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UV-solvent annealing of PDMS-majority and PS-majority PS-\textit{b}-PDMS block copolymer films

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Abstract

The response of polystyrene-block-poly(dimethylsiloxane) (PS-\textit{b}-PDMS) thin films to UV exposure during solvent vapor annealing is described, in order to improve their applicability in nanolithography and nanofabrication. Two BCPs were examined, one with the PS block as majority ($f_\text{PS} = 68\%$, $M_n = 53 \text{ kg mol}^{-1}$), the other with PDMS block as majority ($f_\text{PDMS} = 67\%$, $M_n = 44 \text{ kg mol}^{-1}$). A 5 min UV irradiation was applied during solvent vapor annealing which led to both partial crosslinking of the polymer and a small increase in the temperature of the annealing chamber. This approach was effective for improving the correlation length of the self-assembled microdomain arrays and in limiting subsequent flow of the PDMS in the PDMS-majority BCP to preserve the post-anneal morphology. Ordering and orientation of microdomains were controlled by directed self-assembly of the BCPs in trench substrates. Highly-ordered perpendicular nanochannel arrays were obtained in the PDMS-majority BCP.

Online supplementary data available from stacks.iop.org/NANO/27/465301/mmedia

Keywords: block copolymer, solvent vapor annealing, UV irradiation, microphase separation, directed self-assembly, thin film, nanostructure

(Some figures may appear in colour only in the online journal)

Introduction

Block copolymers (BCPs) are of great interest in nanotechnology due to their ability to self-assemble into two- and three-dimensional microdomain morphologies with periods of a few nm and above \cite{1, 2}. This length scale is beyond the resolution limit of conventional photolithography, and can be achieved by block copolymer self-assembly more economically than by direct-write methods such as electron beam lithography \cite{3–6}. Changing the volume fraction of the blocks and the annealing conditions enables the formation of a variety of morphologies, including spheres, cylinders, double gyroid, lamellae, and perforated lamellae \cite{7–9}, which can be used to form arrays of lines, dots and other features on a substrate \cite{10}. BCPs are particularly attractive in making arrays of high aspect ratio nanochannels \cite{11–13}, which are useful in several applications including etch masks for pattern

5 Equal contribution.

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transfer during the fabrication of memory chips, filtration membranes [14, 15], sensors [16, 17], bulk heterojunction photovoltaic cells [18], and batteries [19].

Nanofabrication based on block copolymer self-assembly typically requires control of the long range order and aspect ratio of the microdomains [20]. Previous studies have shown that chemoepitaxy and graphoepitaxy [21–29], as well as annealing under external constraints such as electric or magnetic field [30], microwave [3], shear [31], and thermal gradients [32, 33], can direct the orientation and morphology of the self-assembled microdomains. Out-of-plane orientation of cylinders or lamellae can be obtained by several methods including the use of top-coat layers [34, 35], a gradient in solvent concentration during solvent annealing [36–38], macromolecular architecture [39], or the use of chemically attractive sidewalls [23]. Exposure of BCP thin films to a solvent vapor can effectively lower the glass transition temperature, decrease polymer chain entanglement, enhance polymer diffusivity and annihilate defects, making solvent annealing an attractive alternative to thermal annealing, at ambient or at elevated [40, 41] temperatures. The final structure is produced as the film collapses in the out-of-plane direction during solvent evaporation, thus the drying process also affects the morphology [36, 37, 42]. Therefore, methods to control the microdomain morphology upon drying are desirable to preserve the ordered structure obtained during solvent annealing.

Exposure of a block copolymer film to photons or electrons can induce chemical changes, and this has been incorporated into annealing processes [43–45]. For example, holographic irradiation of a hybrid film consisting of poly(ethylene oxide)-block-poly(methylacrylate derivative) with an azobenzene (Az) unit (PEO-b-PMMMAz) and 4′-phenyl-4-cyanobiphenyl produced a corrugated relief structure [46]. UV-irradiation has been shown to lock in the self-assembled morphology of BCPs such as poly(α-methylstyrene)-block-poly(4-hydroxyxystyrene) (POMS-b-PHOST) and polystyrene-block-poly(dimethylsiloxane) (PS-b-PDMS) by crosslinking the exposed region, while the unexposed region can be further annealed under a different solvent vapor to change its morphology [47, 48]. Similarly, electron-beam irradiation prior to solvent vapor annealing has been used to induce local cross-linking, preventing morphology changes in the exposed regions of the BCP film [45, 49–51].

Previous studies have focused on the effect of UV exposure before or after annealing in order to stabilize the morphology, but the effect of UV exposure in the swollen state during solvent vapor annealing remains to be studied. UV irradiation can cause both cross-linking of polymer chains and an increase in temperature. Previous in situ observations of solvent vapor annealing found the degree of ordering reached its maximum in the swollen state and subsequent drying degraded the ordering [37]. Therefore, UV exposure during the swollen state may be able to lock in the optimum ordering by cross-linking the morphology and limiting structural collapse when the solvents are removed. This may be anticipated to produce a well-ordered self-assembled morphology with high aspect ratio microdomains.

In this article, we show how a combination of UV exposure and solvent vapor annealing can facilitate self-assembly, reduce defects, and increase the uniformity of self-assembled features in PS-b-PDMS BCPs. This is illustrated for both PDMS-majority and PS-majority BCPs. A particular challenge for PDMS-majority BCPs is deformation of the microdomains even in the dry state, due to the low glass transition temperature of the PDMS block. We demonstrate that UV-solvent annealing can reduce the deformation of the PDMS-majority PS-b-PDMS by partially crosslinking the BCP, producing a variety of well-defined morphologies in thick films including hexagonally close-packed cylinders of PS in a PDMS matrix oriented perpendicularly to the substrate. PS-b-PDMS was chosen because it can be treated to remove the organic PS block and convert the remaining PDMS block into a Si-rich nanostructure which can be sufficiently robust to act as a mask for subsequent pattern transfer processes [8, 52, 53].

The two PS-b-PDMS BCPs were: (1) a 53 kg mol⁻¹ bulk-cylindrical morphology BCP with the PS block as majority [54]; and (2) a 44 kg mol⁻¹ bulk-lamellar morphology with the PDMS block as majority. Although there has been extensive work on thin film morphologies of PS-majority PS-b-PDMS, there is little work on thin film morphologies of such a material. PDMS-majority PS-b-PDMS (Mₐ,PS = 12.0 kg mol⁻¹, Mₐ,PDMS = 22.7 kg mol⁻¹) has previously been prepared as 20 nm thick freestanding silicon-oxygen-carbide nanoporous membranes by forming a BCP film on a C-coated glass substrate, releasing the film by HF etching, picking it up on a TEM grid, and oxygen plasma etching [55]. Recently, PDMS-majority BCPs have been spin-coated onto various polymer and Si substrates, solvent-annealed and etched to make sub-20 nm thick porous films [56].

Materials and methods

Materials

The cylinder-forming PS-majority PS-b-PDMS used here (labeled SD53) has a total number average molecular weight (Mₐ) of 53 kg mol⁻¹, polydispersity index of 1.04, and PDMS volume fraction fPDMS = 0.68. The PDMS-majority PS-b-PDMS used here (labeled SD44) has a PDMS volume fraction fPDMS = 0.67, number average molecular weight of the PDMS block of 28.0 kg mol⁻¹ and of the final BCP of 44.0 kg mol⁻¹ (the polydispersity of the BCP was 1.06). The diblock copolymers were synthesized through anionic polymerization techniques and sequential monomer addition, following the procedures described by Bellas et al [57] Politakos et al [58] and O’ Driscoll et al [59]. The molecular characteristics were calculated and verified by size exclusion chromatography, membrane osmometry and proton nuclear magnetic resonance (¹H-NMR) spectroscopy. Homopolymers of PS (Mₐ = 10 kg mol⁻¹, Mₐ/Mₕ = 1.2) and PDMS (Mₐ = 5.5 kg mol⁻¹, Mₐ/Mₕ = 1.2) were obtained from Polymer Source, Inc.
Film fabrication and characterization
SD53 and SD44 were dissolved into 1 wt% cyclohexane and 5 wt% toluene solution, respectively and spin-coated onto silicon substrates (3000 rpm). After solvent vapor annealing of the resulting thin films (with or without UV post-annealing exposure), the samples were treated first with 5s CF₄/O₂ plasma etch at 50 W and then 22s O₂ plasma etch at 90 W in order to remove PS and reveal the self-assembled microdomain morphology. The film thickness was measured by a Filmetrics F20 spectral reflectometer. The bulk morphology of SD44 was measured in a 3 μm thick sample prepared by drop-casting on a silicon substrate from 5 wt% toluene solution, slow drying, annealing in a vacuum oven at 150 °C at a pressure of 20 Torr for 48 h and then etching. The morphology of the films was revealed through scanning electron microscopy (SEM, Zeiss MERLIN, SEM, acceleration voltage 5 kV, inLens detector). All samples were sputtered with a 2–3 nm thick Au–Pt layer before SEM imaging in order to minimize charging effects. A TA Instruments Q20 Differential Scanning Calorimeter was used to determine the glass transition temperature.

Solvent annealing
The SD53 films were solvent vapor annealed in a small glass chamber (volume 50 cm³) containing 1.5 ml of a liquid solvent mixture. The SD44 thin films were placed into a larger 84 cm³ glass annealing chamber with 20 ml of a liquid solvent mixture such as a toluene and heptane. In both cases the sample was supported above the liquid surface within the annealing chamber. The samples were quenched by rapidly opening the lid of the annealing chamber, and the film deswelled to its original thickness within seconds. For UV-assisted solvent vapor annealing, a quartz cover, which transmits 90% of UV light at 254 nm, was used to cover the annealing chamber [60]. The total annealing time for SD53 films is 60 min, and for SD44 films is 100 min.

We used a solvent vapor generated from a toluene: heptane x:1 volumetric mixture for solvent annealing, where \( x = 5, 2, 1 \) or 1/3. Several annealing procedures were also carried out in acetone vapor. The estimated partial pressure corresponding to the solvent mixture is given in the supplementary material, table S1. Figure S3 shows swelling of SD44 and homopolymers in vapor from a 1:1 toluene:heptane mixture.

UV irradiation was carried out using a XX-115S Shortwave UV Bench Lamp with power of 15 W. This is a mercury lamp with strong emission at 254 nm (ultraviolet UVC) and 365 nm (i-line) wavelengths, and was placed 20 cm above the samples. The power density at 20 cm distance was typically around 3.0 mW cm⁻². Although PDMS is not highly absorbent in the UV range, it can still be effectively crosslinked by UV, forming hydroxyl and silicon oxide groups on the surface [61]. Another study showed that UV irradiation with a power density of 19.0 mW cm⁻² for 6 h is able to crosslink a PS thin film [62], while excessive exposure may lead to polymer degradation [63]. Therefore, although both blocks are cross-linkable by UV, the major effect of the UV is to reduce the solubility in solvent of the PDMS block, as described below. Figure S4 shows the process flow.

Substrate patterning
The gratings were fabricated using a Lloyd’s Mirror Interference Lithography system [64], which uses the intersection of two coherent laser beams in order to create a periodic intensity pattern of light to expose a resist. To make high aspect-ratio trenches, a tri-layer resist stack consisting of 200 nm PFI 88 negative photoresist layer on top, 20 nm SiO₂ layer, and 450 nm anti-reflective coating (ARC) were deposited on a silicon substrate. A helium–cadmium laser emitting at 325 nm was used to expose a grating pattern. After exposure and development of the resist, the grating pattern was transferred into the silica, then into the ARC layer using reactive ion etching (RIE) to produce trenches with approximately vertical ARC sidewalls. To functionalize the trench surface with a thin layer of PDMS brush, a layer of hydroxyl-terminated PDMS (\( M_w = 0.8 \text{ kg mol}^{-1} \)) was spin-coated from a 5 wt% toluene solution, vacuum-baked at 20 Torr, 170 °C for 14 h, and then rinsed in toluene.

Two-step grating substrates were fabricated in a similar manner except that the ARC was 200 nm thick. After exposure and development, the grating pattern was transferred from the photoresist layer into the Si substrate using RIE. Part of the ARC remained at the center of the mesas of the silica trench pattern, forming lines 30 nm thick. This led to a two-step trench topography, figure S1.

Results and discussion
Effect of UV exposure on SD53 swelling ratio
The optical absorbance (logarithm of (incident radiant flux/ transmitted radiant flux)) of an 80 nm thick SD53 film on a Si substrate is shown in figure S1 indicating strong absorbance at 250–300 nm wavelengths, though the polymer was mostly transparent to the i-line peak at 365 nm. Therefore the BCPs as well as the toluene and heptane [65] solvent vapors can absorb at least part of the output of the UV mercury lamp.

The effect of UV irradiation on 80 nm thick PS homopolymer (hPS), PDMS homopolymer (hPDMS), and SD53 was first tested by measuring the film thickness change after films were irradiated and then immersed in liquid toluene for 1 min. Without UV irradiation, the 1 min immersion in toluene completely dissolved all hPS, hPDMS, and SD53 films. However after 20 min UV irradiation (total dose around 450 mJ cm⁻²) the measured dried film thickness, after immersion into liquid toluene for hPS was ~10 nm, for PDMS ~70 nm, and for SD53 ~50 nm. This suggests that the 20 min UV exposure induced cross-linking of hPS, hPDMS and SD53 films, with the greatest resistance to dissolution found in the hPDMS and the least in the hPS. In subsequent experiments, 5 min of UV irradiation was chosen in order to

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only partially crosslink the PS-b-PDMS BCP in the swelled state.

The effect of UV irradiation on the swelling behavior of PS-b-PDMS film was tested by in situ measurement of the swelling ratio of SD53 films with as-cast thickness 80 nm (figure 1). The solvent vapor composition was chosen based on a previous study [37] where it was concluded that the solvent vapors generated from a 5:1 volumetric mixture produced approximately equal swelling of the PS and PDMS blocks of a bulk cylinder-forming PS-b-PDMS BCP, ensuring that the cylindrical morphology forms at the swelled state in the thin film. (It should be noted, however, that crosslinking of the blocks will affect the relative solvent uptake rendering the 5:1 solvent ratio more preferential to swelling the PS blocks.) Without UV irradiation, SD53 films showed a swelling ratio of 2.2–2.3, but when the UV was switched on the swelling ratio of the film increased to 2.6 over ~2 min.

**Effect of UV irradiation on PS-majority SD53 thin film morphology during solvent-annealing**

We first describe the morphology of as-cast SD53 films of different thickness at a saturated swelling ratio of around 2.25, using the vapor from a toluene:heptane 5:1 volumetric ratio. An as-deposited film with thickness 36 nm exhibited micelle-like morphology (figure 2(a)) with period 37 nm. After 1 h solvent annealing without UV irradiation, a SD53 film with 25 nm as-cast thickness produced discontinuous cylinders with poor ordering (figure 2(b)); a 36 nm film formed continuous cylinders with a low correlation length and period 33 nm (figure 2(c)); and a 78 nm film produced double-layer cylinders with breaks in the top-layer cylinders (figure 2(d)). The commensurability between the SD53 film thickness and the natural periodicity of SD53 is an important factor in improving the degree of ordering of the self-assembled morphology [7, 68]. Comparing figures 2(b)–(d), 36 nm as-cast thickness appears to be closest to the commensurate condition under the annealing conditions of the experiment, therefore, the as-cast thickness was fixed at 36 nm and films were treated with UV irradiation during different stages of the solvent annealing.

When UV irradiation was performed on a 36 nm thick film without solvent vapor annealing, the film morphology was similar to the as-cast morphology. The film formed micelles with period 32 nm (figure 2(c)) although the PDMS area ratio became smaller, and the initiation of micelles merging into short cylinders was evident. However, UV irradiation of a swelled film within the first 5 min of solvent vapor annealing produced a mixture of cylinders having different lengths (figure 2(f)). This suggests that partial crosslinking limited the diffusivity during subsequent solvent vapor exposure.

In contrast, UV irradiation during the last 5 min of solvent annealing led to well-ordered cylindrical morphologies in SD53 films with both 36 nm and 80 nm as-cast thickness, with average microdomain grain size around 8 μm² and 1 μm² respectively (figures 2(g) and (h)). This can be compared with the average grain size of samples solvent- annealed with no UV irradiation (figures 2(c) and (d)), which was 10⁻² μm² and 5 × 10⁻³ μm², respectively. (The average grain sizes were estimated based on mapping the grain boundaries from several SEM images using ImageJ software and calculating the grain areas). The ordering improvement is most evident for the commensurate film thickness, 36 nm, but still appeared for the 80 nm thick film. The observations suggest that UV irradiation can lock in the self-assembled morphology of the swelled state, limiting degradation of the ordering induced by deswelling. The period of the UV-annealed morphology of the 36 nm film in figure 2(g) is 34 nm compared to 32 nm in figure 2(c). An in situ study of the solvent vapor annealing of a cylinder-forming PS-PDMS film confirmed that deswelling induces the collapse of the self-assembled lattice structure [69]. The larger period for the UV-solvent annealed sample suggests that UV-induced crosslinking in the swelled state decreased the degree of shrinkage during deswelling.

Compared with non-UV solvent-annealed samples, the improvement of ordering in UV solvent-annealed samples is attributed to two factors: (i) the UV irradiation induced a raise of temperature of the solvent annealing system, thus increasing the solvent vapor pressure and swelling ratio of the sample; (ii) the UV irradiation partially crosslinked the swelled polymer chains, locked in the self-assembled morphology, and minimized the deformation of microdomains during film deswelling. The UV light raised the temperature in the chamber by 3 °C on average, according to a thermocouple suspended in the chamber (the surface temperature of the substrate may have been higher). Heating the solvent reservoir leads to a higher solvent vapor partial pressure (e.g. a 3 °C temperature change at 20 °C would raise...
the vapor pressure of toluene by a factor 1.17 based on its heat of evaporation), which would increase the swelling ratio. The film deswelled and cooled when the light was turned off but did not return to its former swelling ratio by the end of the 60 min anneal, assumed to be a result of cross-linking based on the comparison with the swelling behavior of non-UV solvent annealing (figure 1). A previous study showed that heating the sample (but not the chamber) drove the solvent out of the BCP film and led to deswelling [41], whereas other work showed that heating the entire chamber resulted in an increase in the solvent vapor pressure, which increased the solvent uptake [66, 67]. Our work is more closely related to the latter cases since the UV lamp heated the vapors and the chamber as well as the sample. Increased swelling has been shown to improve the degree of ordering [37].

**Film morphology of PDMS-majority SD44 films after UV-solvent vapor annealing**

The bulk morphology of SD44 consisted of lamellae with a period of 50 nm corresponding to PS and PDMS layer thicknesses of approximately 13 nm and 37 nm, respectively (figure 3(a)). Lamellae formed rather than cylinders despite the deviation of the volume fraction from 0.5 ($f_{PDMS} = 0.67$ for SD44). DSC measurements of SD44 (figure 3(b)) showed a melting temperature of the majority component (PDMS) at $-40^\circ C$ and a glass transition temperature of the minority component, PS, at $96^\circ C$ ($\pm3^\circ C$). Homopolymers, hPDMS and hPS, exhibit glass transition temperatures of $-125^\circ C$ and $107^\circ C$ [70, 71] respectively and the melting temperature of crystalline hPDMS is reported around $-40^\circ C$. The most notable difference between SD44 and SD53 films was the distortion of microdomains that occurred even after drying in solvent-annealed SD44 films prepared without UV irradiation, exemplified in figure 3(d). This is caused by the viscoelastic behavior of the majority PDMS block, and presents a processing challenge for such materials not present in PS-majority BCPs. In this section we show that the cross-linking induced by UV irradiation made the self-assembled nanostructure more robust (figure 3(f)) and enabled formation of a through-thickness pore array.

In order to produce a cylindrical morphology by solvent annealing, the solvent vapor was generated from a toluene: heptane 5:1 volumetric mixture (figure S3) instead of the 5:1 mixture used in the SD53. The increased heptane fraction drives the morphology from lamellae towards PS cylinders. Annealing was carried out for 100 min at a saturated swelling ratio of 2.75 for a 180 nm thick film (figure 3(c)). This led to a PS cylinder morphology with center-to-center periodicity of 44 nm and hole diameter of $\sim14$ nm after etching. The effects of different solvent vapor compositions on morphology will be described below. CF$_4$/O$_2$ and O$_2$ plasma etching showed that the top surface of the etched film consisted of oxidized PDMS with an array of holes (figures 3(d) and (e)).

Although the solvent-annealed SD44 showed a pore array at its top surface, a cross-sectional image, prepared by cooling the sample in liquid nitrogen for 20 s, cracking it using a diamond scriber and etching it, did not show the pores penetrating vertically throughout the thickness of the film (figure 3(d)). This behavior was attributed to deformation of the low glass transition temperature majority PDMS block, even in the dry state. The etching process oxidized only the top layer of the film, and the interior of the film was able to deform during the preparation of the cross-section.

Unlike a PS-majority BCP, which has a stable morphology at room temperature, the PDMS-majority BCP is apparently able to deform even in the dry state at room temperature which limits its utility as a nanochannel film or a pattern transfer mask. To stabilize the microphase-separated structure, 5 min UV exposure at intensity $\sim3$ mW cm$^{-2}$ was...
Figure 3. Self-assembly of SD44 PS-b-PDMS BCP. (a) SEM of the bulk lamellar morphology. The sample was thermally annealed in a vacuum oven at 150 °C at a pressure of 20 Torr for 48 h. PDMS microdomains appear brighter. (b) Differential scanning calorimetry measurement of SD44. The glass transition temperature for the PS block was observed at 96 °C (inset). The melting temperature for the PDMS block was observed at −40 °C. (c) In situ swelling ratio measurement of SD44 film under solvent vapor from a toluene: heptane 1:1 volumetric mixture. The as-cast thickness of the SD44 film was 180 nm. (d), (e), SEM of 180 nm thick SD44 film annealed at room temperature in a solvent vapor generated by a toluene: heptane 1:1 mixture for 1.5 h, followed by reactive ion etching. (d) Cross-section view, (e) top-down view. (f), (g), a film processed in the same way as shown in (d) but exposed to UV light for 5 min before drying and etching. (f) Cross-section view, (g) top-down view.
applied to the film before deswelling (see process of figures 2(f)–(h)), in order to partially cross-link the polymer. Figures 3(f) and (g) shows the cross-section and top-view morphology of the SD44 film prepared in the same way as figures 3(d) and (e) respectively, with the only exception being the use of 5 min UV. The UV-processed film showed pores penetrating the film thickness, although the cross-section cut through some of the pores at an angle. (The granularity in figure 3(e) arises from the metal coating, but the array of pores is clearly visible.)

The orientation of the cylinders is affected by both the annealing process and the surface energies of the blocks. For PS–h-PDMS, a PDMS wetting layer is usually formed at the air/film interface due to the lower surface energy of PDMS (in the swollen state, the interfacial tension of PS with air is 32.1 mN m$^{-1}$ at room temperature, whereas PDMS with air is 20.9 mN m$^{-1}$) [35, 72]. This PDMS wetting layer promotes an in-plane cylinder orientation. However, an out-of-plane orientation can form instead as a result of solvent concentration gradients, especially in thicker films. An in situ study showed a time-dependent cylinder orientation in which the cylinders were initially out-of-plane, but reoriented towards the in-plane direction during solvent vapor annealing [37]. In the present work, we conclude that the combination of film thickness and the solvent vapor annealing led to the out-of-plane cylinders seen in figure 3(d).

**Effect of solvent vapor composition on UV-solvent annealed SD44 thin film morphology**

By varying the solvent or solvent mixture used in the UV-solvent vapor annealing process and therefore the selectivity of the solvent to the two blocks, a wide range of rigid, high aspect ratio self-assembled nanostructures was produced. The morphology transitions are a result of the different affinities of toluene and heptane towards PS and PDMS blocks which changes the effective volume fraction due to their asymmetric swelling [8]. For example, the vapor produced from the 1:1 toluene:heptane mixture caused a swelling ratio of 3.5 for hPS, 2.3 for hPDMS films, and 2.75 for the SD44.

A lamellar morphology was found in a SD44 film with 100 nm as-cast thickness after annealing under acetone vapor (figures 4(a) and (e)). Acetone has a solubility parameter of 19.7 MPa$^{1/2}$, which is closer to that of PS (18.5 MPa$^{1/2}$) than that of PDMS (15.5 MPa$^{1/2}$), thus it is expected to swell PS more, driving the effective volume fraction towards that of a lamellar phase. The out-of-plane orientation of the SD44 lamellae annealed by acetone is attributed to the solvent concentration gradient through the film [35, 37, 73], similar to the formation of vertical PS cylinders in toluene:heptane vapors in figure 3. The top surface of the film has a PDMS wetting layer which is only partly removed in figure 4(a).

A 200 nm thick film annealed in vapor generated by a toluene: heptane 2:1 volumetric mixture (figures 4(b) and (f)) exhibited a porous morphology with poorly ordered, narrow pores. Cylindrical channels oriented out-of-plane were formed in a 180 nm thick film annealed in solvent vapor generated by a toluene: heptane 1:1 mixture, as described in the previous section (figures 3(d), (e) and 4(c), (g)). A mixed morphology containing spheres and cylinders of polystyrene was formed from a 160 nm film annealed in vapor from a toluene: heptane 1:3 mixture (figures 4(d) and (h)). Therefore, increasing the heptane fraction led to morphologies with a qualitatively lower volume fraction of PS; the period of the morphology also decreased from ~45 to ~33 nm with increasing heptane. The structures are less well ordered than those seen in figure 2 for monolayer SD53, but they do illustrate that a range of morphologies including vertical lamellae is enabled by changing the solvent composition. Control of morphology has been reported previously in PS-majority PS–h-PDMS BCPs [1, 6, 7].
Directed self-assembly of SD53 and SD44 films by UV-assisted solvent vapor annealing

The correlation length of the SD44 pore arrays in figures 3(g), and 4(c) is limited to a few periods, but templating the microphase separation using topographical features is expected to improve the ordering [23]. High aspect-ratio gratings (figures 5(a)–(c), trench height 300 nm, width 200 nm; figure 5(d), trench height 300 nm, width 450 nm) were patterned by a Lloyd’s Mirror interference lithography system [64], in which the intersection of two mutually coherent laser beams creates a periodic intensity pattern of light which exposes a resist with a grating pattern. The SD44 was spin-coated onto the PDMS-functionalized gratings, solvent annealed in toluene:heptane vapor, with UV exposure before deswelling, and etched in oxygen plasma.

The templating by the narrower trenches produced an ordered arrangement of out-of-plane channels in the etched BCP, with PDMS wetting the sidewalls. Figures 5(a) and (b) shows results using vapor from a toluene: heptane 1:1 mixture. For an 80 nm thick film (figure 5(a)), a well-ordered close-packed array formed in the trench with rows of cylinders parallel to the trench edges. The vertical fins are remnants of the ARC used to form the trench edges. The center-to-center distance between each hole is 36 nm and the hole diameter is around 14 nm. The center-to-center distance was ∼8 nm smaller than the untemplated morphology (figure 3(e)), a behavior which may be attributed to the physical confinement provided by the trench as well as the surface energy of the trench sidewall that induced preferential wetting by PDMS. Incommensurability between the trench width and the BCP row spacing led to a reduction in period such that six rows of cylinders (unconfined row spacing = 38 nm) could fit within a 200 nm wide trench (confined row spacing = 33 nm).

Figures 5(c) and (d) show results of templated assembly of SD44 after annealing in vapor from a toluene: heptane 2:1 mixture, using the same solvent anneal condition as was used for smooth substrates (figure 4(b)). Figure 5(c) included UV irradiation in the last 5 min of solvent annealing while figure 5(d) was processed without UV irradiation. The sample of figure 5(d) had a wider trench width and exhibited a disordered porous structure, deformed by the flow of the PDMS block. However, the grating template with narrower trenches in figure 5(c) produced what appears to be a perforated lamellar structure in which adjacent PDMS lamellae appear to be interconnected through pores in the PS lamellae, and the ordering of the structure is preserved by UV crosslinking. The 200 nm wide trenches of figure 5(c) each contained seven PDMS lamellae and six PS perforated lamellae implying a
~15% smaller period than that of the drop-cast bulk BCP, similar to the confinement-induced reduction in period seen in figures 5(a) and (b).

Previous studies of cylindrical morphology PS-\textit{b}-PDMS with minority PDMS used trenches with vertical sidewalls and produced in-plane cylinders parallel or perpendicular to the trench walls depending on the annealing process [54]. To examine directed self-assembly of SD53 we used two-step trenches to facilitate flow of the swollen polymer towards the middle of the trench and to promote the formation of in-plane cylinders oriented perpendicular to the trenches [21]. An SEM image of the trench is shown in figure S2.

When a 36 nm thick film of SD53 was spin coated, the film formed in-plane cylinders in a fingerprint pattern independent of the trench structure, rather than the micelles that were observed on the bare Si substrate. After solvent annealing in 5:1 toluene:heptane, the cylinders were contained between and largely perpendicular to the lower trench wall (figure 5(e)), as expected [21]. When UV solvent annealing was used, however, the orientation and periodicity of the cylinders was improved (figure 5(f)) from ~35% of cylinders aligned perpendicular to the trenches in non-UV solvent vapor annealing to 93% in UV solvent vapor annealing. Therefore, directed self-assembly can be combined with UV-assisted solvent annealing to produce both PS-majority and PDMS-majority BCP films with well-ordered 3D microdomain structures.

**Conclusion**

The influence of UV irradiation on the self-assembly of both PS-majority and PDMS-majority PS-\textit{b}-PDMS films was investigated, with the particular aim of stabilizing the microdomain structure of PDMS-majority films which is subject to distortion even in the dry state as a result of the low glass transition temperature of PDMS. UV exposure in the swelled state at the end of the solvent annealing process was effective in partially cross-linking the BCP, which preserved the microdomain structure formed by the solvent anneal. UV exposure also led to an increase in temperature of the annealing chamber which increased the vapor pressure of solvents and the swelling of the films. The UV exposure led in some cases to final microdomain morphologies, i.e. cylinders in the SD53 (\( f_{\text{PDMS}} = 0.32 \)) film and nanochannels in the SD44 (\( f_{\text{PDMS}} = 0.67 \)) film, with better order than those obtained from just a solvent annealing procedure.

The influence of solvent vapor composition on the morphology of the SD44 was further investigated. In bulk the SD44 formed a lamellar morphology but thin films produced a diversity of structures depending on the solvent vapor composition: acetone or toluene-heptane mixtures. These included disordered porous structures and cylinders or lamellae oriented perpendicular to the substrate. Films of SD44 coated onto grating substrates consisting of high aspect-ratio trenches showed enhanced ordering of pores, and a perforated lamellar structure under certain annealing conditions, whereas SD53 coated on grating structures showed in-plane alignment of PDMS cylinders perpendicular to the sidewalls. The perpendicular nanochannel arrays formed from the SD44 PDMS-majority BCP may be useful in pattern transfer for nanolithography as well as other applications such as filtration membranes and sensors. The UV-assisted solvent vapor annealing is extendable to other BCP systems that are susceptible to cross-linking, and thus could provide a simple tool to improve the quality of self-assembled thin films.

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