Cylinder Alignment in Annular Structures of Microphase-Separated Polystyrene-*b*-Poly(methyl methacrylate)

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We present a novel and simple method for generating micron-scale annular structures formed from polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) diblock copolymer on a silicon oxide substrate. This method is based on prewetting of the underlying substrate with a minor polar solvent before spin-casting of the diblock solution. When using this procedure, we also see, using atomic force microscopy, a unique alignment effect which occurs in the cylinder-forming microdomains of PS-*b*-PMMA annuli without the aid of an external alignment field. These aligned microdomains, with controlled nanometer-scale spacing and coherence on the order of microns, facilitate the ongoing exploration of self-organizing nanofabricated surfaces.

Introduction

Microphase separation occurs in diblock copolymer thin films in directions both perpendicular and parallel to the underlying support substrate due to the immiscibility and differential wetting properties associated with the two components of these fascinating materials.[1,2] Microphase separation creates islands and holes via film thickness quantization[3] in the direction perpendicular to the substrate while, under carefully balanced thermodynamic conditions,[4] microphase separation can also expose both polymer components to the air/polymer interface in the direction parallel to the substrate. This latter phenomenon can generate spacially periodic microdomains consisting of the different chemical constituents of the diblock, whose scale and geometry reflect the chemical and physical properties of the polymer. The repeat spacing of such microdomains can be precisely controlled on the nanometer scale by changing, for example, the molecular weight of the diblock copolymer.

One of the strategic goals for these self-organizing materials is to experimentally control the perfection of the resulting nanostructures, leading to their utilization in a variety of fundamental and technological applications including electron transport in confined and periodic geometries. For example, the controllable architectures of these materials may lead to their use in electronic and magnetic nanostructures via selective decoration of individual diblock components[5] with either conductive or magnetic nanoparticles. Another potential application of these periodic diblock microdomains is in nanolithography.[6,7] These efforts are currently hindered by the lack of long-range order in these soft materials, induced by the presence of topological defects such as dislocations and disclinations; that is, the persistence lengths of the spontaneously formed microdomains are limited by the presence of structural defects.[8−10] Various methods have been developed to circumvent this problem, including the use of either externally applied electric[11−14] or shear[15] fields, or controlled solvent evaporation[16] to induce alignment of the microdomains.

In this Letter we introduce a new and simple spin-casting method which produces annular structures from cylinder-forming polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) which exhibit a high degree of long-range, that is, micron-length, microdomain spatial coherence with radial alignment. Using this procedure, microdomain alignment is achieved without the application of any externally applied guiding fields. The system chosen for these experiments was PS-*b*-PMMA supported on a silicon oxide substrate. This combination is known to produce thin films suitable for nanotemplating applications; that is, both diblock components are exposed to the air/polymer interface,[4] thereby providing sites for subsequent selective chemical reaction on the nanometer scale. We address the microphase separation charateristics of these annuli in directions perpendicular and parallel to the substrate; these latter findings are of particular interest, as these structures exhibit a remarkable degree of microdomain alignment clearly visible in the cylinders which form when using these new procedures.

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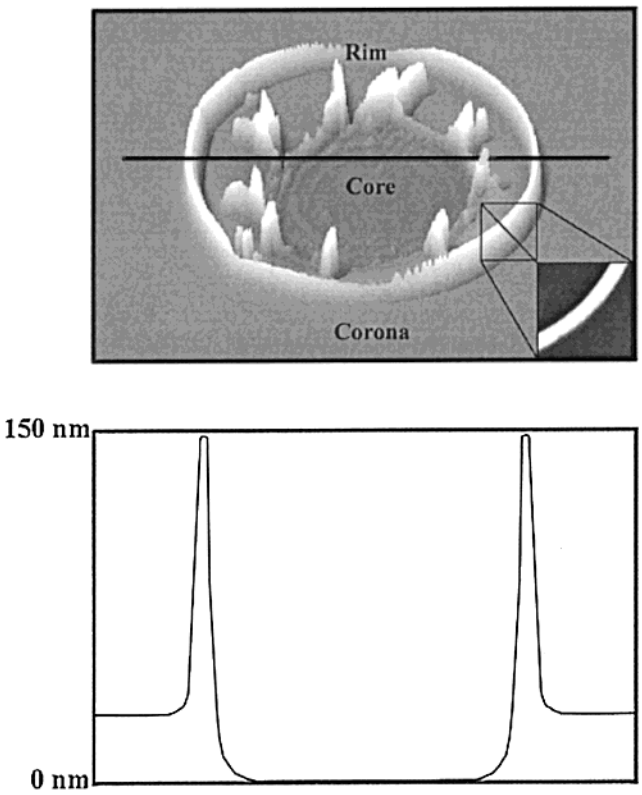

Figure 1. 35 μm × 35 μm AFM image which shows the topology of an annulus before the film is thermally annealed. The image appears rectangular, as a tilted view was used to accentuate the annulus. The 25 μm ring contains three regions: a core, an annular rim, and a corona region. The rim is 3 μm in width and 150 nm in height. An illustrative cross-sectional height map along the solid profile line (35 μm in length) in the AFM image shows only smooth height gradations; that is, no height quantization has occurred. Island and hole height profiles in the core region are not shown. The inset shows a 7 μm × 7 μm AFM image to demonstrate the smooth topology in the rim region.

Experimental Section

The PS-*b*-PMMA used herein was 74% PS by weight, with a molecular weight of 84 000 g/mol and a polydispersity of 1.08. Thin diblock films were prepared on silicon oxide substrates via spin-casting from a toluene solution, as described in detail in our previous papers.[4,8] As before, we have spun-cast diblock films of average thickness 50 nm from a 2% (w/w) diblock/toluene solution. In the current study, one significant modification to the earlier procedure was made in which the underlying support was intentionally prewet with a drop of a "minor" polar solvent. This drop ($\sim$ 5 μL) was placed on the center of the substrate, which was briefly spun for a few seconds to spread the drop uniformly on the substrate and to remove excess solution. This was followed by prompt addition of the diblock copolymer/toluene solution, thus minimizing evaporation of the minor solvent. (No annuli formation was observed when the minor solvent was allowed to fully evaporate before subsequent spin-casting of the diblock solution.) The diblock solution was then spin-coated at 3500 rpm for 1 min. Methanol and acetone were each successfully used as the minor solvent. Subsequent sample thermal annealing was carried out at 513 K for 24 h under an argon atmosphere. Atomic force microscopy (AFM) measurements were then conducted to examine the resulting microphase separation behavior of the diblock copolymer. Contact-mode AFM imaging was performed with a silicon probe tip (applied force 1 nN) using a Topometrix Discoverer.

Results and Discussion

Annuli readily form with an average diameter of 20 μm, ranging from approximately 10−30 μm in size. The annuli density for the conditions used in the study was 40 annuli per 2.5 × 10^5 $\mu$$m^2$. Each ring has three regions: a core (film region inside the rim), the rim itself, and a corona (film region outside of the rim). The average film thickness, as determined by ellipsometry, was 50 nm. Before annealing, we observe only smooth structures which have no microphase separation in any region; that is, no discrete height gradations are observed in the film, as shown in the schematic height map in Figure 1. A rim thus formed is typically 150−200 nm in height and 3−4 μm in width. The mechanistic origin of rim formation has been studied by Brochard-Wyart and co-workers by investigating hole growth (dewetting) of polymer films on nonwettable solid substrates.[17] They have seen the formation of a rim when the radius of a hole reaches a critical value where the threshold radius is determined by factors such as the monomer size and the number of monomer segments in the polymerized material. In analogy to the above mechanism, it may well be that the role of the minor solvent in our experiments is to cause enhanced dewetting of the diblock film from the substrate, leading to annulus formation.

Thermal annealing leads to clearly resolved height quantization due to the wetting properties and mutual

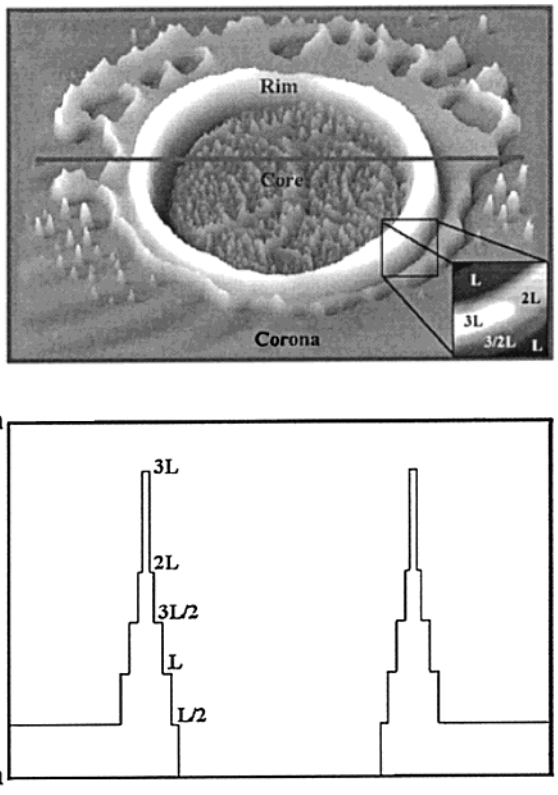

Figure 2. 35 μm × 35 μm AFM image of a 21 μm diameter annulus after thermal treatment at 513 K for 24 h. The image appears rectangular, as a tilted view was used to accentuate the annulus. The irregular topology present in the core region before annealing (Figure 1) is absent after the annealing treatment, leaving only islands and holes. Annealing leads to rim width expansion and rim height contraction, in this instance to 5.5 μm and 130 nm, respectively. This annealing procedure allows the polymer chains to achieve equilibrium heights for each polymer layer. The cross-sectional height map of the ring topology (measured along the 35 μm profile line) clearly shows quantized height gradations. Island and hole height profiles in the core region are not shown. Height quantization occurs for both odd and even multiples of $L/2$ where L is 43 nm. The inset shows a 7 μm × 7 μm AFM image to demonstrate that height quantization has occurred in the rim region after annealing.

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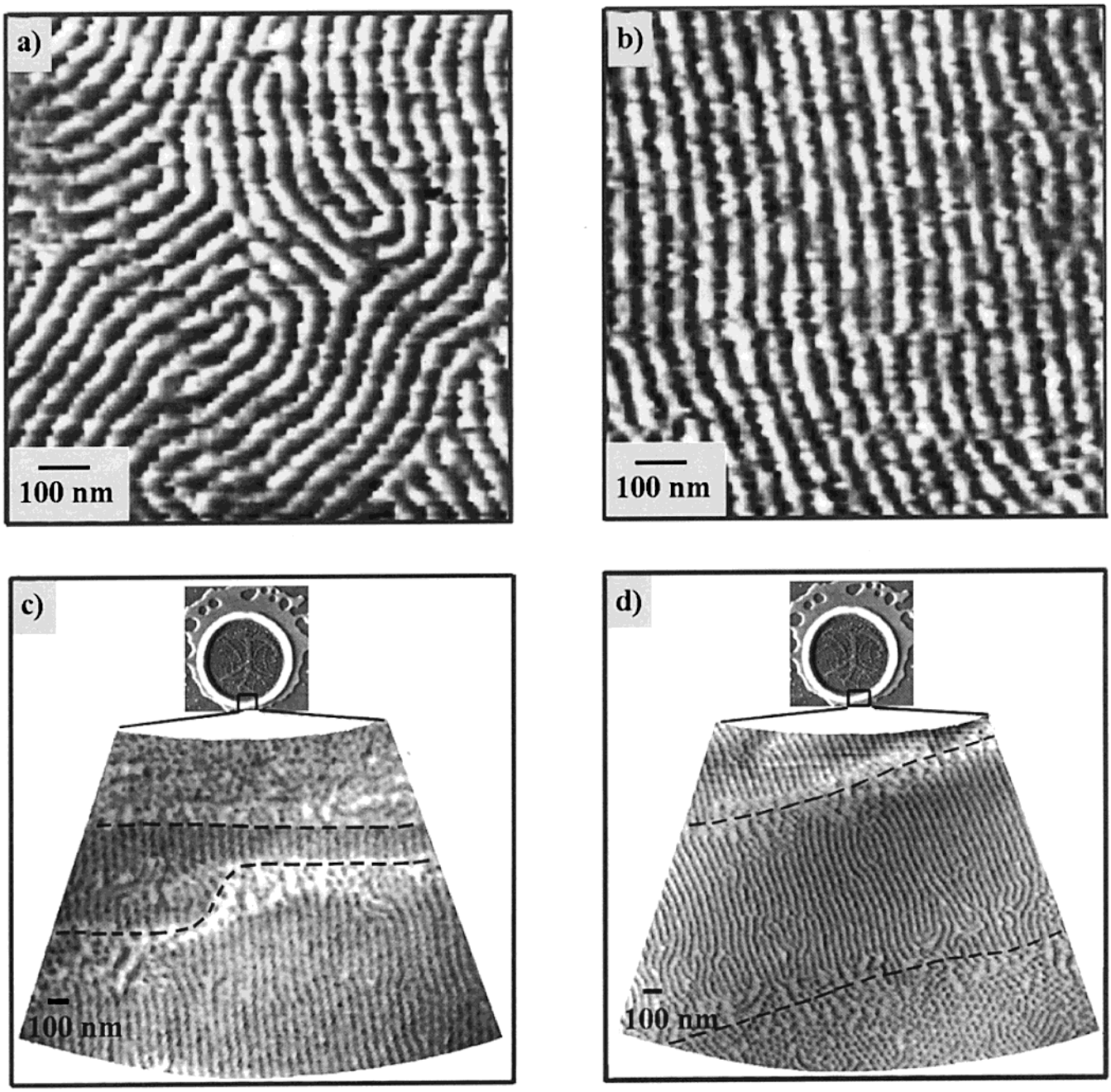

Figure 3. (a and b) Comparative 1 μm × 1 μm AFM images which demonstrate the difference in the degree of cylinder alignment in the L-thick region when using the same annealing conditions (513 K for 24 h) but with or without the addition of the minor polar solvent. (a) Cylinders pack with no preferential alignment when the sample is prepared without the minor solvent. (b) Highly aligned microdomains form with orientation perpendicular to step boundaries when the substrate is precoated using the minor solvent film. (c and d) Two rim images taken at different locations of the same ring which demonstrate radial alignment. Cylinders on nL thick regions align perpendicularly to step boundaries (marked by dashed lines) with extent up to 2 μm (limited by the step width). Radial alignment persists around the entire rim.

incompatabilities of the two blocks in the copolymer (Figure 2). In the case of asymmetric wetting (one component of a given diblock wets the substrate interface while the other component wets the air interface), the polymer film is "odd-number quantized". Here the film exhibits height quantization values which correspond to odd multiples of $L/2$, that is, $(2n+1)L/2$ thicknesses, where n is an integer and L is 43 nm. On the other hand, height quantization values of even multiples of $L/2$, that is, $2nL/2$ thicknesses, can be expected for the case of symmetric wetting, where one component of a diblock wets both the substrate and air interfaces. PMMA is known to wet the silicon oxide/polymer interface due to its lower wetting energy while PS exhibits an affinity for the polymer/air interface.[15] However, at the polymer/air interface, the surface tension difference between PMMA and PS is small enough to produce the appearance of both components at the upper interface when the film is L thick.[4]

The polymer film height in the ring region exhibits both odd and even spatial quantization, up to $3L$ or $4L$, depending on the rim height. Quantized heights are seen in core, rim, and corona regions. The thickness of the film is highest in the middle of its rim. Figure 2 shows an illustrative height map, that is, cross-section, of such a spacially quantized ring. Thermal annealing is found to decrease the rim height to 90−140 nm while increasing the width of the rim to 5−6 μm. The progression of film height quantization varies between annuli, reflecting the

delicate balance of annuli formation energetics; for example, 5*L*/2 terraces were not observed in the annulus presented in Figure 2. However, 5*L*/2 terraces were seen in other annuli on the same substrate. Therefore, the step differences between two neighboring terraces may vary, showing both *L* and *L*/2 thick step differences, in a given annulus. The irregular morphology found in the inner core region before annealing (Figure 1) disappears after annealing, leaving only islands and holes. The morphologies of all *nL* high regions in Figure 2 exhibit lying-down cylinders, that is, cylinders parallel to the substrate, with both PS and PMMA appearing at the polymer/air interface.[4,8] The bright- and dark-shaded areas in the AFM images are PMMA- and PS-rich regions, respectively.[4] The repeat spacing between cylinders is 50 nm.

We now move on to address the unexpectedly large degree of cylinder alignment in the thermally annealed annuli. In the rim regions of these structures, cylindrical polymer microdomains show unique directional preferences. The cylinders formed in *nL* thick regions (as compared to the cylinders typically produced on a silicon oxide substrate without the prespun layer of minor solvent, as shown in Figure 3a) exhibit dramatically decreased orientational disorder; that is, the cylinders are well-aligned over extended regions (Figure 3b). The translational cylinder-to-cylinder spacing remains the same at 50 nm. This microdomain alignment spreads out radially up to 2 μm in length and is oriented perpendicularly to the step boundaries which separate the different film thickness regions in the annular rim, (Figure 3c and d). *The extended length of aligned microdomains is limited by the step width*. In contrast to this, cylindrical microdomains in *L* thick regions far away from a rim (corona regions) do not show any enhanced alignment. The origin of this alignment remains to be explored further. However, a recent study not involving the formation of annuli has shown that lateral microdomain alignment over a large area can be achieved by mechanical strain fields introduced by anisotropic contraction during the drying process of a polymer film.[16] The width of a typical rim in the current study is an order of magnitude smaller than the associated length (circumference). Therefore, lateral shrinkage occurring during the drying process may proceed faster along the short axis of the rims, resulting in aligned microdomains which are perpendicularly oriented with respect to the step boundaries. Another plausible mechanism which may also play a role in this phenomenon is that the polymer domains are left aligned as the minor solvent dries and recedes. Further work on the mechanism of alignment is clearly warranted.

Conclusion

To summarize, we note that the procedures described in this paper can be used to reproducibly generate highly aligned annular structures consisting of microphase-separated cylinders with orientation parallel to the surface and that this alignment occurs without the aid of any external orientation field. These radially aligned cylinders persist around the entire rim of the micron-scale annuli. Moreover, the spacing of these aligned and orientationally ordered cylinders can be tuned by varying easily controlled experimental parameters, such as the molecular weight or volume fraction of the diblock. The use of these new self-organizing and aligned structures for generating novel nanopatterned substrates including nanowires is now being pursued. Other uses are likely given the high degree of control one can impose on the gross and fine morphology of these structures using readily available synthetic methods.

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