Notes

Lamellar Orientation at the Surface of Thin Block Copolymer Films

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Introduction

The orientation of lamellae in thin films of symmetric block copolymers has received considerable attention in recent years.[1−6] These studies have shown that, under near equilibrium conditions, symmetric diblock copolymers such as poly(styrene-*b*-methyl methacrylate), PS/PMMA, exhibit a strong orientation of the lamellae parallel to the surface of the film. It has also been shown that the orientation occurs at both the air/copolymer and the copolymer/substrate interfaces. The orientation is such that PS is preferentially located at the copolymer/air interface. This is explained by the surface energy of PS, which is slightly less than that of PMMA. The surface-induced orientation in solution-cast films was also found to be independent of the thickness of the film.[3] Therefore, under near equilibrium conditions, no lateral lamellar structures can be observed at the surface of diblock copolymers. Previous scanning force microscope studies (SFM) on symmetric PS-*b*-PMMA diblock copolymers show that the lamellae are aligned parallel to the surface and the height difference between adjacent terraces has the dimension of a copolymer bilayer.[4] It has been shown that between terraces, lamellae can align perpendicular to the surface. Since the lamellae must reorient at the lower and higher terraces, each step contains two twist boundaries.[4] This implies that, under near equilibrium conditions, surface perpendicular lamellae can only be observed as defect structures, which are located at lamellar terraces. Surface perpendicular lamellae can be induced by confining films between two rigid surfaces.[5] If there is no preferential adsorption at all, lamellae can be oriented perpendicular to the interfaces. Thickness-induced morphology changes in lamellar diblock copolymer films have been investigated recently by T. M. Morkved and H. M. Jaeger.[6] They have shown that a morphology change from lamellar domains parallel to the substrate to perpendicular domains appears to be unique to a thickness of one lamellar repeat spacing and low annealing temperatures.[6] Contrary, when the thickness is bigger than one lamellar period, the lowest energy structure is always one with lamellae oriented parallel to the *free surface* (polymer−air interface) of the film.

However, the preparation of films under solvent evaporation conditions from solvents that preferentially solvate one of the components may induce an oriented nonequilibrium morphology, in which lamellae are aligned perpendicular to the surface. These nonequilibrium morphologies, which are rapidly lost upon annealing, are not the issue of the present article.

Recently,[7,8] thin films of triblock copolymers such as PS-*b*-PB-*b*-PMMA have been prepared, which can form ordered lateral nanostructures in such a way that, under equilibrium conditions, the lamellae are aligned perpendicular to the surface. Such films not only are of interest as objects for nanotechnological applications but also can be an important addition to study the structural and local mechanical properties of triblock copolymer films, in which all three components are present at the free surface. In the triblock copolymer SBM6, the formation of surface perpendicular lamellae has been observed for the first time.[7,8] SBM6 is nearly symmetric with respect to the PS and PMMA end blocks with a short center block of about 6% PB. The morphology of SBM6 was established by transmission electron microscopy (TEM)[8−11] and scanning force microscopy (SFM).[7,8] As deduced from TEM, SBM6 forms a lamellar-spherical structure, in which PB spheres are located at the lamellar PS/PMMA interface, separated by two alternating periodicities.

In this note we report a scanning force microscope (SFM) study of annealed films of SBM6. The lamellar orientation is analyzed and compared to results on PS/PMMA diblock copolymers reported in the literature.[1−6]

Experimental Section

Materials. The poly(styrene-*b*-butadiene-*b*-methyl methacrylate) triblock copolymer SBM6 was kindly provided by Prof. Dr. R. Stadler, University Bayreuth, FRG. Synthesis and characterization of SBM6 is described elsewhere.[9−11] It has a molecular weight of 225 000 with a polydispersity of 1.11.

Sample Preparation. Films of SBM6 with a thickness in the range between 2 and 20 μm were cast from chloroform solution (10% w/v) on glass cover slides by slowly evaporating the solvent at 25 °C over a period of 1 week. The films were dried at reduced pressure (10^{-2} mbar) for 24 h at 100 °C. To reach equilibrium conditions, the dried films were annealed at reduced pressure (10^{-2} mbar) for 48 h at 160 °C. For SFM analysis, no staining or sectioning was necessary, contrary to the preparation for TEM.

Scanning Force Microscopy. The SFM experiments were carried out with a Nanoscope III (Digital Instruments, Inc., Santa Barbara, CA) in the tapping mode,[13] where the cantilever is oscillated close to its resonance. The change of the vertical cantilever oscillation amplitude is detected, which is caused by the interaction of the tip with the surface. Silicon cantilevers (length 125 μm, width 30 μm, thickness 3−5 μm) with a spring constant between 17 and 64 N/m and a resonance frequency in the range of 240−320 kHz were used. The

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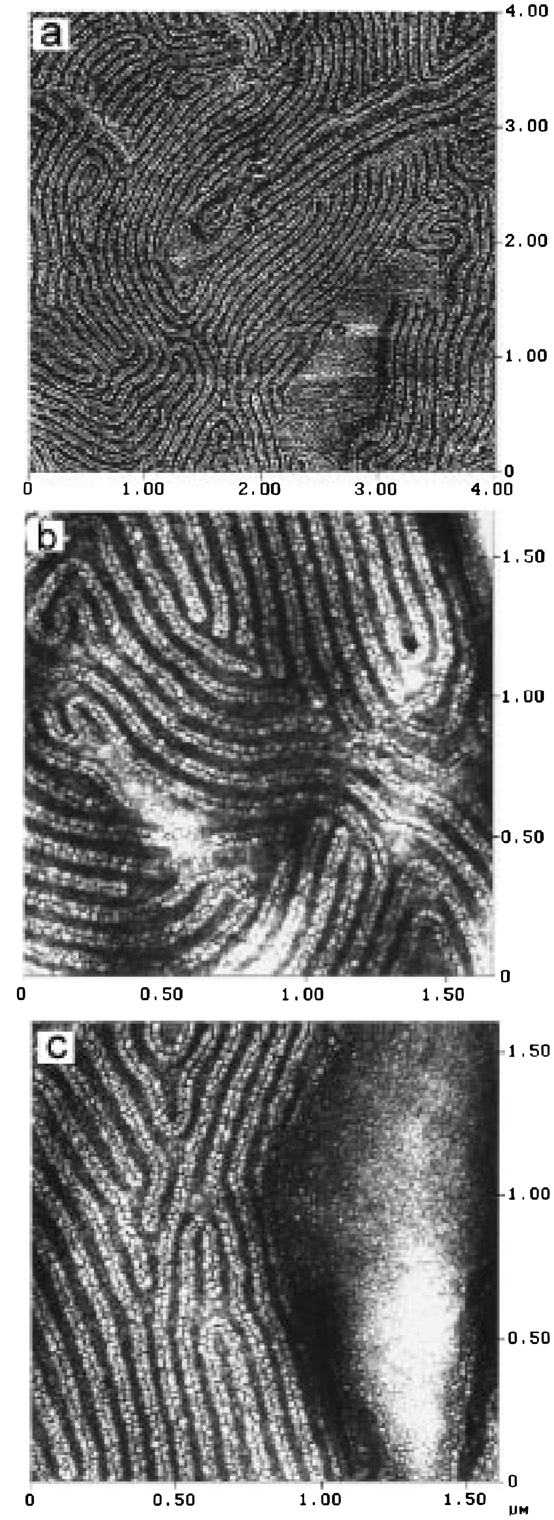

Figure 1. SFM images of thin films of the triblock copolymer SBM6. (a) Phase image, 4 µm × 4 µm, *z*-scale 10°. The PS/PMMA lamellae are mainly oriented perpendicular to the free surface. Only small areas, in which the lamellae are oriented parallel to the observed surface, are visible (lower right in 1). (b) Height image, 1.7 µm × 1.7 µm, *z*-scale 8 nm. PB spheroids are located at the PS/PMMA lamellar interface. The diameter of spheres is about 14 nm. (c) Height image, 1.7 µm × 1.7 µm, *z*-scale 8 nm. Lamellar orientation perpendicular (left) and parallel (right) to the observed surface.

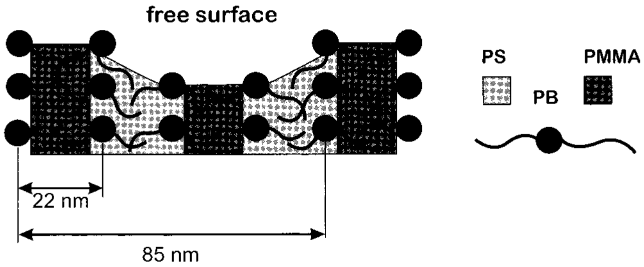

Figure 2. Structural model of the surface reconstructed morphology of the triblock copolymer SPM6 (cross sectional model, side view, molecules are drawn schematically). The vertical shift of neighboring lamellae leads to a characteristic surface profile. This results in a "buckling" of the polymer film at the free surface. The outermost lamellae (dark shaded) are pronounced in SFM. The resulting periodicity at the surface of 85 ± 5 nm is twice the bulk lamellar long period (missing row reconstruction).

cantilever was excited below the free resonance frequency in air at an amplitude of about 10−20 nm. Imaging was performed by displaying the height signal (output of the feedback signal) and the phase signal (phase lag of the cantilever oscillation relative to the driver). Phase images (Figure 1a) and height images (Figure 1b,c) are presented. No filtering techniques were necessary.

Results

Scanning force microscopy (SFM) images of thin films of SBM6 are shown in Figure 1a−c. It should be mentioned that Figure 1a displays more than a particularly well ordered region. It shows the characteristic structure of SBM6, which can be found at any place in the sample. The lamellae are mainly oriented perpendicular to the observed free surface. The overall lamellar long period is 85 ± 5 nm. The surface morphology shows a large number of defects such as lamellar bends and disclinations.

At higher magnification (Figure 1b) polybutadiene PB spheres are visible, which are located at the lamellar PS/PMMA interfaces. The small PB midblocks act as "marker", indicating the phase boundaries between PS and PMMA lamellae. The estimated size of the PB spheres is about 14 nm. The PB spheroids are separated by two alternating periodicities of 22 ± 5 and 63 ± 5 nm. The two alternating periodicities can be explained by a vertical shift of alternating PS and PMMA lamellae. This "surface buckling" is explained in ref 8. A schematic representation of the surface buckling is given in Figure 2.

The large scale SFM image in Figure 1a shows another remarkable feature. Small surface areas exist (i.e., lower right in Figure 1a), in which the lamellae are oriented parallel to the surface. A zoomed region of such an area is shown in Figure 1c. The left part of Figure 1c displays surface perpendicular lamellae, as shown in Figure 1b. In the right part of the image (Figure 1c), the PB blocks can be recognized as small spheroids that are not organized as rows. These small surface areas are attributed to lamellae, which are oriented parallel to the observed surface.

Discussion

The observed surface structure, where the PS/PMMA lamellae are perpendicular to the surface is induced by the small PB midblocks. The surface energies γ of the three components are different (γ_{PS} 40.7, γ_{PB} 25−32, γ_{PMMA} 41.1 mNm^{-1}).[2,12] The lowest surface energy block PB tends to create a free surface contact. As a result, PB spheres always occupy the free surface. Since the small PB blocks are tightly connected between the PS and PMMA end blocks, they cannot undergo large scale phase separation. Then, during film formation, both end blocks are drawn to the free surface. A PS/PMMA interface is formed, which is aligned perpendicular to the free surface. The result is a structure where all three components are present at the polymer/air interface. In our case it is a sequence of alternating PS and PMMA lamellae perpendicular to the surface of the film. Experiments have shown that this orientation is stable upon annealing at 180 °C. The influence of solvent evaporation on film formation has been discussed elsewhere.[7−8]

Surface parallel lamellae occur only as defects (i.e., lower right part in Figure 1a or right part in Figure 1c). This structure may be supported by underlying PS/PMMA lamellae, which are oriented parallel to the observed surface. In this case, the low surface energy of the PB midblock would induce a miscibility of the two end blocks PS and PMMA, which are weakly incompatible in comparison to the PS/PB and PB/PMMA pairs, respectively. In this case it is the minimization of the surface free energy that leads to a thin outermost PB layer, and the PS and PMMA blocks are forced to become miscible in the near surface region. It should be mentioned that these regions are small.

Conclusion

It has been shown that, under near equilibrium conditions, surface perpendicular lamellae are a characteristic feature of PS-*b*-PB-*b*-PMMA triblock copolymers, in which a low surface energy block is connected between the end blocks. In contrast, in diblock copolymers one may observe lamellar structures perpendicular to the surface; these structures are kinetically controlled, and a nonequilibrium structure is frozen in.

Triblock copolymers, when adsorbed from solution, can form ordered lateral nanostructures on a solid substrate, which are stable upon annealing. Such materials may provide supramolecular structures required for nanotechnological applications.

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