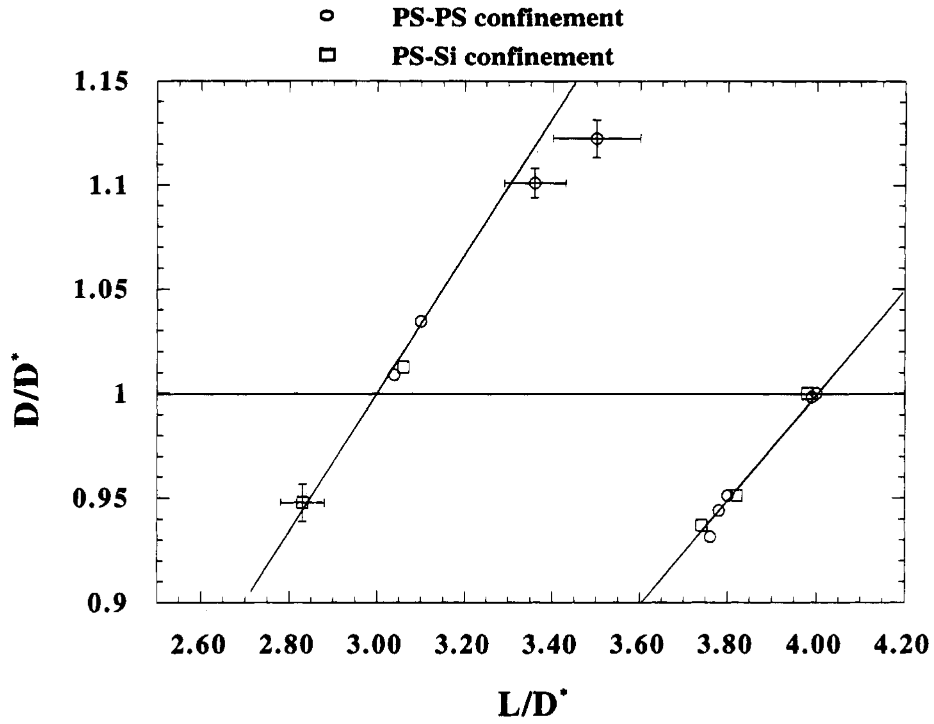

Figure 6. Change in the domain thickness as a function of the film thickness, both normalized with the bulk equilibrium domain spacing D^*, for confinement between two similar (PS–PS) and dissimilar (PS–Si) hard walls. The slanted lines represent the locus of points having single domain spacing in the copolymer, the slope of which is $1/n$, where n is the number of domains.

energetically unfavorable. Furthermore, the PEE block is the wetting component at PS and silicon (and air) interfaces. Enthalpic factors alone cannot explain the segregation of PEE to all the interfaces, viz. PS, silicon, and air. Entropic factors related to the conformational asymmetry between PEP and PEE is the dominant driving force for surface wetting of PEE.[6,7] Issues pertaining to the cause of segregation are discussed in a separate report wherein symmetric wetting of polyolefin block copolymers was found to occur in five different systems.[7] A direct comparison of the results obtained in our confinement studies in this report with Turner's calculations[22] is not possible as contributions from such nonlocal effects have not been considered in this theory. However, an *effective* interfacial energy can be hypothesized that includes contributions from such nonlocal entropic effects. A quantitative description of such a treatment is beyond the scope of this report. Here we simply identify that the strong tendency of PEE to wet the interfaces is due to a reduction in the *effective* interfacial energy arising from the large conformational asymmetry between the PEP and the PEE blocks. We also note that the fact that mechanically stable films with at least 12% domain thickness increase and 6% domain thickness decrease from the equilibrium value (D^*) is supported by entropy-driven wetting in a confined geometry.

A discontinuous first-order-like transition occurs in the number of domains (3–4) for $3.06 \pm 0.02 < L/D^* < 3.74 \pm 0.03$ confined between dissimilar hard walls (PS–Si) (see Figure 3a) and for $3.50 \pm 0.08 < L/D^* < 3.76 \pm 0.03$ confined between similar hard walls (PS–PS) (see Figure 3b). The crossover from 4 contracted domains to 3 expanded domains can be explained on the basis of the differences in the free energies between a film of 3 and 4 domains; at the transition, however, the free energy of the contracted 4 domains must equal to that of the 3 expanded domains. This rationalization is similar to that predicted by Turner's theory.[22] These results are summarized in Figure 6, which shows the change in reduced domain thickness (D/D^*) as a function of the reduced film thickness (L/D^*). The slanted lines represent the locus of points having a single domain spacing in the copolymer in a confined geometry, the slope of which is equal to $1/n$, where n is the number of domains. Clearly, the change in domain thickness is most sensitive to the film thickness when n is small. In the limit of large n ($n \rightarrow \infty$), the change in domain thickness is insensitive to variation in film thickness.

In the study of PS–PMMA block copolymers in confinement, Lambooy *et al.*[14] find that the domain thickness changes with the film thickness and the transition from n contracted to $n - 1$ expanded domains is first-order-like. Similar to the results reported here, formation of asymmetric films is not observed, although in their case this is due to strong polar enthalpic interactions of the PMMA block with the confining layers. Their experimental approach to confinement was somewhat different from this work. The PS–PMMA block copolymer was spun cast on a silicon wafer passivated by an oxide layer, followed by deposition of a buffer layer of PMMA homopolymer over the copolymer. A film of silicon oxide was subsequently evaporated rapidly on the PMMA buffer layer to achieve confinement between "similar" hard walls. The buffer layer guards the diblock copolymer against a degradation during oxide deposition. In our approach, we have shown that a polymer with a glass transition higher than that of the copolymer can act as a hard wall and is effective in suppressing island (or hole) formation that would otherwise occur at the diblock/air interface. In addition, by choice of selective solvents, as we have demonstrated here, simple spin-coating techniques can be used to tailor the specific nature of the confining surfaces.

These findings provide important insights into some of the phenomena observed in block copolymers in the bulk state, such as nonequilibrium domain spacings and order–order transitions. Most small angle scattering experiments on the lamellar phase have been conducted in the strong segregation limit, with solvent-cast samples. Microphase separation occurs in the solvated state and subsequent solvent removal may lead to a mutual entrapment of the microphase-separated grains that have a nonequilibrium domain size, a situation that crudely resembles confinement between hard walls. It is fruitful to point out the differences in confinement effects in bulk and thin films. The aforementioned grains in the bulk state are *microscopic* in size and have *no preferred* orientation unlike in thin films, where the ordering is parallel to the surface. An annealing process can be envisioned in the bulk state, that involves a highly cooperative rearrangement of the grains to obtain the minimum free energy domain spacing. Such a rearrangement would be complicated, involving the movement and annihilation of grain boundaries; these processes would be kinetically limited. However, in thin films, the domain spacings D that are observed, which are different from D^*, are indeed in equilibrium under the constraints of confinement. From the results we have obtained for the thin films in confinement, we simply recognize the phenomenal capability of block copolymers to sustain stretched or contracted conformations and identify that this characteristic of block copolymers could lead to nonequilibrium domain spacings ($D \neq D^*$) in the bulk state, that are difficult or impossible to anneal. The limit of stability for such a compressed (or dilated) lamellae should be evident in mechanical compression experiments with the force applied normal to the plane of the lamellae. Experiments are underway to investigate such effects.

Order–order phase transitions have been observed in certain compositionally off-symmetric diblock copolymers in the bulk state; temperature has been used to access and probe such transition states.[24] At the transition, it is evident that the ensemble of polymer chains reorder by undergoing distortions in chain conformations, and rearrangement, that occur in a highly concerted manner. As we have shown in this report, block copolymers in confinement between hard walls exhibit a remarkable ability to sustain stretched chain conformations (domain thickness). In thin films of certain compositionally off-symmetric diblock copolymers, we speculate that the different extents of frustration caused by confinement can induce or suppress transitions (that are otherwise observed in the bulk), so that the total free energy is minimized. A particularly intriguing example is the lamellar-to-hexagonally modulated lamellar (HML) phase transition that is observed in bulk diblocks, as described by Hamley *et al.*[24] This phase transition, which resembles two-dimensional buckling may be driven by thermally induced reduction of the coil dimensions in PEP–PEE and other polyolefins. In this case, chain rearrangement occurs by in-plane modulation, leading to a partial release of conformational strain between the lamellar and the hexagonal states. We expect that a confining geometry will affect the occurrence of such transitions.

Conclusions

We have demonstrated that the lamellar domain thickness of nearly symmetric PEP–PEE diblock copolymer films, confined between two hard walls, depends on the thickness of the film. In all the cases investigated, the domain thickness adjusted so as to form an integral number of domains. Ordering in the film was always found to be parallel to the surface, regardless of the state of frustration created by the confinement. These results are in qualitative agreement with the theoretical predictions of Shull[21] and Turner.[22] The transition in the number of domains appears to be discontinuous (first-order-like) and always results in a symmetric film with PEE wetting both the confining surfaces. The latter feature is attributed to entropically driven wetting due to conformational asymmetry between the PEP and the PEE blocks.

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