Thin Diblock Copolymer Films on Chemically Heterogeneous Surfaces[†]

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ABSTRACT: We have used scanning force microscopy and transmission electron microscopy to study the microphase separation of P(S-*b*-2VP) block copolymers on chemically structured substrates. Gold was patterned by microcontact printing to form regions of self-assembled alkyl monolayers terminated by $-CH_3$ or −OH. The differences in surface and interfacial energies between the coexisting phases and the boundary surfaces strongly influence the resulting domain structure. We find that excess material accumulates only on layers formed above the H_3C-terminated SAM. For this to happen, single block copolymer molecules diffuse over distances of several micrometers. TEM investigations reveal that the block copolymer is well ordered into lamellae parallel to the substrate over the HO-terminated SAM but that the block copolymer layers on the H_3C-terminated SAM are frequently oriented perpendicular to the substrate. This perpendicular orientation could decrease the edge free energy of the islands that form on this layer.

Introduction

In recent years there has been an increasing interest in the understanding of the influence of boundary surfaces on the morphology of heterogeneous liquids. Generally, the components of a liquid mixture will possess different interfacial energies with a boundary wall. As a consequence, the total free energy of the system can be lowered by accumulating the lower energy component at the boundary surface. In the case of phase-separating mixtures, the effect of the boundary surfaces is even more striking and oscillatory composition profiles are found extending from the boundary surface into the bulk of the sample.[1] While the presence of a boundary obviously influences the surface properties of any heterogeneous bulk sample, thin films are particularly subject to surface effects due to their increased surface-to-volume ratio. Spontaneous formation of multilayers of domains is observed in thin films of phase separating polymer blends. Moreover, the succession of the domains can be influenced by a suitable choice of the boundary surface energies.[2,3]

Similar effects of surface-induced order have been observed in thin films of block copolymers, where two or more polymer chains are covalently linked on a molecular level. The interplay between connectivity and phase separation leads to the formation of microdomains of well-defined molecular size. In the case of symmetric diblock copolymers, lamellar microdomains of thickness L_0 are formed.[4] They can be aligned parallel to the plane of the film by boundary effects. When both boundary surfaces attract the same block, film thicknesses equal to an integer multiple of L_0 result in stable, flat films. Deviations from the quantized thicknesses will lead to the formation of islands or holes in the free surface of the film. When the two boundary surfaces attract different blocks, half-integer multiples of L_0 define the quantized values of film thickness.[5−10]

Up to now, thin film phase separation was studied almost exclusively in the presence of laterally homogeneous surfaces. An interesting situation appears when at least one of the two boundary surfaces has a laterally heterogeneous surface energy. The attraction of different components of the polymer film will be different on neighboring areas of the same surface. The resulting domain structure will be determined by a complex interplay between the different parameters characterizing the structured interface, i.e., the strength of the respective surface attractions, the interfacial energies of the phases of the polymer and the lateral dimensions of the interfacial structure. First experiments of this type were reported for polymer blends deposited onto a line pattern of different chemical composition. The domains were found to line up laterally following the substrate structure.[11] However, a quantitative study of the alignment process has not yet been possible.

In the present paper, we present experiments investigating the domain structure of a diblock copolymer thin film in contact with a chemically patterned substrate surface.

Experimental Section

For our experiments we used poly(styrene-*b*-2vinylpyridine) P(S-*b*-2VP) diblock copolymers with polymerization indices $N_{PS} = 960$, $N_{PVP} = 960$ and $N_{PS} = 510$, $N_{PVP} = 540$, respectively. These will be referred to as 960−960 and 510−540. The PS block of the second polymer was fully deuterated. The polymers were synthesized via anionic polymerization.[12] Patterned self-assembled monolayers (SAMs) were formed by microcontact printing[13] of functionalized alkanethiols on a gold-coated silicon wafer. Lines and grids of H_3C-terminated thiols were transferred onto the Au surface by use of a microfabricated elastomer stamp. The grid allows a straightforward identification of the regions which are covered by H_3C-terminated SAMs (Figure 1). Subsequently, the substrate was immersed into a solution of HO-terminated thiols, allowing this monolayer to form in the empty spaces between the lines of the H_3C-terminated SAM. This procedure should result in a lateral variation of the substrate surface energy between 18[14]

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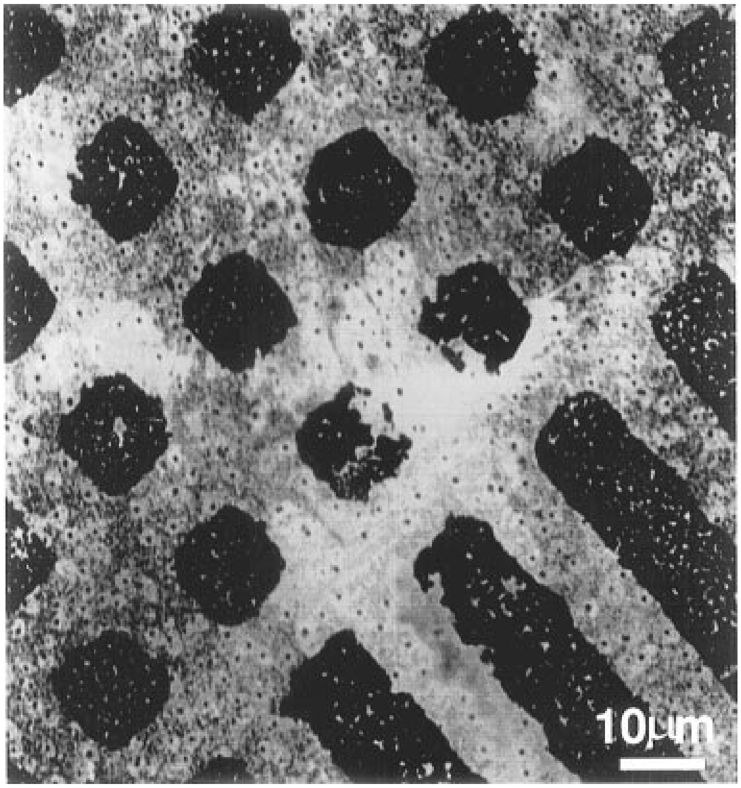

Figure 1. Gold microstructures. An aqueous ferricyanide etch (0.001 M $K_4Fe(CN)_6$, 0.01 M $K_3Fe(CN)_6$, 0.1 M $K_2S_2O_3$, and 1 M KOH)[20] was used after microcontact printing. Gold not protected by the SAMs was removed and the resulting gold microstructures were imaged with an scanning electron microscope (SEM) in backscattering geometry. Light areas correspond to gold; dark areas, to SiO_2.

and 50 mJ m^{-2} [15] on the H_3C-terminated and the HO-terminated regions, respectively. For comparison the surface energies of a native-oxide-covered Si substrate and a stripped Si surface are 36.5 and 44.7 mJ m^{-2},[16] respectively. The width of the lines was varied between 1 and 10 μm. Prior to deposition of the polymer layer, the patterns were imaged by lateral force microscopy.[17]

Thin films of P(S-*b*-2VP) were spun cast onto the patterned substrates from toluene solution. The as cast films were smooth on a nanometer scale. For the 960−960 block copolymer the thickness of the films was varied between 105 and 315 nm. Given an equilibrium lamellar thickness of $L_0 = 70$ nm from the height of the holes and islands, these thicknesses range between $1.5L_0$ and $4.5L_0$. The films were annealed in vacuum at 176 °C for times varying between 4 and 120 h. While island nucleation, growth, and coalescence occurs at early times, a final structure is reached after 6−40 h of annealing, depending on film thickness and grating size. The images we show in Figures 2 and 3 did not change their features after further annealing and in all cases where not otherwise specified, the annealing times chosen were such that the final morphology was achieved. While we discuss our results for the 960−960 diblock copolymer, the same scenario has been found for the 510−540 if the thickness of the films is scaled with respect to their lamellar spacings. This spacing is $L_0 = 55$ nm for the 510−540 diblock copolymer and $L_0 = 70$ nm for the 960−960 diblock copolymer. While we show an image of the 510−540 only in Figure 3, it behaves in all aspects similarly for the 960−960. Given the Flory interaction parameter $\chi \approx 0.1$ for this block copolymer,[18] the annealing temperature is in the strong segregation regime, i.e., well below the order−disorder transition for both block copolymers.

The resulting topography was imaged with scanning force microscopy (SFM) as a function of film thickness. Scanning force microscopy was done with a Nanoscope III SFM from Digital Instruments in contact mode. Experiments were performed with a Si_3N_4 cantilever tip with a nominal force constant of 0.06 N m^{-1}. Forces applied were less than 10^{-9} N. In addition, cross-sectional and plan-view transmission electron microscopy (TEM) micrographs were taken to probe the microstructure of the film. For plan-view TEM the samples were immersed into a 2 mM solution of bromine in methanol. This immersion destroys the gold layer between the polymer film and the silicon substrate, and the film can be easily floated onto deionized water and then picked up with a TEM grid. This procedure provides a "top-down" view of the film. For cross-sectional TEM the samples were sandwiched between a bulk piece of polystyrene and a 10 μm thick PS cover film. Then the PS/P(S-*b*-2VP)/PS sandwich was annealed for 2 min below T_g after which it was microtomed. The PVP was stained by exposure to iodine vapor for 2−6 h to improve contrast in the TEM images.

Results and Discussion

In a first step the microdomain structure of the block copolymer was studied on Au covered silicon substrates coated homogeneously with either H_3C- or HO-terminated thiols. Samples of different thicknesses were annealed at 176 °C for 6 h in vacuum. The surface topography was then imaged with SFM at room temperature. Irrespective of the end groups of the underlying SAM, the films exhibited very similar surface structure. In particular, films with a thickness of $(n + {}^1/_2)L_0$ are flat and featureless, while island and hole structures were observed for films thicker or thinner, respectively, than this quantized value. Since it is known that PS has the lower surface energy, this observation suggests that, in either case, a lamellar structure is formed parallel to the plane of the films, with the PS blocks wetting the vacuum interface and the PVP block wetting the substrate interface. From the surface energies one would expect the H_3C-terminated thiol to attract the less polar PS block rather than the PVP block, but it does not. We shall not pursue this point any further here.

We now turn to the surface morphologies of thin films annealed in the presence of a laterally structured

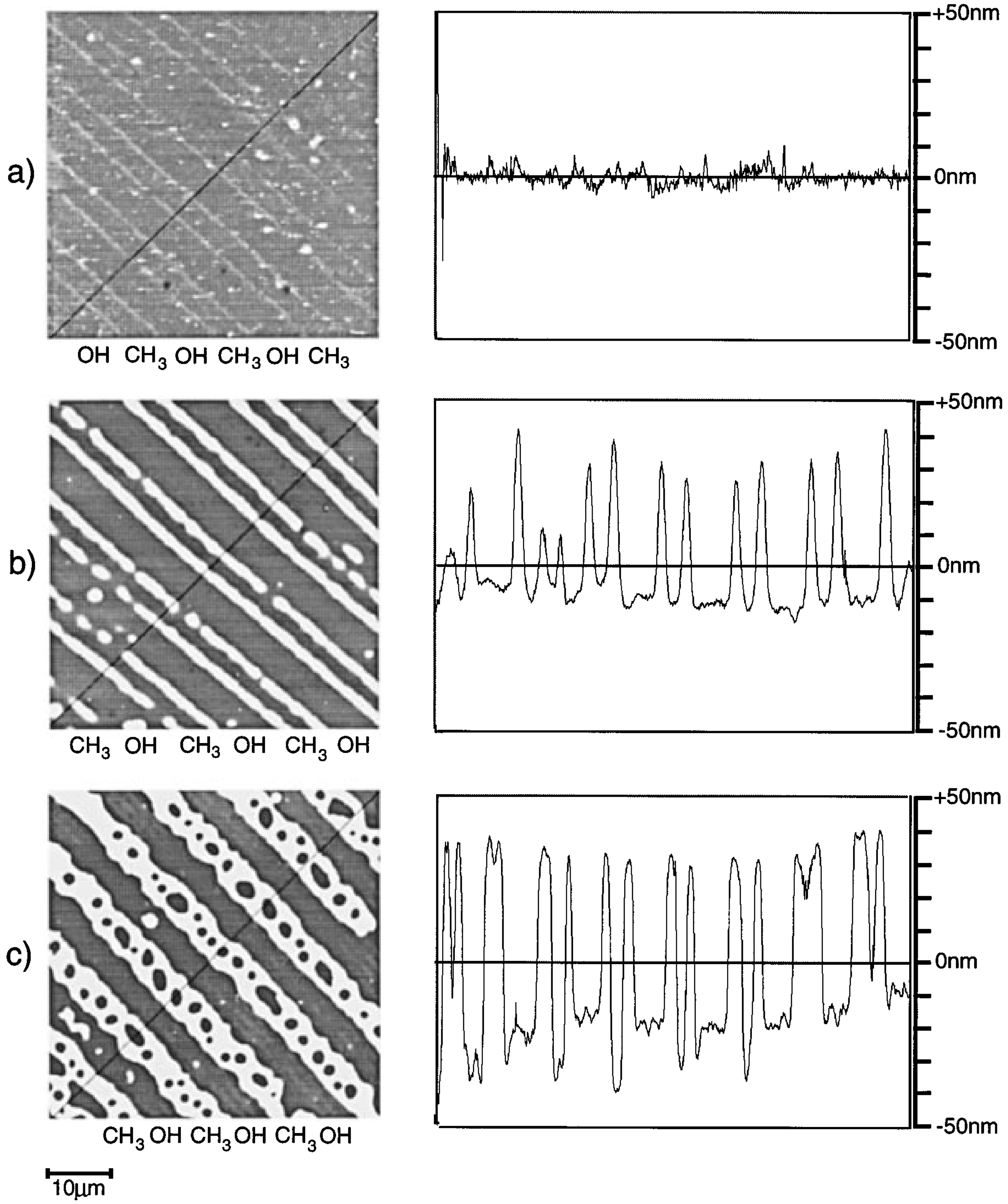

Figure 2. SFM micrographs of 960−960 P(S-*b*-2VP) films of different thicknesses: (a) 106 nm ($\approx 1.5L_0$); (b) 113 nm ($\approx 1.6L_0$); (c) ($\approx 1.8L_0$). The films were annealed for 44 h at 176 °C. The periodicity of the grating is 10 μm. The images show top view SFM images (left) and cross sections (right) taken along the lines indicated in the top view images.

interface. We start with the surface morphology of P(S-*b*-2VP) films with thicknesses around and slightly thicker than $1.5L_0$. Starting with a film of thickness $1.5L_0$ (Figure 2a), the SFM image reveals a rather flat and featureless surface. However, closer inspection shows that the polymer surface appears somewhat rougher on the H_3C-terminated parts of the surface (rms roughness 1.47 nm) compared to a rms roughness of 0.73 nm on the HO-terminated parts. As the film thickness is increased to about $1.6L_0$ (Figure 2b), a characteristic surface morphology has evolved characterized by the accumulation of material in a ridgelike domain located above the boundary lines between the different surface areas. From the cross sections shown in the right hand side of Figure 2, we find that the maximum height of these ridge domains amounts to roughly one lamellar spacing. If we further increase the film thickness to $1.77L_0$ (Figure 2c), a similar surface morphology is observed; however, the ridge-like domains start to grow from the boundary lines into the area above the H_3C-terminated thiol surface. Again, the maximum height of these domains equals one lamellar spacing. In summary, we observe a $2.5L_0$ thick film with isolated holes of depth L_0 on top of the H_3C-terminated SAM, and a $1.5L_0$ thick film with isolated islands on top of the HO-terminated SAM.

As we further increase the film thickness, eventually almost the entire area above the H_3C-terminated SAM

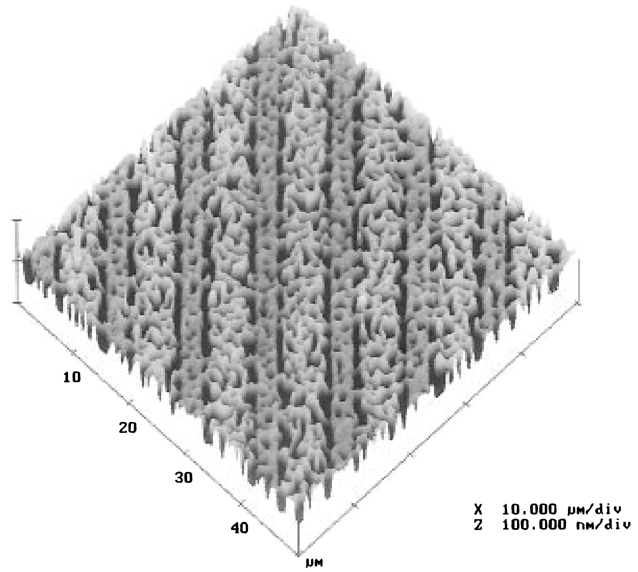

Figure 3. SFM micrograph of a 510−540 P(S-b-2VP) film on a grating of 10 μm periodicity. The film was annealed at 176 °C for 34 h.

is covered with an additional layer of thickness L_0 and islands of the same height are found to develop also above the HO-terminated SAM. As can be seen in Figure 3, for a film of nominal thickness $2.1L_0$, only a few isolated holes appear in the layer (of thickness $2.5L_0$) above the H_3C-terminated SAM, while an interconnected network structure of thickness $2.5L_0$ has formed above the HO-terminated SAM. Both the depth of the holes and the height of the interconnected structure amount to roughly L_0. The same scenario, i.e., accumulation of excess material in the regions above the H_3C-terminated SAM before additional islands are formed above the HO-terminated SAM, is observed for films of nominal thickness between $2.5L_0$ and $3.5L_0$ and $4.5L_0$, respectively (not shown here). We find, however, that the apparent influence of the structured interface on the surface morphology of the film becomes weaker as the film becomes thicker. In particular, the differences between neighboring areas above H_3C- and HO-terminated SAM become less pronounced, and the boundaries between these areas seem to wash out as the film thickness is increased to more than a few lamellae.

Given the experimental results described so far, one may assume that similar to the well-known situation on homogeneous substrates, any material in excess of an integer number of lamellae leads to the formation of lamellar islands on top of an otherwise flat polymer surface. If the excess amounts to more than $L_0/2$, these islands fuse together and holes of depth L_0 are observed. In contrast to the homogeneous substrate situation, however, we observe that the excess material is not distributed randomly over the film surface but accumulates preferentially on top of the copolymer film covering the H_3C-terminated SAM. In particular, it means that single copolymer molecules diffuse over distances of several micrometers to deplete the HO-terminated SAM of their initial uniform film coating. This finding is difficult to understand if we assume that a perfect first lamella is formed irrespective of the underlying substrate surface. Such a lamella would then be terminated by the PS blocks and should result in a laterally homogeneous surface. The laterally inhomogeneous accumulation of parts of a second lamella on such a homogenous surface seems quite unreasonable. We must therefore question whether the near-surface morphology of the polymer film on the structured substrate is indeed characterized by a continuous lamella covering both H_3C- and HO-terminated SAM. As a matter of fact, the observation of slight differences in surface roughness for the $1.5L_0$ thick film indicate that different morphologies may be present on the different surface areas.

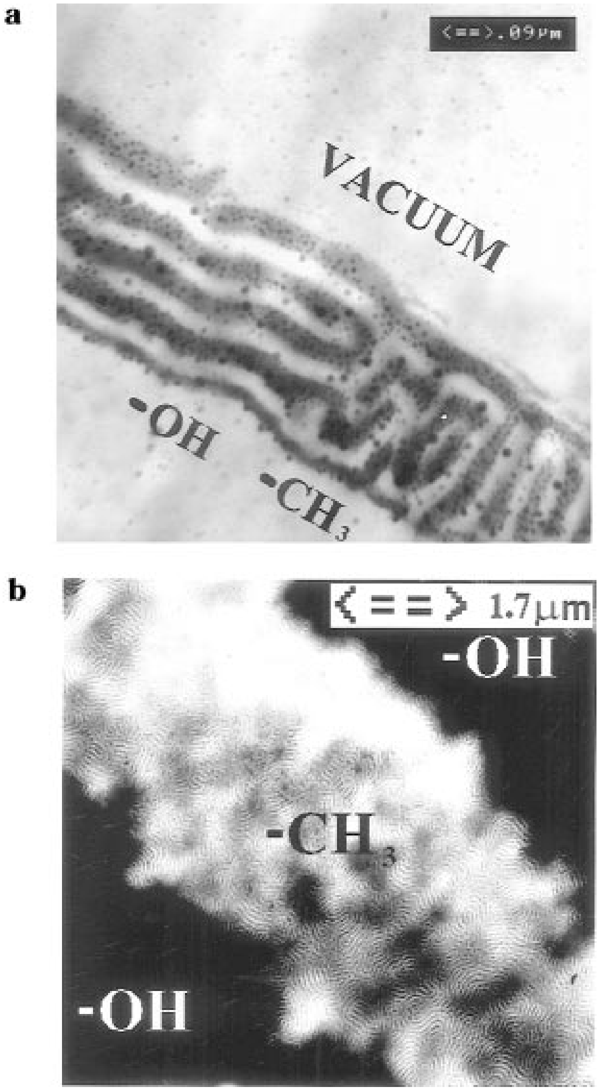

Figure 4. Cross sectional (a) and plan-view (b) TEM micrographs of a 960−960 P(S-b-2VP) diblock copolymer film. The film thickness was 300 nm ($4.3L_0$). The films were annealed at 176 °C for 17 h. Dark regions correspond to the PVP blocks, and bright regions correspond to PS blocks.

To further investigate this issue, we have performed both plan view and cross-sectional TEM investigations of diblock copolymer films which were annealed in the presence of the structured interfaces. Figure 4a shows a cross-sectional TEM micrograph of a 960−960 diblock copolymer film of a thickness around $4.5L_0$. In the image, the PVP domains appear as dark regions while the PS domains appear as bright regions. The microdomain structure is clearly periodic along the plane of the film with a characteristic length given by the periodicity of the underlying substrate structure. Therefore, it is quite straightforward to identify in the TEM micrograph the different regions of the polymer film that were in contact with either H_3C- or HO-terminated SAM during annealing. The different regions are indicated in Figure 4a.

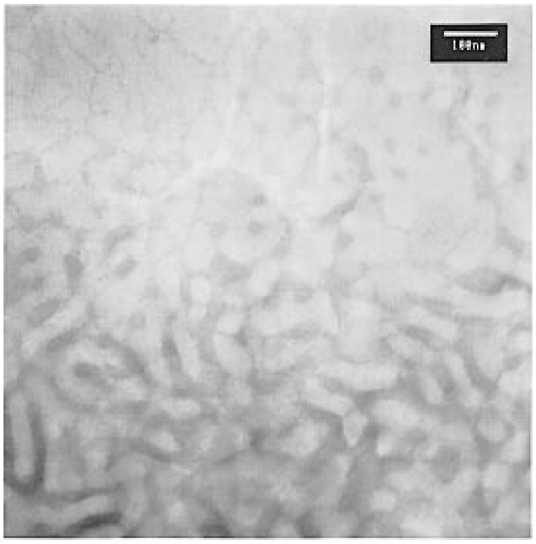

Figure 5. Plan-view TEM micrograph of a 960−960 film of 105 nm thickness ($1.5L_0$) annealed for 17 h at 176 °C on a structured substrate. The section shown is above the H_3C-terminated SAM.

Starting with the regions of the polymer films that were in contact with the HO-terminated areas of the substrate surface, the TEM micrograph clearly reveals that the lamellar microdomains are aligned almost perfectly parallel to the plane of the film. Because the block copolymer was sandwiched in between two polystyrene layers for microtoming, we can not identify from the TEM images the half lamella of PS adsorbed on the vacuum interface, but we can identify the half lamella of PVP adsorbed on the substrate.

The situation is much more complex in the regions of the film which were in contact with the H_3C-terminated substrate areas during annealing. Here, the lamellar microdomains are found to be oriented predominantly perpendicular to the plane of the film. The different morphologies are also revealed in plan-view TEM images (Figure 4b). The regions which were in contact with the HO-terminated SAM appear featureless in agreement with the observation of a nearly perfect alignment of the lamellae parallel to the plane of the film. In contrast, the lamellar structure is clearly revealed in the regions which were in contact with the H_3C-terminated SAM. This result confirms the cross-sectional TEM finding that the microdomains are oriented perpendicular to the plane of the film on the H_3C-terminated SAM.

In thinner films the polymer is no longer able to align its lamellae perpendicular to the H_3C-terminated SAM. As shown in the TEM image in Figure 5, the sheets order now also mostly parallel to the H_3C-terminated SAM, but the alignment is less well developed and the sheets show lots of defects. Plan-view TEM on the same sample in the area of the HO-terminated SAM does not reveal any contrast at all. This corresponds to a perfect alignment of lamellae parallel to the substrate.

The TEM results provide an explanation for the surface morphologies observed with SFM. At the edge of an island, where the thickness can no longer be L_0, the lamellae reorient and show a perpendicular orientation.[19] This high free energy edge structure of an island on a perfectly oriented underlayer may give rise to a chemical potential driving force favoring growth of islands on the less perfectly oriented underlayer over the H_3C-terminated SAM. In fact in the very early stages of annealing we observe that small islands of roughly the same size (less than L_0 high and less than 1 μm in diameter) form over both the H_3C-terminated and HO-terminated SAMs. As the annealing progresses however the islands on the HO-terminated SAM shrink while those on the H_3C-terminated SAM grow, eventually leading to island coalescence on the H_3C-terminated SAM. These results strongly support the hypothesis that it is the free energy of the island edge structures on the two different substrates that drives the very long range transport of block copolymer chains observed on these surfaces.

Conclusion

In conclusion, we have shown how a diblock copolymer responds to a heterogeneous surface during microphase separation. We believe that the perpendicular orientation of the block copolymer lamellae over the H_3C-terminated SAM decreases the edge free energy of the islands that form on that layer over those that form on the parallel lamellae on the HO-terminated substrate, thus providing a chemical potential driving force for transport of individual block copolymer chains over distances of many micrometers on the surface of the block copolymer film.

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