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Ordering Phenomena in Thin Block Copolymer Films Studied Using Atomic Force Microscopy

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ABSTRACT: Ordering phenomena in block copolymers have attracted much theoretical and experimental attention. Most work focuses on lamellar mesophases. We have used atomic force microscopy to study cylindrical mesophase formation in thin films of a commercial styrene–butadiene–styrene (SBS) block copolymer. Complex ordering phenomena occur during annealing. We have found that the orientation of polystyrene cylinders depends on the film thickness. For films that are thinner than two repeat distances the orientation is consistently found to be perpendicular to the surface. Parallel orientations can only exist at specific values of the thickness. If the average thickness of the film is not compatible with the repeat distance, the film develops microscopic variations in thickness such that the thicker regions are an integer of the repeat distance. In the thinner regions, the cylinders orient perpendicular to the surface.

Introduction

Block copolymers comprise two or more blocks of chemically different monomers. If the blocks are sufficiently large and the interactions between them sufficiently adverse, the blocks will segregate.[1,2] Since the blocks are connected, they can only segregate on a microscopic scale. For example, an AB diblock copolymer with A and B blocks of equal molecular weight will form a mesophase structure of A and B lamellae. The thickness of the lamellae is commensurate with the size of the polymer coil. Other structures are formed if the amounts of A and B material are not comparable. Typically, for A contents in the range 20–40%, the A material forms cylinders in a B matrix, and for lower A contents the A blocks form isolated spheres. If the molecular weight distributions of the A and B blocks are small, these spheres and cylinders are ordered into regular lattices.[1,2]

A particularly interesting type of block copolymer is the ABA triblock copolymer where A constitutes a thermoplastic material (e.g. polystyrene) and B an elastomer (e.g. polybutadiene), with A contents in the range 10–40%. These materials find widespread application as so-called thermoplastic elastomers.[2] The individual polymer chains will generally have their thermoplastic end blocks in different domains. At temperatures below the melting point or glass transition temperature of the thermoplastic blocks, these domains effectively act as cross-links for the elastomeric B matrix. The material behaves as a vulcanized rubber in many respects, while at high temperatures the material may be processed with standard thermoplastic processing techniques such as extrusion and injection molding. No vulcanizing steps are needed, and production scrap may be recycled.

It will be clear that the mesophase structure plays a key role in determining the properties of this material.[2] The traditional way of visualizing these small (10 nm scale) structures is by transmission electron microscopy (TEM) of stained samples. In a recent study of styrene block copolymers, it was shown that atomic force microscopy (AFM), operated in the tapping mode, can also be used for this purpose.[3] The AFM samples need only be reasonably flat and can be used as such, without the need for special preparation techniques (such as staining) to enhance contrast. The hard (polystyrene) domains manifest as regions with an apparent lower thickness.[3]

It should be noted here that the origin of the apparent thickness variations is not obvious. In tapping mode AFM, the cantilever is driven to oscillate at a fixed frequency close to resonance (around 300 kHz) and at a fixed power input. The detection system measures the amplitude A of the cantilever oscillations. The tip of the cantilever is then lowered until a fixed, predetermined decrease ΔA of the amplitude is measured. The surface structures that are recorded during a two-dimensional scan are thus "iso-ΔA surfaces". If the various surface elements had identical interactions with the cantilever tip, the iso-ΔA surface would correspond to the actual thickness. However, if the interactions are different, the translation to physical thickness variations cannot be made. We have found previously that the hard polystyrene domains manifest themselves as regions with an apparent lower thickness.[3] A possible explanation for this effect is the fact that the rubbery phase, being above its glass transition temperature, has been able to relax by expanding out of the surface of the film. This would lead to "true" thickness variations. Another explanation is to assume a topographically flat film with rubbery domains that are better able to absorb energy than the polystyrene domain. Hence the tip has to come closer to the polystyrene domains than to the rubbery domains in order to get the same energy loss (i.e. ΔA). In constant force mode AFM of styrene–butadiene diblock copolymers it was observed[4] that the apparent thickness of the rubbery domains is lower which is consistent with their lower hardness.

Previous experiments on thin diblock copolymer films with a lamellar mesophase have shown that the lamellae orient parallel to the surface if there is a specific preference of one of the blocks for the substrate surface.[5] Generally, the film thickness will be incompatible with the lamellar repeat distance. It has been experimentally observed that such films form high-lying plateaus (hills) and low-lying plateaus (valleys) during annealing, such that in both the hills and the valleys the thickness of the film is an integer or half-integer of the lamellar repeat distance.[5–8] In a recent theoretical paper[9] it was

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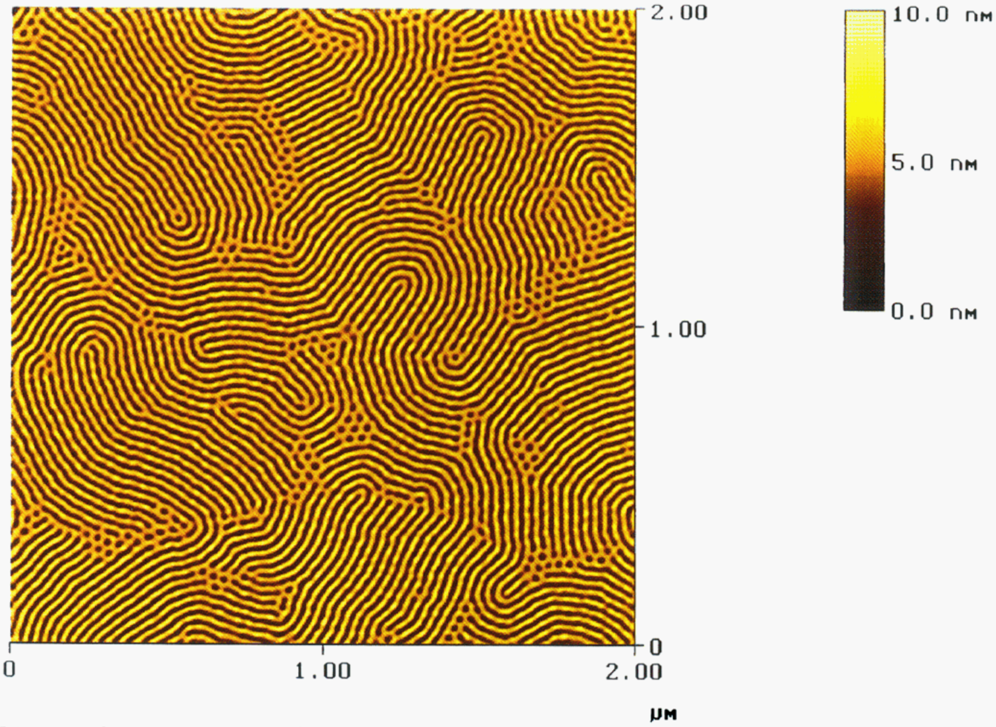

Figure 1. AFM image of a 140 nm thick film of KRATON D-1102C, spin-coated on a silicon wafer. The color height scale is indicated.

shown that the equilibrium structure of a very thin confined symmetric diblock copolymer may be one in which the lamellae are oriented perpendicular to the surface. Confinement implies that hills and valleys cannot be formed.

The interfacial energy effect seems to be less applicable for cylindrical mesophases where it is not possible to cover the entire substrate with one of the components. In this paper we report on the observation of a number of interesting ordering phenomena in spin-coated films of a commercial styrene–butadiene–styrene (SBS) triblock copolymer (KRATON D-1102C, produced by Shell Chemicals Europe).

Experimental Section

Kraton D-1102C is a commercial SBS triblock copolymer that was obtained from Shell Chemicals Europe. It contains about 29% by weight polystyrene, which is equivalent to about 24% by volume. Previous TEM and small-angle X-ray scattering (SAXS) experiments[10,11] have shown that the mesophase structure of KRATON D-1102 consists of hexagonally-ordered polystyrene cylinders. We prepared thin films of KRATON D-1102C by spin coating a solution in toluene on 2.5 in. silica wafers. By varying the spin rate and the concentration of the polymer solution, one can alter the thickness of the film. As toluene is a good solvent for polystyrene as well as for polybutadiene, solvent effects play no role for the initial structure. Spin rates varied between 1000 and 9000 rpm, and solution concentrations between 1 and 3% w. Film thickness values were measured by optical ellipsometry and ranged from 40 to 150 nm. All samples were annealed under vacuum at 115 °C for 96 h. Annealing is essential to obtain well-developed structures. The silica wafers were used as purchased without any special treatment other then rinsing with toluene just prior to spin coating.

All AFM images were recorded with a Nanoscope III from Digital Instruments, operated in the tapping mode in air using microfabricated cantilevers with a spring constant of 30 N m^{-1}. For analysis of the observed surface structures the Nanoscope image processing software was used. Images could be corrected for sample tilt and Fourier filtered to remove low-frequency noise.

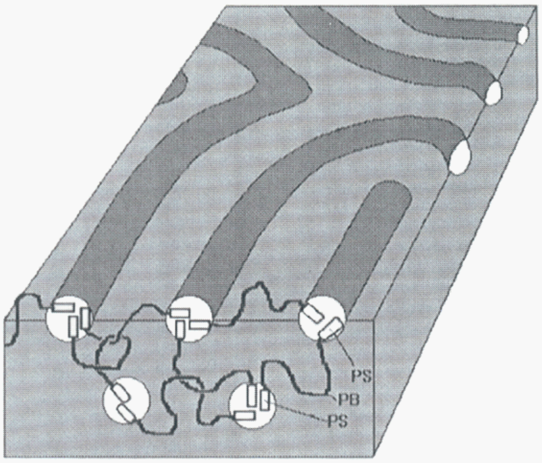

Figure 2. Schematic illustration of the cylindrical domain structure, oriented parallel to the surface, of a polystyrene (PS)–polybutadiene (PB)–polystyrene triblock copolymer.

Results

Figure 1 shows an AFM image of a relatively thick (140 ± 2 nm) sample. As expected, we observe a cylindrical mesophase. In Figure 2 we have schematically illustrated the cylindrical domain structure at the surface of such a triblock copolymer and its relation to the individual polymer chains. The polystyrene cylinders are predominantly oriented parallel to the surface, with a few small areas having a perpendicular orientation. The repeat distance between the cylinders was determined from a power spectrum (Fourier transform) of the image to be 31.1 ± 0.6 nm. Figure 3 shows an AFM image of a thin (42 ± 1 nm) sample for which an entirely different structure is observed. The ordered cylinders are all oriented perpendicular to the surface. Figure 4 is a 2D Fourier power spectrum of the upper left quadrant of the (unfiltered) image corresponding to Figure 3. A hexagonally-ordered structure is clearly manifested. The repeat distance is found to be 31.1 ± 0.5 nm, which is in excellent agreement with the value

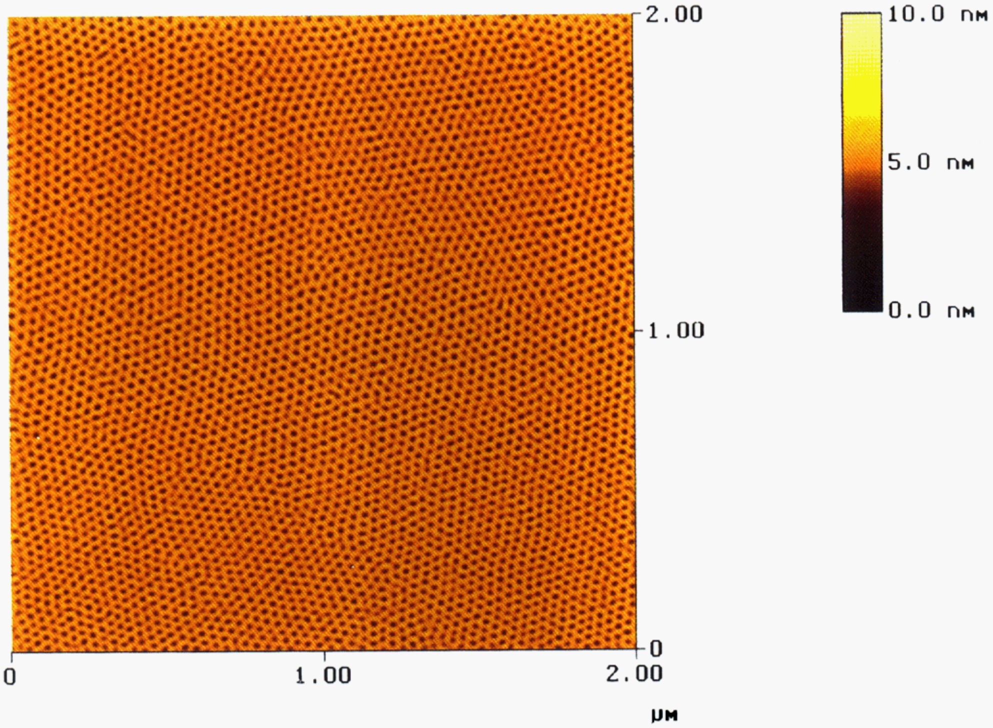

Figure 3. AFM image of a 42 nm thick film of KRATON D-1102C, spin-coated on a silicon wafer. The color height scale is indicated.

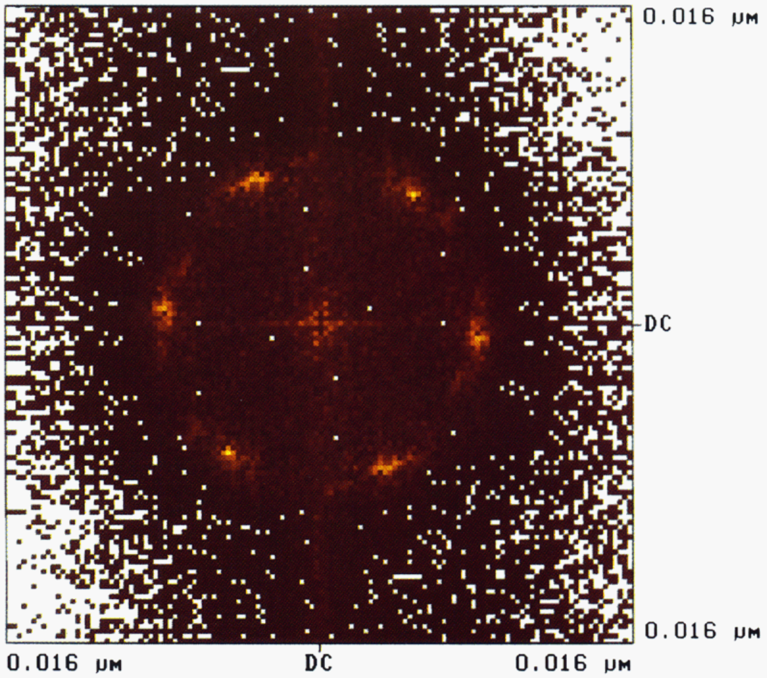

Figure 4. 2-Dimensional Fourier transform power spectrum of the upper right quadrant of Figure 2.

found for the primarily parallel-oriented structures in Figure 1.

Figure 5 shows the AFM image of a sample with intermediate thickness (49 ± 1 nm). Here regions of both mesophase orientations are observed. It should be noted that all AFM pictures have been "flattened" and Fourier filtered. The flattening is done by subtracting a first-order surface, representing height variations related to a possible tilt of the sample. The Fourier filtering typically removes large scale height variations, which are much larger than sizes typical of mesophases. The unfiltered versions of Figures 1 and 3 look similar to the unfiltered images but contain more noise. This is not the case for Figure 5 where the unfiltered images show the presence of micron-sized structures of different thicknesses. Figure 6 shows an AFM image of an unfiltered larger scan of the same sample; the scan of Figure 5 is indicated by a square. The large scale variations in thickness that are removed by the Fourier filtering can be clearly observed, as can a direct correlation between local thickness and mesophase structure. On the hills, the cylinders are oriented parallel to the surface and in the valleys orientation is perpendicular to the surface. This is fully in line with the observations relating to Figures 1 and 3.

Figure 7 is a 3-dimensional image of the structure at the boundaries between the hills and valleys. One observes cylinders diving from the hill into the surface

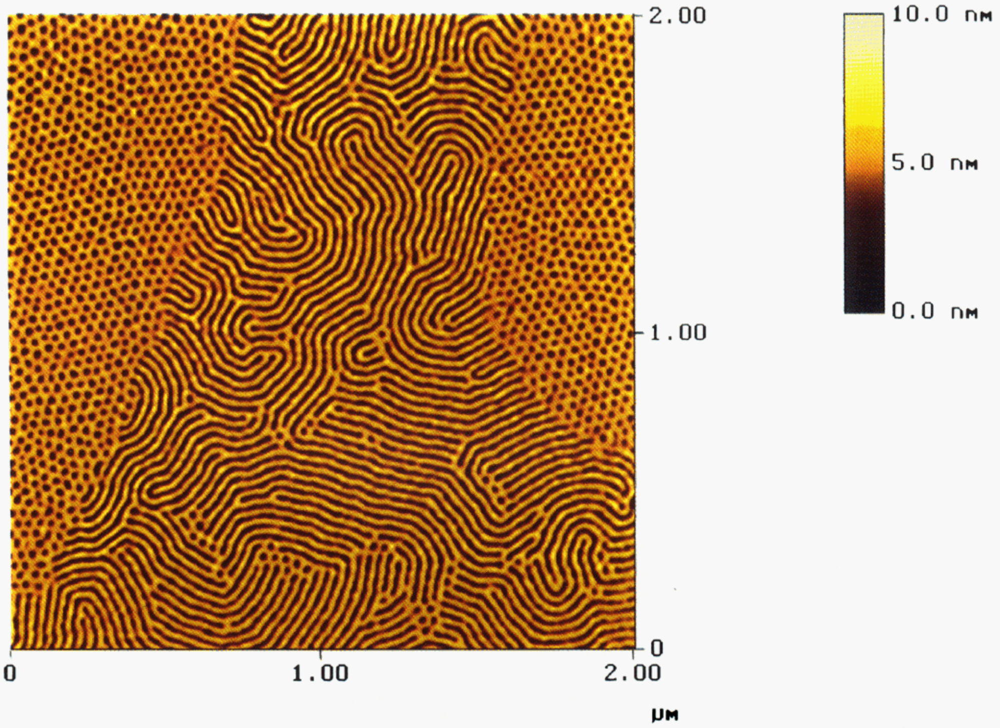

Figure 5. AFM image of a film of KRATON D-1102C, spin-coated on a silicon wafer with an average thickness of 49 nm. The color height scale is indicated.

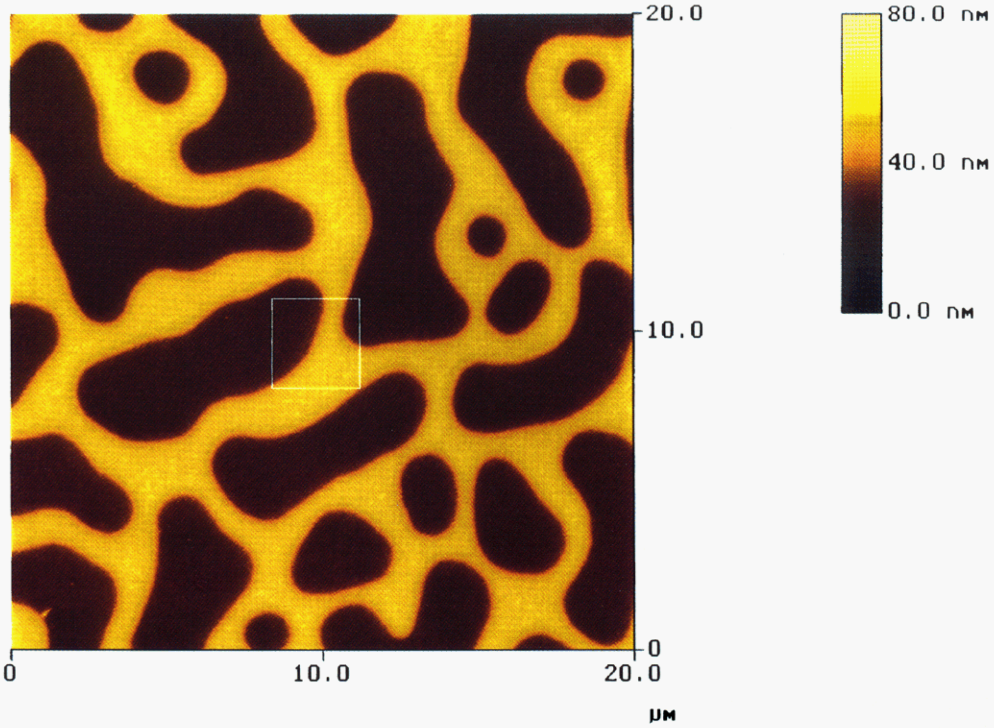

Figure 6. AFM image of an unfiltered large scan. The scan of Figure 5 is indicated by the white square. Note that the color height scale is different from that of Figures 1, 3, and 5.

to a perpendicular orientation. These cylinders take part in the hexagonal ordering in the valleys. Figure 7 also illustrates the high degree of detail that can be achieved by AFM techniques.

Hills and valleys are relatively flat and of constant thickness. This shows that the ordering mechanism is related to special values of the thickness. The average thickness of the film was 49 ± 1 nm. From a large 100 × 100 μm scan we estimate the surface fraction of hills to be about 42 ± 1%. The hills are 25 ± 2 nm above the valleys. From these data we derive the absolute film thicknesses in the hills and the valleys: we obtain respectively 64 and 39 nm with an estimated uncertainty of 2 nm. Within this rather narrow experimental error, the thickness of the hills corresponds exactly to two repeat distances.

Discussion

We explain these observations as follows. In relatively thin films that are only up to a few mesophase repeat distances thick, the presence of bottom and top surfaces imposes an orientation on the mesophase structure such that these surfaces are planes of symmetry. This implies that the orientation of the cylinders

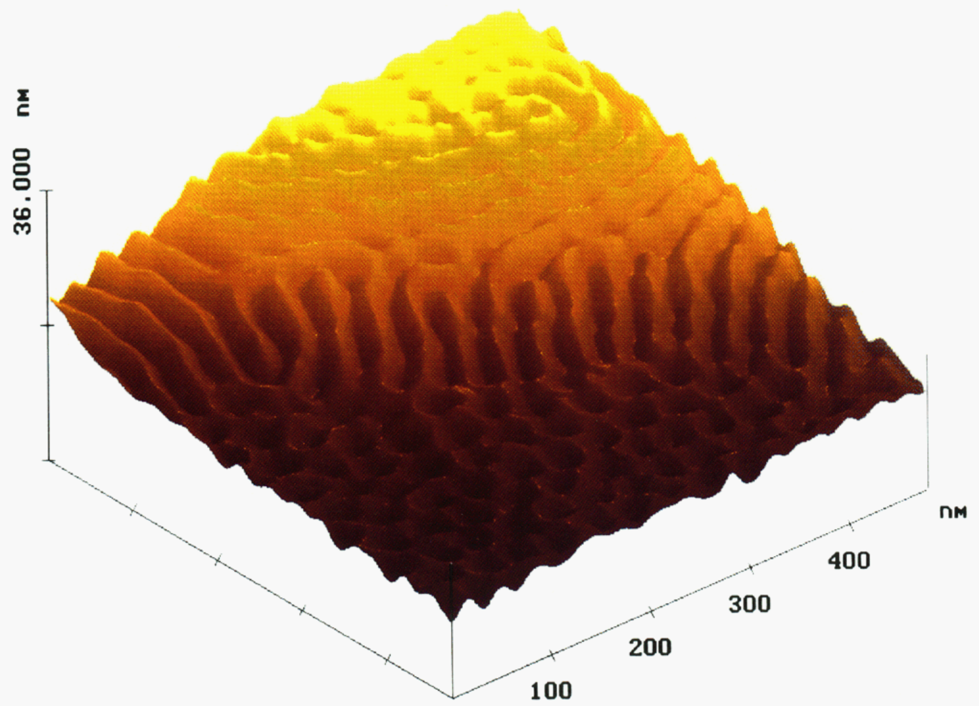

Figure 7. 3-Dimensional image of the film structure at the transition between thick and thin areas (as in Figure 5).

must be parallel or perpendicular to the surface. The parallel orientation is thermodynamically preferred because of the two degrees of orientational freedom compared to one for the perpendicular orientation. In thick films the incompatibility of the film thickness with the cylindrical repeat distance can be distributed over many layers. If the film thickness is of the order of (but not exactly equal to) just a few repeat distances, the structure would become overly distorted with respect to the bulk equilibrium structure. A parallel orientation would cost too much polymer chain configurational freedom. Therefore the equilibrium mesophase structure of very thin films is one in which the cylinders are oriented perpendicular to the surface, such that the equilibrium repeat distances can be maintained. A quantitative theory of this concept would involve surface energy effects and the thermodynamic effects of non-matching interdomain distances in parallel structures and end caps in perpendicular structures.

If the average film thickness is not much less than 2–3 repeat distances, a surface structure of micron scale hills and valleys develops during annealing such that in the higher regions the thickness is equal to an integer number of repeat distances. Here the cylinders orient parallel to the surface. In the lower regions, however, the cylinders orient perpendicular to the surface. The development of these surface structures is similar to what has been observed for lamellar diblock systems.[5–8] Observations on nonlamellar systems are rare. A sample of PS–PB diblocks with 15 vol % PB showed surface damage when scanned by constant force AFM.[4] Thin films of poly(ethene–propene)/polybutene diblock copolymers[12] with a cylindrical polybutene mesophase did not show formation of hills and valleys in contrast to the samples with a lamellar mesophase. The cylinders of poly(vinylpyridine) (PVP) in a PVP–PS–PVP triblock film (24 vol % PVP) were shown (by TEM) to orient parallel to the substrate.[13] Hills and valleys were also observed. Due to the strong interaction of PVP with the silicium oxide surface of the substrate, an almost pure PVP layer was formed at the substrate.

The relation between volume fraction Φ, radius R, and repeat distance L of hexagonally-ordered cylinders is given by

$$\Phi = {}^{2}/_{3}\pi\sqrt{3}(R/L)^2$$

With $L = 31$ nm and $\Phi = 0.24$ one obtains $R = 8.0$ nm. Using standard image analysis techniques we can estimate the surface fraction and average radius of the black cylinders in Figure 3. This gives $\Phi = 0.27 \pm 0.03$ and $R = 8.4 \pm 0.5$ nm. These values are in good agreement with the theoretically expected values and indicate that the black areas indeed correspond to the polystyrene cylinders.

The methods described in this paper provide a convenient way to observe mesophase topology. The use of different film thicknesses produces parallel and perpendicular orientations, such that the structure may be adequately determined. The development of hills and valleys on the surface may be used as a model for the 2-dimensional coarsening processes.[7,14] The possibility of determining domain dimensions with high accuracy can be used to test theoretical models of mesophase formation.

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