

**SIMPLE RSVA-SS PROCESS FOR DIRECTING SELF-ASSEMBLED
NANOSTRUCTURES IN BLOCK POLYMER THIN FILMS**

by

Douglas Michael Scott

A thesis submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Honors Bachelor of Chemical Engineering with Distinction

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NANOSTRUCTURES IN BLOCK POLYMER THIN FILMS**

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ABSTRACT

The nanoscale self-assembly of block polymers (BP) has spurred interest for the generation of nanopattern arrays essential to advanced nanotechnologies. However, applications such as nanolithography typically require high levels of domain alignment achieved through a plethora of techniques with varying degrees of success and practical limitations, inhibiting the adoption of functional BP nanostructures into industrial processes. In this work, a new method termed raster solvent vapor annealing with soft shear (RSVA-SS) was developed and used to align a cylinder-forming triblock terpolymer. This technique, consisting of a solvent vapor delivery nozzle, a poly(dimethylsiloxane) shearing pad, and a motorized stage, was shown to spatially control the orientation of polymer nanostructures and generate a variety of patterns such as straight lines, curves, crossed lines, dashes, and T-junctions. Additionally, the use of a wide slit solvent nozzle demonstrates the scalability of the RSVA-SS process for industrial applications. RSVA-SS promises a facile method for aligning BP nanostructures conducive to future research in nanotechnology without the necessity of substrate pre-patterning.

Chapter 1

INTRODUCTION

A brief overview of block polymer (BP) phase behavior in the bulk and thin film regimes is presented followed by a summary of common annealing techniques for improving the ordering of nanostructure formation in BPs.

1.1 Block polymers

A BP consists of two or more chemically distinct homopolymer chains covalently linked together. Varying the connection of constituent blocks can lead to molecular architectures such as linear, star, and graft copolymers. As a result, the nomenclature of linear BPs is important in indicating the order of block linkages. For example, a BP formed from two chains of A and B respectively is termed an A-*b*-B diblock copolymer while a BP with two A chains spaced by a B chain is termed an A-*b*-B-*b*-A triblock terpolymer (see Figure 1.1).

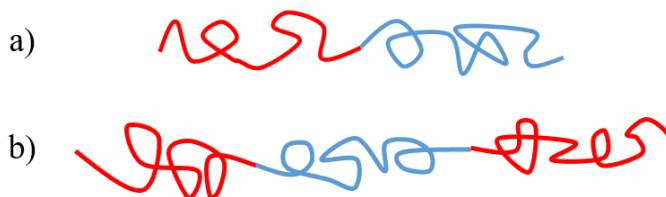


Figure 1.1: Cartoon representations of an (a) AB diblock and (b) ABA triblock.

Unfavorable interactions between the constituent blocks create a thermodynamic drive for phase segregation resulting in nanoscale self-assembly of polymer chains into periodic nanostructures¹. This phenomenon is the primary focus

of BP research as it leads to a plethora of functional morphologies in bulk, solution, and thin film regimes.

The repulsive interactions which drive the self-assembly are quantified by the BP segregation strength, represented by the product of the Flory-Huggins interaction parameter (χ) and the overall degree of polymerization (N). Originally defined on the basis of polymer blends in which constituent homopolymers macroscopically segregate, the value of χ provides a direct representation of unfavorable interactions inherent to a pair of polymers. Additionally, as constituent chains are longer, chemically distinct polymer domains are more easily formed thereby yielding greater segregation. Given the origins of χ and N , the range of segregation strength is dictated by the choice of monomers and extent of polymerization, both which are controlled by a polymer synthesis. Morphology is dependent on the segregation strength and the relative volume fraction (f) of each block which dictates the geometry of the self-assembly. Early studies using self-consistent field theory created phase diagrams showing the effects of these factors on morphology². Common stable morphologies formed in the bulk regime are lamellae, gyroid, cylinders, and spheres. Without adequate segregation strength ($\chi N < \sim 10.5$) and/or highly asymmetric volume fractions, the driving forces for phase segregation are minimal enough to produce a disordered phase. Because χ is inversely proportional to temperature, the necessary temperature in which a BP matrix transitions from ordered to disordered phases is designated as the order-disorder transition temperature T_{ODT} .

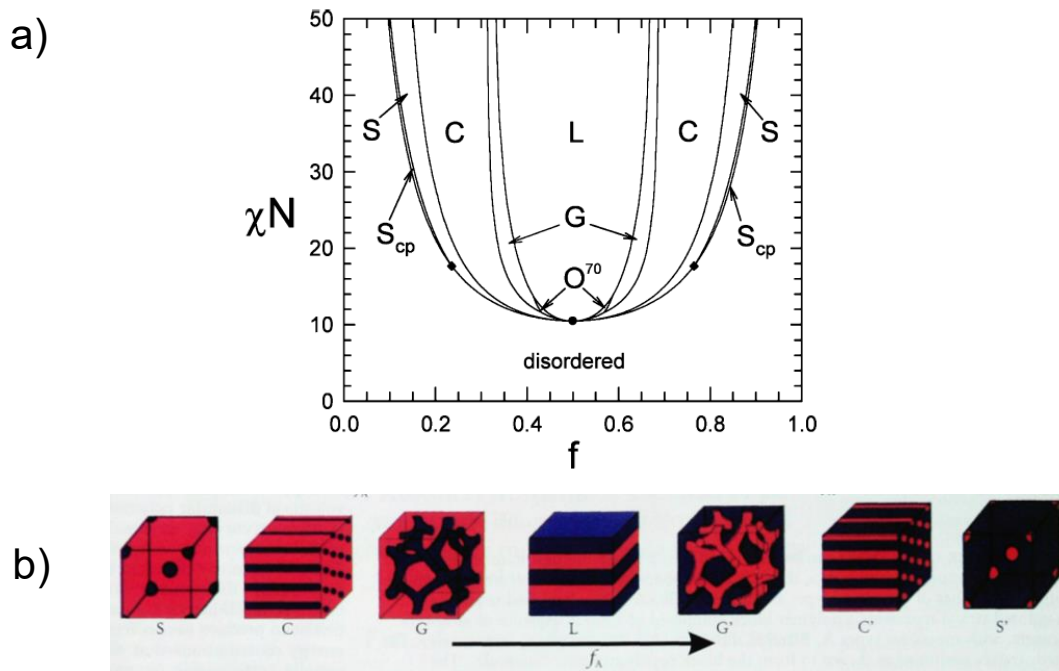


Figure 1.2: (a) Phase diagram detailing morphology as a function of segregation strength (χN) and volume fraction (f). (b) Cartoon depictions of self-assembled morphologies: (left to right) spheres, cylinders, gyroid, lamellae. Adapted from Bates, F.S. *et al.*, *Physics Today* **1999**, 52 (2), 32-38. Copyright 1999 American Institute of Physics.

In a BP morphology, another characteristic parameter known as the domain spacing (L_0) indicates the periodicity of the nanostructure formed. Empirical correlations relating domain spacing to segregation and size parameters (χ and N) have been developed for both the strong and weak regimes³.

1.2 Thin film regime

The phenomenon controlling the self-assembly of BPs in thin films has been found to expand the parameter space to consider the effects of film thickness and block-surface interactions. First, domain alignment relative to the substrate is an

added physical attribute dictated by the interaction between the surfaces (free surface and substrate surface) and the constituent blocks. Considering cylinders and lamellae in the bulk regime, both perpendicular and parallel variations are present in thin films. If two blocks shared similar surface interactions, both domains can be exposed at the surface, eliciting a perpendicular orientation. Conversely, a difference between boundary surface energies would result in segregation of the block(s) with most similar surface energies to each, producing a parallel orientation with symmetric or asymmetric wetting conditions. In parallel orientations, island and holes are formed at the free surface to relieve chain compression or stretching associated with incommensurability between film thickness (t) and number of domain spacings. Commensurability is dictated by wetting conditions: (nL_0 for symmetric wetting and $(n + 0.5)L_0$ for asymmetric wetting)⁴.

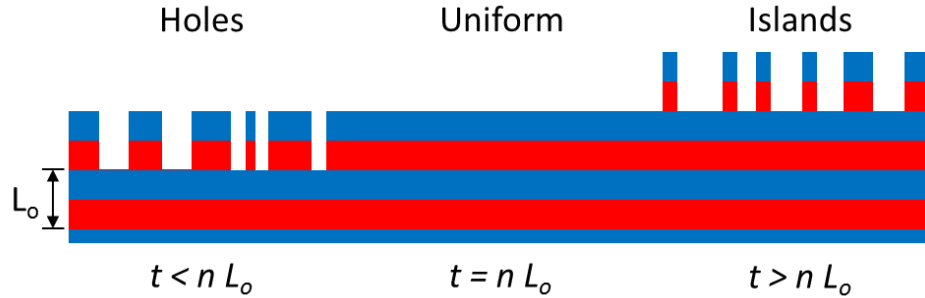


Figure 1.3: Island/hole formation resulting from commensurability conditions and symmetric wetting.

1.3 Annealing Processes

After casting directly from a solution, BPs typically are trapped in nonequilibrium structures, yielding poor ordering of domains. To overcome the

associated kinetic barriers to equilibrium structures with long-range ordering, two approaches to annealing BP thin films can be taken: thermal and solvent vapor annealing. By raising the temperature of a polymer sample, chains can adopt a wider distribution of configurations and more easily reptate, allowing reorganization towards equilibrium structures. For glassy polymers, annealing temperatures must be, at minimum, above the glass transition temperatures (T_g 's) of the constituent blocks to access mobility in rubbery regime. Though thermal annealing is a simple technique easily performed using heating stages and ovens, treatments prove inadequate for high molar mass polymers and thermally sensitive or thermally responsive polymers. Additionally, the process can be prohibitively long in duration⁵.

In this work, solvent vapor annealing (SVA) is employed as the principle ordering method. By exposing a thin film to vapors of a good or adequate solvent for all constituent blocks, the film uptakes the solvent and swells. The plasticizing effects of solvent molecules between chains effectively lowers the T_g of swollen blocks below ambient room temperature and subsequently impart mobility to the polymer chains. Upon removing solvent via evaporation, structures with longer range ordering and fewer defects are attained. Without the time limitations associated with thermal annealing, SVA has been shown to be a more effective technique⁶. Furthermore, with a large library of solvents and corresponding mixtures, SVA generally is applicable to all polymer systems.

1.4 Motivations for Directed Self-Assembly

Significant research effort in polymer science and engineering over the past three decades has sought to produce and control BP morphologies for a plethora of applications including nanofiltration^{7, 8}, drug-delivery^{9, 10}, energy storage¹¹, photonics

^{12, 13}, and nanolithography ^{14, 15}, all of which benefit from nanoscale interfaces and features. Specifically, in the area of nanolithography, the demand to minimize features in dense integrated circuits and data storage has reached a critical turning point in which past technologies can no longer be employed to achieve future technological nodes ¹⁶. A promising solution to this impasse is directed self-assembly (DSA) of BP morphologies to fabricate nanolithographic masks, enabling higher resolution patterning with 193nm and extreme ultraviolet (EUV) lithography.

Current techniques for DSA include graphoepitaxy ^{17, 18}, chemical prepatterning ^{19, 20}, both of which require substrate modification and thereby yield prohibitively slow processing. Magnetic and electric fields have been explored in DSA applications however both are limited to only specific polymer systems ^{21, 22}. With regard to these limitations, a new approach to DSA must be developed without the need for modified substrates and be universally applicable to all polymers. As shown by Register, Chaikin, and Panagiotopoulos, BP domain alignment was found to correlate highly with the direction of applied shear fields both experimentally as well as through simulation ^{23, 24, 25}. In these studies, shear forces were imparted to single-layer polymer film through a poly(dimethylsiloxane) (PDMS) elastomer and moving weight. However, the shearing process required a processing rate of approximately 400 nm/s, inadequate for industrial purposes.

Chapter 2

Description of Techniques and Procedures

To conduct studies on thin films, it is important to understand the methods used to generate films as well as characterize their morphology. Throughout the thesis work, flowcoating and atomic force microscopy (AFM) were essential for these respective purposes.

2.1 Flow Coating

BP thin films are cast from solutions prepared using good solvents for both constituent blocks. To cast films for this project, a flow coater was used. The basic components of this system are a motorized stage, glass blade, and blade mounting stage with adjustable height and tilt (α).

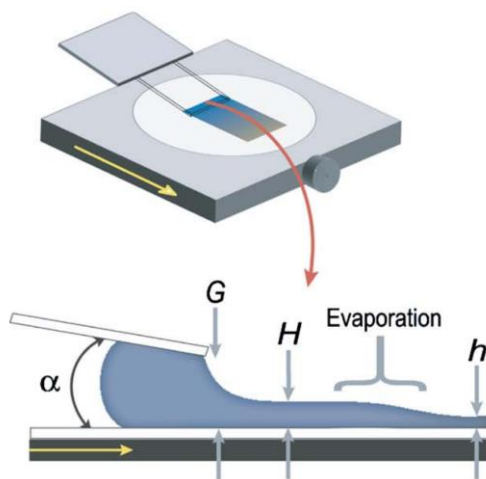


Figure 2.1: Reprinted from reference 26. Schematic of flow coating polymer solution to substrate. The gap height (G), deposited solution height (H) and dried film height (h), blade tilt angle (α) are illustrated.

Flow coating is a high throughput method for generating a library of film thicknesses on one single substrate. Before operation, polymer solution is injected between the glass slide and the substrate and is held in place by capillary forces. As the substrate rapidly accelerates to an initial velocity and moves beneath the slide, frictional forces drag out the solution onto the substrate which subsequently evaporates, generating a thin film. The deposition of solution onto the substrate is dictated by the instantaneous velocity of the motorized stage. As a result, by accelerating the motorized stage, the rate of solution deposition is increased proportional to velocity and a gradient thickness film can be fabricated²⁶. An extra displacement at end of the coating process is implemented to prevent solution backflow.

For this thesis work, solutions of cylinder-forming poly(styrene-*b*-isoprene-*b*-styrene) (SIS) were cast into films using flow coating according to the following procedure: (1) inject 50 μL of a 2.3% wt. solution of SIS solution in tetrahydrofuran between silicon substrate ($N<100>$, Wafer World, Inc.) and a glass slide with a gap height of 200 μm ; (2) rapidly accelerate the motor stage to an initial velocity (v_0) of 10 mm/s and then slowly accelerated at a constant rate (a) of 0.4 mm/s² for a displacement (Δx) of 75 mm to generate a ~ 115 nm thick film of constant thickness. A small acceleration is required to account for the gradual loss of solution volume underneath the blade during coating. The SIS polymer was obtained from DEXCO (V4211) with a total molecular weight of 118 kg/mol, domain spacing of 29 nm (from SAXS), and volume composition of $f_s = 0.134$, $f_I = 0.732$, and $f_S = 0.134$.

2.2 Atomic Force Microscopy

AFM is a high resolution imaging technique used to characterize surface properties such as composition and topography. The basis of the technique involves bringing a probe tip into close proximity of a surface where molecular interactions deform the cantilever of the probe. By reflecting a laser off of the cantilever into a four-zone photodetector system, the angular deflection of the cantilever can be determined and translated to useful data signals such as sample height. A feedback loop connecting the deflection of the cantilever and the piezoelectric tube scanner adjusts the height of the tip to maintain constant low interaction forces²⁷.

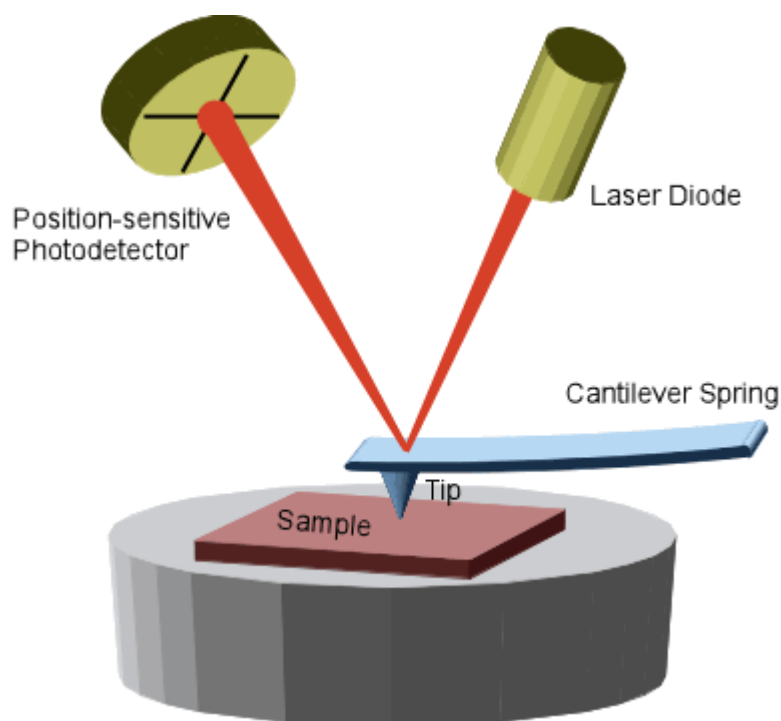


Figure 2.2: Representation of AFM operation showing key components of microscope. Reprinted from reference 28.

For AFM, two modes of operation are commonly used: contact and tapping. In contact mode, a tip is continuously drawn across a sample while in constant interaction with the surface. As the underlying topology of the sample changes across a scan path, the prior mentioned feedback loop adjusts the tip heights to maintain interaction and avoid severe physical contact with tall structures which may damage the tip or sample. A major drawback in using contact mode for soft matter samples such as polymers is the potential for damaging the sample and the probe tip due to dragging. To mitigate this unfavorable effect, tapping mode only allows a tip to oscillate on the sample surface at a specified frequency over a scan path. The result is a high resolution image without sample damage. In addition to height imaging, tapping mode offers direct measurement of surface stiffness/softness as a result of characteristic phase shifts between the driver and response frequency oscillations²⁹. Because differences in modulus are directly linked to local changes in surface compositions, phase images are advantageous for directly discerning the morphology and ordering of BP thin films.

Chapter 3

Design of Raster Solvent Vapor Annealing with Soft Shear

3.1 Prior Developments

Raster solvent vapor annealing with soft shear (RSVA-SS) was designed as a combination of two methods for directing self-assembly in BP thin films: raster solvent vapor annealing (RSVA) and soft shear (SS).

3.1.1 Raster Solvent Vapor Annealing

Raster solvent vapor annealing (RSVA) is a technique previously developed by Seppala *et. al.*³⁰. The process involves suspending a flat tip nozzle directing a solvent-rich nitrogen stream from a bubbler system into a thin film situated below on a motorized stage. As a result, solvent enters the film only in the region directly beneath the nozzle (the annealing zone) and the degree of swelling can be tuned by the vapor flow rate. With this method, only targeted regions within a single film are exposed and solvent vapor annealed to create spatial control of the nanostructure alignment. Prior studies have demonstrated the area-selective reorientation of SIS cylinders from parallel to perpendicular relative to the substrate³⁰.

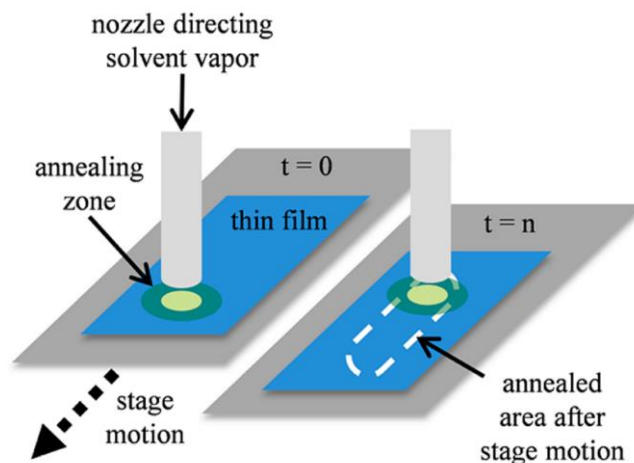


Figure 3.1: Illustration of RSVA showing the progression of an annealing zone over time. Reprinted from reference 30.

3.1.2 Soft Shear

Another method created to impart shear fields on BP thin films for aligning nanostructures was demonstrated by Qiang *et al.* using a laminated solvent permeable elastomer (PDMS) and solvent vapor annealing³¹. A brief summary of this technique, termed “soft shear,” is presented. The solvent vapor swells both the PDMS pad and the underlying BP thin film. The PDMS is expanded significantly and the BP is plasticized. After adequate levels of expansion, solvent is slowly removed from the system at a constant specified rate, resulting in deswelling and contraction of the PDMS pad. During contraction, a shear field is imparted on the underlying BP thin film by which nanostructures are aligned. After processing, the low surface energy of the PDMS pad allows for non-destructive removal. In the study, orientation was highly correlated to the shape of the laminated PDMS pad resulting from the isotropic deswelling front but the polymer under the center of the pad remained unaligned due to minimal shearing.

3.2 Process Description & Experimental Procedures

Combining the set-up of the RSVA process with the sample preparation of soft shear experiments, the raster solvent vapor annealing with soft shear (RSVA-SS) process was created. The mechanism for aligning nanostructures using this method is described as follows: as a portion of the sample moves into the annealing zone of the nozzle, solvent diffuses into the PDMS pad laminated upon a BP thin film. This process can be understood as the progression of a swelling front followed by a deswelling front which produces the intended shear forces. The speed of the motorized stage and sample beneath the nozzle is termed the raster speed (v) and is usually set at $10\text{ }\mu\text{m/s}$ to achieve adequate alignment (see section 4.3). The flow rate of a toluene vapor stream through a needle nozzle was held constant at 20 mL/min , adequate for solvent transport into a PDMS pad and SIS thin film.

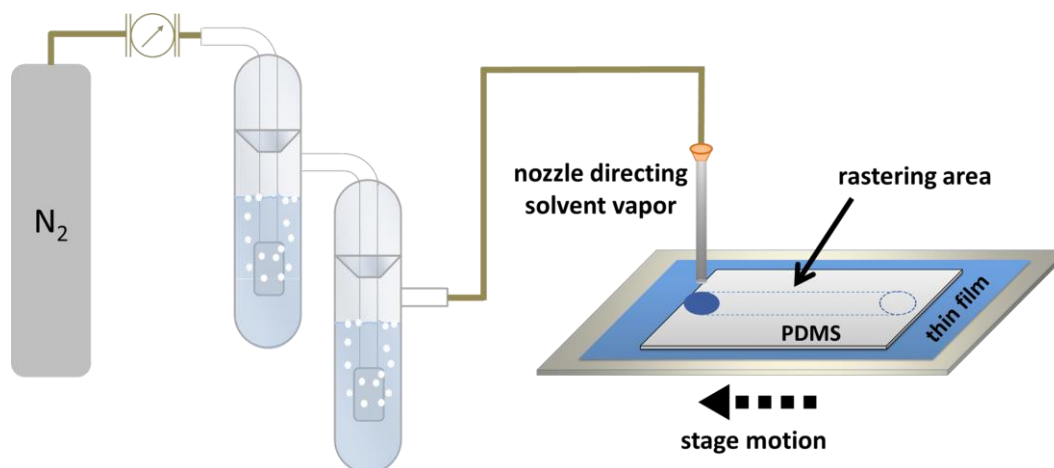


Figure 3.2: Schematic of RSVA-SS process. Reprinted from reference 32.

Chapter 4

Results

4.1 Single Raster Pass: 1-D and 2-D

Single linear RSVA-SS passes with a needle nozzle were conducted vertically, horizontally, and diagonally relative to rectangular PDMS pads laminated on SIS thin films. As shown in Figure 4.1 (a – b), the alignment of SIS cylinders were correlated highly with raster direction and independent of PDMS pad shape unlike prior soft shear techniques³¹. Raster speed (v) was set to 10 $\mu\text{m/s}$ and the typical dimension of the PDMS pads was 20 mm $\times$ 10 mm $\times$ 0.3 mm. Though only the surface morphology was evaluated in this study, the alignment of cylindrical nanostructures throughout film thicknesses was previously investigated with grazing-incidence small-angle X-ray scattering (GISAXS) and found to correlate with the surface alignment for film thicknesses ranging between 40 nm and 1 μm which includes the film thickness of the study (~ 115 nm)³³.

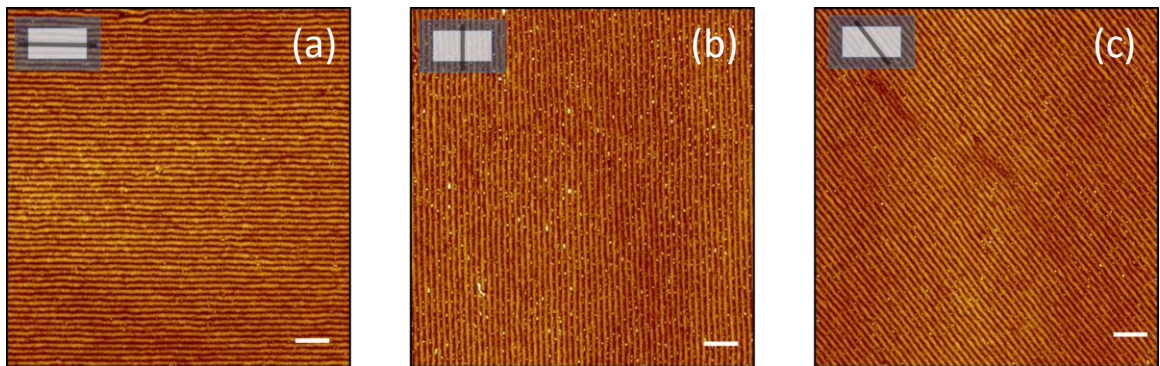


Figure 4.1: AFM phase images of (a) horizontal, (b) vertical, and (c) diagonal RSVA-SS single passes. Scale bars represent 200 nm. Reprinted from reference 32.

Given this correlation over a one-dimensional raster path, it was hypothesized that BP domain alignment would follow the instantaneous velocity of the film beneath the solvent nozzle in two-dimensions. Two motorized stages were stacked to enable XY directional capabilities and controlled by a computer code previously written to create a “UD” shaped raster path. After processing, multiple areas in the rastered path were examined using AFM and the ability for the RSVA-SS to conduct 2-D patterning of BP thin films was confirmed. This result highlighted the versatility of the RSVA-SS process in efficiently writing 2-D patterns of ordered BP nanostructures in the absence of substrate modification.

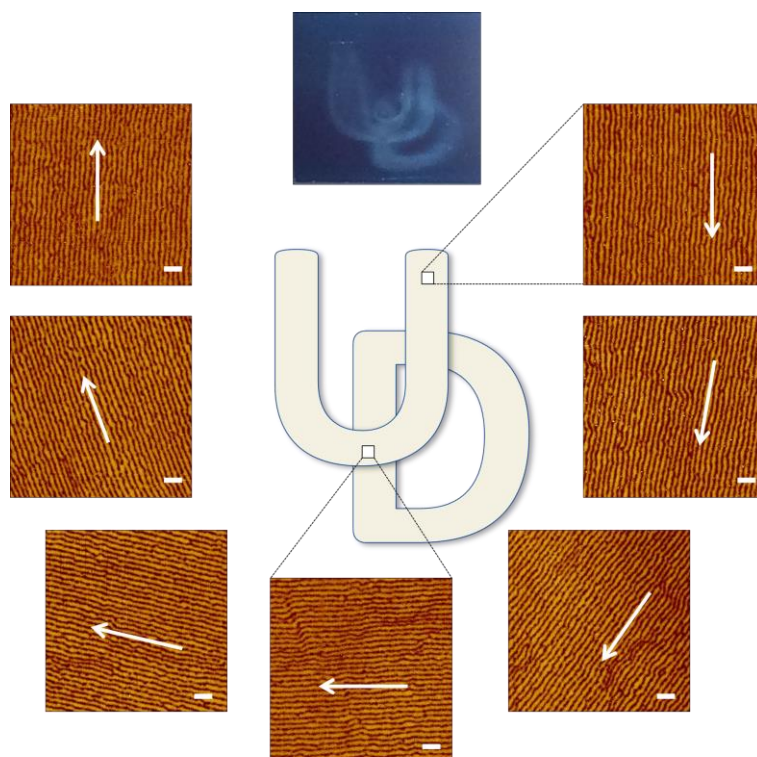


Figure 4.2: “UD” shaped 2-D patterning showing alignment highly correlated with the curvature of the raster pathway. A macroscopic optical image of the SIS thin film post-processing is shown above. Scale bars represent 200 nm. Reprinted from reference 32.

4.2 Slit Nozzle

To increase the area of the annealing zone, a slit nozzle with two inlet ports and a widening channel was fabricated. After conducting a single raster pass using the wide slit nozzle, the alignment of polymer domains was checked at multiple points along a set displacement (Figure a – c). Consistent alignment of SIS cylinders was found for each studied area throughout the 5 cm width of the processed area. These results demonstrated the scale-up potential of the RSVA-SS process for large area patterning.

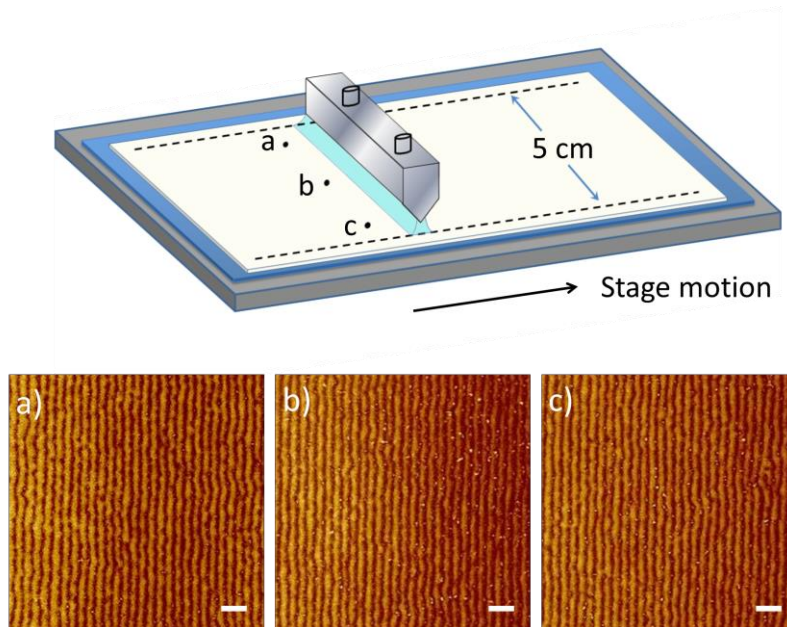


Figure 4.3: Schematic of RSVA-SS process utilizing a wide slit nozzle with AFM phase images of three points at a set displacement. Reprinted from reference 32.

4.3 Dashes and Crossed Lines

Varying raster speed, and therefore the exposure time of a given area of PDMS to solvent flow, was seen to significantly affect the degree of alignment imparted on

BP nanostructures. The results of four raster speeds are exhibited in figure 4.4. At slower speeds (*e.g.* 10 $\mu\text{m/s}$), the prolonged exposure to solvent enabled greater solvent uptake by the PDMS pad and underlying thin film. Upon deswelling, the PDMS pad undergoes significant contraction and imparts large shear forces on the highly plasticized BP film to generate alignment. As raster speed is increased, less solvent uptake results and eventually no appreciable shearing occurs.

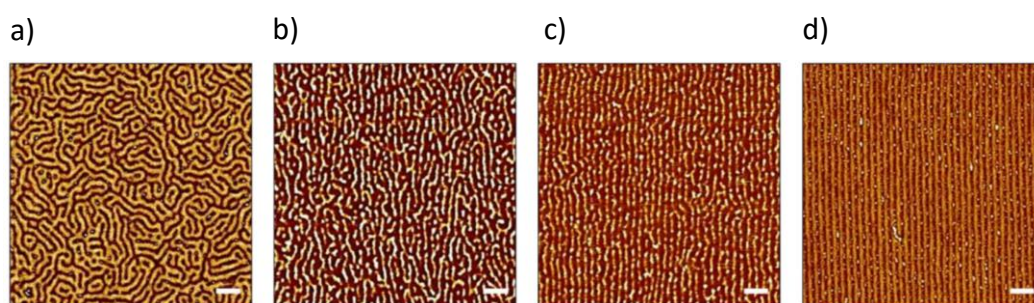


Figure 4.4: AFM phase images of SIS cylinders aligned using RSVA-SS single passes at different raster speeds: (a) 100 $\mu\text{m/s}$; (b) 50 $\mu\text{m/s}$; (c) 20 $\mu\text{m/s}$; (d) 10 $\mu\text{m/s}$. Scale bars represent 200 nm. Reprinted from reference 32.

The effect of raster speed on nanostructure alignment was utilized to produce a dash pattern. Along a one-dimensional raster path, the motorized stage speed was alternated between 10 $\mu\text{m/s}$ (“slow”) and 100 $\mu\text{m/s}$ (“fast”) at distinct displacements associated with dash size. Distinct areas of aligned and disordered cylinders were observed in the “slow” and “fast” regions, respectively. However, due to the lack of a swelling front at the “slow” - to - “fast” boundary, a wide transition from aligned to disordered was created. For applications requiring higher resolution, modulating raster speed of the RSVA-SS process would be inadequate in comparison to the accuracy achieved by methods such as graphoepitaxy and chemical pre patterning.

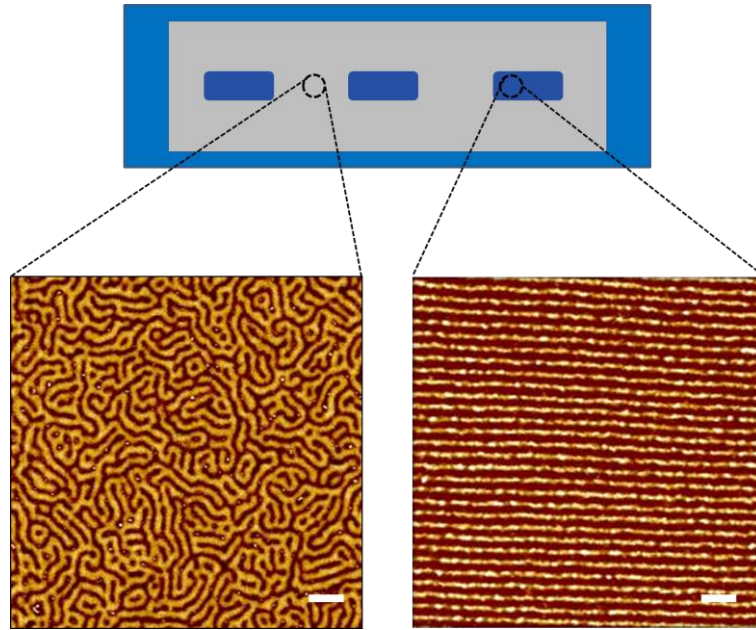


Figure 4.5: Schematic of dash pattern with accompanying AFM phase images showing both disordered (“slow”) and aligned (“fast”) regions. Scale bars represent 200 nm. Reprinted from reference 32.

The ability to overwrite previously aligned nanostructures was tested by performing a single pass RSVA-SS, replacing the deformed PDMS pad with a new one, followed by a second raster pass orthogonal to the first pathway. As expected, alignment correlated with each raster direction occurred away from the junction of the pathways. At the junction, however, only the alignment of the second pass was present confirming the overwriting capability of the RSVA-SS process. In further testing, a resistance associated with reordering previously aligned nanostructures was perceived.

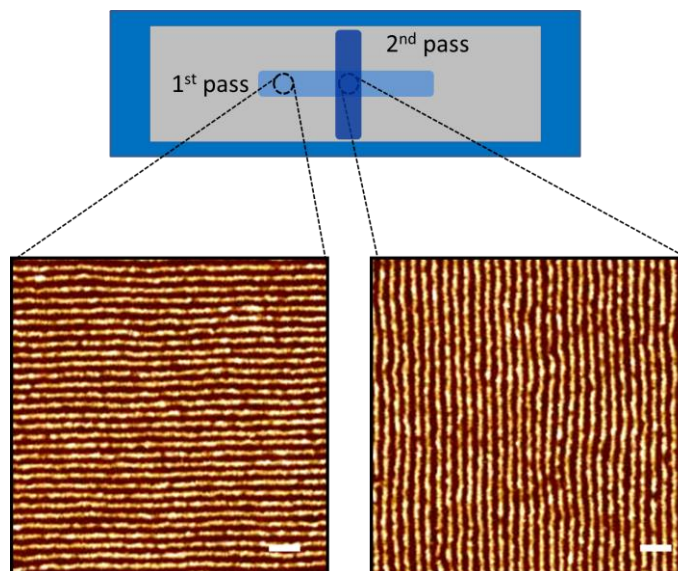


Figure 4.6: AFM phase images of a double-pass RSVA-SS demonstrating the ability to overwrite previously aligned SIS cylinders. Scale bars represent 200 nm. Reprinted from reference 32.

4.4 Bell-jar Erase & Rewrite

In addition to aligning structures with RSVA-SS, a simple bell-jar SVA of a polymer thin film can erase pre-existing order by enabling chain mobility. Once the BP domains return to an isotropic disordered state, RSVA-SS can rewrite a new pattern in the BP domains.

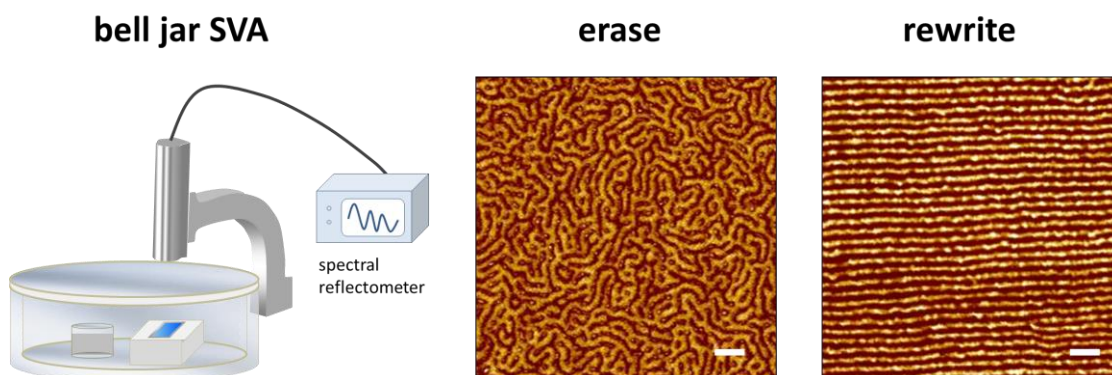


Figure 4.7: Schematic of bell-jar SVA setup with spectral reflectometer to analyze film swelling. AFM phase images are shown of post-annealed disordered BP domains (“erase”) and realignment from RSVA-SS “rewrite.” Scale bars represent 200 nm. Reprinted from reference 32.

4.5 Alignment boundaries

In following section, the experimental trials which led to utilizing a channeled PDMS pad for sharp alignment boundaries are presented.

4.5.1 Stiffness transition

The ability for a PDMS to expand and subsequently contract and produce a shear force on underlying is strongly dependent on the modulus (stiffness) of the pad. Therefore, it was hypothesized that a change in pad stiffness along a raster would yield alignment in the low modulus region of the pad while poor or no alignment would be generated in the stiff portion. Thus, a PDMS was half covered by a mask and underwent ultraviolet ozone (UVO) treatment to convert the pad surface to silicon oxide.

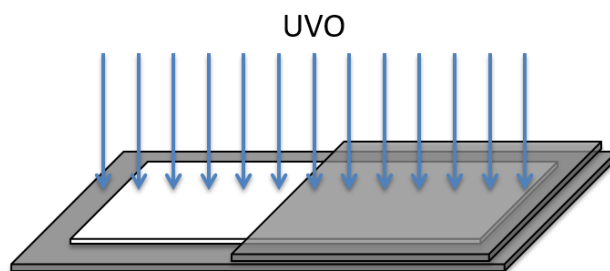


Figure 4.8: Schematic showing UVO treatment of PDMS pad for stiffness transition.

After rastering across the stiffness transition of pad, the artifacts of trapped bubbles at the interface were shown under an optical microscope. An explanation for this result is the inability for the swelling front to advance into the stiff portion causing an accumulation of solvent at the interface creating bubbling under the pad. Though this result and method was unacceptable in achieving a sharp alignment boundary, an interesting result was found at the interface of a trapped bubble: a change from slightly ordered cylinders with poor coordination lengths to a completely disordered morphology.

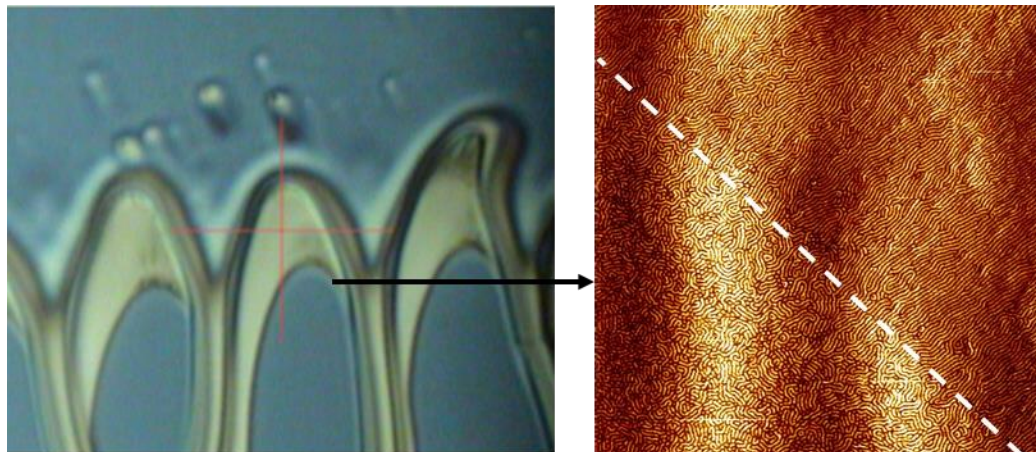


Figure 4.9: Optical image of trapped bubble artifacts (left) and AFM phase images of the edge of bubble with the approximate alignment boundary designated (right).

4.5.2 Trapped air bubble

Given the prior results, the use of a bubble to generate a boundary with nanometer resolution was tested. While laminating a PDMS pad on a SIS film, an air bubble was trapped beneath the pad. After rastering across the diameter of the bubble, the alignment at the interface was characterized with AFM. A sharper boundary between ordered and disordered morphologies was found. It is important to note from the optical image of the interface that the RSVA-SS processing was seen to create film defects. However, from phase imaging, the alignment of nanostructures remained independent of the defect height profiles.

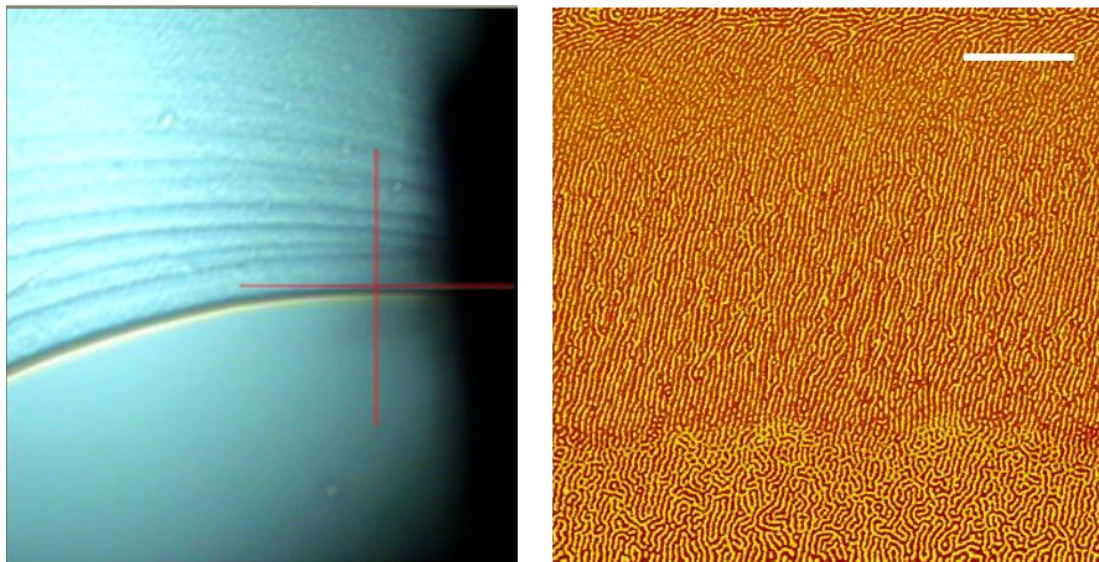


Figure 4.10: (Left) optical image of bubble interface after RSVA-SS processing (left). (Right) AFM phase image of interface. Scale bar represents 600 nm.

To eliminate the undesirable curvature of the interface, a coverslip shard was embedded in a PDMS film and subsequently removed after curing the PDMS. Therefore, when laminated, a bubble with the same shape as shard was produced. Rastering across a straight bubble edge, a sharp alignment boundary was produced as shown in figure 4.11.

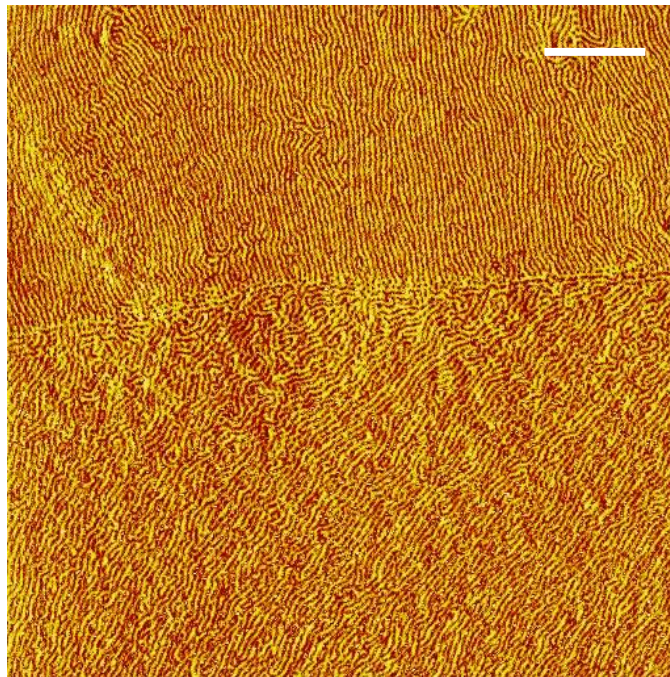


Figure 4.11: AFM phase image of the alignment boundary created from rastering across a straight bubble edge. Scale bar represents 600 nm.

4.5.3 Channeled PDMS pad

PDMS pads with channels were fabricated using a lithographic SU-8 template (see appendix B). Initial tests with laminated channels without openings yielded undesirable bubbling as solvent became trapped in the channel, thereby creating pressure and delaminating the pad at the interface. A simple solution for this was to cut open the channel ends for excess solvent to escape. Rastering across a channel produced the boundary shown in figure 4.12. Though the resolution is poorer than previously observed, significant deviations in lab temperature affecting solvent uptake in the bubbler system and edge roughness of the channel strongly affect the shearing front up to the interface.

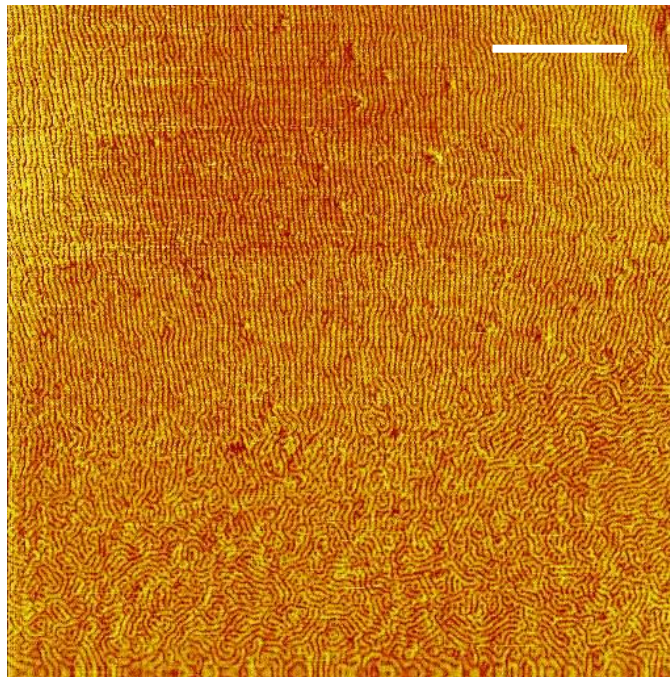


Figure 4.12: AFM phase image of alignment boundary generated by RSVA-SS and a channeled PDMS pad. Scale bar represents 800 nm.

4.5.4 T-junction & RSVA-SS Resolution Limit

The preceding work to sharpen the interface of an alignment transition laid the groundwork to achieve transitions between two regions of separately aligned domains. Such a transition can be represented by a T-junction where domain alignment rotates by 90° across an interface. Experimentally, creating this junction would require an initial RSVA-SS pass with a standard PDMS pad followed by a second pass across a channeled pad with the channel aligned parallel to the prior raster path.

In the initial procedure, both raster passes were conducted utilizing the needle nozzle. This selection presented challenges in achieving the T-junction given the effect of degrading alignment away from the needle exposure area (4 mm in width). Therefore, unless the pad channel was laminated perfectly to enclose the highly

aligned region of the first pass pathway, tapering effects near the periphery of the raster path would create a wide transition region between horizontally oriented cylinders and vertically oriented cylinders. To solve this impasse, the slit nozzle was employed for the first raster pass, thereby aligning cylinders in the entire film without any tapering alignment effects. Upon rastering in an orthogonal direction across a channel, an interface was generated with three distinct regions: horizontally aligned, disordered (“as-cast”), and vertically aligned SIS cylinders.

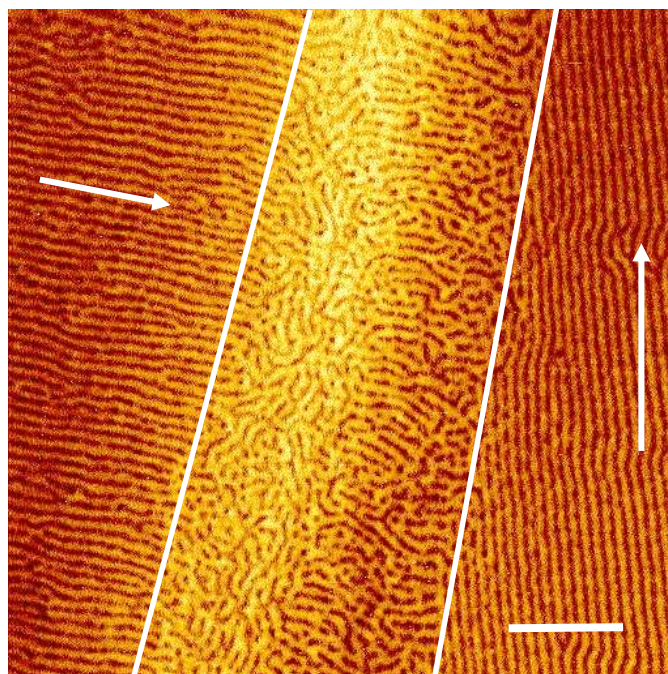


Figure 4.13: AFM phase image of a T-junction attempt with SIS cylinders. Visual guides designate region boundaries and nanostructure alignment. Scale bar represents 400 nm.

The “as-cast” region measured approximately 0.8 - 1 μm in width with a height profile varying 100 nm across the interface. This height profile suggested the shear

force to realign the nanostructures was in excess and thus the edge of the channel “shoveled up” a sample of disordered polymer. If true, the interfacial width could be minimized if the shear force imparted on the film during the second raster pass was tuned to allow for both nanostructure realignment and avoid the described “shoveling” effect. With the current experimental setup available, such control would be difficult to achieve because conditions such as temperature and humidity significantly impact PDMS swelling and shear. However, at the current progress of this work, the resolution limit for RSVA-SS technique has been minimized to 0.8 μm .

Chapter 5

Future Work & Considerations

In this study, only a cylinder-forming SIS polymer was processed using RSVA-SS to demonstrate the ability to align BP nanostructures. A logical progression from this work would be to apply RSVA-SS and promote long-range ordering for a library of morphologies such as hexagonally-packed spheres and cylinders useful for nanoscale filtrations and dot arrays, bicontinuous gyroids for material and energy transport applications, as well as through-film perpendicular lamellar nanostructures for lithography and templating. With regard to perpendicular lamellae forming polymers, shear fields alone have been proven to be inadequate for patterning these nanostructures in thin films³⁴.

A potential solution to this challenge lies in coupling RSVA-SS with solvothermal annealing³⁵. By placing the laminated film sample upon a motorized heating stage and properly balancing heat input with solvent uptake, chains throughout the film thickness would be granted greater mobility, allowing surface shear fields to propagate through the film and align the lamellae. This approach could also be amended to high molecular weight polymer systems in which entanglements greatly restrict chain mobility for shear alignment.

The resolution limit of RSVA-SS in this work highlights an important limitation in applying the technique to nanolithography where nanoscale features such as sharp bends and jogs are required. Combining RSVA-SS with previously established DSA methods would both overcome this limitation while maintaining the unique process viability. While chemical pre patterning has already been developed into a continuous process through IMEC³⁵, RSVA-SS may enable shorter processing

times by quickly patterning less complex feature areas which do not required substrate modification.

Lastly, findings from Majewski *et al.* indicate a pathway-dependent method for ordering block polymer thin films through subsequent thermal annealing after rapid shear from laser zone annealing (LZA)³⁶. After shearing, it is postulated that “latent alignment” is induced in a film and can be thermally annealed to reduce the number of kinetic defects in the polymer nanostructures. The shear forces associated with RSVA-SS are not commensurate with those produced in LZA, the reproducibility of this reported phenomenon was tested by placing a RSVA-SS processed film in an oven for 2h at 160°C. Before and after phase imaging demonstrates the emergence of latent alignment and confirms the benefits of thermal annealing, a step easily amended to the continuous RSVA-SS process. Future studies to optimize the required post-RSVA-SS processing time as well as resulting improvement of feature resolution should be conducted.

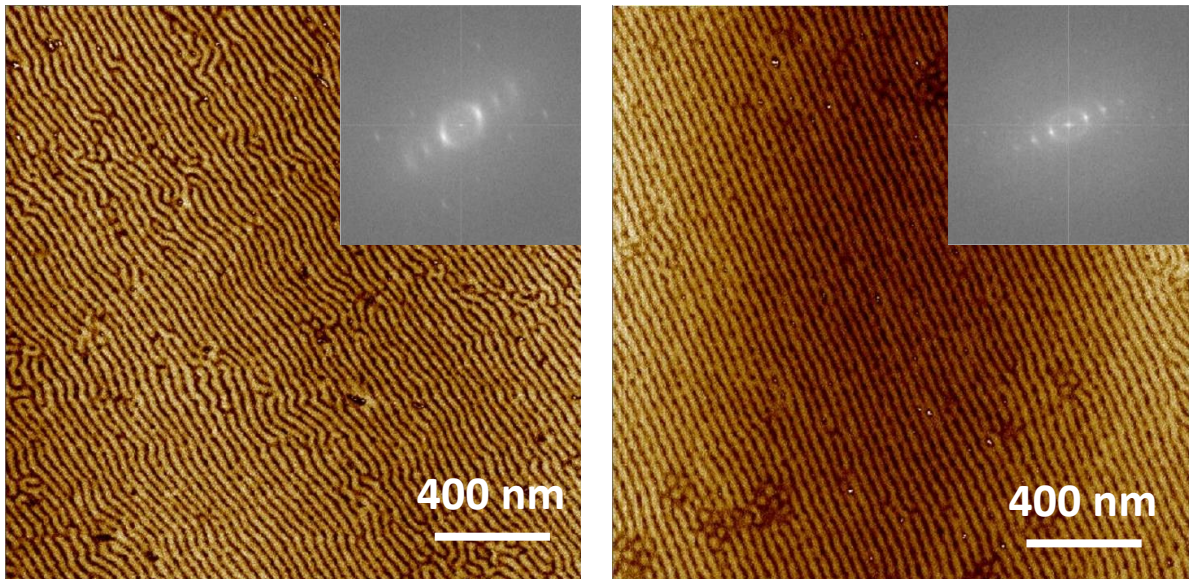


Figure 5.1: AFM phase images and fast Fourier transform (FFT) of RSVA-SS processed SIS cylinders before thermal annealing with poor alignment (left) and after thermal annealing with significantly improved alignment (right).

Chapter 6

Conclusions

Through an assortment of demonstrations, RSVA-SS has proven to be a versatile and facile technique for writing nanostructures patterns into BP thin films. Simple linear patterns as well as complex patterns such as curved, crossed, and dashed lines were achieved easily with cylindrical SIS nanostructures. By incorporating channels into a PDMS pad, alignment transitions were achieved, specifically a T-junction with 0.8 μm resolution.

The promise of RSVA-SS also must be assessed with the inherent limitations of the technique and opportunities for enhancement. Greater control over laminate swelling and associated shear forces as well as combinations with other DSA methods would improve the resolution of features such as T-junctions and dashes, enabling both macro- and nanoscale features to be simultaneously patterned. For applications such as nanolithography which demand an even higher degree of feature resolution, post-process thermal annealing has been shown to elicit latent alignment to minimize defects and extend coordination lengths of self-assembled domains. Extending beyond cylinder-forming polymer systems to enhance ordering in spherical, lamellar, and gyroid structures further would demonstrate the versatility of RSVA-SS to impact a wide range of applications.

With an industrially viable processing rate, no requirement for prohibitively slow substrate modification, and a wide slit nozzle for large area patterning, RSVA-SS exhibits noteworthy potential for the large scale application of BP DSA currently lacking in the field of nanotechnology.

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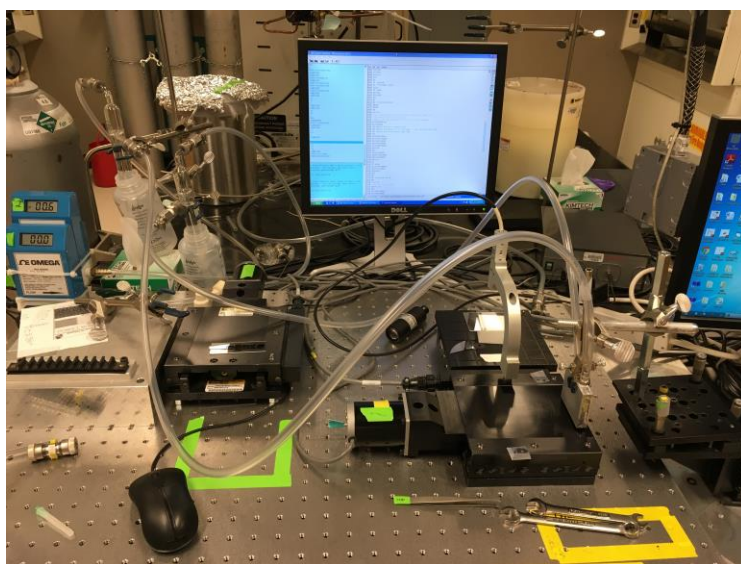
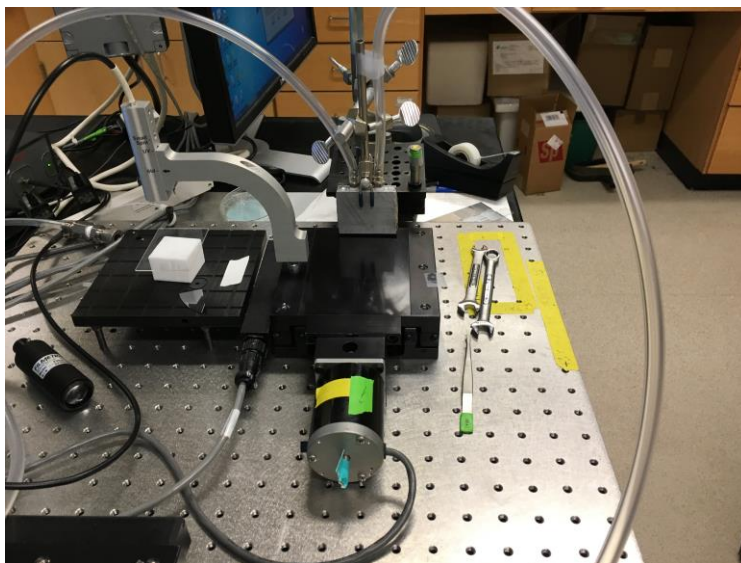
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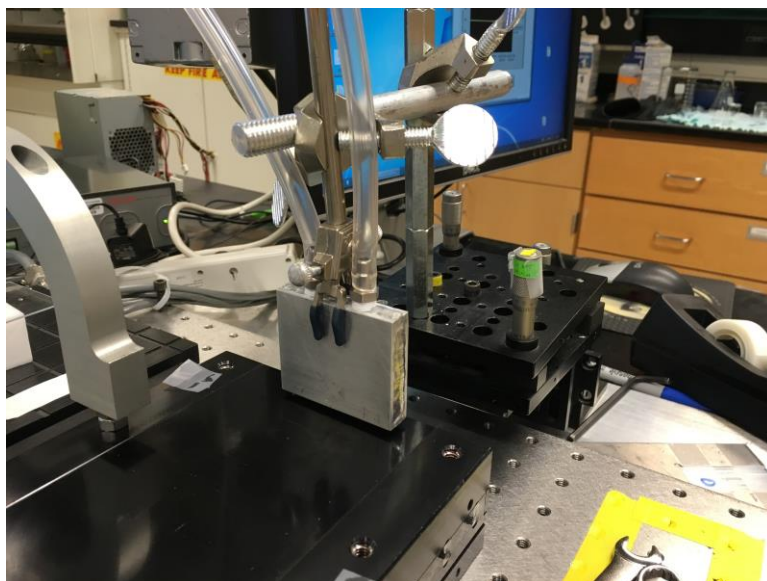
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Appendix A

Laboratory Images of RSVA-SS Set-up

Images of a standard RSVA-SS set-up are shown below. In the images, the wide slit nozzle is mounted above a motor stage and is connected to two separate solvent bubblers.





Appendix B

Fabrication of Channeled PDMS Template

Channeled PDMS pads were fabricated using a SU-8 epoxy template. The procedure for making a template is described as follows (see Figure B1): SU-8 epoxy resin is spin-coated onto a UVO-treated silicon wafer and subsequently baked atop a hot stage to preliminarily set the film. Next, a printed photomask is laminated on the film (Figure B2) and the uncovered areas of SU-8 are exposed to UV light for crosslinking. After additional baking steps, the template is submerged in developing solvent to remove the non-crosslinked SU-8 and expose the crosslinked features (Figure B3).

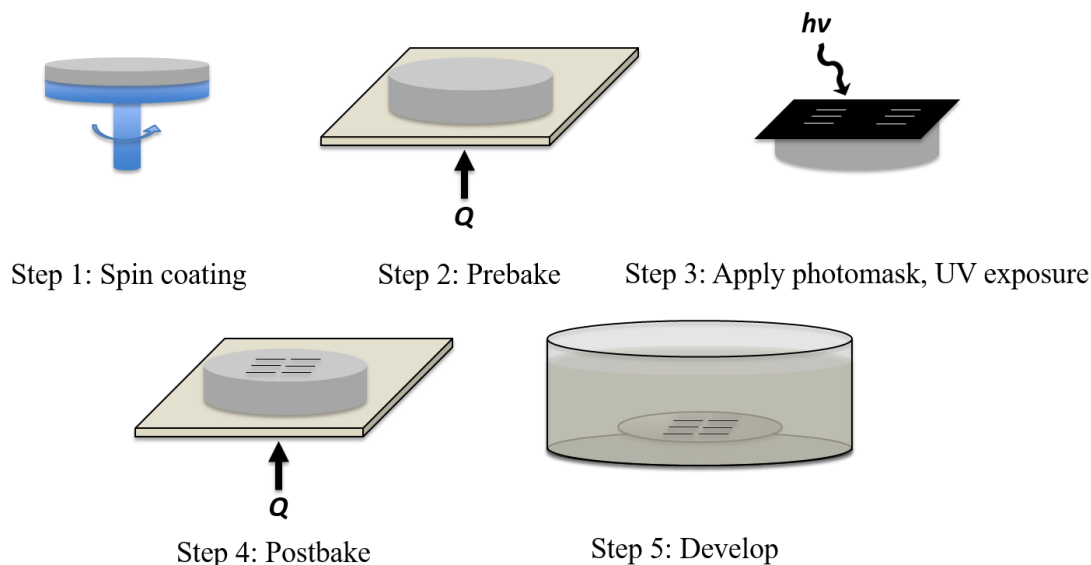


Figure B1: Schematic representing steps for fabricating the SU-8 template

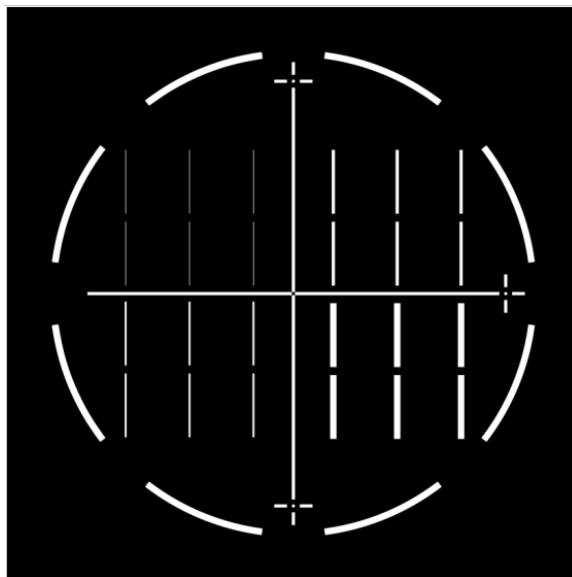


Figure B2: Design of photomask used to generate the SU-8 template. Credit: Ming Luo.

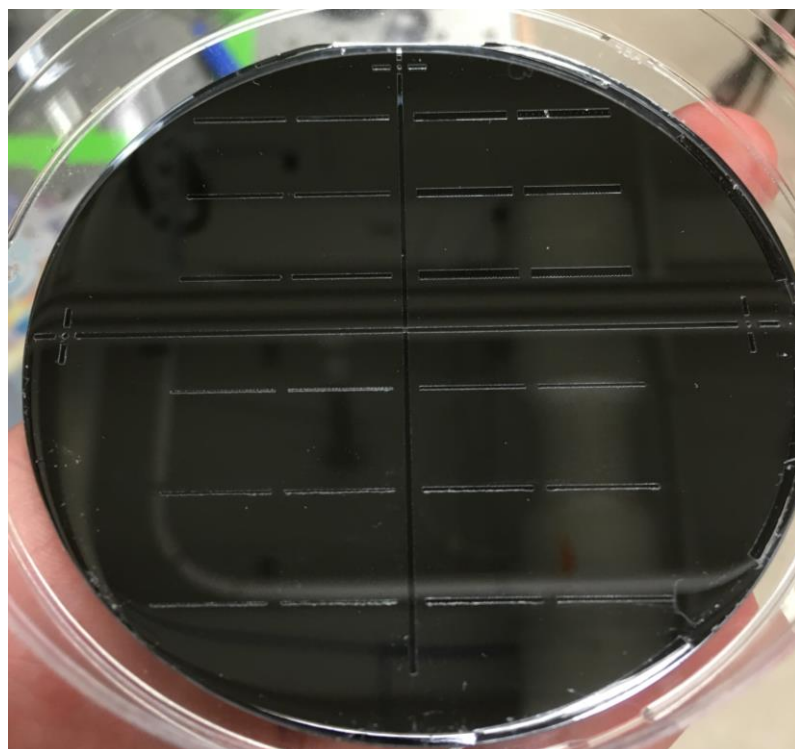


Figure B3: Photo of a finished SU-8 template with features.