Templated Self-Assembly of Block Copolymers: Effect of Substrate Topography**

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It is widely assumed that self-assembly will be the basis of an extensive range of applications in nanotechnology,[1] and self-assembled systems are expected to become increasingly valuable for the fabrication of nanoscale or molecularly-based devices. One important class of self-assembly consists of systems in which organized patterns or structures with a characteristic length scale form spontaneously, for instance by spinodal decomposition or by island, micelle or domain formation. These self-assembling systems, by themselves, typically produce structures that lack long-range order and contain a population of uncontrolled defects. However, long-range order can be imposed if self-assembly takes place on a template or guide,[2–8] a process described as templated self-assembly.

Block copolymers are well-known examples of self-assembling systems, in which chemically distinct blocks microphase-separate into the periodic domains. The domains can adopt a variety of morphologies (lamellar, double gyroid, cylindrical, or spherical) and length-scales, depending on the polymer chemistry and molecular weight.[9] Self-assembled block copolymer domain structures have been used as masks to pattern high-density silica, germanium, and other microelectronic and magnetic materials.[10–13] Many practical applications such as patterned magnetic recording media require nanostructures with precise positions.[14] Here, we show how templated self-assembly can be achieved in a block copolymer using a pre-patterned substrate, to obtain arrays of domains with long-range order. Significantly, the confinement width of the patterned substrate is an order of magnitude larger than the domain size of the polymer, and thus templated self-assembly makes it possible to control the location of nanoscale features using considerably coarser substrate features, producing hierarchical structures. In particular, we have investigated the importance of the commensurability between the period of the block copolymers and the period of the template.

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Substrates with topographical features or chemical heterogeneities have previously been used to influence the position and/or orientation of block copolymer domains.[5–8] Substrates with shallow steps separated by distances of several micrometers have been shown to lead to long-range ordering of a spherical-morphology polystyrene–polyvinylpyridine block copolymer, in which ordered areas up to two hundred domains wide were created perpendicular to the steps.[5] In this system, since the length-scale of the template is very large compared to the domain size, the effects of incommensurability are negligible, and defects result primarily from entropic effects. In comparison, at the opposite extreme of template length-scale, lamellar domains in polystyrene–polymethylmethacrylate have been oriented perpendicular to the film plane by using chemically heterogeneous stripes formed lithographically on a substrate, provided that the stripe width is very similar to the width of the lamellar domains.[6,7] Defects in the lamellar domain structure are observed when there is a mismatch between the period of the substrate pattern and that of the block copolymer. In other experiments, thin films of lamellar-morphology block copolymers have been confined within a few times the natural domain spacing by two rigid plates. The lamellar periodicity deviates from the bulk value to satisfy the boundary conditions imposed by the confining surfaces.[8] These experiments show that the domain morphology, periodicity and ordering of self-assembled block copolymers can be influenced by substrate features, but to date there has been no direct observation of how block copolymers behave when templated by in-plane substrate features with characteristic sizes of a few times the domain period. In this work, we will describe the behavior of a spherical-morphology block copolymer in various topographical confinements, in particular the effects of incommensurability, and we will demonstrate the use of template features to deliberately introduce defects in the ordered domain arrays.

A polystyrene (PS)-*block*-polyferrocenyldimethylsilane (PFS) block copolymer[15] was chosen, in which the organometallic PFS forms spherical domains within a PS matrix. The molecular weight was 32 kg mol^{-1} for the PS and 10 kg mol^{-1} for the PFS, corresponding to 20 vol.-% of PFS. The choice of an organic–organometallic block copolymer leads to high etch-selectivity between the two blocks, enabling direct structural analysis.[13,16] The substrates consisted of thermally-oxidized silicon, patterned with square-wave profile grooves of 50 nm depth using interference lithography and reactive ion etching. The grooves had a period of 400 nm, and their widths were varied between 200 and 270 nm. The block copolymer was spin-cast from a 1.5 wt.-% toluene solution to form a conformal coverage on the gratings, and then annealed at 140 °C for typically 48 h to obtain good phase separation. The anneal resulted in the block copolymer film residing only within the valleys of the substrates.[17] The film was etched by an oxygen plasma to remove the exposed PS, which revealed the spatial arrangement of the PFS spherical domains.[13] Results from secondary ion-mass spectroscopy suggest that there is a PFS wetting layer next to the substrate. In addition, cross-sectional

scanning electron microscopy (SEM) images of partially etched films demonstrate that the annealed film consists of a monolayer of PFS spheres and a ~ 10 nm thick brush layer with PFS molecules wetting the silica substrate, as shown schematically in Figure 1b.

Figure 1a shows an SEM plan-view image of the PFS domains on a smooth substrate, after annealing and etching. Its associated pair-distribution function (PDF) is shown in Fig-
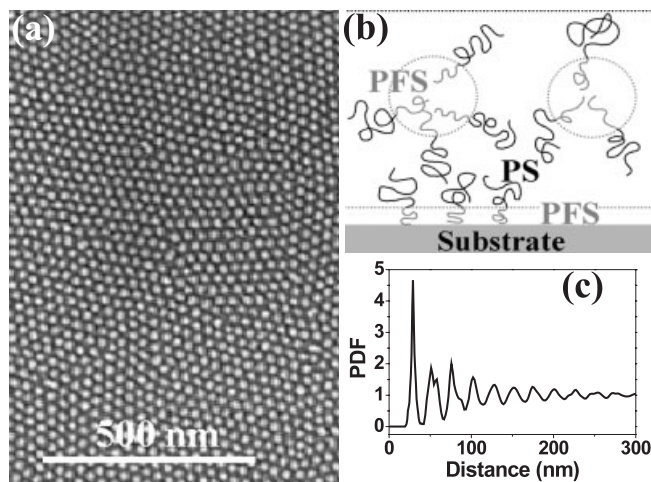

Fig. 1. PS-PFS polymer spin-coated onto a smooth silica surface. a) SEM image of PFS spherical domains. b) Schematic of the arrangement of the polymer chains in the domains and at the silica surface. c) Pair distribution function calculated from the SEM image.

ure 1c. The first peak in the PDF indicates that the distance between first-nearest neighbors, or the averaged center-to-center spacing of the domains, is $a_o = 28.6$ nm. The PFS spheres show short-range ordering with a 280 nm correlation length. Within the correlation length, the spheres are close-packed with a sixfold symmetry. The spacing between parallel close-packed rows is $d_o = (a_o/2)\sqrt{3} = 24.8$ nm.

In contrast, Figure 2a shows the domain morphology for the same polymer but now confined within a 233 nm wide shallow groove. Again, a monolayer of spheres is formed, but now 9 rows of spheres are oriented parallel to the sides of the groove to give a well-ordered, close-packed array. Also, a brush layer is found both at the bottom and sidewall of the silica grooves. The rows of spheres faithfully follow the variations in groove width, conforming to the sidewall variations. The number of rows of spheres is plotted vs. groove width in Figure 2b. The groove width is expressed in terms of the corresponding number of ideal block copolymer periods. The number of ideal periods is calculated as (groove width minus the thickness of the brush layers) divided by the equilibrium row width d_o (24.8 nm). The width is measured as an average over a groove length of 400 nm. The number of rows is quantized, for example, 9 rows are found in grooves with widths between 8.25 and 9.25 ideal periods, then this jumps to 10 rows for widths of 9.25 to 10.25 ideal periods. The periodicity of the block copolymer domains is compressed or expanded in order to comply with the groove width. When the groove
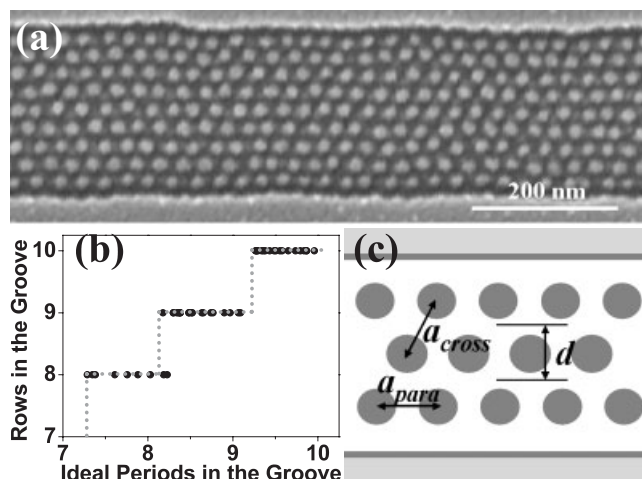

Fig. 2. PS-PFS polymer confined within grooves in a silica substrate. a) SEM image of a section of one groove, showing 9 rows of PFS spheres. b) The number of rows in the groove vs. groove width, showing the widths at which 8, 9, or 10 rows are stable. The groove width is expressed in terms of how many rows would ideally fit within the groove, calculated from the equilibrium row spacing. c) Schematic of the structure showing the row spacing d and the domain spacings a_{para} and a_{cross}.

width is incommensurate with the ideal period, it is apparently easier to accommodate an additional row such that the domain array is on average slightly compressed. This represents an interesting comparison with the vertical confinement of a lamellar system where, for instance, 9 parallel lamellae were found if the film thickness was held within the range from 8.5 to 9.5 periods.[8] The formation of a well ordered array for all the groove widths shown in Figure 2b may also be compared with the case of hard spheres packed within grooves, where incommensurability between the sphere diameter and groove width leads to a loss in ordering.[4]

The preferential wetting layer on the vertical sidewalls of the groove is assumed to drive the domain ordering,[18] and generates a gradient in the domain spacing and domain size. First, the center-to-center spacing of the PFS spheres is no longer the same in the direction parallel to the groove (a_{para}) and in the direction across the groove (a_{cross}), shown in Figure 2c. The averaged spacing a_{para} is 29.3 ± 0.3 nm, slightly larger than the averaged center-to-center spacing a_o found for the film on the smooth substrate. Second, the spacing d of rows parallel to the grooves is not uniform across the groove. Figure 3a shows how the row spacing d varies across the groove width for grooves of different widths. Clearly, the row spacing is smaller near the sides of the grooves, and expands to a nearly uniform value near the center of the grooves. The rows at the center of the groove are compressed or expanded compared to the equilibrium spacing (indicated by the dotted line at $d_o = 24.8$ nm). Grooves with 8 or 10 rows also show this structural gradient. In comparison, the rows within a 466 nm wide groove show the same reduced spacing near the groove edge, but away from the groove edge the row spacing approaches d_o.

The reduction in the row spacing near the groove edges is also associated with a change in the size of the PFS spheres.
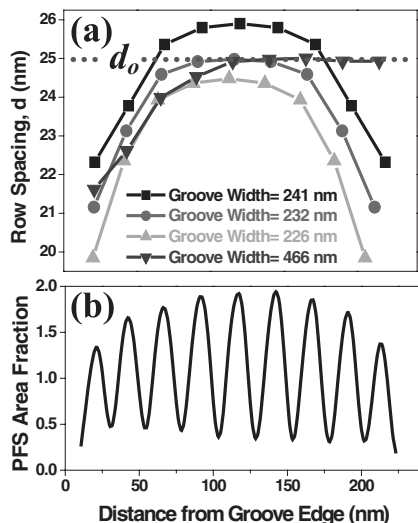
Fig. 3. a) The row spacing d for each of the rows of domains, in four different grooves. In each case the rows are more closely spaced near the groove edges. Three of the grooves, with widths 226, 232, and 241 nm, contain exactly 9 rows of domains. The fourth groove is much wider, but still shows a smaller row spacing near the edge. The dotted line shows the equilibrium row spacing d_o, on a smooth substrate. b) The PFS domain area fraction (arbitrary units) across a 232 nm wide groove. The size of the PFS spheres is smaller near the edges of the groove and larger at the center of the groove.

Notably, the two rows closest to the groove steps show a significant reduction in sphere diameter compared to spheres at the center of the rows. From Figure 3b, the sphere area within the edge row is 75 % of that of the center row and the diameter is 85 % of that of the center row. By following the evolution of the domain structure with annealing time, we observe initially that small domains form and grow to a stable size over a few hours. Subsequent annealing leads to improvements in the ordering of the domains but not to changes in their size. This implies that the observed non-uniform domain sizes and row spacings are in fact equilibrium states for the confined polymer, rather than being kinetically trapped features. The size and spacing variation at the groove edges is believed to be related to the presence of the PFS wetting layer at the vertical sidewalls which decreases the concentration of PFS blocks available for domain formation in the vicinity of the step edge. This indicates that the surface chemistry of the confinement edges affects domain spacing over several periods, and can be used to induce gradients in the spacing and size of self-assembled structures. More uniform domain size and spacing may be expected when using a substrate preferentially wetted by the majority block. Therefore, by adjusting the confinement width, surface chemistry of the substrate, and molecular weight of the block copolymer, a range of gradient features can be designed and fabricated with templated block copolymers, which is difficult to achieve with assembly of hard spheres.

The topographical confinement described here not only controls the row spacings and feature dimensions of templated block copolymers, but also induces defect formation in the block copolymer arrays. Point defects (i.e., missing domains) and point edge dislocations (i.e., a change in the num-

ber of domain rows within the groove) can be purposefully generated in the close-packed arrays by the sidewall features of the grooves. A sharp edge feature such as a small protrusion causes a local vacancy (a missing domain) as shown in Figure 4a. This locally pins the position of the sphere array and suggests a convenient means for aligning the lateral posi-
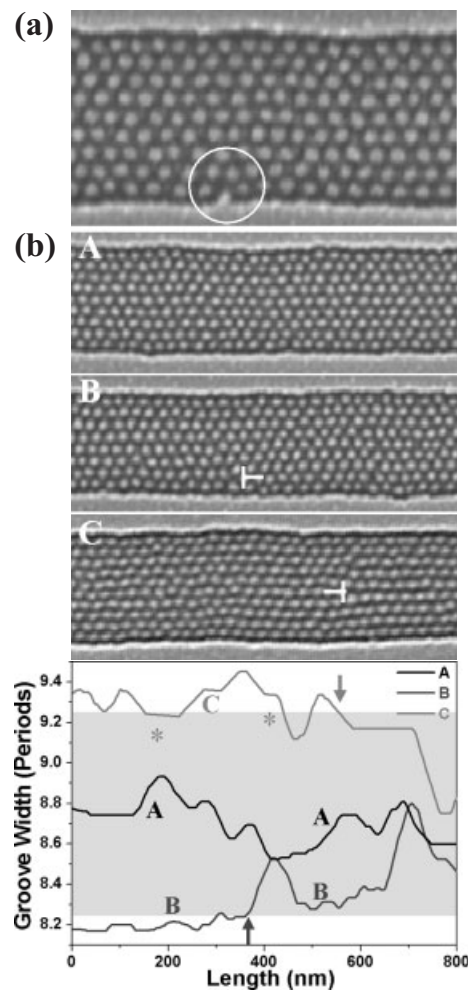

Fig. 4. a) A point defect (a missing domain) forms where there is a small, sharp protrusion at the groove edge, but the overall array is undisturbed. b) Three grooves, A, B, and C, showing how the number of domain rows adapts to changes in groove width. The lower plot shows groove width along the length of each groove. The shaded region represents the groove widths at which 9 rows form. In B and C, dislocations accompany a change in the number of rows, from 8 to 9 in B, and 10 to 9 in C, associated with changes in groove width.

tion of the array. To pin the array structure, the radius of curvature of the edge feature must be in the same range as the domain size, less than about 50 nm in this polymer. A blunt edge feature with a larger radius of curvature perturbs the block copolymer arrangement as a long-range effect. In the presence of a blunt edge feature, the block copolymer array can either expand or contract to maintain an ordered arrangement, or dislocations can be generated to change the number of rows and accommodate the variation in groove width. Figure 4b shows polymers in three grooves along with a corresponding plot of the groove width vs. distance along the

groove. In groove A, 9 ordered rows of spheres form regardless of the variation of the groove width, because the groove width remains within the ideal 8.25–9.25 periods (shown shaded), where a 9 row structure is stable. In groove B, as the width increases gradually from 8.15 to 8.8 ideal periods, the number of rows increases from 8 to 9 via the formation of a defect (a dislocation) at the location where the groove width enters the shaded region (marked by an arrow). In groove C, the groove width decreases gradually, and the number of rows changes from 10 to 9 with the formation of a dislocation, at the position marked with the arrow. There are other places, e.g., the position marked with a star, at which the width of groove C briefly enters the 9-row region, but the system does not change to 9 rows, presumably because the strain energy associated with the formation of two additional dislocations would exceed the energy penalty from the non-equilibrium number of rows over such a short distance. This behavior is reminiscent of that seen in lattice-matched films growing on substrates, in which the film can grow epitaxially up to a certain critical thickness, at which point strain-relieving dislocations can nucleate.[19]

In conclusion, topographical confinement is seen to template the formation of nanoscale domains in a PS-PFS block copolymer, leading to a quantized number of rows within a groove. Unlike the packing of hard spheres,[3,4] the block copolymer system behaves elastically and can conform to various groove widths, leading to arrays with tunable row spacings that depend on the commensurability between the groove and the ideal polymer period. The variation in domain size and spacing across the groove, believed to be a result of interfacial interaction, can be used to make gradient nanostructures. The rows of domains conform to the sidewall variations, with the rows exhibiting a high correlation to the sidewall profile. The tolerance of domain alignment to roughness in the sidewalls of the topographical template is important in using templated self-assembly for nanofabrication, since it is typically difficult to prepare topographical templates with perfectly smooth edges. Small-scale, abrupt sidewall features can lead to defects such as vacancies (missing spheres), which can be used to pin the lateral position of the array, while longer-range changes in groove width lead to dislocation formation. By utilizing this behavior, tailored periodic arrays or defect-engineered structures can be created by design of the topographical features. Significantly, the requisite template periodicity is an order of magnitude larger than the domain size of the polymer, allowing control of the location of nanoscale features using considerably coarser substrate features. Such hierarchical structures can have applications in fields such as photonics or microfluidics, especially given the ability to precisely position engineered defects and periodicity in the structures.[20,21]

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Synthesis of Ordered Mesoporous Carbon with Bimodal Pore System and High Pore Volume

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Mesoporous carbons, which possess the properties of thermal stability, high resistance to acid and base, and biocompatibility, are very attractive for applications in many areas, such as adsorption of dyes, purification of water, catalysis and as

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