THE ORIENTATION OF MICRODOMAINS AND THE PROGRESSION OF SHEAR ALIGNMENT IN BLOCK COPOLYMER FILMS: THE ROLES OF KEY MATERIAL, FILM, AND PROCESS PARAMETERS

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Abstract

Block copolymers provide attractive templates for nanopatterning at size scales inaccessible to conventional fabrication techniques. To serve effectively for most applications, however, the need to impart well-defined orientational and/or positional order to these microdomains is paramount. Shear alignment, has the powerful ability to macroscopically align microdomains in the direction of the applied shear simply by applying a stress at the film’s surface. The primary goal of this dissertation is to investigate the influence of key material, film, and process parameters on the ease and quality of alignment in sheared block copolymer films.

One important parameter which influences block copolymer thin film morphology is film thickness. To probe this effect rapidly and systematically, a film casting technique known as flowcoating was utilized. Previously, the quantitative relationship between the film thickness profile and the flowcoating process parameters was unclear. We illuminate this process by comparing experimental film thicknesses with a model based on a Landau-Levich treatment; the model thus provides a design approach which allows a user to produce polymer thin films of virtually any desired thickness profile. Via flowcoating, the influence of film thickness on block copolymer thin film morphology was then investigated using a series of polystyrene-poly($n$-hexyl methacrylate) (PS-PHMA) diblocks varying in composition and molecular weight.

The influence of additional material, film, and process parameters was then investigated using the same series of PS-PHMAs. To quantitatively compare the
alignment process across the different block copolymer films, a melting-recrystallization model was fit to the data, which allowed for the determination of two key alignment parameters: the critical stress needed for alignment, and an orientation rate constant. Collectively, these results provide useful scaling rules which enable predictions of the level of alignment which will occur under particular shearing conditions.

Lastly, a separate aim of this dissertation was to explore a means for manipulating block copolymer film morphology, not through shear, but by controlling the environmental conditions at the film’s surface during thermal processing in order to generate polymeric coatings with thermally switchable wetting properties (i.e., hydrophilic vs. hydrophobic).
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<td>AFM</td>
<td>atomic force microscopy</td>
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<tr>
<td>AIBN</td>
<td>azobisisobutyronitrile</td>
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<tr>
<td>BCC</td>
<td>body-centered-cubic</td>
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<td>BMA</td>
<td>n-butyl methacrylate</td>
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<tr>
<td>CA</td>
<td>contact angle</td>
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<td>CZA</td>
<td>cold zone annealing</td>
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<td>DDFT</td>
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<td>DMSO</td>
<td>dimethyl sulfoxide (deuterated)</td>
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<td>DPE</td>
<td>diphenylethylene</td>
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<td>DRI</td>
<td>differential refractive index</td>
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<td>DSC</td>
<td>differential scanning calorimetry</td>
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<td>FWHM</td>
<td>full width at half maximum intensity</td>
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<td>GI-SAXS</td>
<td>grazing incidence small-angle X-ray scattering</td>
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<td>$^1$H-NMR</td>
<td>proton nuclear magnetic resonance spectroscopy</td>
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<td>HEMA</td>
<td>2-hydroxyethyl methacrylate</td>
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<td>Interactive data language</td>
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<td>LS</td>
<td>light scattering</td>
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<td>poly(ethylene-alt-propylene)</td>
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<td>P2VP</td>
<td>poly(2-vinylpyridine)</td>
</tr>
<tr>
<td>RMS</td>
<td>root mean square</td>
</tr>
<tr>
<td>SAXS</td>
<td>small-angle X-ray scattering</td>
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<tr>
<td>SCFT</td>
<td>self-consistent field theory</td>
</tr>
<tr>
<td>SEC</td>
<td>size-exclusion chromatography</td>
</tr>
<tr>
<td>SPM</td>
<td>scanning probe microscopy</td>
</tr>
<tr>
<td>SS-LZA</td>
<td>soft shear with laser zone annealing</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscope</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
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</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TM-AFM</td>
<td>tapping mode atomic force microscopy</td>
</tr>
<tr>
<td>TREOS</td>
<td>three-angle light scattering</td>
</tr>
<tr>
<td>WAXS</td>
<td>wide-angle X-ray scattering</td>
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“I wouldn’t be who I am today, if not for those I’ve loved along the way …”

Eric Church
Chapter 1: Introduction

Introduction

1.1 Dissertation Objective

The desire to fabricate structures at ever-decreasing size scales has led to the development of a myriad of micro- and nano-processing techniques which have, in turn, fueled some of the greatest technological innovations in human history. However, many of the most successful and widely used fabrication techniques (like photolithography) are beginning to reach their size limits. \(^1\) Therefore, the need to discover and refine methods which can achieve higher and higher resolutions is paramount.

One potential avenue with which to address this critical issue is through the use of self-assembled materials, specifically block copolymer thin films. \(^2\)-\(^4\) Under the right conditions, the different blocks will locally phase-separate, producing a variety of periodic patterns and geometries (for example, spheres or cylinders of one component dispersed in a matrix of a second component) on the size scale of 10-100 nm. \(^5\) These patterns can then be used as templates to produce nanostructures such as metal nanodots \(^6\), nanowire polarizer grids \(^7\), and nanopore arrays \(^8\) to name a few. To be useful for many applications, however, the structures fabricated must have well-defined positional or orientational order. Therefore techniques are needed which can provide such order to the phase-separated microdomains contained in the block copolymer template. Several
methods have been created to impart order to block copolymer thin films; one which shows great promise is shear alignment.

Shear alignment is the process of ordering microdomains by applying a shear stress to the surface of a block copolymer. This technique has long been shown to align bulk polymer samples\textsuperscript{9}, but more recently has also been demonstrated to impart alignment to certain thin-film systems\textsuperscript{10-13} The current knowledge of the underlying physics of shear alignment as well as the body of experimental data available to help understand the phenomenon are, however, extremely limited to this point.

The primary aim of this dissertation is to address these limitations and more fully understand the shear alignment process so that block copolymers can be used more widely in nanofabrication. Specifically, we investigate the influence of a variety of parameters, including film thickness, block copolymer composition, and molecular weight, on the progression and terminal quality of alignment in sheared cylinder-forming block copolymer thin films. To achieve this, a series of block copolymers with controlled composition and molecular weight were synthesized and their thin film morphology, both pre- and post-shear, assessed using atomic force microscopy and a variety of image analysis techniques. To support our efforts to examine the role of film thickness on alignment quality, a series of experiments generating films with gradient thickness profiles via flowcoating\textsuperscript{14} was also conducted. Using these data, we attempt to identify design rules which will allow for precise fabrication of films with designed thickness profiles.

An additional goal of this work is to explore a route for manipulation of block copolymer film morphology, not through application of shear, but by controlling the
environmental conditions at the film’s surface during processing. Specifically, we attempt

to create coatings with thermally switchable wetting behavior based on block copolymers

which possess both hydrophilic and hydrophobic segments. Our approach is to control

which block wets the air interface by manipulating the environmental humidity while

cooling through the material’s order-disorder transition temperature. This should provide

a rapid, and fully reversible, route towards production of switchable coatings which

would be of great interest as electronically reconfigurable printing plates.15

1.2 Dissertation Organization

The preceding section presented a general overview of the motivation and scope of this dissertation. Chapter 2 provides background information on many of the fundamental concepts pertaining to this work, including discussion of both the bulk and thin film physics of block copolymers. Also reviewed in detail are many of the methods employed to order or manipulate block copolymer thin film morphology. Chapter 3 presents the experimental techniques used throughout the dissertation and includes discussion of polymer synthesis and bulk characterization, techniques for thin film production, characterization, and manipulation, and methods for microscopy and image analysis. Chapter 4 presents an experimental investigation of flowcoating. The parameters which dictate the film thickness profile are examined and compared with a Landau-Levich treatment. Chapter 5 describes the synthesis of a series of cylinder-forming polystyrene-poly(\textit{n}-hexyl methacrylate) block copolymers, which provide a convenient system for investigation of shear alignment phenomena. The thin film morphologies of these block copolymers are investigated as a function of film thickness.
Chapter 1: Introduction

for both nonaligned and shear-aligned thin films. Chapter 6 examines the effects of a variety of material, film, and process parameters on the alignment behavior (alignment quality vs. stress and time) of the same cylinder-forming block copolymers employed in the preceding chapter. To quantitatively interpret the results, the data are compared to a melting-recrystallization model. Chapter 7 presents our approach for creating coatings with thermally switchable surface energies using amphiphilic poly(ethylene oxide)-poly(dimethylsiloxane) block copolymers. Lastly, Chapter 8 summarizes the key conclusions of the dissertation and suggests several prospective areas for future research.
1.3 References


Chapter 2

Background

The purpose of this chapter is to introduce many of the fundamental concepts which will be built upon in this thesis. First, block copolymers and their bulk physics will be presented. This will include some discussion on applications of these materials including their use as nanolithographic templates. Second, the physics of block copolymer thin films will be discussed, with a particular emphasis on the “extra” forces which can greatly influence their thin film morphology. Finally, the majority of the chapter will focus on methods to control the order and morphology of block copolymer thin films. This will contain a survey of the many techniques used towards this end, including a discussion of the shear alignment techniques which are central to this thesis work.

2.1 Introduction to Block Copolymers

A polymer is a large, chain-like macromolecule composed of many smaller chemical repeat units, or monomers. The degree of polymerization, \( N \), is the number of repeat units which form a single chain. A homopolymer consists of a single type of repeat unit. For example, polystyrene (PS) is a homopolymer of \( N \) covalently linked styrene (S) monomers. A copolymer, however, contains two or more chemically distinct repeat units. For copolymers, the sequence with which the different monomer types add to the
polymer chain can have great effects on the material’s properties. As such, copolymers are classified based on their monomer arrangement. Statistical copolymers are composed of monomer units whose sequence distribution obeys known statistical laws; a special type of statistical copolymer is a random copolymer, whose distribution of repeat units is truly random along the chain. An alternating copolymer has two different types of repeat units which are alternately arranged along the chain (i.e., if A and B are the monomer types, the chain sequence is as follows: -A-B-A-B-A-B-). The above copolymers typically possess properties which are intermediate to the properties of the corresponding homopolymers. Alternating copolymers are produced when the growing end of a polymer chain rigorously adds a monomer of the opposite type. The converse case, when a growing chain adds only a monomer of the same type, yields a block copolymer (i.e., the chain sequence would be -A-A-A-B-B-B-; although block copolymers are not actually synthesized in this way, see the discussion on anionic polymerization in Chapter 3). These block copolymers, and the techniques used to understand and manipulate them, will be the primary focus of the remaining chapter. For more information concerning polymers in general, please refer to the wealth of literature available on the topic.1-3

The simplest type of block copolymer is the linear diblock: di- indicating that there are two blocks, and linear referring to their connectivity or “architecture” (branched and star type polymers are also possible).4-7 Linear triblocks (and higher order materials) are also common. These include ABC-type triblocks, for which all three blocks are chemically distinct, and ABA-type triblocks, which have identical endblocks. Perhaps the most fascinating aspect of block copolymers is their phase behavior, illustrated in the following example. Consider a mixture of A and B homopolymers which are chemically
dissimilar, and therefore at most blend ratios will thermodynamically phase separate. This causes the A and B chains to macroscopically partition into two phases: one rich in A, the other in B (see Figure 2.1a, this is analogous to the phase separation commonly seen in small molecules; e.g., oil and vinegar). Upon addition of some A-B block copolymer to this mixture (see Figure 2.1b), the block copolymer preferentially partitions to the A-B interface and acts as a surfactant or emulsifying agent, stabilizing

![Figure 2.1](image-url)  

**Figure 2.1** Diagrams showing A/B polymer/polymer phase behavior for three cases: (a) blends of A and B homopolymers undergo macroscopic phase separation, (b) addition of A-B diblock stabilizes the interface, producing intermediate-scale phase separation, (c) pure A-B diblock yields microphase separation, with periodic features of the length scale of the polymer chains.\(^6\)
intermediate-scale drops of one homopolymer in a matrix of the other. Now imagine a melt consisting entirely of A-B block copolymers. Like the previous case, the block copolymers situate their block junctions at the A-B interface, but rather than stabilize larger droplets, the chains can only form domains on the length scale of the polymer chains themselves (see Figure 2.1c). This phenomenon is referred to as microphase separation (although the features are actually on the nanoscale). Therefore, under the appropriate conditions, most block copolymers will microphase-separate, self-assembling into periodic nanoscale features rich in either A or B, with the covalent bond between the A and B blocks confined to the microdomain interface.

Great efforts, both experimentally and theoretically, have been made to better understand the phase behavior of block copolymer melts. Phase separation in all materials depends on both enthalpic and entropic contributions. The latter always favors mixing; however, in polymers this effect is greatly reduced due to the covalent bonds between monomer units, which restrict their ability to independently sample all space. Therefore, the enthalpic contribution (usually positive, though not always) typically drives the energy of mixing in polymeric systems. Mixing in polymer blends can be modeled via the Flory-Huggins treatment:

$$\Delta G_m = \frac{f_A}{N_A} \ln (f_A) + \frac{f_B}{N_B} \ln (f_B) + f_A f_B \chi$$

Equation 2.1

where $\Delta G_m$ is the change in free energy due to mixing (a negative value favors mixing, positive always produces phase separation), $R$ is the universal gas constant, $T$ is the absolute temperature, $f$ is each component’s volume fraction, and $\chi$ is the Flory-Huggins interaction parameter. The Flory-Huggins interaction parameter can be thought of as the effective degree of incompatibility between the two polymers. It is typically observed to
decrease with increased temperature and is theoretically predicted to be inversely related to temperature: \( \chi \sim V_r (\delta_A - \delta_B)^2 / RT \), where \( V_r \) is a reference molar volume and \( \delta \) is the solubility parameter for each component. The first two terms on the right hand side of Equation 2.1 represent the entropy of mixing; their contribution is small because \( N \) is large for polymers. The rightmost term represents the enthalpic contribution, which is dominated by \( \chi \). Therefore, the larger the \( \chi \) the greater the driving force for macroscopic phase separation in polymer blends and microphase separation in block copolymers.

As mentioned previously, because of the covalent bond between the blocks, block copolymers can only microphase-separate on nanoscopic length scales. At equilibrium, the chains will self-assemble such that they balance the surface area between the two blocks and the degree of chain stretching beyond their non-constrained dimensions (this is typically expressed as the polymer’s radius of gyration, \( R_g \), which is the average root-mean-square distance between the chain segments and the chain’s center of mass\(^3\)). As such, when the polymer is symmetric (i.e., the A and B blocks have equal volume fraction), or nearly symmetric, the chains will form lamellar structures (parallel, alternating domains of A and B chains). In general, as one block increases in volume relative to the other, the interfaces curve (again, to balance the competition between chain stretching and minimizing surface area) and the lamellar morphology transitions to a bicontinuous gyroidal phase. As the polymer continues to become more asymmetric, hexagonally-packed cylinders and then body-centered-cubic (BCC) spheres of the minority component are formed, embedded within a matrix of the majority component (see Figure 2.2).\(^4\)\(^-\)\(^7\) The domain/repeat spacing of these features, \( d \), is predicted to scale as \( d \sim aN^{2/3} \chi^{1/6} \), where \( a \) is the statistical segment length.\(^4\) This phase behavior has been
Figure 2.2 (a) Phase diagram\(^8\) (generated by self-consistent field theory) for an AB diblock copolymer, showing the regions for hexagonally-close-packed spheres (S\(_{cp}\)), body-centered-cubic spheres (S), hexagonally-packed cylinders (C), gyroid (G), orthorhombic Fddd (O\(^{70}\)), and alternating lamellae (L). (b) Representations of the most commonly observed morphologies, arranged as a function of volume fraction.
mapped out both experimentally\textsuperscript{7} and theoretically (mostly using self-consistent mean field theory, SCFT)\textsuperscript{8-10} and is shown in Figure 2.2.

The lowest curve on the diagram represents the order-disorder phase transition, or the point at which the periodically arranged microdomains decay into a homogeneous melt. Because $\chi$ is temperature dependent, this transition is observed at a fixed temperature, termed the order-disorder transition temperature ($T_{ODT}$); this temperature is one of the most important physical properties of a block copolymer. Theory\textsuperscript{9} predicts that for a symmetric diblock, $\chi N$ at the $T_{ODT} = 10.5$. Because $\chi N$ at $T_{ODT}$ is positive, if either $\chi$ or $N$ is sufficiently small, the block copolymer will never order; though $\chi$ increases with decreasing $T$, at some point the polymer melt will vitrify into a rigid, glassy solid (this occurs at the material’s glass transition temperature, $T_g$) and thus be unable to self-assemble. Conversely, if $\chi N$ is very large, the polymer will always be ordered as the material will thermally degrade before its $T_{ODT}$ can be reached. Therefore, not all polymers have practically accessible order-disorder transitions.

The phase diagram in Figure 2.2 is for a relatively specific case. The phase behavior can be dramatically altered by changing any of numerous conditions. Dispersity, or the heterogeneity in the polymer chains’ $N$, has been shown to shift or skew the phase diagram and can either widen the phase space for certain morphologies or enable the expression of new ones.\textsuperscript{11-12} Employing tri- or multiblock copolymers and changing the polymer architecture (e.g., linear vs. star polymer) can all impact the phase behavior.\textsuperscript{13} In the case of a linear ABA triblock with A blocks of equal length (i.e., two linear AB diblocks coupled together), the difference is modest; the phase diagram is qualitatively similar, but shifted vertically (positively, to reflect the greater $N$ of the triblock). When
employing ABC triblocks, however, a wide array of morphologies becomes available. Exploring the vast phase space of three-component (or more) multiblocks is a daunting task, but due to the richness of structures and functionalities possible, will likely be a key area of study in block copolymer science moving forward. An additional factor which can influence the shape of the phase diagram is the conformational asymmetry of the blocks (which reflects the mismatch of the pure component densities and persistence lengths), defined as the ratio of the statistical segment lengths. The conformational asymmetry essentially skews the phase diagram such that the block with the smaller segment length has a disproportionately larger volume fraction contribution, thus creating an asymmetric phase diagram.

All of the phase behavior discussed above deals with amorphous (non-crystalline) polymers which are in the melt (above the $T_g$ of all of the blocks). Upon reaching the $T_g$ the melt vitrifies, thereby “locking in” the melt structure present at $T$ slightly greater than $T_g$. It is also possible to have one or more crystallizable blocks present in the copolymer. Upon cooling beneath the melting temperature, $T_m$, this can yield an interesting variety of solid-state structures. Essentially, nanostructure formation in semicrystalline block copolymers is a competition between the crystallite growth and the block incompatibility, $\chi N$. When the polymer is disordered (i.e., $\chi N$ is very small), crystallization dominates, creating alternating crystalline/amorphous lamellae. This is also generally the case for weakly microphase-separated systems; the crystals will “break out” of their microdomains, causing structural rearrangement into lamellae. When $\chi N$ is large, however, the crystal growth is confined to the microdomains (i.e., it is too energetically
costly for the crystallizing chains to break out) so the crystal growth is templated by the pre-existing (and preserved) melt structure.

The diffusive and rheological properties of block copolymers in the melt have also been studied. From classic reptation theory, the self-diffusion coefficient, $D_S$, for long (entangled), linear homopolymers scales with the inverse of the polymer’s molecular weight squared.\textsuperscript{3, 18} However, $D_S$ for microphase-separated block copolymers shows a much stronger scaling with molecular weight. Lodge and Dalvi,\textsuperscript{19} and later Yokoyama and Kramer,\textsuperscript{20} proposed that the enhanced dependence was due to a thermal activation barrier which must be overcome for chains to “hop” between microdomains, given by:

$$D_S \sim D_0 \exp(-\beta \chi N_{MB})$$

\textbf{Equation 2.2}

where $D_0$ is the self-diffusion coefficient of a hypothetical disordered block copolymer melt at the temperature of interest, $N_{MB}$ is the degree of polymerization of the minority block, and $\beta$ is a constant of order unity. This strong diffusive scaling actually presents some practical constraints for these materials including a limit to the accessible feature sizes (at very high $\chi N$, the ordering kinetics become prohibitively slow) and generally high melt viscosities (thus hindering processability). The ordered microstructure of block copolymer melts also affects their rheological behavior.\textsuperscript{21} One example of this is that the low-frequency linear viscoelastic response does not show a terminal relaxation time such that the material flows like a liquid. In addition, the rheological properties are extremely sensitive to the material’s history; in particular, application of shear or extensional flow can orient the microdomains, which lowers the polymer’s modulus at low frequency (\textit{i.e.}, it becomes easier for the material to flow in the shear direction). Indeed, much work has been done to orient block copolymer microdomains in the bulk via shear (both steady and
large amplitude oscillatory).\textsuperscript{22-31} In general the microdomains macroscopically orient in the direction of the applied shear; lamellae-forming block copolymers can actually orient in two ways: with their lamellar normal parallel to the shear gradient direction (low shear frequency) or to the vorticity direction (high frequency).\textsuperscript{26-28}

Due to their nanostructure, block copolymers have found utility in a wide range of applications. In general, these applications leverage block copolymers’ ability to incorporate advantageous and often dissimilar properties (\textit{e.g.}, high mechanical strength, ion conductivity, chemical compatibility) from multiple materials into a single polymer. The most commercially significant application of block copolymers is as thermoplastic elastomers. These are materials which combine the benefits of both elastomers (low modulus, high extensibility, good recovery) and plastics (melt processability).\textsuperscript{32} They perform similarly to conventional vulcanized rubbers, but rather than possessing permanent chemical crosslinks, rely on physical crosslinks formed by the endblocks of asymmetric microphase-separated ABA triblocks; the short endblocks are glassy ($T_g > T$) and aggregate into spheres or cylinders, while the rubbery ($T_g < T$) midblock is long and can bridge between two separate glassy domains, thus creating an elastically effective strand. In addition to thermoplastic elastomers, numerous other applications for block copolymers are emerging including their use as membranes for selective material transport,\textsuperscript{33} bulk heterojunctions in organic photovoltaics,\textsuperscript{34} and controlled release drug delivery.\textsuperscript{35}

In addition to their ability to combine advantageous material properties, block copolymers are also attractive as patterning templates for advanced lithographic processes due to the minute length scales at which they self-assemble (\textasciitilde 10-100 nm).\textsuperscript{36-42}
Patterning at these sizes is difficult to achieve via conventional lithographic methods (typically light-based); therefore, great efforts are being made to this end. The general strategy of block copolymer nanolithography is to first deposit a thin film of block copolymer such that only a single layer of microdomains (a monolayer) forms. Then selective etch processes are performed such that the two blocks are etched away at different rates; upon sufficient etching, the pattern of the microdomains is transferred to the underlying substrate (see Figure 2.3a). The block with the lower etch rate locally “masks” the substrate so that it is exposed to the etching agent for less time, and thus less material is removed. The first successful demonstration of block copolymer nanolithography was by Park et al.\textsuperscript{43} They developed methods to transfer the microdomain patterns of sphere-forming polystyrene-polybutadiene (PS-PB) into an SiNx substrate to produce regularly spaced holes/dots (about 15-20 nm deep/thick) with a periodicity of $\sim$ 40 nm, thereby producing a feature density of $\sim 10^{11}$ holes per cm$^2$. The prospect of producing such immense feature densities using relatively simple, macroscopic manipulations has spurred great interest in advancing block copolymer nanolithographic techniques.

One successful application of this approach to produce functional devices is the use of cylinder-forming block copolymers to create nanowire-grid polarizers for very short-wavelength light.\textsuperscript{44-46} For wire-grid polarizers to be effective, the pitch of the grating must be less than the wavelength of the radiation being polarized. Because of this constraint, compact wire-grid polarizers are typically only available for relatively long wavelengths of light (microwaves and far/mid-infrared). However, by transferring the pattern of aligned (methods to induce this alignment will be discussed at length in Section
Figure 2.3 (a) Schematic of the production of wire-grid polarizers using block copolymer nanolithography. Scanning electron micrographs of polarizers made from cylinder-forming (b) PS-PHMA\textsuperscript{44} and (c) polystyrene-poly(ferrocenylisopropylmethylsilane)\textsuperscript{46}; scale bars indicate 250 nm. (d) Plot displaying the enhancement of polarizing efficiency with increase in wire height.\textsuperscript{46}
2.3) monolayers of polystyrene-poly(n-hexyl methacrylate) (PS-PHMA) block copolymers to an underlying substrate, Pelletier et al. produced wire grids with a 33 nm pitch (see Figure 2.3b), enabling the polarization of wavelengths ranging from visible to ultraviolet light. Further decreasing the pitch size (e.g., by using a block copolymer with a smaller periodicity), will continue to shift the polarization effectiveness into the far ultraviolet regime. In addition, the polarization efficiency increases with wire height; this has been achieved both by increasing the polymer domain spacing (thus increasing the monolayer thickness) and also by employing specialty block copolymers which have higher differential etch rates between the two blocks (see Figures 2.3c, d). One of the chief challenges to the above approach is understanding and manipulating the block copolymer thin film structure prior to and during pattern transfer. This will be the central focus of the remainder of this chapter.

2.2 Physics of Block Copolymer Thin Films

When confined to a thin film (typically tens to hundreds of nm, or one to several microdomain layers), several factors, in addition to those already discussed for block copolymers in the bulk, become relevant in dictating microdomain morphology. First, surface interactions become important. Each block will have a different surface/interfacial energy, or strength of attraction or repulsion for both the top surface (often referred to as the free surface, typically air) and the bottom surface (often a hard substrate, e.g., the oxide coating on a silicon wafer). If one block (vs. the other block) greatly prefers a surface, the polymer will present that block at that surface. If neither block prefers a particular surface, then the system is said to have “neutral” wetting
conditions. If the same block wets both surfaces, the system has symmetric wetting conditions, while if each surface is preferred by a different block, the system has asymmetric wetting conditions. As an example, consider the illustrations in Figure 2.4 which show thin films of cylinder-forming diblocks (minority block A forms cylinders, shown in red, while the surrounding matrix, majority block B, is transparent). If B wets both the substrate and the free surface, one expects the A cylinders to orient in-plane (parallel to the substrate or lying down) with the surrounding B matrix exposed at both interfaces (Figure 2.4a). If A prefers one of the surfaces, it will wet that surface, producing a “wetting layer” of block copolymer chains. The wetting layer typically

![Figure 2.4](image_url)

**Figure 2.4** Common structures observed when cylinder-forming block copolymers are confined to a thin film: microdomains oriented (a) in-plane or (b) out-of-plane with the substrate, (c) the formation of wetting layers at the substrate and/or the free surface, and (d) terracing.
consists of either a half-lamella (as shown in Figure 2.4c) or a hemi-cylinder layer\textsuperscript{51} with a thickness of approximately half a microdomain layer. If the substrate is neutral to A and B, however, then the cylinders could either lie in-plane, or orient out-of-plane (perpendicular to the substrate or standing up), thus exposing both A and B at both surfaces (Figure 2.4b). In a truly neutral condition there is no interfacial energetic difference between these two options, and instead other factors will determine the through-plane orientation.\textsuperscript{52}

The second major factor influencing thin film morphology is that of commensurability.\textsuperscript{53-54} To understand commensurability, consider the same cylinder-forming A-B diblock with symmetric wetting conditions (block B wets both the substrate and the free surface). In the bulk, the block copolymer has a preferred domain spacing, \( d \). If a film is laid down such that the thickness of the film equals \( \sim d \), then the thin film structure will resemble a slice containing one complete period of the bulk structure. This single-period film is referred to as a monolayer. It is then straightforward to consider additional thin films which are integer multiples of this film thickness which would then contain \( n \) periods of the bulk structure. Now imagine a thin film which is \( n + \frac{1}{2} \) layers thick: if the bulk spacing and structure were preserved, block A would have to be present at either the free surface or the substrate, which is enthalpically disfavored. What if instead the block copolymer deviated from the bulk periodicity and formed a single cylinder layer, with B still wetting both the substrate and the free surface, but with \( d \) now equal to 1.5 times the value exhibited in bulk? This option has a strong entropic penalty associated with stretching the chains to reach this much larger period. The effects on thin
film structure which result from differences between the film thickness and the preferred bulk spacing are referred to as commensurability effects.

When a film is of incommensurate thickness, typically one of three things can happen. First, if the difference between the thickness and bulk spacing is small, the chains may simply stretch to a new periodicity, despite the entropic penalty, or can undergo a structural transition (e.g., spheres elongate or coalesce to form cylinders or vice versa\(^55\)). Second, if the surface energy penalty is small, and therefore the surfaces are only slightly non-neutral, the microdomains could orient out-of-plane. While this exposes both A and B at each surface thus producing an enthalpic penalty, once the cylinders are standing up there is no longer a preferred spacing in the confined direction, so the film can be arbitrarily thick without encountering commensurability effects. Third, the film can undergo terracing or the formation of islands and holes (see Figure 2.4d)\(^56-60\). When a film terraces, the polymer will reorganize such that some regions of the film thicken to the next complete integer domain spacing (islands), while the remaining regions thin to the thickness corresponding to the next smallest integer layer (holes). For example, in a 1.5 layer film, half the film will form regions 2 layers thick, while the remaining half adopts a monolayer thickness. Thermodynamically, terracing addresses the problems of commensurability; however, this process will also create additional surface area. In addition, terracing can be slow, so in some cases block copolymers will forgo this route for the more kinetically favorable options discussed earlier. Since commensurability effects lead to a strong dependence of morphology and often orientation on film thickness, much work has been done to understand this relationship, and film thickness must be carefully controlled during thin film experiments.
An excellent illustration of many of these effects can be seen in work done by Knoll et al. studying thin films of cylinder-forming PS-PB-PS linear triblocks (PS cylinders in a PB matrix). They examined, both experimentally and theoretically (via dynamic density functional theory, DDFT), the phase behavior of this polymer as a function of film thickness in the vicinity of monolayer and bilayer film thicknesses (see Figure 2.5). At commensurate film thicknesses the cylinders orient in-plane as the matrix prefers to wet both interfaces. At a submonolayer thickness, the film terraces, forming two regions: a thin region covered with a disordered wetting layer (dis) and monolayer-thick region forming in-plane cylinders (C\(_{\parallel,1}\)). Along the terrace edge there is a relatively sharp thickness gradient (~ 0.1-0.2 nm height change per nm along the gradient). At these thicknesses the cylinders stand out-of-plane (C\(_{\perp}\)) to relieve the incommensurability. A similar situation is observed for slightly thicker terraced films (between 1 and 2 layers thick); as the film thickness increases from one to two layers, the film makes perforated lamellae (PL, alternating lamellae in which the majority component microdomains penetrate the minority lamellae, forming a continuous phase) followed by out-of-plane cylinders, and finally, when a bilayer is reached, the in-plane cylinder morphology is recovered.

It is clear that interfacial and commensurability effects have strong influences on block copolymer thin film morphology; however, the degree to which these effects persist as the film becomes thicker remains an active area of study. Stein et al. examined the lattice packing of sphere-forming polystyrene-poly(2-vinylpyridine) (PS-P2VP) as a function of the number of layers of spheres using grazing incidence small-angle X-ray scattering (GI-SAXS). In bulk, this block copolymer packs into the familiar
Figure 2.5 (a, b) Atomic force micrographs (tapping mode) of thin films of cylinder-forming PS-PB-PS triblock copolymer showing disordered regions (dis), out-of-plane cylinders (C⊥), one (C||,1) and two layers (C||,2) of in-plane cylinders, and perforated lamellae (PL). (c) Schematic height profile of the micrographs shown in (a, b). (d) Simulations of the system using DDFT.58

BCC lattice. When confined to a monolayer, the spheres instead possess hexagonally close-packed symmetry (this is generically true for monolayers of all sphere-forming block copolymers); this morphological transition is attributed to the frustrated packing that emerges when a BCC lattice (a three-dimensional structure) is confined to a quasi-two-dimensional thin film. They found that the hexagonal packing persisted up to 3 layers of spheres, but at 4 layers coexistence between hexagonally packed spheres and a metastable face-centered orthorhombic structure was observed. As the number of layers was further increased (up to 23 layers) the hexagonal phase gradually vanished and the
orthorhombic phase asymptotically transitioned to a BCC-like structure (i.e., the bulk morphology was recovered). While this is just one example and the quantitative effects may not be generalizable, this study clearly illustrates that the influence of thin film confinement effects can persist (at least in part) over very large length scales (greater than 10× the polymer’s domain spacing).

2.3 Directed Self-Assembly

To be useful for most applications, particularly nanolithography, the microdomains within block copolymer thin films must have a high degree of orientational, and sometimes translational or positional, order. This order can either be local, allowing for the fabrication of extremely small features (sizes of tens of nm), or more long-range, which would enable the creation of arrays with ultrahigh resolution and large areal coverage, characteristics useful in applications such as magnetic data storage and nanowire grids. Much work has been done to understand the underlying physics which control block copolymer thin film morphology (see the previous section for a review on this topic). Further work has focused on controlling the orientation of microdomains using a variety of methods and materials. The following section serves as an introduction to some of the dominant approaches by which researchers have attempted to control microdomain orientation in thin films. For a more comprehensive review or more details regarding the concepts and techniques discussed here, the reader is referred to the listed references.37-38, 40, 62-68
2.3.1 Alignment via Shear

One method which has been shown to impart strong in-plane alignment to block copolymer thin films is the application of shear stress at the film’s surface. As discussed previously, shear has long been known to orient block copolymer microdomains in the bulk\(^{22-23, 25-26, 69-72}\). The first observation of this phenomenon was by Keller et al.,\(^69\) who noticed that an extruded rod of PS-PB-PS showed scattering patterns “comparable with that of atoms in a crystal lattice except that the scale of the periodicity is in the range of 300 Å.” As a consequence of the shear and extension applied during the extrusion process, the microdomains were (nearly) perfectly oriented in the extrusion direction.

More recently, several methods have been developed to adapt this shear alignment approach for thin films (including simple rubbing techniques used to align liquid crystalline materials\(^{73-74}\)). Angelescu et al. achieved alignment in monolayers of a cylinder-forming block copolymer by placing a smooth, cross-linked poly(dimethylsiloxane) (PDMS) pad in contact with the film and applying a lateral force (“pad shear” method, see Figure 2.6a).\(^75\) They showed that given sufficient stress the cylinders align in the shear direction over the entire area under the pad. They later applied this technique to align sphere-forming block copolymers.\(^76\) Interestingly, alignment in monolayers of spheres was impossible to achieve via shear, and only bilayer (or thicker\(^77\)) films shear aligned. They attributed this behavior to the high degree of mechanical isotropy of the spheres’ hexagonal lattice and the need for layers of spheres to slide past one another for the system to order. In some instances, the shear induced the spheres to coalesce, forming continuous cylinders.\(^78\) For both spheres and cylinders, the degree of alignment is highly sensitive to the film thickness, with the highest quality of alignment
Figure 2.6 Schematics of several methods to shear align polymer films: (a) pad shear\textsuperscript{75-76}, (b) rheometer shear\textsuperscript{79} (adapted from Wu \textit{et. al}\textsuperscript{77}), and (c) channel flow\textsuperscript{80}.
occurring in films in close proximity to their preferred monolayer thickness. The pad shearing technique has also been shown to align lamellae-forming block copolymers which are oriented out-of-plane with respect to the substrate, although the quality of alignment in these systems was diminished.81

Additional methods have been developed to shear-align block copolymer thin films. Wu et al. employed a nonsolvent fluid as the medium to impart stress at the film’s surface.77 The shear was applied by sandwiching a viscous silicone (PDMS) oil layer between the substrate-supported thin film and a rheometer plate. Rotation of the parallel plate transmits a shear stress through the silicone oil to the film’s surface (“rheometer shear” method, see Figure 2.6b). A related shear alignment technique, the “channel flow” method developed by Pelletier et al., utilizes pressure driven flow of the same nonsolvent fluid through a channel which directs the fluid across the film’s surface (see Figure 2.6c).80 The chief advantage of both of these techniques, as compared to the elastic pad shearing approach, is their ability to apply a range of stresses to a single sample, varying in position. This markedly increases the throughput and reliability of experiments intended to investigate how the quality of shear alignment varies with stress. Also, these methods avoid any “pre-shearing” caused by unintended or uncontrolled thermal expansion of the pad during specimen heating prior to applying the shear stress.

Some of the factors which influence the ease and ultimate quality of alignment in shear-aligned films have been previously studied. Using films of sphere-formers (two to six layers thick), Wu et al. showed that beneath a threshold stress no alignment is observed, and that upon exceeding this threshold the layers align in the “easy shear” direction over a relatively narrow range of shear stresses and eventually plateau to a
terminal alignment quality. They further showed that with increased temperature and time the breadth of this transition narrowed and the value of the threshold stress decreased. To model this behavior, they proposed a “melting-recrystallization” mechanism of alignment. They argued that any polymer grains which are misaligned relative to the direction of the applied shear experience an effective reduction in their $T_{ODT}$, and that with sufficient stress, the most misaligned grains will selectively melt and reorder in the shear direction. The resulting model equations nicely reproduced the dependence of alignment quality on applied shear stress. Pelletier et al. then modified this model for cylinder-formers and also found good agreement with the experimental data. To further test the core premise of this model, that the grains which are most misaligned with the shear direction are preferentially destroyed, Marencic et al. first aligned a polygrain film, via shear, and then systematically probed the effects of applied stress and misorientation angle on re-orientation of the microdomains. They showed that the stress required for alignment increased monotonically as the difference between the microdomains’ orientation and the shear direction decreased.

Later, Marencic et al. explored the terminal quality of alignment, achieved at large applied stresses, of sphere- and cylinder-formers. They discovered that in these well-aligned films, the quality of order is limited by the persistence of isolated dislocations in the microdomain lattices. In addition, the maximum order observed in cylinder-formers was limited by small-amplitude undulations of the cylinders about their axes (i.e., even at zero dislocation density, cylinder-formers did not show perfect order). Theoretical and simulation studies have also been employed to better understand shear
alignment in block copolymer thin films;\textsuperscript{85} these include Monte Carlo\textsuperscript{86} and molecular dynamics simulations.\textsuperscript{87-90}

\subsection*{2.3.2 Electromagnetic Fields}

Electric\textsuperscript{91} and magnetic\textsuperscript{92} fields can be used in much the same way as shear/flow fields to orient microdomains over relatively large length scales. The driving force behind electric-field alignment arises from differences in the dielectric constants of the two blocks. Amundson \textit{et al.} first utilized electric fields to orient bulk block copolymers.\textsuperscript{93} Later, other groups successfully applied this approach to orient microdomains in thin films. Morkved \textit{et al.} demonstrated this by achieving in-plane alignment of cylinder-forming polystyrene-poly(methyl methacrylate) (PS-PMMA) in the direction of the applied electric field (\textgtrsim 30 kVcm\textsuperscript{-1}).\textsuperscript{94} This method was later scaled up by Mansky \textit{et al.} to produce in-plane alignment over macroscopic length scales (2 cm\textsuperscript{2}, comparable to those attained by shear alignment).\textsuperscript{95} In both cases, the requisite electric field strength was achieved by lithographically depositing electrodes directly onto the substrate. Experiments have also demonstrated that an electric field applied across the thickness of the film can overcome the preferred interfacial interactions, which prompt in-plane orientation, thus causing the microdomains to reorient out-of-plane,\textsuperscript{96-97} to produce the out-of-plane orientation, the film is sandwiched between two electrodes (with a spacer to prevent shorting). This technique has successfully reoriented both symmetric\textsuperscript{98} and asymmetric\textsuperscript{99} materials, and in some cases can induce sphere-to-cylinder transitions,\textsuperscript{100} similar to those seen with application of shear. In some cases, inorganic salts,\textsuperscript{101} which can selectively complex with the blocks, or electro-responsive nanoparticles\textsuperscript{102} are added
to help enhance dielectric contrast, thus lowering the critical electric field needed and improving the alignment response. Electric-field approaches are thus powerful in their ability to control both in-plane and out-of-plane alignment, and on a relatively local scale. The primary disadvantages are the high voltages (~30 kV/cm) required for alignment, and the limitations on block chemistry imposed by the need for dielectric contrast.

Like electric fields, magnetic fields can also be used to align block copolymers over relatively large length scales, although to this point, magnetic-field alignment has primarily been limited to bulk materials, not thin films. The driving force for this method is anisotropy in the magnetic susceptibility of the blocks; this susceptibility can be ferro-, dia-, or paramagnetic in origin. As such, this method is typically reserved for aligning relatively exotic materials which possess the requisite anisotropy (e.g., side-chain liquid crystalline block copolymers, rod-coil block copolymers, semi-crystalline materials, and surfactant mesophases). One advantage of magnetic-field alignment (vs. electric-field) is that the fields are applied “at a distance”, not in direct contact with the material, enabling greater scalability of the technique. In addition, dielectric breakdown is not an issue for magnetically-aligned materials (as it is for electric fields), although very large field strengths are needed (>1 T). This technique has shown particular promise in the synthesis of thick, chemoselective transport membranes. Recently, Majewski et al. used magnetic-field alignment to produce highly-aligned cylinders of poly(ethylene oxide)-poly(6-(4′-cyanobiphenyl-4-yloxy)-hexyl methacrylate) (PEO-PMA/CB) block copolymers doped with Li⁺ (see Figure 2.7). These materials possess an order of magnitude increase in ionic conductivity as compared to the non-aligned materials,
making these attractive as conductive polymer electrolyte membranes for use in battery applications.

![Figure 2.7](image)

**Figure 2.7** Two-dimensional small-angle X-ray scattering patterns showing the progressive increase in alignment quality of PEO-PMA/CB (doped with Li\(^+\)) with applied magnetic field (B). The inset shows the maximum peak intensity (black) and width of the peak at half the maximum peak intensity (FWHM, red) for the Lorentzian fit to the scattering data for the microdomains (triangles) and liquid crystal mesogens (circles).\(^{104}\)

### 2.3.3 Solvent Vapor Annealing

Recently, solvent vapor annealing has become a popular technique for enhancing or directing microdomain order in thin films.\(^{105-113}\) Upon exposure to compatible solvent vapors, the film will swell, thus diluting the polymer chains. This can serve much the same role as thermal annealing; the solvent vapor plasticizes the chains, leading to an
effective reduction in the polymer’s $T_g$, and therefore great enhancement of the chains’ mobility.\textsuperscript{67} This approach is particularly attractive when ordering via thermal annealing is slow (\textit{i.e.}, polymers with very high molecular weights\textsuperscript{114}), or when the material is thermally sensitive/responsive. In some cases, the solvent can preferentially swell specific blocks\textsuperscript{115} which can lead to changes in the polymer’s domain spacing,\textsuperscript{116} morphology (\textit{e.g.}, sphere-to-cylinder transition)\textsuperscript{117-120}, or interfacial wetting behavior (\textit{i.e.}, which block(s) prefers to wet the substrate and free surface). In addition, directional swelling and deswelling (solvent removal/evaporation) of the film can introduce morphological changes, particularly changes to the in- vs. out-of-plane orientation of the microdomains.\textsuperscript{118, 121-122} This reorientation appears to be primarily affected by solvent evaporation rate; however, the direction of this relationship does not appear to be universal (\textit{i.e.}, increasing solvent evaporation rate has been shown to induce both in-plane\textsuperscript{123} and out-of-plane\textsuperscript{124} orientations in different systems). This point nicely illustrates a chief advantage and challenge of the solvent vapor annealing technique: a variety of film manipulations are possible, but the wealth of effects and process variables can be difficult to control and reproduce. In addition, because the morphologies produced by this technique are “frozen in place” as the material vitrifies (upon solvent removal) and are only metastable, any subsequent reannealing/processing above the material’s $T_g$ might completely rearrange the solvent-annealed structure.

Solvent vapor annealing can be performed very simply by enclosing a sample into a chamber alongside a reservoir of liquid solvent (the “bell jar” approach\textsuperscript{68, 107}). This technique, while effective, is difficult to control and often yields inconsistent annealing results. Additional solvent vapor annealing techniques have since been developed to
provide more control to the annealing process. One technique, described as proximal injection, uses a solvent-swollen elastomer pad, placed in close proximity to the film (~ 1 mm above the film’s surface), to deliver a steady supply of solvent vapor to the film.\textsuperscript{125} Another approach, developed by Cavicchi and Russell, implements a solvent anneal by flowing a controlled concentration of solvent vapor (by adjusting the flow rates of a pure N\textsubscript{2} and a solvent-infused N\textsubscript{2} stream, see Figure 2.8a) through an annealing chamber.\textsuperscript{126} They showed that by changing the concentration of solvent, and thus the swollen film thickness, a cylinder-forming polymer could possess in-plane, out-of-plane, or mixed orientations of cylinders (see Figure 2.8b-e). Solvent vapor annealing using mixed solvents has also garnered much attention for its ability to precisely tune solvent selectivity between the blocks. Albert \textit{et al.} developed a microfluidic mixing device (see Figure 2.8f) which enables the creation of discrete gradients in solvent composition or concentration, enabling the rapid and systematic probing of these parameters on block copolymer self-assembly.\textsuperscript{127} Relatively local control of self-assembly is also possible using “raster” solvent vapor annealing strategies in which the solvent is delivered using a vapor delivery nozzle which is scanned across the film (see Figure 2.8g). In this method, the degree of annealing can be precisely controlled by the rastering speed.\textsuperscript{128} Solvent annealing can also be combined with traditional thermal and microwave\textsuperscript{129} annealing strategies to further enhance the ordering rate.
Figure 2.8 (a) Setup for controlled solvent annealing.\textsuperscript{126} (b-e) Atomic force micrographs (phase images) showing the progression of morphologies in thin films of cylinder-forming polyisoprene-poly(lactic acid) after increasing degrees of solvent annealing: (b) as cast, no order, (c) all in-plane cylinders, (d) mixed in- and out-of-plane cylinders, and (e) all out-of-plane cylinders.\textsuperscript{126} (f) Design for microfluidic device which enables gradient solvent vapor annealing.\textsuperscript{127} (g) Illustration for raster solvent vapor annealing apparatus.\textsuperscript{128}

Solvent vapor annealing can also be combined with other techniques for directed self-assembly to produce features with long-range lateral order. Qiang \textit{et al.} recently demonstrated a method to combine solvent annealing with shear alignment (so-called “soft-shear”) by placing a flat, cross-linked PDMS capping layer (the same material used in the previously discussed pad shearing technique) in direct contact with a block
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copolymer thin film and swelling both the cap and the film using a common, good solvent. The expansion/contraction of the PDMS pad during solvent swelling/deswelling imparts shear at the film’s surface. The strength of the applied shear depends on the annealing time, rate of solvent removal, and the physical properties of the pad (i.e., the crosslink density). The shear is either applied radially outward from the pad’s center (in the case of a uniformly swollen pad, i.e., solvent annealing via the “bell jar” approach, see Figure 2.9a) or in a (nearly) uniform direction, parallel to a flowing vapor stream. In the former approach, the strain in the pad’s center is isotropic, so no local alignment occurs. In the latter method, the alignment orientation and quality can be further controlled by adjusting the pad’s shape and aspect ratio (e.g., a high-aspect-ratio rectangular pad globally aligns the microdomains in the pad’s long dimension, while a small-aspect-ratio pad aligns the features diagonally to the solvent flow; see Figure 2.9b).

2.3.4 Zone Annealing

Uniform annealing strategies can increase block copolymer grain sizes to microns or greater, but generally do not provide any preferential orientation. As discussed previously, zone-casting and directional solvent annealing techniques also create large grains, but they can impart directionality as well (e.g., orientation in the direction of the evaporation front). Analogous results are possible with directional thermal annealing strategies, generally termed “zone annealing.” This was first employed by Hashimoto et al. who showed that sweeping a strong temperature gradient through a bulk sample of lamellar block copolymer oriented the material. Heating the block copolymer above
**Figure 2.9** Soft-shear alignment of thin films of a polystyrene-polyisoprene-polystyrene cylinder-forming triblock as revealed by atomic force microscopy. (a) A circular pad is used to orient the cylinders radially outward from the pad’s center by uniformly swelling and deswelling the pad with solvent vapor. White arrows indicate alignment direction. (b) Rectangular pads induce orientation in the general direction of solvent vapor flow; the precise alignment direction can readily tuned by adjusting the aspect ratio of the pad. All scale bars indicate 500 nm.\textsuperscript{131}

its $T_{ODT}$ was key to the process; as the material cools, lamellae grow from the disordered phase with their planes normal to the direction of the temperature gradient. Angelescu \textit{et al.} adapted this approach to generate very large grains in monolayers of cylinder-forming block copolymer using a sweeping solidification front.\textsuperscript{134} They showed that the defect densities in the film were dramatically reduced; this order could be further enhanced by employing an oscillatory front.
These zone refinement techniques, later termed hot zone annealing (HZA), were limited to materials with thermally accessible $T_{ODT}$. Berry et al. later developed a cold zone annealing (CZA) strategy in which the film is annealed above its $T_g$, but below its $T_{ODT}$, thus expanding the range of applicable materials. They showed that CZA (similar to HZA) speeds up the polymer’s ordering kinetics, dramatically reduces lattice defects, and imparts some directionality to the microdomains.\textsuperscript{135-137} While CZA typically produces in-plane order of block copolymer cylinders, increasing the “sharpness” of the thermal gradient (CZA-S) has been shown to induce out-of-plane orientation of the cylinders.\textsuperscript{138} A major advantage of zone annealing is the potential for scalability; Singh et al. demonstrated relatively large-scale roll-to-roll fabrication of oriented microdomains using these techniques.\textsuperscript{139}

Zone annealing can also be combined with shearing techniques to further enhance the orientational order of the microdomains.\textsuperscript{140-141} This so-called cold zone annealing with soft shear (CZA-SS) can be achieved by placing a PDMS pad in contact with the film and passing the system across a thermal gradient. The differential thermal expansion between the pad and film imparts a shear which creates high degrees of orientational order (see Figure 2.10a-c). More recently, Majewski et al. employed lasers to create intense photothermal gradients to induce the differential expansion between the pad overlayer and block copolymer film.\textsuperscript{142} The laser provided highly localized control of the shear fields, enabling the creation of both uniformly aligned patterns as well as perpendicular junctions (see Figure 2.10d-f).
Figure 2.10 (a) Schematic of CZA-SS apparatus with (b) in-plane and out-of-plane views of the sample. (c) Atomic force micrographs of PS-PMMA block copolymer thin films after (i) conventional thermal annealing, (ii) thermal annealing with a cross-linked-PDMS overlayer, (iii) cold zone annealing, (iv) cold zone annealing with a sharp thermal gradient, (v) and CZA-SS. Insets show corresponding Fourier transforms; scale bars indicate 200 nm. (d) Schematic of soft-shear laser zone annealing apparatus and scanning electron micrographs showing (e) uniformly aligned PS-PMMA and (f) a perpendicular junction pattern, both generated by SS-LZA. Arrows indicate shear/sweep direction.
2.3.5 Substrate Modification

An alternate route to ordering block copolymer microdomains is through modifications of interfacial interactions, particularly between the film and the substrate. Generally, there is an energetic preference of one block over the other to wet each interface (this is why most block copolymer thin films prefer to orient in-plane). Modifications of the substrate chemistry or topography, however, can manipulate or eliminate this preferential wetting to control the in- vs. out-of-plane orientation of the microdomains as well as create both local and long-range in-plane ordering.

One common method of modifying surface energy is through the use of self-assembled monolayers, or the deposition of a single layer of a small molecule, with a desired chemical functionality.143-144 Similarly, substrates such as silicon wafers can be treated with acids to control the presence of Si-H or Si-OH groups at the surface.145 A more systematic route to control surface energy is through grafting a random copolymer layer to the substrate.146-159 Mansky et al. first demonstrated this concept by synthesizing poly(styrene-r-methyl methacrylate) (P(S-r-PMMA)) statistical copolymers which were end-functionalized with hydroxyl groups.146 Upon deposition of the polymer onto a silicon substrate and a subsequent thermal anneal, these hydroxyl groups readily react with the native silicon oxide layer, creating an end-grafted polymer brush layer. The surface energy of the resulting substrate could then be easily tuned by changing the ratio of monomers in the statistical copolymer. Later, In et al.149 used a similar approach to create surfaces which were chemically neutral to PS-PMMA. They synthesized random terpolymers of styrene, methyl methacrylate, and 2-hydroxyethyl methacrylate; the latter monomer contains a reactive hydroxyl side group which, like the hydroxyl end group in
the previous approach, provides a means of chemically grafting the terpolymer to the native oxide of a silicon substrate. When a PS-PMMA block copolymer was deposited onto the grafted layer, lamellar microdomains oriented either in-plane or out-of-plane (indicating a “neutral” wetting condition) depending on the composition, and therefore surface energy, of the underlying grafted layer. This method thus provides a particularly useful means to control the in- vs. out-of-plane orientation of block copolymer microdomains and to induce preferential wetting of either block onto the substrate. PS-PMMA is the most commonly studied system for this approach due to its relatively neutral wetting conditions at the free surface (at 220 °C\(^{160}\)); however, the method has been shown to be fairly generalizable\(^{152}\). Recently groups have employed a “topcoat” strategy, in which a neutral layer is deposited at the top surface as well, to further enhance the ability to produce out-of-plane features via this strategy\(^{161-163}\). The ultimate in- vs. out-of-plane orientation of block copolymer microdomains is a competition between preferential wetting and commensurability effects. As a consequence, there remains a thickness dependency to this approach (i.e., not all film thicknesses will yield out-of-plane microdomains, see Figure 2.11).

While the above approaches uniformly modify the chemistry/surface energy of the entire substrate, additional techniques which can provide local or periodic control of the substrate chemistry have been developed. Broadly these methods are referred to as “epitaxy” (in true epitaxy, the deposited layer “crystallizes” in registry with the pattern on the underlying substrate\(^{164}\)). These techniques often rely on established lithographic techniques (e.g., ultraviolet or electron-beam lithography) to create a template pattern which directs the overlying block copolymer self-assembly. This enables the creation of
Figure 2.11 (a-d) Atomic force microscope phase images of lamellar PS-PMMA films of various thicknesses cast onto “neutral” substrates composed of P(S-r-PMMA) copolymers chemically grafted to Si wafers; black scale bars indicate 500 nm.\textsuperscript{150} (e-g) Cross-sectional transmission electron micrographs of PS-PMMA films (~ 12 domain spacings thick) showing the increased influence of the neutralized substrate on the through-film morphology as the block copolymer $M_n$ increases: (e) 50 kg/mol, (f) 74 kg/mol, (g) 113 kg/mol.\textsuperscript{158}

truly local chemical patterns on the substrate which in turn can lead to precise control of the translational as well as orientational order within the thin film.\textsuperscript{165-170} For example, one can impart in-plane alignment to perpendicularly oriented lamellae by first creating a precise striped pattern on the substrate such that the wetting conditions alternate stripe to stripe (one stripe is wet by block A, the next by block B).\textsuperscript{171-174} If the periodicity of this striped pattern matches the periodicity of a lamellar block copolymer, then the
microdomains should perfectly register with the underlying pattern, allowing more interesting patterns to be created, such as jogs, bends, or perpendicular\textsuperscript{175-176} junctions rather than simple parallel line patterns (see Figure 2.12). To accommodate the local microdomain bending present in some of these patterns, it is often necessary to blend homopolymer into the block copolymer to allow for local variation in microdomain size and spacing (as illustrated in Figure 2.12d-g).\textsuperscript{176}

In addition to surface chemistry, topographic relief structures can also be used to control local in-plane orientation and order; this is typically referred to as graphoepitaxy.\textsuperscript{177-191} These techniques have been used to create oriented grains up to several microns in the short in-plane dimension, and even longer in the orthogonal in-plane dimension (\textit{e.g.}, parallel to a long step edge). As an illustration of this method, consider a cylinder-forming block copolymer, placed in a trough with a depth equal to approximately a monolayer thickness and a width of approximately 10 cylinder periodicities (see Figure 2.13a). Upon thermal annealing, preferential wetting against the trough wall will drive alignment of the cylinders parallel to the trough walls (similar to how surface/substrate wetting conditions induce in- vs. out-of-plane orientation, see Figure 2.13b) and this alignment then persists across the width of the trough. Furthermore, if a thicker film is deposited, the aligned microdomains within the trough will induce the layers above to also align. The microdomains can also be made to orient orthogonally to the trough wall by creating neutral wetting conditions at the wall (using the methods discussed above).\textsuperscript{188, 190} Combining graphoepitaxy with solvent and zone annealing\textsuperscript{191} strategies can significantly enhance the ordering kinetics, further increasing its attractiveness as an ordering technique. In addition to the controlled relief structures
Figure 2.12 Illustrations of (a) the typical thin film behavior for a lamellar block copolymer (parallel domains) and the use of chemical patterning of the substrate (via electron-beam lithography) to produce (b) dense arrays of perpendicular domains and (c) mixtures of parallel and perpendicular domains in order to produce isolated features. Scanning electron micrographs of ternary blends (PS-PMMA block copolymer with PS and PMMA homopolymers) directed to assemble into (d) nested arrays of jogs, isolated (e) PMMA and (f) PS jogs, and (g) arrays of T-junctions.\(^{176}\)
Figure 2.13 (a) Illustration of “graphoepitaxy” using lithographically patterned “troughs” to produce aligned cylindrical domains.\textsuperscript{183} (b) Atomic force micrograph showing cylinder-forming polystyrene-polyisoprene (PS minority) aligned within the trough due to preferential PS wetting of the trough wall.\textsuperscript{184} Scanning electron micrographs of sphere-forming polystyrene-poly(ferrocenyldimethylsilane) (PS majority) similarly aligned within troughs which are (c) 500 nm, (d) 320 nm, and (e) 240 nm wide.\textsuperscript{178}
discussed above, periodic substrate topography/roughness has been shown to promote out-of-plane alignment,\textsuperscript{192-195} and in some cases can produce lateral order of the standing microdomains.\textsuperscript{196}

Epitaxial techniques are powerful because they provide precise and flexible control over the patterns created, enabling the creation of the isolated, and arrays of, complex features required for nanocircuit design and other advanced nanolithographic applications. The disadvantage of many of these approaches, however, is that they require a nominal 1:1 relationship between the feature size or frequency of the required substrate prepatterning and the final oriented block copolymer microdomain, limiting their cost-effectiveness and ultimate efficacy as a nanolithographic tool. Work has been done to address this limitation by employing techniques which use the block copolymer to “frequency multiply” the underlying substrate pattern, retaining the epitaxial match. These techniques work by generating either chemical\textsuperscript{197-198} or topographic\textsuperscript{199-202} relief patterns (\textit{e.g.}, posts) whose periods are an integer multiple of the microdomain periodicity. The block copolymer microdomains (\textit{e.g.}, out-of-plane cylinders) will then conform to the lattice created by the guiding pattern and fill in the missing lattice points. This creates an array of points with perfect translational order and at a higher density than the original substrate pattern. Figure 2.14 shows a recent example of frequency multiplying to produce highly-ordered spherical arrays using (relatively) sparse prepatterning.
Figure 2.14 (a) Top-down and side-view illustrations of block copolymer chains packing around a single “guide post”. (b) Scanning electron micrographs showing the relatively poor ordering of a monolayer of sphere-forming PS-PDMS in the absence of any external guides. Additional micrographs showing enhanced ordering of the spheres using sparsely-patterned guide posts functionalized with (c) PDMS- and (d) PS-grafted layers. Insets show Fourier transforms of the corresponding images.$^{199}$

2.5.6 Emerging Techniques and Advanced Materials

Despite the great traction made in directed self-assembly of block copolymer thin films, there is still a constant effort to continue to develop strategies and materials which can increase the efficacy of block copolymer nanolithography. Much of this work has been in the development of materials which have either smaller features sizes or have improved pattern transfer properties. Principally, the minimum achievable resolution via block copolymer lithography depends on the polymer domain spacing. To minimize $d$, materials with exceptionally high $\chi$ (which remain microphase-separated even at very low $N$) are employed. Recently, this has been achieved using various Si-containing polymers$^{203-205}$ to produce features sizes of $<10$ nm. To further push the boundary of $\chi$, 

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Kim et al. demonstrated that preferential, epitaxially patterned substrates can suppress fluctuations and therefore increase the effective $\chi_N$ of the block copolymer film, enabling the system to remain ordered at higher than expected temperatures (i.e., the bulk $T_{ODT}$) or lower molecular weight. In addition to feature size minimization, identification of materials with exceptional etch contrasts is also paramount. Several strategies have been employed to increase etch selectivity including employment of the Si-containing blocks mentioned above. In addition, the use of metal-containing blocks such as poly(ferrocenylsilane)s (PFS) or materials which can be complexed/impregnated with metal ions during a post-deposition step have shown remarkable promise. Also, some effort to improve the sustainability of these approaches has been made by utilizing biodegradable materials (i.e., poly(lactic acid)).

Block copolymers which can be used to make novel or highly-useful two-dimensional and three-dimensional nanostructures are also of great interest to the community. A primary example is the creation of square or rectangular arrays using block copolymer films; these structures are compatible with integrated circuit design which is generally based on a rectilinear system. Unfortunately, block copolymers do not typically make such patterns, but instead provide templates for lines or hexagonal arrays. Several strategies have been developed to create such square packing. Tang et al. created blends of A-B and B'-C type diblocks, where the B and B' blocks can hydrogen bond. Thin films of these blends displayed long-range square-packed order (see Figure 2.15a). More recently, groups have utilized the substrate pre-patterning approaches discussed above to guide the microdomains into rectangular arrays. Kim et al. oriented PS-PEO (in-plane) lamellae orthogonally to prepatterned corrugations/trenches on the
Figure 2.15 Recent methods to generate square- or rectangular-packed patterns in block copolymer thin films. (a) Binary blends of poly(ethylene oxide)-poly(styrene-r-4-hydroxystyrene) (PEO-P(Sr4HS)) and poly(styrene-r-4-vinylpyridine)-poly(methyl methacrylate) (P(Sr4VP)-PMMA) self-assemble into square arrays due to hydrogen bonding between P(Sr4HS) and P(Sr4VP): (left) Transmission electron micrograph with Fourier transform inset, (right) a cartoon illustrating the chain packing.\textsuperscript{211} (b) Scanning electron micrographs showing three-dimensional structures fabricated by creation of post templates (via electron-beam lithography).\textsuperscript{212}
substrate, producing 20 nm half-pitch gratings. More recently, Tavakkoli et al. produced square patterns using a bilayer of cylinder-forming block copolymer assembled on a prepatterned substrate with strategically located posts (see Figure 2.15b). The posts expertly guide the first layer of cylinders in one direction and then orient the second layer at a controlled angle relative to the underlayer. More complex three-dimensional structures are also being explored either by employing techniques like nanoimprint lithography or through stacking of films to hierarchically build multilayers. The chief advantage of the latter approach is that each layer can be manipulated separately and then its morphology fixed, typically through a crosslinking reaction, allowing for exceptional control of the three-dimensional structure. Recently, this approach was used by Jung et al. to create multilayered PS-PMMA films. The first layer consisted of out-of-plane cylinders which were cross-linked via reactive azido groups which were incorporated into the PS backbone. Upon deposition of a second layer, consisting of lamellae-forming PS-PMMA, the microdomains oriented out-of-plane due to interactions between polymer chains at the interface. Upon removal of the PMMA domains, they produced a nanostructure which enhanced the light extraction efficiency in GaN light-emitting diodes.

In addition to novel morphologies, advanced deposition techniques which can control the local microstructure (i.e., morphology and domain periodicity) of block copolymer films along a substrate are needed to develop more complex structures and films. A recently developed method, titled electrohydrodynamic jet printing, achieves this by applying a voltage to a micro/nano nozzle to induce a continuous stream of block copolymer solution to deposit on a substrate. In addition to its relative simplicity, the
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The chief advantage of this technique is the local control of film deposition, enabling the creation of hierarchical patterns with both micro- and nanoscale features (see Figure 2.16a-e). By employing multiple nozzles/solution reservoirs, the user can easily control the thickness of the film deposited as well as the specific polymer/blend deposited, thus mixed morphology and periodicity patterns are possible. This tunability provides a wealth of complex patterning options. In addition to depositing block copolymers, this method can also be used to deposit functionalized polymer layers (which are subsequently grafted to the substrate) to chemically modify the substrate prior to block copolymer deposition. This enables local control of the in- vs. out-of-plane orientation of the microdomains (see Figure 2.16i-iii).
Figure 2.16 Examples of the local control enabled via electrohydrodynamic jet printing techniques. (a-e) Scanning electron micrographs showing the deposition of polymer into complex patterns at multiple length scales using symmetric PS-PMMA (oriented out-of-plane due to a neutralized substrate) using two different molecular weights: (b, c) 74 kg/mol, $d = 41$ nm, black dashed box, (d, e) 51 kg/mol, $d = 27$ nm, blue dashed box.\textsuperscript{218} This technique can also be used to locally deposit a substrate-neutralizing polymer graft layer (i – iii).\textsuperscript{219}
2.4 References


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Chapter 3

Experimental Methods

The following chapter serves as an overview of the experimental methods employed in this work. Included are both specific details (e.g., equipment used) as well as discussion of the principles behind many of the techniques. This chapter does not contain all of the experimental information, as some of the details are reserved for the relevant chapters (e.g., the precise synthetic procedures and characterization of the polymers employed in the thesis).

3.1 Polymer Synthesis and Bulk Characterization

3.1.1 Synthesis

The specific procedures used for polymer synthesis are detailed in the appropriate chapters: anionic synthesis of polystyrene-poly(\(n\)-hexyl methacrylate) is discussed in Chapter 5, free-radical polymerization of statistical copolymers of poly(styrene-\(r\)-2-hydroxyethyl methacrylate) (P(S-\(r\)-HEMA)) and poly(\(n\)-hexyl methacrylate-\(r\)-2-hydroxyethyl methacrylate) (P(HMA-\(r\)-HEMA)) is described in Chapter 6, and catalytic coupling of poly(ethylene oxide) (PEO) and poly(dimethylsiloxane) (PDMS) is explained in Chapter 7. The following includes a general discussion on anionic and free radical polymerization.
Anionic polymerization is part of a class of “living” polymerization techniques in which the rate of initiation is comparable to or faster than the rate of propagation and proceeds without transfer or termination reactions.\(^1\) This approach enables the synthesis of polymers with controlled molecular weights and narrow distributions (dispersity, \(D \leq 1.1\)) using various vinyl or heterocyclic monomers. These reactions are often initiated using alkali metal complexes (e.g., sodium or potassium naphthalide) or organometallic compounds (e.g., alkyllithiums) to produce a nucleophilic “living end”. Upon initiation, a stoichiometric number of chains (1 chain per initiator) polymerize in a chain-growth fashion, with all chains growing at roughly equivalent rates (this, coupled with their near simultaneous initiation, is responsible for the low \(D\)). At full monomer conversion, the length of an anionically-polymerized chain is dictated by stoichiometry: \(N = \frac{[M]_0}{[I]_0}\), where \(N\) is the degree of polymerization and \([M]_0\) and \([I]_0\) are the starting molar concentrations of monomer and initiator, respectively. In the absence of impurities, spontaneous termination does not occur; therefore, the living end of the chain will remain active even after complete monomer consumption. This enables successive monomer additions and thus provides a synthetic route towards production of well-defined block copolymers. In principle, any number of monomer additions can be made, allowing for synthesis of ABC triblocks, -ABABA- multiblocks, etc., though not all crossovers (e.g., from monomer A to B) are possible. A primary challenge of executing controlled anionic polymerizations is rigorous removal of all terminating or chain transferring impurities (these include water and oxygen). Therefore, great effort is made to purify all reactants, solvents, etc., prior to reaction initiation.
Free-radical polymerization was employed to make HEMA-containing statistical copolymers. Unlike anionic polymerization, in free-radical polymerization propagation is fast relative to initiation, and there is intrinsic termination either through the combination of two chain ends or through disproportionation (the transfer of an H radical from one chain to another). This mechanism produces a relatively broad distribution of chain sizes ($D \sim 1.5 - 2.0$ depending on the termination mechanism) and molecular weights which depend on the reaction kinetics given by:3

$$\nu_n = \frac{k_p [M]}{\beta_i (k_i k_p f_i [I])^{1/2}} \quad \text{Equation 3.1}$$

$$\frac{d[M]}{d\tau} = k_p [M] \sqrt{\frac{k_d f_i [I]}{k_i}} \quad \text{Equation 3.2}$$

$$[I] = [I]_0 e^{-k_d \tau} \quad \text{Equation 3.3}$$

where $\nu_n$ is the kinetic chain length (the degree of polymerization of the growing chain prior to termination), $k_d$, $k_p$, and $k_i$ are temperature dependent rate constants (given by $k = K_1 \exp(-K_2/RT)$, where $K_1$ and $K_2$ are constants) for disassociation of the initiator (which generates free radicals), propagation of the chain, and termination of the free radical, respectively, $\beta_i$ accounts for the mode of termination ($\beta_i = 1$ for disproportionation, and $\beta_i = 2$ for coupling), $f_i$ is the efficiency of disassociation of the initiator (for a good initiator, typically close to 1), $\tau$ is time, and $[M]$ and $[I]$ are the instantaneous reactant concentrations.3 Free-radical polymerizations are comparatively easy to execute, as the polymerizations can often be done in bulk (without a solvent), and the monomers require less rigorous cleaning prior to use; they are degassed to remove oxygen, and any inhibitors which have been added to stabilize the monomer (e.g., 4-tert-butylcatechol) are removed, typically by passing through a column packed with inhibitor removal particles.
Free-radical polymerization also provides a convenient means to make statistical copolymers by charging two or more monomer types into the reactor during polymerization. The copolymer composition is dictated by the reactivity ratios of the monomers, which are the ratios of the rate constants associated with a chain end adding a unit of the same type vs. one of the alternate type. The composition is then given by the Skiest equation:

\[
F_A = \frac{r_A f_A^2 + f_A f_B}{r_A f_A^2 + 2 f_A f_B + r_B f_B^2}
\]

where \( F_A \) is the instantaneous molar composition of the copolymer, \( r_A \) and \( r_B \) are the reactivity ratios (defined as \( r_A = k_{AA}/k_{AB} \) and \( r_B = k_{BB}/k_{BA} \), where \( k_{ij} \) is the rate constant of a chain ending in \( i \) adding a monomer of type \( j \)), and \( f_A \) and \( f_B \) are the instantaneous mole fractions of the monomers. Because the monomers are selectively consumed, \( f_A \) and \( f_B \) will change as the reaction proceeds, leading to a drift in the copolymer composition over time/conversion. To minimize this effect, free-radical copolymerizations are typically terminated well before the reaction’s completion (~20 % conversion).

3.1.2 Molecular Weight Characterization by SEC

Size-exclusion chromatography (SEC, sometimes referred to as gel permeation chromatography, GPC) is a chromatographic method used to determine the molecular weight and dispersity of polymers. A small sample of a dilute solution of the polymer (typically 0.1-1 wt. % or sufficiently dilute that the chains are well isolated in solution), using the same solvent which serves as the mobile phase of the system, is injected at the inlet to a packed column. The column packing (the stationary phase) is highly porous and contains a wide distribution of pore sizes. As the flowing mobile phase (solvent) carries
the sample through the column, each polymer chain will “explore” the porous network; however, the chain can sample only pore spaces which are sufficiently large to accommodate the chain’s size. As a result, very large molecules are limited in the pore space they can explore and will thus pass through the column packing relatively quickly. Small molecules, however, can explore a much larger fraction of the column’s volume and take correspondingly longer to move through the column. Therefore, the elution time of a polymer from the column is correlated to the polymer’s size in solution and molecular weight, $M$. Since polymers are polydisperse, not all of the chains in a sample elute at the same time; the distribution of elution times then provides a direct measure of the distribution of chain sizes, and therefore, the polymer’s dispersity, $D$. SEC thus allows for the determination of different moments of the molecular weight distribution. The first moment is the number-average molecular weight, $M_n$, while the second moment is the weight-average molecular weight, $M_w$. The polymer’s dispersity is defined as the ratio of these two moments: $D = M_w/M_n$.

While the SEC columns separate the molecules based on size, a suitable detection method(s) is needed to determine when and how much polymer is eluting. The two types of detection used in this work are differential refractometry (DRI) and light scattering (LS). Other detection methods are possible (e.g., differential viscometry and ultraviolet absorbance); however, these were not employed here. DRI measures the difference in refractive index ($n_f$) between the solvent and the sample. For example, because PS has a larger $n_f$ than tetrahydrofuran (THF), when PS elutes from the columns the DRI shows a positive peak whose intensity is proportional to the concentration of PS in the effluent. DRI provides only a relative measure of molecular weight as it only captures the elution
time, \( \tau_e \), of the material which must be compared to a calibration curve (given by Equation 3.5, where \( A, B, C, \tau_0, \) and \( n_0 \) are all fit parameters, examples shown in Figure 3.1) obtained from the \( \tau_e \)s of chemically identical polymer standards of known molecular weight.

\[
\log(M) = A_0 + B_0 \tau_e + C_0 (\tau_e - \tau_0)^{n_0} \quad \textbf{Equation 3.5}
\]

The SEC systems employed in this work were calibrated using polystyrene (PS), although in principle any polymer may be used. Therefore, using the calibration curve, one only measures the PS-equivalent molecular weight of a polymer (if analyzing PS, the calibration curve may be used to directly determine the absolute molecular weight). To measure the absolute molecular weight for polymers via DRI, one must know the R-factor, which is defined as the ratio of the molecular weight measured from the calibration curve to the absolute molecular weight of the polymer. The R-factor effectively shifts the calibration curve vertically (see Figure 3.1) to account for the differences in hydrodynamic volume between the calibrant and the polymer of interest. The R-factor for a particular polymer must be determined separately using an absolute molecular weight determination method (e.g., light scattering, discussed below). The R-factor for block copolymers can be approximated using a variety of combining rules with the R-factors of the constituent homopolymers.\(^4\) In this work we employ the Chang combining rule (see Equation 3.6) which has been shown to yield accurate results for some of the most commonly studied block copolymers:

\[
R_{BCP} = \frac{M_A}{M_{BCP}} = 1 + (1 - w_A)(R_B - 1) \quad \textbf{Equation 3.6}
\]

where A and B represent the constituent homopolymers, \( w_A \) is the weight fraction of component A, \( R_{BCP} \) is the combined R-factor and \( M_{BCP} \) is the block copolymer molecular
weight, taken as the weight-fraction-weighted average of the individual block weights:

\[ M_{BCP} = w_A M_A + (1 - w_A) M_B. \]

**Figure 3.1** SEC calibration curves for PS, polyisoprene, and polybutadiene homopolymers measured in THF at room temperature. Solid curves show best fits to Equation 3.5. The calibration curves are approximately parallel, which enables the R-factor approach for molecular weight determination.\(^5\)

The second SEC detection method used in this work is static light scattering. Light scattering is an absolute molecular weight determination technique which measures \(M_w\) and relies on differences in \(n_f\) between the polymer and solvent for scattering contrast. This technique employs monochromatic light which is launched at the solution and
scatters with an intensity that is proportional to the molecular weight of the polymer and
the concentration of polymer in the solution. The angular dependence of this scattering
can be used to construct a Zimm plot and subsequently determine both the molecular
weight and size of the chains in solution (i.e., radius of gyration). To utilize light
scattering, one must know the concentration of polymer in solution which can be
obtained from a combination of the DRI data and the specific refractive index increment,
$dn_f/dc$, which is the change in refractive index of the solution as a function of the polymer
concentration (typically on the order of $\sim 0.1$ mL/g). The $dn_f/dc$ must be separately
determined for each polymer-solvent pair of interest by precisely measuring the $n_f$ of
multiple solutions of known concentrations and fitting to a line (the slope of this line is
$dn_f/dc$). Like the R-factor, the $dn_f/dc$ for block copolymers can be approximated with a
combining rule. In this case, a simple weight-fraction-weighted average is used (i.e.,
$dn_f/dc_{BCP} = w_A \times dn_f/dc_A + (1 - w_A) \times dn_f/dc_B$). Therefore light scattering data, using the
appropriate $dn_f/dc$, can be used to measure the absolute $M_w$ of a polymer without reliance
on external calibration. This $M_w$ can subsequently be used to determine a homopolymer’s
R-factor.

Two different SEC systems were utilized in this work: one with an HPLC-grade
toluene mobile phase and another with HPLC-grade THF. The former system consists of
a Waters 590 HPLC pump, two Polymer Labs PLgel Mixed-C 30 cm columns, and a
Waters 410 Differential Refractometer with a Precision Detectors PD2020 Dual-Angle
Light Scattering Detector built into the Waters 410 box, all operating at 40 °C. This GPC
system was primarily employed for analyzing PDMS homopolymers and PDMS-
containing block copolymers; PDMS has an index of refraction that is similar to THF,
thus the DRI signal obtained is very weak. PDMS in toluene, however, produces a large, but negative, DRI signal, making it much more amenable to analysis. All of the other polymers were analyzed using the second SEC system (THF mobile phase) which is composed of a Waters 515 HPLC pump, two 30 cm Agilent PLgel Mixed-C columns operating at 35 °C, and Wyatt OptiLab T-rEX (differential refractometer) and miniDAWN TREOS (three-angle light scattering) detectors, both operating at 658 nm and 25 °C. This system also possesses the capacity for viscometry (using a Viscostar II) and ultraviolet absorbance (with a Waters 2487 Dual λ Absorbance Detector) measurements, although these data were not employed for analysis of the present polymers. Both systems operate with a 1 mL/min flow rate and are calibrated with PS as described above. The specific refractive index increments of the relevant homopolymers were measured in THF at 25 °C and 658 nm using a separate Wyatt OptiLab rEX (DRI).

3.1.3 Composition Determination by $^1$H-NMR

Proton nuclear magnetic resonance ($^1$H-NMR) spectroscopy is a ubiquitous and powerful organic chemistry technique used here primarily to measure the compositions of block copolymers (i.e., measuring the ratio of hydrogens from monomer A to hydrogens from monomer B), compute the $M_n$ of low molecular weight polymers (via end-group analysis, see Chapter 7), and to track reaction completion (see Chapter 7). $^1$H-NMR spectroscopy enables the “counting” of all the protons in a sample, and operates by first aligning the nuclear spins by application of a strong external magnetic field, and then measuring the strength of field needed (which corresponds to a frequency) to switch the spin states between a base energy level (spin aligned with the magnetic field) and a
higher energy level (anti-aligned). The frequency of these transitions is measured and converted into the classical NMR spectrum which displays signal intensity vs. chemical shift (see Figures 5.2, 7.2, and 7.3 for representative examples). The strength of the chemical shift (measured in ppm) is related to each proton’s local electron environment. For example, a proton surrounded by a relatively dense electron cloud (produced by adjacent electron donors, e.g., saturated alkanes) shows a smaller chemical shift (closer to 0), while a proton which “feels” less electron density (one that is close to electron withdrawing groups, e.g., aromatic protons) shows a much greater shift. The number of peaks in the spectrum corresponds to the number of distinct types of hydrogens present in the sample, while the area of each peak provides information about the relative number of protons of that type. Typically, small molecules show sharp, well defined peaks in $^1$H-NMR spectra, while polymers show broader and more complex peaks due to variations in local environment, through monomer sequence stereoirregularity.

All of the present $^1$H-NMR work was conducted using a 500 MHz Bruker AVANCE. Unless otherwise noted, samples were prepared in deuterated chloroform (CDCl$_3$, peak position 7.24 ppm) at ~ 10 mg/mL. Phase and baseline corrections were applied to all spectra using MestReNova NMR software; this software was also used for numerical integration of the peaks.

3.1.4 Nanostructure Characterization by X-ray Scattering

X-ray scattering is a technique used to measure the characteristic size or spacing of nano- or Ångstrom-scale features. In a typical experiment, monochromatized and collimated X-rays are transmitted through a sample. As the beam passes through the
material, the X-rays coherently and elastically scatter, and the scattered signal is measured by a detector (see Figure 3.2a). The coherent interference of the scattered X-rays is described by Bragg’s Law\(^{10}\) (see Figure 3.2b):

\[
n_B \lambda = 2d_B \sin(2\theta_B)
\]

Equation 3.7

where \(n_B\) is an integer order of reflection, \(\lambda\) is the wavelength of the incident (and scattered) beam, \(d_B\) is the Bragg spacing (which corresponds to a structural length scale in the sample), and \(2\theta_B\) is the scattering angle. Therefore, if \(2\theta_B\) can be measured, a characteristic spacing, \(d_B\), can be determined via Equation 3.7. In general, X-ray scattering experiments are categorized by the magnitude of the scattering angle: wide-angle X-ray scattering (WAXS, typically 5 – 60°) is used to probe length scales corresponding to polymer crystal planes (typically a few Å), while small-angle X-ray scattering (SAXS < 5°) allows for detection of larger (~ 5 – 100 nm) length scales useful for measurement of domain spacings in microphase-separated block copolymers and crystallite size in semicrystalline polymers.

For crystalline polymers, WAXS is used to measure crystallinity and determine crystal structure. The scattered intensity is measured as a function of scattering angle which produces a series of sharp peaks which correspond to scattering from specific lattice planes. Because polymers are only semicrystalline, diffuse scattering from the polymer’s amorphous fraction may also be observed. These “amorphous halos” appear as broad humps superimposed onto the crystalline scattering.\(^9\) In this work, one-dimensional WAXS was used to monitor the crystallinity in PEO-containing block copolymers. These WAXS experiments were performed using a Philips-Norelco wide range goniometer,
Figure 3.2 (a) Schematic of X-ray scattering experiment operating in transmission. A collimated beam strikes a sample. The transmitted X-rays are blocked by a beamstop, while the scattered beam (with angle $\theta_B$) intensity and position/scattering angle is measured by a detector. (b) Schematic of Bragg scattering.$^9$

operating in reflection, with a graphite crystal focusing monochromator. The scattering angle is calibrated with a polycrystalline quartz sample exhibiting a peak at $2\theta = 26.66^\circ$. 
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For microphase-separated block copolymers, SAXS was utilized to determine the bulk morphologies (e.g., spheres, cylinders, lamellae) and interlayer spacings. Typically, SAXS data are plotted as scattering intensity vs. a scattering vector, $q$, defined as follows:

$$ q = \frac{4\pi \sin(\theta)}{\lambda} $$  \hspace{1cm} \text{Equation 3.8}

The measured scattering intensity, $I(q)$, is proportional to the product of the form, $P(q)$, and structure, $S(q)$, factors for the material. The form factor is the contribution to scattering intensity from the shape and size of the individual scattering entities (e.g., spheres, cylinders), while the structure factor accounts for scattering due to the arrangement of entities (e.g., body-centered cubic, hexagonally packed). Together, these lead to expressions for the expected scattering patterns for various block copolymer morphologies, shown in Figure 3.3. As an example, a block copolymer forming hexagonally-packed cylinders has a scattering pattern with peaks at $q/q^*$ ratios of $1$, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, and $\sqrt{9}$, where $q^*$ is the scattering vector magnitude at the primary (highest intensity) peak at low $q$. The location of the higher-order peaks enables determination of the block copolymer morphology, while the value of $q^*$ allows for calculation of the feature spacing by combining Equations 3.7 and 3.8 and setting $n_B = 1$:

$$ d_{\text{bulk}} = \frac{2\pi}{q^*} $$  \hspace{1cm} \text{Equation 3.9}

where $d_{\text{bulk}}$ is the characteristic spacing between block copolymer microdomains.

One-dimensional SAXS patterns were performed using CuK$_\alpha$ radiation (monochromatized, $\lambda = 1.542$ Å) from a PANalytical PW3030 generator (operating at 40 kV, 30 mA) with long-fine-focus Cu tube, a slit-collimated Anton Paar compact Kratky camera (evacuated to ~ 150 mtorr to minimize scattering by air), an MBraun OED-50M
position sensitive detector, and a home-built hotstage.\textsuperscript{11} Samples were mounted in copper hotstage cells (\(\sim 0.8 – 1.6\) mm thick) with thin (\(\sim 20\) \(\mu\)m) mica sheets as windows. Data were corrected for empty beam scattering, sample thickness and transmittance, compared to a polyethylene standard for absolute intensity, and desmeared.\textsuperscript{11}

\textbf{Figure 3.3} Representative one-dimensional SAXS patterns for some common block copolymer morphologies with the predicted \(q/q^*\) ratios labeled.\textsuperscript{12}
3.1.5 Thermal Characterization via DSC

Differential scanning calorimetry (DSC) is a technique for measuring thermal properties and transitions of materials (e.g., glass transition temperature, $T_g$, or melting temperature, $T_m$). DSC measures the precise amount of heat required to increase the temperature of a sample. The sample is placed in a metal pan, and the energy required to heat/cool the sample is compared with that needed for an empty reference pan; this differential heating method enables highly precise measurements of the input energy. In a typical experiment, the sample is cycled through fixed-rate heating and cooling steps and either the heat flow or heat capacity is plotted vs. system temperature (see Figure 3.4). If the sample undergoes a first-order phase transition (e.g., melting/crystallization), a peak is observed (if the data are plotted “endo up”, then a positive peak corresponds to melting, while a negative peak indicates crystallization). DSC can also detect second-order transitions such as the glass transition, which appears as a step change in the heat flow data. In addition to simple temperature scan experiments, DSC can also be used for more sophisticated thermal analyses including isothermal crystallization experiments which allow for measurements of the degree of crystallization (proportional to the area of the crystallization peak) as a function of annealing time.

DSC experiments were performed using a PerkinElmer DSC 7 equipped with a Type II intracooler and calibrated using the onset melting temperatures of indium ($T_m = 156.60 \, ^\circ\text{C}$) and tin ($T_m = 231.88 \, ^\circ\text{C}$) and the enthalpy of melting of indium ($\Delta H_m = 28.45 \, \text{J/g}$). A small amount of sample (between 5 – 15 mg) was placed in a crimped aluminum pan and placed in one furnace, while an empty aluminum pan is placed in the second furnace and used for the reference. Samples were typically scanned at 10 °C/min over the
temperature range of interest through multiple heating and cooling cycles. A baseline is collected using an empty sample pan scanned using the same temperature protocol.

![Figure 3.4](image)

**Figure 3.4** Representative thermograms (on heating, 10 °C/min) for a semicrystalline polymer (poly(ethylene terephthalate), PET) showing heat flow normalized by mass (mW/mg) vs. temperature.\(^{13}\) Common polymer thermal transitions seen by differential scanning calorimetry include (a) the glass transition (a step change in the heat flow), (b) crystallization (a negative peak), and (c) melting (a positive peak). As shown above, these transitions are heavily influenced by the polymer’s thermal history.

### 3.1.6 Solution Viscometry

For precise determination of polymer solution viscosities we employ a glass Schott-Geräte Ubbelohde dilution viscometer.\(^{14}\) Dilute solution viscometry operates on the simple principle that the time required for a precise volume of solution to flow through a properly-sized capillary is proportional to the solution’s viscosity. Therefore,
by comparing the flow time of a polymer solution to the flow time of a liquid of known viscosity, one can determine the solution’s viscosity via:

\[
\frac{\tau_{\text{solution}}}{\tau_{\text{reference}}} = \frac{\mu_{\text{solution}}}{\mu_{\text{reference}}}
\]

where \( \tau \) is the measured flow time and \( \mu \) is the solution viscosity. All measurements were performed at 20 °C; the temperature was maintained by submerging the viscometer and test liquid in a temperature-controlled water bath. Pure toluene (purchased from EMD Millipore, ACS grade), which has a viscosity of 0.59 cP at 20 °C, was used as the reference liquid.

3.2 Thin Film Techniques

3.2.1 Film Casting

This thesis employs a variety of methods to cast polymer films. The most straightforward casting method is simply melting polymer onto a substrate and allowing it to spread. This produces thick (>10 \( \mu \)m) films useful for the WAXS experiments discussed in Chapter 7; however, the technique is limited to polymers with an accessible glass transition temperature, \( T_g \), and order-disorder transition temperature, \( T_{ODT} \) (microphase-separated block copolymers are highly viscous and tend not to flow under their own weight; this phenomenon actually provides a quick test for microphase separation: if the material does not flow when heated above its \( T_g \), then it is most likely microphase-separated\(^{16} \)). To avoid these pitfalls and to produce the substantially thinner films needed for the majority of the work, solution casting techniques are employed instead. In this approach the solid polymer is dissolved in a good solvent and the solution
cast onto a substrate. As the solvent evaporates a dry polymer film is left behind. Drop casting a polymer solution produces a comparatively thin film, and is locally flat, but macroscopically is non-smooth.

Thin (<100 nm) and macroscopically flat (i.e., uniform thickness) films can be generated via spin-coating (see Figure 3.5). In this method the polymer solution is deposited onto a substrate, and then the substrate is rapidly accelerated to a set rotational speed. Centrifugal force causes the solution to flow radially outward, forming a thin, 

![Figure 3.5 Illustration of spin-coating. (a) A polymer solution is deposited onto a substrate. (b) The substrate is rotated at high speed, spreading the solution across the substrate and ejecting the excess solution. (c) The excess solvent quickly evaporates and leaves behind a dry film (d).](image-url)

Figure 3.5 Illustration of spin-coating. (a) A polymer solution is deposited onto a substrate. (b) The substrate is rotated at high speed, spreading the solution across the substrate and ejecting the excess solution. (c) The excess solvent quickly evaporates and leaves behind a dry film (d).
uniform coating on the substrate; the excess liquid flies off the substrate. The solvent evaporates and the film vitrifies as the substrate continues to rotate. The final thickness of the dry film is primarily dictated by the spin speed and the solution’s properties (e.g., viscosity, polymer concentration, etc.) and can be reasonably well modeled (within ~10% of the actual film thickness) by Equations 3.11-3.13:

\[
k = \left( \frac{c_0 D_g}{\nu_g \rho} \right) \left( \frac{P^*_v M}{RT} \right) \Omega^{1/2}
\]

Equation 3.11

\[
t_{\text{wet}} = \left[ \frac{3\mu_0}{2\rho \Omega^2} \right] \left( k (x^0_1 - x_{1\infty}) \right)^{1/3}
\]

Equation 3.12

\[
t_{\text{dry}} = (1 - x^0_1) t_{\text{wet}}
\]

Equation 3.13

where \( k \) is a mass transfer coefficient, \( c_0 \) is a numerical constant which depends on the Schmidt number of the overhead gas, \( D_g \) is the diffusion coefficient of the solvent in the gas, \( \nu_g \) is the kinematic viscosity of the gas, \( \rho \) is the solution density, \( P^*_v \) is the vapor pressure of the solvent, \( M \) is the molecular weight of the solvent, \( \Omega \) is the spin speed, \( t_{\text{wet}} \) is the wet film thickness (no significant solvent evaporation), \( t_{\text{dry}} \) is the dry film thickness (after all solvent has evaporated), \( \mu_0 \) is the initial solution viscosity, \( x^0_1 \) is initial solvent mass fraction in the coating solution, and \( x_{1\infty} \) is the solvent mass fraction that would be in equilibrium with the solvent mass fraction in the gas. \(^{18}\) In practice, rather than using the above equations, it is often easier to achieve the precise, desired film thickness by first generating a calibration curve (by producing multiple films, each with a fixed and known spin speed) for a particular solution (a polymer-solvent pair at a fixed solution concentration).
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For the present work, films were typically produced by dissolving ~0.5-5 wt. % polymer in toluene. The solutions were prepared the same day of their usage or were stored in a refrigerator (to minimize solvent evaporation) and used within several days. To spin the film, an amount of solution sufficient to cover approximately one-third to one-half the area of the substrate was pipetted onto the substrate which is held in place on the spin-coater chuck by pulling a slight vacuum. The substrate was then immediately accelerated at a rate of 10,000 rpm (rotations per minute) per second to the desired spin speed: typically between 1,000 – 6,000 rpm. Above 6,000 rpm, the vacuum became insufficient to consistently affix the substrate to the chuck (i.e., the substrate is ejected off the chuck prior to reaching the full spin speed). However, below 1,000 rpm deviations in the film thickness greater than 2 nm become common. After accelerating to the set rotation speed, the sample is held at that speed for at least 30 seconds (this is typically sufficient when casting from toluene, however, if a less volatile solvent is used then longer spin times may be required). During this time the solvent evaporates (typically within the first 5 seconds of spinning, this can be observed by eye as the film suddenly changes color). After spinning for a fixed time, the sample is decelerated (~ 1000 rpm/second) and removed from the spin coater.

Spin-coating has emerged as the most common method for generating polymer thin films due to its ease of use, reproducibility, and ability to make exceedingly smooth films (with average roughnesses of ~ 1 nm or less). The primary limitation to spin-coating, however, is that only flat (uniform thickness) films can be generated. An alternate coating method, termed flowcoating, has the ability to produce both thin films of a uniform thickness or ones which possess a thickness gradient. This technique was
first invented by Stafford et al.\textsuperscript{19}, and is discussed at length in Chapter 4. To produce a film, polymer solution is placed between a fixed blade and a substrate which rests upon a programmable translation stage. Once the solution is in place, the stage is made to move, gradually drawing solution from the reservoir and producing a film on the substrate with thickness $t_{\text{wet}}$. If the stage accelerates, solution is drawn out at a disproportionately faster rate, leading to a greater $t_{\text{wet}}$. The solvent then evaporates, leaving behind a dry polymer film of thickness $t_{\text{dry}}$.

A flowcoater was constructed based on the design by Stafford et al.\textsuperscript{19} using a Newport Corp. one-dimensional stage (ILS150CC, max velocity = 100 mm/s, max acceleration = 400 mm/s$^2$, on-axis accuracy 5 ± 2.5 $\mu$m) and motion controller (ESP300). At one end of the stage a metal holder which can stably mount a glass slide (Fisher pre-cleaned microscope slide, 75 mm × 25 mm × 1 mm, which served as the fixed blade) was placed above the stage. The mount contains four screws, each capable of independently adjusting the blade: the blade height (gap between the substrate and the blade, $G$, see Figure 4.1), blade angle (pitch or angle between the substrate and blade in the direction of motion, $\alpha$), blade tilt (roll or angle between the substrate and blade in the transverse direction), and the position of the blade in the transverse direction can all be carefully controlled. For details on operation of the device and an investigation of the parameters which dictate the coated film thickness, please refer to Chapter 4.

For all coating methods, unless otherwise noted, silicon (Si) wafers were used as the supporting substrate. The Si wafers were purchased from Silicon Quest (3 inch diameter, 381 ± 50 $\mu$m thick, highly polished on one side) and were liberally rinsed with
toluene prior to use. All of the wafers possessed a native SiOₓ layer ~ 2.2 ± 0.3 nm thick (this was accounted for when measuring polymer film thicknesses, see Chapter 3.2.3).

3.2.2 Film Floating

In some cases it is desirable to produce a free-standing (rather than substrate-supported) film; e.g., to stack multiple films, or to image via transmission electron microscopy. This is typically achieved by releasing a film from its substrate by floating the film onto water (see Figure 3.6). This requires that either the substrate be water soluble (e.g., a single crystal of NaCl), or that the film readily releases upon exposure to water. One approach to achieve the latter is through deposition of a sacrificial release layer onto the substrate, prior to the polymer film deposition. The main requirements of the release layer are that it must be a uniform thickness (low roughness) film, it must not interact with the polymer or casting solvent upon deposition of the polymer layer, and it must readily absorb or dissolve in water. Previously, our group has had success using poly(4-styrenesulfonic acid) (PSS), commercial liquid dish detergent (e.g., Ajax antibacterial dishwashing liquid), or table sugar (sucrose).

3.2.3 Ellipsometry

Ellipsometry is an optical technique used to measure the thickness (t) and index of refraction (nᵢ) of polymer thin films. When operating in reflection mode (transmission is also possible), polarized light is launched at a substrate-supported film, passes through the film, reflects off the substrate, and travels to an analyzer and detector (see schematic in Figure 3.7). The ellipsometer measures changes in polarization between the incident
Figure 3.6 Illustration of floating a block copolymer film onto water, thus releasing it from the underlying Si substrate, using a sacrificial release layer (PSS).22

and reflected light using the complex reflectance ratio given by:

\[
\frac{r_p}{r_s} = \tan(\Psi)e^{i\Delta}
\]  

Equation 3.14

where \(r_p\) and \(r_s\) are the amplitudes of the \(p\) (oscillating parallel to the plane of incidence) and \(s\) (oscillating perpendicular to the plane of incidence) components, respectively, of the reflected light, \(\tan(\Psi)\) is the amplitude ratio upon reflection, and \(\Delta\) is the phase shift. The technique thus measures two raw quantities (\(\Psi\) and \(\Delta\)) independently, and using various models uses these quantities to calculate two material properties, most commonly a film thickness and an index of refraction for a single layer of a film (although additional calculation combinations are possible, e.g., the film thicknesses of two separate layers). This work uses a Gaertner Scientific LS116S300 single wavelength ellipsometer (laser wavelength, \(\lambda = 632.8\) nm) to measure polymer film thicknesses. Previously, our group has found that this machine cannot accurately/reproducibly measure \(t\) and \(n_f\) simultaneously for very thin films (<50 nm). Therefore, in these cases \(n_f\) (whose value is primarily dependent on the material’s density) is first measured on a relatively thick film.
(~ 100 – 200 nm), and then this value is input (and assumed independent of thickness) when measuring sub-50 nm films.

![Figure 3.7 Schematic of an ellipsometer operating on a polymer thin film.](image)

### 3.2.4 Contact Angle Goniometry

The surface energy of a material is typically measured by observing the wetting behavior of liquids on that surface. This is often characterized by a contact angle (CA), which is the angle at which the liquid/vapor interface meets a solid surface (see Figure 3.8a). Typically, CA measurements are performed using water as the liquid phase and ambient air as the vapor phase. When the water CA is <90°, the surface is said to be hydrophilic or wettable. Conversely, a surface whose water CA is >90° is labeled hydrophobic, or non-wettable (superhydrophobic surfaces actually have water CAs >150°). According to Young’s equation (Equation 3.15), derived by performing a tension/force balance on a sessile drop, the equilibrium (or Young’s) CA_{Equil} is uniquely
Figure 3.8 (a) Illustrations of sessile droplets displaying their equilibrium or Young’s contact angle.\textsuperscript{23} (b) Illustrations of advancing (left) and receding (right) contact angles.\textsuperscript{23} (c) Photograph of Ramé-Hart contact angle telescope-goniometer.\textsuperscript{24}
defined by the interfacial tensions ($\gamma$) between the three components (solid-S, liquid-L, and vapor-V) by:

$$\cos(CA_{\text{Equil}}) = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$  \hspace{1cm} \text{Equation 3.15}

In practice, $CA_{\text{Equil}}$ is difficult to observe directly, but is instead bounded by a surface’s advancing ($CA_{\text{Adv}}$) and receding ($CA_{\text{Rec}}$) contact angles; these are the angles formed just prior to de-pinning of the sessile drop upon advancing or receding, respectively, across a surface (see Figure 3.8b). The difference between $CA_{\text{Adv}}$ and $CA_{\text{Rec}}$ define the contact angle hysteresis. Typically, rough surfaces show large hysteresis, while smooth/ideal solid surfaces show little or none; in these cases the observed $CA \approx CA_{\text{Equil}}$.

The simplest method to measure the CA is through contact angle goniometry (see Figure 3.8c) which measures the angle visually.\textsuperscript{23} The goniometer consists of a horizontal stage above which is a fine needle attached to a motor driven syringe/pump. The sample is placed onto the stage and a small volume (< 5 $\mu$L) of liquid is placed on the surface, forming a sessile drop. The drop can then be imaged using a high resolution camera which is mounted beside the stage. The CA is then measured through various analyses of the drop shape profile. The present work employed a Ramé-Hart contact angle goniometer (model 500-F1) to observe the water CA on various polymer films. The sessile water droplet mass was ~ 2.5 mg, and the images were analyzed using Ramé-Hart’s DROPimage Advanced software. CA values were determined using the “circle method” in the software. The goniometer is kept in a clean room to minimize impurities/contamination on the polymer films and in the droplet liquid.
3.2.5 Pad Shearing

As discussed in Chapter 2, application of shear at the surface of a block copolymer thin film can orient the microdomains in the direction of applied shear. Multiple apparatus have been developed to implement this approach; this thesis will employ two of these: pad shearing and rheometer shearing. The pad shearing technique enables macroscopic alignment (areas of cm² or larger) of microdomains using a fixed, and sufficiently large, stress across the whole of the pad. This technique is particularly advantageous for device fabrication where globally aligned features are desired (e.g., polarizing grids²⁵-²⁷) or in cases where large stresses (≥ 6 kPa) are needed for alignment.

For the pad shearing technique, a smooth, cross-linked elastomer pad is placed in direct contact with the film²⁸-²⁹ This pad is prepared using a mixture of Dow Corning Sylgard 184 (a cross-linkable PDMS), at a weight ratio of 1:15 curing agent to elastomer. Changing this ratio alters the stiffness of the pad which seems to impact the final quality of the alignment; this was never rigorously optimized, but a ratio of 1:15 seems to consistently yield “good” pads which produce the best alignment. After rigorous mixing of the Sylgard components, the material is immediately cast onto an as-received Si wafer. Curing the Sylgard in contact with the (nearly) atomically smooth Si wafer ensures that the resulting pad possesses as little roughness as possible, promoting maximum contact between the pad and block copolymer film during shearing. After allowing the mixture to rest for ~ 15 minutes (to allow all of the visible air bubbles, introduced during mixing, to escape the viscous liquid) it is cured at ~60 °C for 2 hours and then overnight at room temperature.
The cross-linked pad is trimmed to a prescribed size (with a typical area 1 – 5 cm²) and the smooth side (cured in contact with the Si wafer) is placed in direct contact with the supported block copolymer film which rests on a hot plate and has been preheated to a temperature well above the $T_g$ of both blocks of the copolymer (for the present work, $T = 150 \, ^\circ\text{C}$ is employed for all shearing experiments). After placing the pad down, the system is allowed to equilibrate for ~ 10 min. A normal force (typically ~ 10 N) which is sufficiently large to prevent any noticeable slip between the pad and polymer film is applied. A precise shear stress is then imparted using a weight and pulley system (see Figure 2.6a) to apply a lateral force. The shear is applied for a prescribed time (typically 30 min) during which the pad translates a small, but measurable, distance (typically 0.01-1 mm, depending on the magnitude of the stress, the thickness of the film, and the polymer being sheared; see Chapter 6.7 for further discussion). Upon completion of shearing, the system is cooled to room temperature (at ~ 10 °C/min) with the stress still in place; it is necessary to shear the film while cooling through the $T_g$ of one or both blocks to ensure that the aligned morphology is locked in upon vitrification. Once cooled, the stress, normal force, and PDMS pad are carefully removed.

### 3.2.6 Rheometer Shearing

The rheometer shearing technique (discussed in Chapter 2, see Figure 2.6b for a schematic of the setup) provides an alternate means of shearing block copolymer films. Unlike the pad shearing approach, which applies a uniform stress across the entire sheared area, rheometer shearing applies a stress gradient. This enables investigation of
the dependence of block copolymer alignment quality on applied shear stress using only a single polymer film.

The rheometer shearing technique is executed as follows.\textsuperscript{30-33} Supported block copolymer films are fastened with polyimide tape (purchased from Fisher) directly to a Peltier heating plate, which is attached to an AntonPaar MCR-501 rheometer which is fitted with a 25 mm diameter parallel plate. Highly viscous PDMS oil (DMS-T72, purchased from Gelest, room temperature kinematic viscosity $\approx 2 \times 10^7$ cSt) is placed on the surface of the film, after which the parallel plate is carefully lowered (so as not to exceed a normal force of 2 N on the rheometer tool, to prevent damage to the instrument) until the PDMS layer between the plate and block copolymer film is $\sim 0.2$ mm thick (the oil is trimmed around the plate’s edge when the gap height is $\sim 0.21$-$0.22$ mm). Employing such a high viscosity oil minimizes leakage of oil from the gap and makes removal of the oil upon completion of the experiment easier (most of the highly viscoelastic PDMS can be “peeled” off in a manner similar to a solid pad). Once the oil no longer exerts a measurable upward normal force on the plate, indicating that any stresses in the oil have relaxed, the Peltier plate is heated to the shearing temperature (150 °C, well above $T_g$ for the polymers employed in this thesis) and allowed to equilibrate for 15 min. The shear is then applied by rotating the top plate with a constant torque, thus creating a radially-varying shear stress gradient such that the stress at the film’s center is zero and increases to a maximum at the plate’s edge (this gradient is shown in Figure 6.1b). After shearing for a prescribed time ($\tau_{\text{shear}}$), the system is cooled beneath the $T_g$ of at least one of the blocks of the copolymer with the stress still applied. After completion of the process, a circular outline around the shearing plate is scribed into the substrate, to
later identify the center of the sheared area. Once the plate is raised, the excess PDMS oil on the film surface is removed first by peeling off (as described above) and then “sponging” off any residual oil using a cross-linked PDMS pad (described in Section 3.2.5); the PDMS oil preferentially wets the pad and detaches from the block copolymer film surface.

To subsequently compute the stress applied during rheometer shearing (discussed in Chapter 6.2), the rotation axis of the sheared area must be determined. This procedure was developed by Marencic and is summarized here. The sample is placed on a moveable stage (with controlled, ~ 20 µm resolution) with an optical microscope (~ 10× magnification, both the stage and optical microscope are attached to the atomic force microscope used for sample imaging, see Chapter 3.3.1) which is used to record the location in Cartesian coordinates (relative to an arbitrary reference position on the film) of twenty or more points along the scratches etched into the sample upon completion of shear and which outline the position of the rheometer tool (see Figure 3.9). The circle (with radius \( r_0 = 12.5 \text{ mm} \), the radius of the parallel plate tool) of best fit to these points is computed, from which the axis of rotation (the center of the best-fit circle, \((x_0, y_0)\)) is determined. The radial distance \( r \) from the center of the sheared area for a particular position \((x, y)\) along the film is then simply computed by:

\[
r = \sqrt{(x-x_0)^2 + (y-y_0)^2}
\]

Equation 3.16
3.3 Microscopy and Image Analysis

3.3.1 Atomic Force Microscopy

Atomic force microscopy (AFM, a form of scanning probe microscopy, SPM) is a versatile, high resolution (nm to μm scale) imaging technique commonly used to characterize block copolymer thin film morphology. In AFM, a sharp tip or probe (~10 nm radius), which is attached near the end of a flexible cantilever, is scanned across the surface of a sample and the interactions between the tip and sample are measured and used to produce a spatially resolved image (see schematic in Figure 3.10). While modern AFMs can feature numerous imaging modes and functionalities, the most common are the contact and tapping modes. When operating in contact mode, the tip is dragged across the film’s surface and the vertical deflection (height or z-position) of the cantilever is monitored. This allows for the production of a height image which provides a three-dimensional (length × width × height) representation of the scanned surface.
Figure 3.10 (left) Schematic of AFM operating in tapping mode to image a block copolymer thin film. (right) Scanning electron micrograph of an AFM tip.\(^{38}\) Scale bar indicates 2.5 \(\mu\)m.

Alternatively, when operating in tapping mode, the cantilever is made to oscillate at or near its resonance frequency (which is dictated by the cantilever’s dimensions and Young’s modulus) and made to “tap” along the surface. This enables the independent measurement of both the height image, as the AFM controller adjusts the cantilever height to maintain constant oscillation amplitude, and also a phase image. As the tip interacts with the sample, a phase lag is produced between the signal from the controller which drives the cantilever oscillation and the output signal back to the controller. This phase lag or shift is correlated to the mechanical properties (\textit{i.e.}, stiffness) of the surface. Therefore, by monitoring the phase lag as the probe scans the sample, a two-dimensional mapping of the surface’s local stiffness can be generated. This feature is especially vital for imaging block copolymer thin films. When there is the appropriate mechanical contrast between blocks (\textit{i.e.}, one glassy block and one rubbery block), phase imaging
allows for the direct, and nondestructive, observation of the thin film morphology (e.g., dots vs. lines or nonaligned vs. aligned). Typically, softer (rubbery) materials appear darker in an AFM phase image, while harder (glassy) materials appear brighter. Occasionally the phase image contrast can become inverted; this is often attributed to whether the AFM tip is interacting with the surface in a repulsive (“standard” contrast) or attractive (“inverted” contrast) manner.

All AFM imaging was performed using a Digital Instruments (now Bruker) Dimension 3000 equipped with a movable stage and optical microscope. The substrate-supported sample is placed on the stage and moved to the desired imaging spot. Force modulation mode probes (purchased from NanoWorld, force constant = 1.2 – 5.5 N/m, resonance frequency = 60-90 kHz) were used for tapping mode imaging. These probes, while designed for operation in force modulation mode, prove excellent for phase imaging as the relatively long and flexible cantilevers enable exceptional phase contrast for the materials employed, thus providing clearer images. To detect the tip oscillation and/or deflection, a built-in laser is positioned to reflect off the top side of the cantilever and the laser’s reflection is monitored by a position-sensitive detector. Immediately prior to engaging the probe with the surface, the cantilever resonance frequency is determined using the device’s autotuning function. This must be done regularly (every time a new tip is used, or after that same tip has been used for ~ 10 images) as small changes in the cantilever resonance frequency during use can dramatically alter the image quality. After autotuning, the amplitude set point (the average distance of the cantilever away from the sample) is set to 1.000 V, and the drive amplitude (the size/amplitude of the cantilever oscillation) is set such that the root-mean-square amplitude is ~ 1.50 V. The tip is then
engaged with the surface. Once engaged, the phase image is brought into focus by first reducing the amplitude set point (to ~ 0.8 V) and increasing the drive amplitude (as much as needed, but no more than ~ 5× the starting value); both of these adjustments cause the tip to tap on the surface more strongly, allowing the relatively subtle mechanical contrast of the blocks to become more visible. The controller gain settings (proportional gain = 0.5000, integral gain = 0.7800) may also be adjusted to further improve the phase image, but fine adjustment of these parameters often produces only modest changes in the final image quality. All images, unless otherwise noted, were taken at a 2 μm × 2 μm scan size with 512 × 512 pixel resolution. Figure 3.11 shows a representative pair of height and phase images of a block copolymer film.

The position of the tip is controlled by piezoelectric actuators. These are materials which translate a fixed amount upon application of a voltage. As the piezoelectrics age, the specific relationship between voltage and translation distance will change; because of this, the piezos must be calibrated regularly (annually, or as needed) by imaging samples of known feature sizes. In addition, upon initial application of the voltage, the piezo may not instantly translate the full distance, but instead will gradually approach it with time; this creates an apparent time-dependent stretching of the image called piezo drift. To minimize piezo drift, the tip is engaged with the surface, but the image is not collected until the image no longer appears stretched or distorted. Even so, some piezo drift may be unavoidable, but can be removed by subsequent image processing (see Chapter 3.3.3).
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Figure 3.11 Representative tapping mode atomic force micrographs of a cylinder-forming block copolymer film: (left) height image, and (right) phase image. The scan area is $2 \times 2 \, \mu\text{m}^2$ and the z-position (height or phase shift) gray scale is displayed to the right of each image. The glassy cylinders appear as bright lines or dots, while the rubbery matrix appears dark. Interestingly, the microdomain pattern is observable in both the height and phase images, while the film’s topography can be seen only in the height image. For phase images, the magnitude of the z-position contrast is arbitrary, thus it will not be displayed alongside the phase images presented later in the thesis.

3.3.2 Transmission Electron Microscopy

Transmission electron microscopy (TEM) was not extensively employed in this thesis, and used only to generate the image shown in Figure 5.5c. As such, the present discussion of the topic is brief; for more information, please refer to the available references. TEM was conducted using a Philips CM-100 (40-100 kV, tungsten filament) with a single-tilt goniometer stage, and an attached high-resolution digital camera. Samples were prepared by spin-casting films from solution onto NaCl single
crystals (polished infrared crystal window, purchased from Sigma-Aldrich) and floating the film on water (see Chapter 3.2.2). The film was collected onto a TEM grid (purchased from Electron Microscopy Sciences, 400 mesh copper), allowed to dry overnight, and imaged without any further sample preparation (i.e., the film was not stained with a heavy metal, as is commonly employed for TEM of polymers).

3.3.3 Image Filtering

Prior to further analysis of the micrographs, a Fourier filtering process was typically performed. This eliminates irreproducible sample-to-sample and AFM probe-to-probe noise which could interfere with subsequent calculations. To execute the image filtration, a discrete Fourier transform of the real-space micrograph is taken. In nonaligned samples the first-order peaks yield an approximate ellipse; the elliptical, rather than circular, profile is a result of thermal and piezo drift in the AFM which causes asymmetric stretching of the image (though the magnitude of this asymmetry was typically <0.5 nm in real space). To correct for this, an ellipse is fit to the first-order peak which is subsequently stretched into a circle with a radius equal to the average of the major and minor axis lengths, thus resizing the image. This stretching was not performed for images of aligned cylinders, whose Fourier space image contains only two sharp peaks, which cannot be fit to an ellipse. After stretching, the image is filtered to remove both high- and low-frequency noise using a bandpass mask, and an inverse Fourier transform is performed to convert the image back to real space. The resulting image is used for subsequent image analysis. For nonaligned or sixfold symmetric patterns we employ an annulus which is fit over the first-order peaks as a mask (see Figure 3.12).
Figure 3.12 Representative images displaying the Fourier filtering process using a “ring” for nonaligned or sixfold-symmetric patterns: (top left) raw AFM phase image, (top right) Fourier transform of the original image showing the annular filter mask, (bottom left) intensity removed by the filter, and (bottom right) the final filtered image in real space. Real space images are $2 \times 2 \ \mu m^2$. 
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For the well-aligned images we instead utilized two circular masks centered around the two primary peak positions (see Figure 3.13). In both cases the size of the mask (in the former case the width of the annulus, in the latter case the diameter of the circles) was fixed at a value of \( D_{FFT} \) (where \( D_{FFT} \) is the distance in Fourier-space from the center to the position of maximum peak intensity). Figures 3.12 and 3.13 display examples of the image filtering for two representative images. All filtering was done using software written in Interactive Data Language (IDL).\(^{34}\)

### 3.3.4 Computation of Fractional Coverage of Lines

The fractional areal coverage of lines (in-plane cylinders) vs. dots (spheres or out-of-plane cylinders) in a particular micrograph, hereby denoted \( F \), was computed using ImageJ.\(^{40}\) ImageJ is an image analysis software created and provided (free) by the National Institutes of Health. To compute \( F \), first the filtered micrograph is thresholded such that the dispersed glassy domains (the dots and lines) can be treated as particles (see Figure 3.14 for representative examples of the process). Using the “analyze particles” tool on ImageJ, each domain is identified, outlined, and binned based on either its size or circularity (both approaches yield the same result) with smaller, more circular particles labeled as “dots”, while the larger, less circular particles were deemed “lines”. The total area of dots and lines is then computed by summing the areas of the particles in each bin, and \( F \) is obtained simply by dividing the area of lines by the total area of particles (dots and lines).
Figure 3.13 Representative images displaying the Fourier filtering process using a “two spots” or circular masks for aligned patterns: (top left) raw AFM phase image, (top right) Fourier transform of the original image showing the “two spots” filter mask, (bottom left) intensity removed by the filter, and (bottom right) the final filtered image in real space. Real space images are $2 \times 2 \, \mu m^2$. 
Figure 3.14 Representative images illustrating the calculation of the fractional coverage of lines in an image, $F$. (top left) Filtered AFM phase micrograph. Scale bar indicates 500 nm. (top right) Thresholded image showing the dispersed microdomains in black and the matrix in white. (bottom) Images outlining the “particles” identified by the software with larger, less circular particles binned as lines (bottom left) and smaller, more circular particles binned as dots (bottom right). For the present image, $F = 0.66$. 
Chapter 3: Experimental Methods

3.3.5 Order Parameter Calculations

The quality of alignment in the micrographs of sheared samples was assessed using an orientational order parameter, $\psi_{2\alpha}$, defined as follows:

$$\psi_{2\alpha} = \langle \cos \left[ \alpha (\theta_i - \theta_0) \right] \rangle$$  

**Equation 3.17**

where $\theta_i$ is the direction of microdomain orientation, $\theta_0$ is the direction of applied shear, $\alpha = 1$ is used to characterize all-line patterns while $\alpha = 3$ is used for hexagonally-packed dot patterns or mixtures of dots and lines ($\alpha$ thus reflects the number of planes of rotational symmetry in the image), and the angle brackets indicate that the an average is taken over all microdomains in the image. The order parameter is equal to 0 when the microdomains are randomly oriented, 1 when they are perfectly aligned in the direction of shear, and -1 when anti-aligned. Before computation of $\psi_{2\alpha}$, the micrographs were filtered (see Chapter 3.3.3).

Typically, $\psi_6$ is used to analyze the alignment of sphere-forming block copolymer thin films. While the alignment of sphere-formers is not a subject of this thesis, it was still necessary to employ $\psi_6$ when analyzing systems which displayed mixed morphologies consisting of both in-plane cylinders (which appear as lines in the AFM image) and out-of-plane cylinders (hexagonally-packed dots). To compute $\psi_6$ the following approach, developed by Marencić\textsuperscript{34}, was employed. Using IDL, a Fourier transform is performed on the real space image which yields an angular distribution of first-order peaks whose intensity corresponds to the areal density of grains in the real-space image with that particular orientation. The angular distribution is binned into 1° increments (Figure 3.15 shows an example of this distribution for an image of a relatively well-aligned film) and exported to Microsoft Excel where the remaining data
Figure 3.15 Angular distribution of pixel intensity in a representative AFM micrograph transformed into Fourier space. The black curve shows the raw data, while the red shows the data with an isotropic background subtracted. With the background subtracted, the calculated $\psi_6$ of this micrograph is 0.897.

Manipulations are performed. From the angular distribution the order parameter is computed as follows:

$$\psi_6 = \frac{\sum_i R(\theta_i - \theta_0) \cos(6(\theta_i - \theta_0))}{\sum_i R(\theta_i - \theta_0)}$$

Equation 3.18
where the sum \( i \) is taken over all bins (0 - 359°) and \( R \) is the angular distribution of pixel intensity in the Fourier space. Typically, the angular distribution possesses a substantial background intensity caused by noise in the original micrograph. This dramatically reduces the calculated \( \psi_6 \) and undermines this approach’s ability to accurately convey the degree of alignment in the image. Therefore, the background intensity was removed by subtracting a horizontal line set at a value equal to the average intensity of the background (see Figure 3.15; if this difference resulted in a negative value then the intensity for that angle was set to zero).

For highly-aligned images which do not show any dots, \( \psi_2 \) may be computed instead using a script written in IDL (method described previously\(^{34, 39, 41-42} \)). This is done by determining the intensity gradient for each pixel; this gradient is assumed orthogonal to the cylinder axis (and thus orientation). The order parameter is then computed by:

\[
\psi_2 = \frac{1}{N_{\text{pixels}}} \sum_i \cos(2(\theta_i - \theta_0))
\]

Equation 3.19

where \( N_{\text{pixels}} \) is the number of pixels in the image. Notice that here there is a factor of 2 in the cosine term indicating the twofold symmetry of this lattice (rather than the factor of 6 present in Equation 3.18 for the hexagonal lattice). Both methods for computing \( \psi \) will yield values of 1 when the microdomains are perfectly aligned in the direction of applied shear and values of 0 when they are randomly oriented. However, due to differences in their definition, the difference between \( \psi \) and unity for well-aligned films are different by a factor of 9 between \( \psi_2 \) and \( \psi_6 \). This means that in the example image shown in Figure 3.15, in which \( \psi_6 \) was found to be 0.897, one would expect a \( \psi_2 \) of ~ 0.989; when \( \psi_2 \) was computed using our algorithm we obtained an actual value of \( \psi_2 = 0.990 \) which is in excellent agreement with the expected value.
3.3.6 Dislocation Finding Algorithm

The density of dislocations was computed for highly-aligned films (which display no dots) using an algorithm in which a square trace is created and the total number of cylinders entering and leaving the trace is counted.\textsuperscript{33-34} If this total is even, meaning that the same number of cylinders are entering and exiting the trace, then no dislocation is deemed present. Conversely, an odd number of cylinders indicates that a defect is potentially present. The length of the edges of this square trace was iteratively varied, beginning first with a maximum trace length of 6 cylinder spacings. The trace length was then reduced by 1 pixel and the search repeated, disregarding any dislocations which have already been found so as not to double count. This iteration continues until a minimum trace length of 2 cylinder spacings is employed. Only images which are highly aligned and which have been aggressively filtered (using the two-circle filtering method) were counted for defects. The more aggressive filtering was needed to ensure that no artificial “breaks” in the cylinders, which would be counted as defects, are present in the images.\textsuperscript{33-34} After all potential defects are found they are each outlined with a circle (see Figure 3.16a) so that the defects could be manually inspected to ensure that a defect was actually present. The only defects observed in the well-aligned images were isolated dislocations (see Figure 3.16b).
Figure 3.16 (a) Representative TM-AFM phase image (PS-PHMA 21-77, $t = 30$ nm) showing the output of the dislocation finding algorithm for an image with a relatively low dislocation density. (b) Higher magnification view of an isolated dislocation. Scale bar = 500 nm.
3.4 References


42. Pelletier, V. *Physics and Technology of Sheared Cylinder-Forming Diblock Copolymer Thin Films*. Ph.D. Thesis, Princeton University, **2005**.
Chapter 4: Creating Controlled Thickness Gradients in Polymer Thin Films via Flowcoating

Creating Controlled Thickness Gradients in Polymer Thin Films via Flowcoating

4.1 Introduction

As previously discussed, the creation of thin (< 200 nm) polymer films is a subject of intense interest, with applications in diverse fields such as medicine,\textsuperscript{1-2} optics,\textsuperscript{3} and microelectronics.\textsuperscript{4-5} Numerous methods exist to deposit thin polymer films including spin-coating,\textsuperscript{6} dip-coating,\textsuperscript{7} layer-by-layer assembly,\textsuperscript{8} and physical,\textsuperscript{9} chemical,\textsuperscript{10} and laser deposition.\textsuperscript{11} An additional method, invented by Stafford et al. and titled flowcoating, has the useful advantage of being able to generate both flat films and films which possess a thickness gradient.\textsuperscript{12} The basic setup of a flowcoater is displayed in Figure 4.1, with the hardware discussed previously in the Experimental section. Due to the technique’s ease of use and potential for integration into large-scale production methods,\textsuperscript{13} numerous efforts have utilized this approach for deposition of thin films. Accordingly, applications of this technique range from studies of polymer thin film physics,\textsuperscript{14-16} biomaterial properties,\textsuperscript{17-19} and block copolymer phase behavior,\textsuperscript{20-26} to nanoparticle assembly\textsuperscript{27} and device fabrication.\textsuperscript{28-29} Flowcoating is also popular due to its amenability to high-throughput and combinatorial experiments which leverage the technique’s versatile
Figure 4.1 (a) Schematic of flowcoating process with relevant experimental parameters labeled. (b) A photograph showing the flowcoater, coating a toluene-polymer solution onto a Si wafer (scale bar indicates 1 mm).

capacity to produce films with a thickness gradient.\textsuperscript{30-36} This allows for the rapid investigation of the influence of film thickness on properties using only a few samples—sometimes only one. High-throughput approaches like flowcoating thus save time, conserve material, and minimize unintended sample-to-sample variation.

The primary control parameter which dictates film thickness ($t_{dry}$) is the coating blade velocity, $U$. The stage can be made to run at a constant $U$ producing a flat film, not unlike one produced by spin-coating, or the stage can operate with a non-zero
acceleration and produce a film with a thickness gradient. To this point, however, the fundamental fluid mechanics which govern this coating process as well as the quantitative relationship between the numerous experimental parameters and the final film profile are yet to be fully understood. Le Berre et al. developed a model for this process using Landau-Levich theory, based on the lubrication approximation, which states that the length scale in the direction of the gap is much smaller than the length scale in the flow direction. Landau-Levich theory predicts that all coating flows of this nature should have a solution of the following form:

\[
\frac{t_{\text{wet}}}{L} = c_1 Ca^{2/3} = c_1 \left(\frac{\mu U}{\gamma}\right)^{2/3}
\]

Equation 4.1

where \(t_{\text{wet}}\) is the coated solution film thickness far away from the meniscus prior to solvent evaporation, \(L\) is a characteristic length scale, \(c_1\) is a numerical constant, and \(Ca\) is the capillary number which is defined in terms of the solution viscosity \(\mu\), \(U\), and the solution surface tension \(\gamma\). \(Ca\) is a dimensionless parameter comparing the relative strength of viscous forces and surface tension in the system. The solution from Le Berre et al. matched this form, with the characteristic length scale \(L\) identified as the radius of curvature of the rear meniscus \(R_c\), and the numerical constant \(c_1 = 1.34\). Lau independently solved the problem, yielding a similar solution. Experiments performed by Le Berre and by Lau, all using aqueous solutions or suspensions, showed qualitative agreement with this model, including the proper scaling with \(U\). However, the experimental films were typically 2-3 times thicker than the model prediction; this was attributed by Lau to solute-induced Marangoni effects, which are known to occur in the presence of surface-active components and can lead to thickening by a factor of up to
2.5. If true, then when no surface-active components are present, as is typically the case when coating polymers from organic solvents, this model may indeed provide a useful quantitative guide for the creation of films with desired thicknesses and thickness gradients, though this has yet to be demonstrated.

The purpose of this study is to explore the relationships between the experimental parameters associated with flowcoating and the final polymer film thickness. First, the dependence of film thickness on $U$ and $Ca$ are rigorously tested; next, the characteristic length scale proposed by Le Berre and Lau is examined and used to experimentally determine the prefactor $c_f$. The result is a design equation which allows a user to produce polymer thin films with precise and broadly tunable film thickness profiles.

4.2 Materials, Method, and Initial Experiments

Figure 4.1 shows a side-view schematic of the coating process, with all relevant experimental parameters labeled, and a side-view photograph of coating in progress. In addition to the gap dimensions (e.g., the gap between the substrate and blade, $G$, the angle between the blade and the substrate, $\alpha_0$, and the blade tilt/roll), additional experimental parameters can be controlled including stage velocity, $U$, and acceleration, $A$, and solution reservoir volume, $V$. These, along with properties of the solution such as polymer concentration, $C$, viscosity, $\mu$, and surface tension, $\gamma$, can influence the film thickness.

The following polymers were used in this study: an experimental grade polystyrene (PS) provided by Dow Chemical (XP6069.02, number-average molecular weight $M_n = 112$ kg/mol, dispersity $D = 2.8$), three additional PS homopolymers
synthesized in-house with molecular weights of 16.7 kg/mol ($D = 1.7$), 416 kg/mol ($D = 1.2$), and 1500 kg/mol ($D = 1.8$), poly(methyl methacrylate) (PMMA, $M_n = 46.4$ kg/mol) and poly(ethylene glycol) (PEG, typical $M_n = 8$ kg/mol) purchased from Sigma Aldrich, and two polystyrene-polyisoprene-polystyrene (PS-PI-PS) triblock copolymers (D1111, 22 wt. % PS; D1163, 15 wt. % PS) and two polystyrene-polybutadiene-polystyrene (PS-PB-PS) triblock copolymers (D1102, 28 wt. % PS; D1493, 75 wt. % PS) provided by Kraton Polymers. The polymer solutions were made at the desired concentration (by weight) and stored in a refrigerator. All solutions were allowed to warm to room temperature (20 ± 2 °C) prior to their use in coating experiments. Solvent and solution viscosities at 20 °C were measured via capillary viscometry.$^{43}$ Toluene was purchased from EMD Millipore; mixed xylenes were purchased from EM Science; and ethyl acetate and cyclohexane were purchased from Fisher. All solvents were used as received. Tables 4.1-4.4 list the relevant solvent, polymer, and solution properties for the materials used in this section.

### Table 4.1 Solvent Properties at 20 °C

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Density (g/mL)$^{44}$</th>
<th>Viscosity (cP)</th>
<th>Surface Tension (mN/m)$^{45}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>toluene</td>
<td>0.87</td>
<td>0.59$^{46}$</td>
<td>28.5</td>
</tr>
<tr>
<td>xylenes (mixed)</td>
<td>0.87</td>
<td>0.65</td>
<td>29.2</td>
</tr>
<tr>
<td>ethyl acetate</td>
<td>0.90</td>
<td>0.43</td>
<td>24.0</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>0.78</td>
<td>0.66</td>
<td>25.2</td>
</tr>
</tbody>
</table>
Tables 4.2, 4.3, and 4.4.
As indicated in Figure 4.1, the direction of motion is denoted as the x-direction, with the x-coordinate of the coating gap progressively increasing during coating due to the stage motion; the orthogonal direction in the plane of the substrate is denoted the y-direction, and the z-direction corresponds to the film thickness. A piece of silicon wafer (approximately 3.0 cm × 6.0 cm) was placed on the stage, beneath the fixed blade. The blade was changed between each coating run. Once positioned, a scratch was made on the substrate to indicate the exact location in x on the wafer where coating begins. The gap height and blade angle were then set to the desired values and the blade was made to be approximately level with the substrate in the y-direction. A fixed volume $V$ of polymer solution was loaded, via syringe, into the gap where it was held in place by capillary forces, thus creating the solution reservoir. The setup was examined to ensure that the reservoir’s contents were evenly distributed along the width of the blade (i.e., uniform distance between front and back menisci). An uneven distribution indicated a need to readjust the y-direction blade tilt. The thicknesses of all films produced for this study were measured along x at several locations in y to ensure uniformity in the y-direction (thickness variation in y < 3% of the average film thickness).

After loading the solution, the stage was made to travel the first 3 mm at a constant $U = 0.1$ mm/s, to remove any startup effects the flow may experience. In all figures in this chapter, x = 0 is taken as the position at the end of this 3 mm constant-velocity travel, regardless of the subsequent velocity profile. For typical runs, at x = 0 the stage was then programmed to either rapidly accelerate to a constant velocity, or to accelerate continuously (with a constant acceleration $A$) over the remaining length of the substrate (typically 40 − 50 mm), in both cases depositing a film over the entire substrate.
Once coating of the film began, often a moving evaporation front (typically 5-20 mm away from the blade for toluene solutions) could be observed. Subsequently, $t_{\text{dry}}$ was measured via ellipsometry at known positions along the substrate. For films prepared at nonconstant velocity, $U$ was determined from the position ($x$) along the film using basic equations of motion. Some representative film thickness profiles are shown in Figure 4.2.

The flowcoated films contained negligible quantities of trapped solvent. PS films were flowcoated from toluene at 100 and 200 nm thickness, with the initial thickness measured within an hour of flowcoating; these films were then annealed in air at 150 °C for 30 min, cooled to room temperature, and the thickness remeasured. The 100 nm film showed a thickness decrease of only 0.9%, while the 200 nm film showed a decrease of only 1.6%; analogous spin-coated PS films showed very similar thickness changes following annealing. While these thickness changes represent upper bounds on the minute amount of trapped solvent in the present films, the amount could potentially be larger for solvents of much lower volatility or much stronger affinity for the polymer.
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4.3 Capillary Number Dependence

Films were deposited from solution (112 kg/mol PS, 1 wt. % in toluene) by coating at constant acceleration rates of 0.05, 0.10, 0.50, 1.0, and 5.0 mm/s². In addition several films were made with uniform thickness, using a constant $U$ of 0.5, 1.0, 5.0, or 10.0 mm/s. All films were produced with $V = 50 \mu\text{L}$, $G = 200 \mu\text{m}$, and $\alpha_0 = 7^\circ$. Figure 4.3 shows the dry film thickness $t_{dry}$ plotted vs. instantaneous coating velocity $U$ on a log-log scale. A best-fit line to the data yields a slope, $m = 0.642 \pm 0.009$ (± indicates one
Figure 4.3 Dry film thickness, $t_{\text{dry}}$, vs. stage velocity, $U$, on a logarithmic scale for a solution of 1 wt. % of PS (112 kg/mol) in toluene. A best-fit line to the data produces a slope of $0.642 \pm 0.009$.

standard deviation), very close to the 2/3-power dependence predicted by Landau-Levich theory. The precise agreement between the flat ($A = 0$) and gradient ($A \neq 0$) films confirms that instantaneous stage velocity, not stage acceleration, is the relevant control parameter.

A wider array of tests was performed by changing the properties of the coating solution: polymer molecular weight and concentration, as well as polymer and solvent type (with $V$, $G_s$, and $\alpha_0$ all still fixed at the previous values). These results are shown in
Figure 4.4. To compare across solutions, the ordinate is plotted in terms of \( Ca \), while the abscissa displays the wet film thickness prior to evaporation, \( t_{\text{wet}} \), which was computed from \( t_{\text{dry}} \) via:

\[
\frac{t_{\text{dry}}}{t_{\text{wet}}} = \frac{\frac{w_{\text{polymer}}}{\rho_{\text{polymer}}}}{\frac{w_{\text{polymer}}}{\rho_{\text{polymer}}} + \frac{w_{\text{solvent}}}{\rho_{\text{solvent}}}}
\]

Equation 4.2

where \( w \) is the weight fraction of the component in solution and \( \rho \) is the density of the pure component. Note that volume additivity is assumed for the solutions, an approximation estimated to be accurate to within 0.1% for the relatively dilute solutions employed here.\(^{49-50}\) In computing \( Ca \), the viscosity determined by capillary viscometry was used; thus any shear thinning which may occur at the coating velocity is assumed to be negligible. It was also assumed that the solution surface tension is approximately equal to that of the pure solvent, which should hold as long as total loading of polymer in the solution is low and the polymers are not surface active, which should be the case for the systems studied here (small fractions of polymer dissolved in a good solvent of moderate surface tension).\(^{51}\)

The data generally appear quite linear on the log-log plots of Figure 4.4, except at low \( Ca \) where some upward curvature is observed. To capture the proper scaling exponent for this coating flow, only data in the linear region \((Ca > 10^{-4})\) were considered when generating best-fit lines; the cause of, and threshold for, the deviations observed at low \( Ca \) will be discussed below. The resulting slopes of the best-fit lines are displayed in the corresponding plots in Figure 4.4. All four panels show a dependence on \( Ca \) close to the predicted 2/3 power; moreover, all four panels are essentially identical, as shown by
Figure 4.4 Plots showing $t_{\text{wet}}$ vs. $Ca$, where the coating solutions were varied as follows: (a) PS molecular weight, (b) PS concentration, (c) solvent type, and (d) polymer type. Each plot shows the best-fit line (with slope $m$, and ± indicating one standard deviation) for $Ca > 10^{-4}$.

The “master” curve in Figure 4.5, with a best-fit slope of $0.662 \pm 0.006$. This provides compelling evidence that, in the range of $Ca$ considered ($10^{-4} < Ca < 10^{-2.58}$), the flowcoating process is indeed a Landau-Levich flow and robustly follows the predicted $2/3$ dependence.
Figure 4.5 “Master” plot combining all data from Figure 4.4. The best-fit line to all the data with $Ca > 10^{-4}$ yields a slope of $0.662 \pm 0.006$.

While velocity ($\sim 0.5 - 20$ mm/s) and viscosity ($\sim 0.5 - 5$ cP) were each varied over at least a decade in generating the data of Figure 4.5, one limitation in this work was the comparatively narrow range over which the solution surface tension could be varied (approximately 20%, by changing solvent). Performing experiments over a wide range of $\gamma$ is difficult, as most organic solvents have comparable surface tensions; in principle, aqueous solutions could also be employed, but considerable effort must be taken to eliminate even trace levels of surfactants, otherwise Marangoni effects may strongly affect the film thickness.$^{37,40}$
4.4 Characteristic Length Scale

In addition to the $2/3$-power dependence of film thickness on $Ca$, Landau-Levich theory predicts that there should exist a characteristic length scale, $L$, with which the film thickness should scale linearly; this characteristic length scale depends on the coating geometry.\textsuperscript{39} Perhaps surprisingly, both previous work\textsuperscript{12} and our own experiments show that the gap height, $G$, between the blade and the substrate is not a useful predictive length scale in this flow. Instead the length scale proposed by Le Berre\textsuperscript{37} and Lau\textsuperscript{40}, derived by calculating the curvature of the static meniscus and using this to obtain a complete solution to the Landau-Levich flow problem, will be used. Because the lateral pressure gradient in the solution reservoir is zero,\textsuperscript{37} the radius of curvature in the front and rear menisci can be equated. The rear meniscus height and wetting conditions are typically easier to measure than the curvature; thus the following expression for the rear meniscus curvature is chosen as the characteristic length scale, $L$:

$$L = \frac{H}{\cos \theta_1 + \cos \theta_2 - \frac{H^2}{2 l_{cap}^2}}$$

\textbf{Equation 4.3}

where $H$ is the height of the rear meniscus, $\theta_1$ and $\theta_2$ are the back meniscus wetting angles as shown in Figure 4.1, and $l_{cap}$ is the capillary length, equal to $(\gamma/\rho g)^{1/2}$, where $g$ is acceleration due to gravity. The rear meniscus height, $H$, is somewhat ill-defined and difficult to accurately measure in the experimental setup (with an approximate measurement uncertainty of $\sim 9\%$). We chose instead to indirectly determine $H$ by approximating the solution reservoir volume as a trapezoidal prism. One can then use simple geometry to compute $H$ from $a_0$, $G$, $V$, and the blade width, $B$ (here, simply the width of the glass slides used, $B = 25$ mm).
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Although held constant up to this point, $V$, $G$, and $\alpha_0$ may each be varied over some range. Therefore to test the length scale proposed by Equation 4.3, these parameters were adjusted ($20 \mu\text{L} < V < 200 \mu\text{L}$, $100 \mu\text{m} < G < 400 \mu\text{m}$, $5^\circ < \alpha_0 < 10^\circ$) and the calculated $H$ and $L$ were applied in the analysis of the measured film thicknesses according to Equation 4.1. For simplicity, these experiments were all done using one solution (1 wt. % of 112 kg/mol PS in toluene), so that $\theta_1$, $\theta_2$, and $l_{\text{cap}}$ were not varied. $\theta_1$ and $\theta_2$ were assumed to equal the static contact angles of pure toluene on silicon with native oxide, and on glass, respectively. For both substrates the contact angle was measured to be $\theta_1 = \theta_2 = 15 \pm 4^\circ$ and the contact angle hysteresis (difference between advancing and receding contact angles) was found to be less than the measured error. All flat films were produced using $U = 10 \text{ mm/s}$, hence $Ca$ was fixed. Figure 4.6 shows $t_{\text{wet}}/Ca^{2/3}$ vs. $L$ for films produced using a variety of $G$, $\alpha_0$, and $V$. If true Landau-Levich flow is observed, these data should describe a line through the origin with a slope equal to $c_1$, the numerical constant predicted to be 1.34. The data in Figure 4.6 do indeed conform well to a linear dependence, indicating that film thickness does scale linearly with $L$; a linear fit yields a slope of $1.58 \pm 0.02$. The difference between the experimentally determined $c_1$ and the predicted value ($\sim 18\%$) could reflect the method used to evaluate the rear meniscus height $H$, wherein the reservoir volume was approximated by a trapezoidal prism. This approach likely underpredicts the true $H$ leading to an apparent increase in the measured value of $c_1$. A further consideration is that $H$ has been assumed constant during coating; however, as coating progresses and solution is drawn out, the reservoir volume, and therefore the back meniscus height, gradually decreases. However, calculations suggest that this effect is small for the films of Figures
4.2-4.6 (< 2% expected change in film thickness); moreover, this effect would actually
decrease, not increase, the apparent value of \( c_1 \).

**Figure 4.6.** Plot showing \( t_{wef}/Ca^{2/3} \) vs. the characteristic length scale, \( L \), proposed by Equation 4.3. \( L \) was varied by changing the front gap height (\( \Delta G \)), the blade angle (\( \Delta \alpha_0 \)), and the solution reservoir volume (\( \Delta V \)). The slope of the best-fit line, which according to Equation 4.1 should correspond to \( c_1 \), equals 1.58 ± 0.02. All films produced using a single solution of 1 wt. % PS (112 kg/mol) in toluene.
4.5 Deviations From Landau-Levich Flow at Low $Ca$

In the preceding analysis, it was assumed that evaporation is negligible during the coating process but then occurs rapidly after coating. Should coating occur too rapidly relative to evaporation, as when using low-volatility solvents, the wet film can flow prior to solvent evaporation, smoothing out the thickness gradient. Conversely, should coating occur too slowly relative to evaporation, one can enter a different coating regime: one which is driven by evaporation rather than Landau-Levich flow. In the evaporation-dominated regime, film thickness actually decreases in proportion to the stage velocity; the hypothetical wet film thickness prior to drying can be determined simply by balancing the rate of evaporation and the rate of coating:

$$t_{\text{wet}} = \frac{Q_{\text{evap}}}{B \times U}$$

Equation 4.4

where $Q_{\text{evap}}$ is the volumetric flow rate (as liquid) of the evaporating solvent. In this study no deliberate attempt was made to systematically investigate the evaporation-dominated regime as the apparatus is not equipped to control evaporation rate. However, positive deviations from the scaling predicted by Equation 4.1 were observed at low $Ca (< 10^{-4})$ which likely indicates an approach to the crossover into the evaporation-driven coating regime. The velocity at which this crossover is expected to occur, $U^*$, can be predicted by setting Equations 4.1 and 4.4 for $t_{\text{wet}}$ equal, and solving for $U$:

$$U^* = 0.839 \left( \frac{\gamma}{\mu} \right)^{2/5} \left( \frac{Q_{\text{evap}}}{BL} \right)^{3/5}$$

Equation 4.5

$Q_{\text{evap}}$ was estimated as the product of the gap height $G$ and blade width $B$, multiplied by the evaporative flux of toluene $[\text{m}^3 \text{ liquid toluene/m}^2\text{s}]$ measured from a full Petri dish
placed next to the flowcoater over a fixed time, yielding $Q_{evap} \sim 10^{-12}$ m$^3$/s. For the toluene solutions used in this study, this yields a range of $U^* \sim 0.1 - 0.2$ mm/s and range of crossover capillary numbers, $Ca^*$, $\sim 6 \times 10^{-6} - 2 \times 10^{-5}$. While this estimate is only approximate, it suggests that the lowest end of the measured data ($Ca \sim 2 \times 10^{-5}$) may indeed be in the vicinity of the crossover to the evaporation-driven regime. Le Berre showed that for velocities within approximately a factor of five of the crossover, positive deviations from Landau-Levich scaling can be observed. Therefore a conservative lower bound above which the data can be expected to be well described by the Landau-Levich model should be $\sim 5 \times Ca^* = 10^{-4}$, providing the basis for the lower-$Ca$ limit used in the analysis of the data in Figures 4.4 and 4.5.

4.6 Designed Film Profiles

With the successful confirmation of the proposed $L$ and the robust adherence of the film thickness to a $Ca^{2/3}$ dependence, Equations 4.1 and 4.3 together constitute the necessary design rules for creating any desired film thickness profile. To test this idea, several complex velocity profiles were programmed and used to deposit films from a 2 wt. % solution of 112 kg/mol PS in toluene. The corresponding predicted dry film thickness profiles were then calculated, using the experimentally determined value of $c_1 = 1.58$. In addition, when calculating $L$ from Equation 4.3, a correction to the reservoir volume, $V$, was applied, decrementing $V$ at any point in the process by the volume of solution used to create the film up to that point. In most cases this correction produces a negligible difference in predicted thickness profile, as in the results of Figures 4.2-4.6;
however, for the thicker films, this correction was necessary to obtain a precise quantitative match between the model and experiments.

The measured and calculated film thicknesses are displayed in Figure 4.7. Case 1 depicts a profile which includes several near-step-change increases in stage velocity. Case 2 explores the simple scenario of a constant-acceleration ramp in stage velocity (data are the same as shown in Figure 4.2). As in case 1, differences between the predicted and measured profiles of no more than 1-2 nm were observed. In the film with $A = 0.1 \text{ mm/s}^2$, the initial part of the profile does appear flatter and the film thicker than expected; this can be attributed to the low velocity (and therefore low $Ca < 3 \times 10^{-5}$) at which these films were created, since at $Ca < 10^{-4}$ there are deviations from the predicted Landau-Levich flow due to an approach to the evaporation-driven coating regime. In case 3 an effort was made to produce a roughly linear thickness gradient, by connecting several program segments of varying acceleration (constant $A$ within each segment). Finally, case 4 shows a film with a trapezoidal thickness profile, thus demonstrating the device’s ability to controllably produce both positive and negative thickness gradients on a single sample. In total these four cases illustrate both the precise degree of control attainable using the design rules embodied in Equations 4.1 and 4.3, and the broad range of thickness profiles which may be created.
Case 1 (top left) shows rapid increases in velocity from $U = 1 \text{ mm/s}$ to $U = 5 \text{ mm/s}$ (at $A = 10 \text{ mm/s}^2$) to $U = 10 \text{ mm/s}$ (at $A = 20 \text{ mm/s}^2$). Case 2 (top right) contains profiles generated with constant accelerations of $A = 0.1$, $0.5$, $1.0$, $2.5$, and $5.0 \text{ mm/s}^2$. Case 3 (bottom left) shows an approximately linear profile with a positive slope, created using numerous step increases in acceleration. Case 4 (bottom right) displays a single profile containing sections with positive, zero, and negative thickness gradients. All films were deposited from a solution of $2 \text{ wt. % PS (112 kg/mol)}$ in toluene.
4.7 Conclusions

The flowcoater design by Stafford et al. produces polymer thin films whose thickness is governed by Landau-Levich flow: the film thickness scales with $Ca^{2/3}$, and is proportional to a characteristic length scale $L$ which is dictated by the height of the rear meniscus (through the solution reservoir volume, blade tilt angle, and gap height) and the contact angles of the solution on the blade and substrate. Numerous coating solutions prepared from different polymers and organic solvents all yielded film thicknesses in excellent quantitative accord with the model, thus displaying the versatility of the method. Additionally, the scaling holds true over a wide range of $Ca$ and $t_{dry}$ (over an order of magnitude in both cases), though deviations from the model are observed for $Ca < 10^{-4}$ as the evaporation-driven coating regime is approached. Most importantly, this rigorously-tested model can now be used as a design equation, enabling the user to create polymer films with tailored thickness gradients. These results should allow for more convenient and widespread use of this device for a variety of polymer thin film experiments, especially studies which can benefit from the high-throughput potential offered by thickness-gradient films.
Chapter 4: Creating Controlled Thickness Gradients in Polymer Thin Films via Flowcoating

4.8 References

Chapter 4: Creating Controlled Thickness
Gradients in Polymer Thin Films via Flowcoating


Cylinder Orientation and Shear-Alignment in Thin Films of PS-PHMA Diblock Copolymers

5.1 Introduction

Currently there is enormous interest in the use of block copolymer thin films as patterning templates for production of materials with nanoscale features; polystyrene-poly(n-hexyl methacrylate) block copolymers (PS-PHMA) forming PS cylinders are of particular interest for nanolithography. When aligned via shear, thin films of PS-PHMA have been used to create nanowire polarizing grids for deep ultraviolet light. A primary advantage of PS-PHMA for this application is that the two blocks etch at sufficiently different rates to permit an all-dry etching process during pattern transfer; this etch contrast can be further enhanced through heavy metal staining. A major challenge, however, has been the relatively poor quality of alignment achieved in PS-PHMA thin films compared with other cylinder-forming polymers. This is in part because the thin film morphology of PS-PHMA, both before and after shear, often consists of mixed patterns of in-plane cylinders and hexagonally-packed dots, which reflect either cylinders
which have transformed into discrete spherical microdomains\textsuperscript{14} or cylinders which have reoriented out-of-plane with the substrate.\textsuperscript{15} Due to PHMA’s\textsuperscript{16} low surface energy (as compared to PS\textsuperscript{17}) and the generally attractive interactions between poly(alkyl methacrylates) and silica,\textsuperscript{18} when cast as a thin film onto a substrate with a silica surface, the PHMA matrix is expected to wet both interfaces, thus prompting in-plane cylinder formation at film thicknesses which correspond to approximately integer multiples of the bulk interplanar spacing. When at an incommensurate thickness, however, the cylinders would need to be strained from their equilibrium dimensions to maintain a parallel orientation in a film of uniform thickness; the polymer could avoid this energetically unfavorable strain by reorienting the cylinders to be perpendicular to the substrate, or by terracing into islands and holes such that the entire film is composed of discrete regions of the next-highest and next-lowest integer-layer film thickness.\textsuperscript{19-20} However, previous work using PS-PHMA diblocks shows that they do not terrace under the annealing conditions employed, and instead produce the mixed morphologies described above.\textsuperscript{13} Some previous studies have observed similar switching between, and coexisting mixtures of, parallel and perpendicular cylinders as a function of film thickness; however, these have either been along terrace edges, where the thickness gradient is steep,\textsuperscript{21-22} or in cases where the film contains large amounts of residual solvent.\textsuperscript{23} An important implication of PS-PHMA’s tendency not to terrace is that it makes it difficult to identify the precise film thickness at which a monolayer of cylinders will form; however, identifying this thickness is critical to achieving successful alignment. Previous work on a cylinder-forming PS-poly(ethylene-\textit{alt}-propylene) diblock copolymer (PS-PEP) showed that the quality of shear-induced alignment suffered dramatically if the film thickness deviated by

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more than 2 nm from the monolayer thickness. It is thus likely that film thickness may strongly influence alignment quality in PS-PHMA films as well.

This work aims to investigate the thin-film structure as a function of film thickness for various cylinder-forming PS-PHMA diblocks in both the non-sheared (but thermally annealed) and shear-aligned states. Furthermore, we investigate the effect of block copolymer composition and molecular weight on this behavior; if the PHMA matrix wets both the air and substrate interfaces, perpendicular PS cylinders must be “capped off” at both ends with hemispheres or similar structures of high curvature, so we expect that moving the polymer more firmly into the cylinder-forming region of the phase diagram might dampen the orientational switching because of the increased energetic cost for this necessary surface reconstruction. To rapidly probe the influence of film thickness, we employ flowcoating to create films which possess thickness gradients that are negligibly shallow on the scale of the microdomain period, yet produce a wide range of thicknesses across the macroscopic film. Atomic force microscopy is then used to characterize the thin-film morphology, both before and after shear alignment.
5.2 Synthesis and Bulk Characterization of PS-PHMA Diblocks

This study required two complementary sets of PS-PHMA diblocks: one which varies in composition across the entire cylinder-forming region of the phase diagram (i.e., variable PS content, but fixed molecular weight), and another with fixed composition, but systematically varying in overall molecular weight. Polymers which form the latter series have previously been synthesized by Brian T. Michal (B.S.E. 2010) as part of his senior thesis project.\textsuperscript{24} To obtain the complementary set of polymers, we performed sequential living anionic polymerization of styrene (S) and \textit{n}-hexyl methacrylate (HMA) in a manner similar to Michal; PS-PHMA diblocks were synthesized using the same chemistry, but in different apparatus as described below. Tetrahydrofuran (THF) and methanol were purchased from Fisher Scientific. Both were degassed and the THF was dried over the purple sodium-benzophenone complex for several days prior to use. S, HMA, and diphenylethylene (DPE) were purchased from Sigma-Aldrich. S and DPE were vacuum transferred from dibutyl magnesium after several freeze-pump-thaw cycles, while HMA was titrated with trioctyl aluminum, turning the monomer a green-yellow color,\textsuperscript{25} prior to vacuum transfer. Trialkylaluminums are known to initiate free-radical polymerization of alkyl methacrylates in the presence of oxygen, so the HMA was degassed via freeze-pump-thaw cycles prior to titration.\textsuperscript{26} These three reagents were all distilled into evacuated flasks and either used immediately for polymerization or stored in a glove box freezer at -20 °C. Sec-butyllithium and anhydrous LiCl were purchased from Sigma-Aldrich and used as received.

The reactions were performed at \textasciitilde10 wt. % solids inside the cold well of an MBraun UNILab glovebox with N\textsubscript{2} atmosphere (O\textsubscript{2} and H\textsubscript{2}O concentrations \textless0.1 ppm).
THF was used as the reaction solvent and was cooled to -78 °C (using a dry ice–isopropanol bath) prior to any monomer addition to prevent side reactions between the living anion and the HMA carbonyl group. To further prevent these side reactions, LiCl was added at 10 eq relative to initiator prior to the start of the reaction. Throughout the polymerization, the reactor was vigorously mixed via magnetic stirring. A small amount of S (~40 μL) was added to the reactor, which was then titrated with sec-butyllithium until a persistent yellow-orange color appeared, indicating that all reactive impurities had been removed. The calculated charge of initiator was then immediately added. The remaining charge of S was then added to the reactor dropwise, turning the reaction a bright orange color. The S block was allowed to react for 15 minutes, after which 2-3 eq of DPE were added (turning the reaction mixture red) to further reduce the nucleophilicity of the active site, and allowed to react for 5 minutes. A small reactor aliquot was taken for first block characterization. HMA was then added to the reactor at a rate of ~2 mL/min and allowed to react for 30 minutes. Finally, the reaction was terminated with methanol. Most reactions contained a minor quantity of terminated PS block (<5% of PS chains), which was removed via liquid-liquid fractionation using toluene (solvent) and acetonitrile (non-solvent); the homopolymer content in the fractionated diblocks was below the detectability limit by size-exclusion chromatography (SEC, see Figure 5.1). All of fractionated polymers were analyzed via SEC for molecular weight and dispersity determination and 1H-NMR (see Figure 5.2 for a representative spectrum) to measure the weight fraction of PS, $w_{PS}$, by comparing the peak areas of the PS aromatic protons (6.3-7.2 ppm) and the PHMA methylene protons (3.7-4.2 ppm).
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Figure 5.1 Representative SEC chromatographs showing normalized differential refractive index (DRI) signal vs. PS-equivalent molecular weight for PS-PHMA 34-77: (solid black line) PS aliquot taken during the reaction, (dash-dot red line) unfractionated diblock from an aliquot taken immediately after reaction completion, (blue dotted line) PS-rich “light” (dilute) fraction, and (green dashed line) block copolymer-rich “heavy” (concentrated) fraction.
Figure 5.2 Representative $^1$H-NMR spectrum of PS-PHMA. The peak area corresponding to the aromatic protons (6.3-7.2 ppm), labeled A, is compared to the peak area corresponding to methylene protons (3.7-4.2 ppm), labeled B, to compute $w_{PS}$. 
Chapter 5: Cylinder Orientation and Shear-Alignment in Thin Films of PS-PHMA Diblock Copolymers

The absolute weight-average molecular weight ($M_w$) of each diblock was then determined by four methods: 1) from the $M_w$ of the PS block using the SEC differential refractometry (DRI) data (elution times calibrated with PS standards), combined with the diblock $w_{PS}$; 2) from the $M_w$ of the PS block using the SEC light scattering (LS) data (the refractive index increment, $dn/dc$, for PS was measured to be 0.1834 mL/g), combined with the diblock $w_{PS}$; 3) from the SEC LS data on the fractionated diblock, using a weight-fraction-weight $dn/dc^{29}$ (the $dn/dc$ of PHMA was measured to be 0.0753 mL/g), and 4) from the SEC DRI data on the fractionated diblock using a weighted R-factor, determined using the Chang combining rule$^{30}$ (measured $R_{PHMA} = 0.809$). The results from the 4 methods are shown in Table 5.1. Note that for the polymers synthesized by Michal$^{24}$, the requisite light scattering data for the PS block aliquot were unavailable and thus calculation of $M_w$ via Method 2 was not possible. For all of the methods, we chose to use the dispersity, $D$, measured from the DRI data to compute $M_n$ from $M_w$ (the DRI data likely yields an upper bound on the true $D$, while the LS analysis software provides a lower bound on $D$). The four methods show reasonable agreement with each other; the modest differences between Methods 1 and 2 with 3 and 4 may reflect the effects of fractionation to remove the minor quantity of terminated PS first block, suggesting that the results from Methods 3 and 4 be considered more reliable.

The bulk morphologies were determined using one-dimensional small-angle X-ray scattering (SAXS). All but two of the polymers listed in Table 5.1 were bulk cylinder-formers. These will be the primary focus of study for the remainder of the chapter, although the thin film morphologies of PS-PHMA 17-96 (sphere-former) and 50-74 are briefly discussed (see Chapter 5.6). The primary utility of these two polymers is
Table 5.1 Summary of PS-PHMAs

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<tr>
<th>PS-PHMA</th>
<th>PS $M_w$ [kg/mol]</th>
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<th>PS-PHMA $D$</th>
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<th>Weighted $R$ Factor</th>
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<td>-</td>
<td>382</td>
<td>429</td>
</tr>
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*LS data for PS aliquots for PS-PHMAs synthesized previously (21-77, 31-108, 60-191, 87-256) were unavailable.
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that they demonstrate that the cylinder-forming region of the phase diagram is effectively bracketed between $0.15 < w_{PS} < 0.40$. The bulk interlayer spacings between microdomains ($d_{bulk}$) were measured at 150 °C via $d_{bulk} = 2\pi/q^*$, where $q^*$ is the primary peak position in the SAXS pattern. Figure 5.3a shows a plot of $\log_{10}(d_{bulk})$ vs. $\log_{10}(M_n)$ for the series of PS-PHMA with fixed $w_{PS}$, but which vary in $M_n$, using the different molecular weight determination methods. All of the methods show a comparable, monotonic increase in interlayer spacing with molecular weight, with a power law exponent of $\sim 3/4$. This is a bit larger than the expected 2/3 scaling; this discrepancy is likely a result of the unintended, positive correlation between $M_n$ and $w_{PS}$ in this polymer series (i.e., the polymers with larger $M_n$ also have higher $w_{PS}$ which can increase $d_{bulk}$). Figure 5.3b quantifies the size of this effect by plotting the domain spacing normalized by the predicted molecular weight scaling ($M_n^{2/3}$) vs. $w_{PS}$ for the series of PS-PHMA which vary in composition. Excluding the non-cylinder-forming polymers (the points at $w_{PS} = 0.15$ and 0.40), the data shows that Methods 1 and 2 yield very strong dependencies of $d_{bulk}$ on composition; this seems unphysical. Based on this observation, and the inability of these methods to capture the effects of fractionation (as discussed above), we conclude that Methods 1 and 2 likely do not properly reflect the true molecular weights of these materials. Though Methods 3 and 4 both produce reasonable scaling trends, we selected Method 3 as our best estimate of molecular weight as this approach relies on fewer assumptions and utilizes the LS data, which is an absolute (calibration-independent) technique. Henceforth, all of the PS-PHMA are referred to as PS-PHMA A-B, where A and B denote the PS and PHMA block $M_n$ values, respectively, as determined by Method 3.
Figure 5.3 Plots of (a) log$_{10}(d_{\text{bulk}})$ vs. log$_{10}(M_n)$ for the fixed- $w_{ps}$ series and (b) $d_{\text{bulk}}/M_n^{2/3}$ vs. $w_{ps}$ for the fixed-$M_n$ series of PS-PHMA diblocks using the four different methods of molecular weight determination: Method 1 (black squares), Method 2 (red circles), Method 3 (green triangles), and Method 4 (blue downward-triangles).
5.3 Pre-Shear Morphology

Supported thickness-gradient films were prepared by dissolving PS-PHMA in toluene (1-5 wt% polymer) and flowcoating\textsuperscript{32} at a constant acceleration onto silicon wafers (with native oxide); film thicknesses were measured via ellipsometry. Typical film thickness profiles ranged from ~20 to ~100 - 200 nm along a 45 mm length of substrate. After deposition, the films were thermally annealed under vacuum at 150 °C (well above the glass transition temperature for both blocks) for 2 hours. Preliminary experiments via atomic force microscopy (AFM) showed that after annealing for 2 hours no significant changes in surface morphology were observed on a practical time scale (up to 24 hours). In addition, to ensure that residual solvent was not influencing the surface morphology,\textsuperscript{23} the thickness gradient films were compared with several spin-coated films of representative thicknesses annealed under the same conditions. The same morphologies were observed in both sets of films, \textit{i.e.} at a given thickness, the same structures (all lines, all dots, mixtures of lines and dots) were observed in both the spin-coated and flowcoated films.

The thermally annealed (non-sheared) PS-PHMA thin films displayed an interesting morphological dependence on film thickness, composition, and molecular weight; PS-PHMA 21-77, with the lowest PS content and molecular weight of all the cylinder-forming polymers studied, showed the strongest thickness dependence. Figure 5.4 shows some representative micrographs illustrating the dramatic orientational switching that occurs as a function of PS-PHMA 21-77 film thickness, with patterns ranging between complete coverage by hexagonally-packed dots to complete coverage by fingerprint-like lines. As previously mentioned, we employ the terms “dot” and “line”
Figure 5.4 AFM phase images of PS-PHMA 21-77 at thicknesses of (a) 20 nm, (b) 30 nm, (c) 40 nm, (d) 60 nm, (e) 75 nm, and (f) 130 nm. Line patterns are cylinders oriented parallel to the substrate while dot patterns are inferred to reflect cylinders oriented perpendicular to the substrate. Panel (g) displays a line trace along the diagonal dashed line in image (e), demonstrating the “pseudo-terracing” observed at thicknesses containing mixtures of dots and lines. Scale bar = 500 nm.
Chapter 5: Cylinder Orientation and Shear-Alignment in Thin Films of PS-PHMA Diblock Copolymers

when describing the observed morphology in recognition that AFM, a surface characterization technique, provides no direct information on the through-film structure. Because these PS-PHMA diblocks form cylinders in bulk, and because PHMA is expected to wet both the substrate and free surface, the line patterns should reflect PS cylinders which are parallel to the substrate. The dot patterns, however, are more ambiguous. They could be cylinders which have reoriented themselves to be perpendicular to the substrate; however, due to differences in the PS and PHMA surface energies, a “capping layer” of PHMA would be expected to cover the tops of the cylinders, thus allowing for accommodation of the strain introduced by incommensurability between the film thickness and the cylinder layer spacing, without exposing the higher-energy PS to the surface. An alternative interpretation of the AFM images is that under confinement, the cylinders rearrange into hexagonally-packed-spheres; this particular polymer is close to the bulk sphere-forming boundary (the sphere-to-cylinder transition occurs at $0.15 < w_{PS} < 0.21$) so a sphere-like thin film morphology is conceivable. For films of approximately a monolayer thickness, there is no distinction between PS spheres and perpendicular PS cylinders, given the expected presence of PHMA at both the substrate and air interfaces. For films of multilayer thicknesses, where such a distinction is meaningful, simulations of this system by Nikoubashman et al. indicate that the dot-like surface patterns reflect perpendicular cylinders and persist through the thickness of the film, between PHMA layers which cover both interfaces.

To confirm this prediction, two complementary tests were performed. In both cases a ~75 nm film of PS-PHMA 21-77 was spin-cast onto a salt crystal and thermally annealed, revealing the expected coexistence of dots and lines (see Figure 5.5a). The film
Figure 5.5 Micrographs showing a 75 nm film of PS-PHMA 21-77. AFM phase images of (a) top and (b) bottom sides of the film. (c) TEM micrograph of an identically prepared film. Scale bar indicates 500 nm.

was then floated onto water by dissolving the substrate. For the first experiment, the film was picked up by lowering the smooth side of a Si wafer onto the top side of the floating film. The film stuck to the wafer and was then removed from the water, yielding an inverted (flipped upside down) film, such that the surface which had previously been in contact with the substrate was now in air, and vice versa. This enabled AFM imaging of the underside of the film (see Figure 5.5b) which showed a similar morphology as the top side (mixed dot and line patterns). In the second experiment, the floating film was picked up using a transmission electron microscope (TEM) grid and was subsequently imaged by TEM (see Figure 5.5c). TEM allows for imaging of the through-film structure, which also displayed the mixed dot and line morphology. The source of contrast in the TEM images is uncertain as no heavy-metal staining was performed. One possibility is electron beam damage; if one block is selectively depolymerized (likely PHMA, similar to what occurs during pattern transfer via dry etching processes) the mass differential could produce sufficient contrast for imaging (with the more strongly depolymerized PHMA
domains allowing more electrons through, thereby appearing brighter, compared to PS). While neither of these methods unambiguously confirmed the through-film structure (this may be possible using grazing incidence SAXS, however we did not attempt these experiments), they both are consistent with Nikoubashman’s interpretation. We therefore conclude that the dots observed in the experiments reflect out-of-plane cylinders.

At thicknesses which exhibited coexisting dots and lines (typically around 1.5 and 2.5 cylinder layer spacings), film thickness variations were also observed; the height trace displayed in Figure 5.4g shows an example. Note that the height gradient created in these films by flowcoating (maximum gradient of $3 \times 10^{-6}$ m thickness change/m lateral change) is several orders of magnitude smaller than the slopes evident in Figure 5.4g (approximately $2 \times 10^{-2}$). Consistently, the height changes observed in the AFM images are gradual and correspond to approximately half the thickness of a layer of in-plane cylinders. This is in contrast to typical terracing of block copolymer thin films, in which changes of a full integer layer thickness are observed and there is little thickness variation except at the boundaries between terrace heights. Further complicating this behavior, while all of the dots are found in the thinner regions of the film, both dots and lines are observed at these thicknesses. This height variation, which we term “pseudo-terracing”, is present in these films whenever significant fractions of dots and lines coexist, yielding a typical root-mean-square (RMS) height variation of ~6 nm over the 2 $\mu$m $\times$ 2 $\mu$m AFM image. By contrast, films presenting all-line patterns were quite flat (RMS height variation <0.5 nm), while films presenting all-dot patterns showed a greater height variation (though still <3 nm RMS), consistent with the reduced energetic penalty for height variations in a film presenting perpendicular cylinders, as height variations do not
distort the cylinder cross-section or spacing for perpendicular cylinders (leaving the additional surface area created by these height variations as the only energetic penalty).

To quantitatively understand the influence of film thickness on morphology, the fractional coverage of lines, \( F \), was computed via ImageJ\textsuperscript{35} for each image and plotted vs. a normalized film thickness \( t/d \), where \( t \) is the absolute film thickness as measured by ellipsometry, and \( d \) is the interplanar spacing between layers of parallel cylinders, which is also the thickness corresponding to a monolayer of in-plane cylinders. \( d \) was measured in two ways: on the bulk polymer by SAXS at 150 °C (\( d_{\text{bulk}} \) listed in Table 5.1) or by imaging relatively thick films (~ 200 nm) by AFM at room temperature, and then using the Fourier transform of the image to compute an average cylinder periodicity, \( p \), and then assuming hexagonally-packed cylinders:

\[
d_{\text{AFM}} = \frac{\sqrt{3}}{2} p_{\text{AFM}}
\]  

\textbf{Equation 5.2}

The two approaches yield similar values of \( d \) (PS-PHMA 21-77: \( d_{\text{AFM}} = 31.0 \pm 0.4 \) nm; PS-PHMA 30-86: 38.9 ± 0.7 nm; PS-PHMA 34-77: 39.0 ± 0.4 nm; PS-PHMA 48-88: 47.2 ± 0.8 nm, averages and ± 1 standard deviation from 10 images); \( d_{\text{AFM}} \) was used to normalize film thickness. Figure 5.6 displays \( F \) vs. \( t/d \) for PS-PHMA 21-77, clearly showing the oscillatory nature of the switching between dot and line patterns. At low \( t/d \), nearly complete switching between all-dot and all-line patterns is observed; as the film thickness increases, the depth of the valleys decreases, and for \( t/d > 3 \), \( F \) plateaus to ~1, indicating that above a certain film thickness the orientation is no longer dependent on film thickness. For \( t/d < 3 \), the maximum \( F \) values occur at thicknesses corresponding approximately to integer numbers of layers of in-plane cylinders, while the local minima
Figure 5.6 Plot of $F$, fractional coverage of in-plane cylinders, vs. $t/d$, film thickness normalized by thin film interlayer spacing, for PS-PHMA 21-77. Error bars represent ±1 standard deviation of $F$ from multiple images (3 or more) taken at the same film thickness.

In $F$ occur between 0.2 and 0.5 layers above the previous integer thickness. A practical consequence of these results is that if one desires a monolayer of in-plane cylinders, as is typically employed for nanopatterning applications, this polymer offers only a very narrow range of suitable film thicknesses (<3 nm).
The same analysis was performed on thickness-gradient films of the three other
PS-PHMA diblock copolymers in the composition series, as shown in Figure 5.7, revealing the influence of
polymer composition on in- vs. out-of-plane orientation. With increased PS fraction, the
peak centered around \( t/d \sim 1 \) begins to broaden while simultaneously the valley at \( t/d \sim 1.25 \) starts to vanish. Furthermore, only the diblock with the lowest \( w_{PS} \) possesses a local
valley between \( 2 < t/d < 3 \). For \( w_{PS} = 0.30 \) and above, the switching has completely
vanished, yielding films whose orientation is nearly independent of film thickness for \( t/d \gtrsim 1 \). This result indicates that as the polymer’s composition is shifted more firmly into
the cylinder-forming regions of the phase diagram, it becomes more energetically
unfavorable for the cylindrical microdomains to reorient out-of-plane; this is likely due to
the increased energy required to form the high-microdomain-curvature “capping layers”
required in the out-of-plane orientation to prevent the PS cylinders from contacting the
free and substrate surfaces. Pseudo-terracing is observed for PS-PHMA 30-86 at \( t/d \)
between \( \sim 1.1 \) and 1.5, but neither terracing nor pseudo-terracing is observed for PS-
PHMA 34-77 or 48-88. The Nikoubashman simulations show that at incommensurate
thicknesses, the in-plane cylinder cross-section can stretch into an ellipsoidal shape,
elongated in the thickness direction. Those simulations also demonstrate excellent
quantitative agreement with our experimental \( F \) vs. \( t/d \) data for PS-PHMA 21-77 and 30-
86. Collectively, these results show that when exclusively in-plane cylinders are desired,
one way to dramatically expand the window of suitable film thicknesses is to increase the
minority block content to values \( >0.30 \).

The same analysis outlined for the above composition series was used on PS-
PHMA 31-108 (\( d = 39.6 \) nm), 60-191 (\( d = 57.2 \) nm), and 87-256 (\( d = 85.4 \) nm). These
Figure 5.7 Plot of $F$, fractional coverage of in-plane cylinders, vs. $t/d$, film thickness normalized by thin film interlayer spacing, for the composition series of PS-PHMA. All films with $t/d > 3$ showed $F > 0.99$. Error bars represent ±1 standard deviation of $F$ from three or more images taken at the same film thickness.

Results, along with those for PS-PHMA 21-77 (thus comprising the molecular weight series) are displayed in Figure 5.8. Over the range of film thicknesses studied, none of the higher-$M_n$ polymers possessed a thickness at which $F \sim 1$; the tendency for dot patterns to persist even in the vicinity of a monolayer appears to increase with increasing molecular weight. Furthermore, neither PS-PHMA 60-191 nor 87-256 showed a clear monolayer
Figure 5.8 Plot of $F$, fractional coverage of in-plane cylinders, vs. $t/d$, film thickness normalized by thin film interlayer spacing, for the molecular weight series of PS-PHMA.

thickness, $t_{mono}$ (as indicated by a local maximum in $F$), thus for subsequent studies which required casting a monolayer film (Chapter 6) we employed films with $t = d$.

5.4 Sheared Morphology

To examine whether film thickness influences the quality of in-plane cylinder alignment after shear, the same gradient films used to investigate the nonaligned thin film morphology were shear-aligned orthogonal to the direction of the thickness gradient at an
applied shear stress of ~10 kPa at 150 °C. The shear was applied for 30 minutes, after which the system was cooled back to room temperature with the applied stress still in place, thus fixing the post-shear morphology. Preliminary experiments, in which uniform-thickness, monolayer films of PS-PHMA were shear-aligned, showed that these conditions were sufficient to produce the maximum alignment quality, *i.e.* no significant improvement was achieved with further increases in stress or time, across the entire sheared area (see Figure 5.9a). At low stresses, alignment was still observed; however, the cylinders were not aligned in a uniform direction, but instead oriented radially outward from the center of the sheared area (see Figure 5.9b). This alignment was not induced by the externally applied shear, but by thermal expansion of the poly(dimethylsiloxane) (PDMS) pad similar to that observed in previous “soft shear” studies. Therefore, to “override” any pre-alignment caused by this effect, a sufficiently large stress must be applied.

Figure 5.10 shows the results for PS-PHMA 21-77. At some thicknesses, coexisting dots and lines remain even after shear. As a result, the quantification of alignment quality for these images must be done using the orientational order parameter $\psi_6$, rather than $\psi_2$, to correctly account for patterns with sixfold symmetry. Due to differences in their definitions, the deviation from unity for well-aligned films differs by a factor of 9 between $\psi_2$ and $\psi_6$, *i.e.* $(1- \psi_6) = 9(1- \psi_2)$ in the limit $\psi \rightarrow 1$. Therefore, to keep all comparisons consistent, we chose to exclusively employ $\psi_6$ for this portion of the study, even for films which showed all-line (twofold symmetry) patterns. In general it is observed that the higher the fractional coverage of in-plane cylinders pre-shear ($F$), the greater the quality of in-plane alignment post-shear ($\psi_6$). This is reflected in the
Figure 5.9 AFM micrographs of different positions on a monolayer film of PS-PHMA 34-77 which have been in contact with a PDMS pad. (a) Films sheared with a stress of 10 kPa show alignment in the direction of shear across the whole area of contact with the pad, while (b) films which were not actively sheared, displayed alignment induced by thermal expansion of the PDMS pad. The scale bar indicates 500 nm.
Figure 5.10 AFM phase images of shear-aligned PS-PHMA 21-77 at thicknesses of a) 20 nm, b) 30 nm, c) 44 nm, and d) 120 nm. Arrows indicate shear direction in each panel. Scale bar = 500 nm. (e) Plot of orientational order parameter, $\psi_6$, as a function of normalized film thickness, $t/d$, for PS-PHMA 21-77 (red squares connected by red lines to guide the eye). Error bars represent ±1 standard deviation from three or more images taken at the same film thickness. For comparison, the $F$ vs. $t/d$ data (black line) for this polymer (from Figure 5.6) are also shown.
remarkably similar trajectories of $F$ vs. $t/d$ and $\psi_6$ vs. $t/d$ shown in Figure 5.10. For all images with $\psi_6 > 0.8$, only well-aligned line patterns are observed. In these cases the alignment quality is primarily limited by a combination of isolated dislocations and undulations in the cylinders’ trajectories; this will be discussed at greater length below.

At the lowest thicknesses ($t/d < 0.8$), for which all-dot patterns were present in the absence of shear, once sheared there is a partial dot-to-line transition (see Figure 5.10a) in which it appears that the dots are aligning in the direction of applied shear and in some cases elongating and connecting to form continuous cylindrical microdomains. This behavior is consistent with previous experimental\textsuperscript{38} and simulation\textsuperscript{39} results for similar block copolymer thin film systems. For $1 < t/d < 3$, the local maxima in $\psi_6$ correspond to well-aligned films containing integer numbers of layers of cylinders. In this thickness range, films of non-integer thicknesses show either a large number of dots or a very high defect density in all-line patterns. At $t/d > 3$ all images show well-aligned in-plane cylinders whose alignment quality is approximately independent of film thickness.

A moderate annealing treatment was performed in an attempt to reduce the cylinder undulations present in the sheared films. A monolayer of PS-PHMA 21-77 ($t = 28$ nm) was shear-aligned and placed in a hot stage mounted in the AFM, to allow imaging of closely similar regions of the film following different annealing durations. After annealing at 150 °C for 10 minutes, the film was cooled to room temperature and imaged by AFM; the film was then reheated to 150 °C for 10 more minutes, cooled to room temperature, and imaged again. Figure 5.11 displays the micrographs; both unfiltered images (top row) and images filtered with the two-Fourier-spot mask appropriate for highly aligned line patterns (bottom row) are shown. Compared to the as-
Figure 5.11 AFM phase images showing a monolayer ($t = 28$ nm) of PS-PHMA 21-77 after shear alignment and subsequent annealing: (a) unfiltered and (d) filtered images of the as-sheared film, (b) unfiltered and (e) filtered images after 10 minutes of annealing at 150 °C, and (c) unfiltered and (f) filtered images after 20 minutes of annealing at 150 °C. The filtering was performed using two circular masks centered around the first-order peaks; note that this filtering, which is appropriate only for highly-aligned line patterns, distorts the small patches of dots present in panel (c) into clusters of dislocations. Scale bar = 500 nm.
sheared film, the 10 minute anneal produced no noticeable change in the cylinder undulations, while further increasing the annealing time to 20 minutes generated additional defects in the lattice, notably small patches of dots, without reducing the undulations. The fact that small patches of dots are formed after 20 minutes indicates that the polymer chains do have substantial mobility under these conditions, yet the undulations persist.

Analogous studies were performed on the other cylinder-forming PS-PHMA diblocks in the composition series (see Figure 5.12). PS-PHMA 30-86 displayed a qualitatively different relationship between $\psi_6$ and $t/d$; unlike PS-PHMA 21-77, which possessed a strong oscillation in both $F$ and $\psi_6$, PS-PHMA 30-86 showed almost no dependence of $\psi_6$ on $t/d > 1$. All thicknesses which showed a significant fraction of dots pre-shear, show no dots post-shear. This is again consistent with the notion that as $w_{PS}$ is increased, away from the sphere-cylinder phase boundary, then out-of-plane orientation (with its associated capping layers) becomes correspondingly less stable, and the cylinders more readily lie in-plane. The two highest-$w_{PS}$ polymers, PS-PHMA 34-77 and 48-88, show almost no dependence of $\psi_6$ on thickness above $t/d \sim 0.8$. This is perhaps unsurprising given that these polymers possessed nearly complete coverage of in-plane cylinders ($F \sim 1$) pre-shear. To further compare the alignment behavior of the four polymers, Figure 5.13a shows alignment quality as a function of composition for both monolayer and four-layer films. For monolayer films, there is a monotonic increase in $\psi_6$ with increased $w_{PS}$; however, for the thicker films, there is no obvious trend with composition. This suggests that the compositional effects on alignment quality are magnified in the monolayer films desired for nanopatterning.
Figure 5.12 Plots of orientational order parameter, $\psi_6$, and fractional coverage of lines, $F$, as a function of normalized film thickness, $t/d$, for PS-PHMA (a) 30-86, (b) 34-77, and (c) 48-88. Error bars represent ±1 standard deviation from three or more images taken at the same film thickness. Representative images for non-sheared and sheared films at $t/d \sim 1$: (d) non-sheared and (e) sheared PS-PHMA 30-86, (f) non-sheared and (g) sheared PS-PHMA 34-77, (h) non-sheared and (i) sheared PS-PHMA 48-88. Scale bar = 500 nm; arrows indicate direction of applied shear in each panel.
Figure 5.13 Alignment quality vs. (a) $w_{PS}$ for films with $t/d = 1$ (red squares) and $t/d = 4$ (blue diamonds) and vs. (b) $M_n$ for $t/d = 1$. Each point represents the average value from 10 AFM micrographs; error bars represent ±1 standard deviation.
The complementary experiments on the molecular weight series of PS-PHMA were conducted (see Figure 5.14); gradient thickness films were sheared using 10 kPa of stress at $T = 150 \, ^\circ C$ for 30 minutes. As $M_n$ increases, the sensitivity to film thickness diminishes (the films are well-aligned over a wider range of $t$), despite these films displaying predominantly out-of-plane cylinders pre-shear. This behavior contrasts with that in the composition series, where the greater the degree of in-plane alignment pre-
shear, the better the alignment quality post-shear. In addition, the quality of alignment at a monolayer thickness does not show a convincing correlation with molecular weight (see Figure 5.13b).

5.5 Limitations on Alignment Quality

To investigate the maximum orientational order achievable by shear alignment in these systems, the four shear-aligned polymers in the composition series were imaged at integer values of $t/d$. At these thicknesses, all of the polymers displayed a high degree of alignment with complete coverage of in-plane cylinders (no dots) and relatively few isolated dislocations, which were the only lattice defects observed; a high-magnification AFM image of a typical dislocation is shown in Figure 5.15b. Because exclusively all-line patterns were present, we characterized the alignment in each image via $\psi_2$, rather than $\psi_6$, to allow for quantitative comparison with previous work on other cylinder-forming block copolymers. For such well-aligned samples, the measured quality of order is primarily limited by two factors: undulations in the cylinders’ trajectories and the frequency of dislocations. To determine to what degree these dislocations diminish the order in films of each polymer, the density of dislocations for each image was computed and normalized by the square of the cylinder periodicity ($p_{AFM}$). These results are plotted in Figure 5.15a, where each point reflects a single AFM micrograph. Compared with previous work on cylinder-forming PS-PEP, the normalized dislocation densities for well-aligned PS-PHMA diblocks are relatively high ($<2 \times 10^{-3}$ for PS-PEP vs. up to $11 \times 10^{-3}$ for PS-PHMAs), although there is substantial variation between the PS-PHMAs. To examine these differences, the data are grouped by diblock and also by whether the image
Figure 5.15 (a) $\psi_2$ order parameter vs. normalized dislocation density for monolayers (open symbols) and multilayers (closed symbols, up to 4 layers) of PS-PHMA 21-77 (red squares), 30-86 (orange diamonds), 34-77 (green triangles), and 48-88 (blue circles). Red line shows best-fit to all PS-PHMA 21-77 data (mono- and multilayer), while the black line shows the analogous best-fit of the combined data for PS-PHMA 30-86, 34-77, and 48-88. (b) High-magnification AFM of a typical dislocation (PS-PHMA 21-77, $t = 30$ nm). Representative micrographs of aligned monolayer films of (c) PS-PHMA 21-77, (d) 30-86, (e) 34-77, and (f) 48-88 show the relative strength of undulations present in well-aligned films. Scale bars indicate 200 nm.
Table 5.2 Slopes and y-intercepts from fits of $\psi_2$ vs. normalized dislocation density

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Monolayer</th>
<th></th>
<th>Multilayer</th>
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<tbody>
<tr>
<td></td>
<td>slope</td>
<td>y-intercept</td>
<td>slope</td>
<td>y-intercept</td>
</tr>
<tr>
<td>21-77</td>
<td>-3.4 ± 1.0</td>
<td>0.9947 ± 0.0020</td>
<td>-4.1 ± 3.0</td>
<td>0.9946 ± 0.0010</td>
</tr>
<tr>
<td>30-86</td>
<td>-1.1 ± 0.2</td>
<td>0.9993 ± 0.0004</td>
<td>-0.9 ± 0.2</td>
<td>0.9987 ± 0.0005</td>
</tr>
<tr>
<td>34-77</td>
<td>-1.1 ± 0.2</td>
<td>0.9992 ± 0.0007</td>
<td>-0.8 ± 0.3</td>
<td>0.9986 ± 0.0008</td>
</tr>
<tr>
<td>48-88</td>
<td>-1.1 ± 0.3</td>
<td>0.9986 ± 0.0020</td>
<td>-1.0 ± 0.4</td>
<td>0.9995 ± 0.0019</td>
</tr>
<tr>
<td>30-86, 34-77, 48-88</td>
<td>-1.2 ± 0.2</td>
<td>0.9990 ± 0.0006</td>
<td>-0.9 ± 0.2</td>
<td>0.9988 ± 0.0005</td>
</tr>
<tr>
<td>simulations</td>
<td>-1.3 ± 0.1</td>
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*All ± indicate one standard deviation

was taken at a monolayer ($t/d \sim 1$) or multilayer ($t/d \sim 2, 3, 4$) thickness; no significant differences in alignment quality or dislocation densities were observed between the multilayers of different integer thicknesses. For each of the data clusters, a best-fit line was computed; the results of these fits are displayed in Table 5.2. The slope of the best-fit line reflects the quantitative influence that an individual dislocation has on the order in the system, while the y-intercept shows the maximum quality of order possible in the absence of any local defects. The y-intercept thus provides a value for the maximum quality of alignment achievable with these polymers at integer film thicknesses. For each individual polymer, there are no significant quantitative differences in slope or y-intercept between monolayer and multilayer films. Furthermore, PS-PHMA 30-86, 34-77, and 48-88 all have similar best-fit parameters; however, PS-PHMA 21-77 shows substantially different values. This is evident directly in Figure 5.15a, where all the points for PS-PHMA 30-86, 34-77, and 48-88 cluster together (fit collectively by the black line), while the data for PS-PHMA 21-77 lie apart (fit by the red line). The difference in y-intercept, $b$, between PS-PHMA 21-77 ($b = 0.9945 \pm 0.0010$) and the other three
polymers \((b = 0.9993 \pm 0.0007)\) reflects a real difference in the maximum alignment quality between the two groups, resulting from differences in the undulations in the cylinders’ trajectories present after shear. Figure 5.15c shows a well-aligned image of PS-PHMA 21-77 which contains no nearby defects; however, as can be seen from the micrograph, the cylinders possess short-period undulations of substantial amplitude around the average orientation of the microdomains. The presence of these undulations is consistent with previous work on shear alignment of other cylinder-formers,\(^6\), \(^9\), \(^{12}\) annealing the film following the shear does not eliminate or reduce these undulations (see Figure 5.11), indicating that they are not transient structures produced by the shearing process. AFM images for the other three polymers (Figure 5.15d-f) show comparatively straighter lines with undulations of much smaller amplitude; however, undulations are always observed for even the best-aligned samples.

The difference in slope, \(m\), between PS-PHMA 21-77 \((m = -3.3 \pm 0.9)\) and the other three polymers \((m = -1.2 \pm 0.2)\) is also highly significant. Elastic continuum simulations by Marencic \textit{et al.}\(^9\) predict a slope of -1.3, in good agreement with the value for the three higher-\(w_{ps}\) diblocks (-1.2), but considerably less than observed for PS-PHMA 21-77. Physically, \(m\) indicates the impact of an isolated dislocation on the lattice order; since the dislocation fields in all the diblocks have approximately the same shape and splay, it is unclear why a quantitatively different slope is observed for PS-PHMA 21-77 than for the other three diblocks, and in the simulations. A possible explanation may lie in the observation that images of PS-PHMA 21-77 often appeared to reveal enhanced undulations of the cylinder trajectories near a dislocation core, but this was not present in every case and proved difficult to quantify.
Collectively, these results show that high degrees of alignment can be achieved for all four polymers, as high as $\psi_2 \sim 0.999$ in the most favorable cases. The diblock with lowest $w_{PS}$, PS-PHMA 21-77, showed consistently poorer alignment as measured by $\psi_2$, however, it also exhibited comparatively few dislocations. Conversely, while the three high-$w_{PS}$ polymers all possessed comparable alignment behavior, PS-PHMA 48-88 showed a higher density of defects; unlike the other three polymers, in no case did we observe a defect-free image in a 2 $\mu$m $\times$ 2 $\mu$m micrograph of PS-PHMA 48-88, and the highest defect densities ($>10^{-2}$) were observed in PS-PHMA 48-88 films. It is interesting that the two polymers at the edges of the cylinder-forming composition window show the poorest quality of alignment ($\psi_2$), but for different reasons: PS-PHMA 21-77 because of pronounced undulations (despite a relatively low defect density), and PS-PHMA 48-88 because of a relatively high defect density (despite minimal undulations). Thus, both of these disturbances must be considered to maximize the quality of order in the film, which is obtained for compositions in the middle of the cylinder-forming region.

5.6 Non-Cylinder-Forming PS-PHMA Thin Films

The PS-PHMA diblock copolymers with the lowest and highest PS weight fraction, PS-PHMA 17-96 and 50-74, did not form cylinders in the bulk (as assessed by SAXS). Their thin film morphologies were investigated as a function of film thickness via AFM using flowcoated films which possessed a thickness gradient and which were thermally annealed for long times (~ 24 hours) at 150 °C. PS-PHMA 17-96 (a bulk sphere-former) showed hexagonally-packed dot patterns at all thicknesses studied (18 to 107 nm). Unlike all the other PS-PHMA s studied, this polymer terraced (formed islands
and holes), but only for film thicknesses up to 30 nm. Films which were 35 nm thick or
greater did not terrace, but were always flat and showed all-dot patterns. Figure 5.16a-b
shows some representative AFM micrographs.

SAXS revealed only a single clear peak for PS-PHMA 50-74. Investigation of the
thin film morphology, by preparing gradient films and annealing at the conditions listed
above, showed a complicated dependence of morphology on film thickness. At sub-
monolayer thicknesses, fingerprint-like line patterns are observed (see Figure 5.16c). It is
unclear whether these are in-plane cylinders or instead lamellae which are oriented
perpendicular to the substrate. Near the monolayer thickness, hexagonally-packed dots
are observed. These are likely not indicative of cylinders which are oriented
perpendicular to the substrate; in AFM phase contrast images, the glassy PS domains
appear lighter, while the rubbery PHMA domains are darker. Therefore the dark dots (see
Figure 5.16d) are most likely PHMA which has perforated an overlying PS layer,
suggesting a perforated lamellar structure. At film thicknesses above a monolayer,
mixtures of the line patterns and the PHMA dots (perforated lamellae) are observed (see
Figure 5.16e).
5.7 Conclusions

The thin-film structure of two series of PS-PHMA diblock copolymers, one with compositions spanning the cylinder-forming region of the phase diagram and the other spanning a range of molecular weights, were investigated. For incommensurate film thicknesses, these polymers do not terrace, but diblocks of lower PS weight fraction ($w_{ps}$)
showed continuous height variations with an amplitude corresponding to roughly half a cylinder layer spacing (“pseudo-terracing”). The PS-PHMA diblock with the lowest PS content and molecular weight showed the most dramatic effect of film thickness on morphology: non-sheared films of incommensurate thickness formed perpendicular cylinders rather than the usual parallel arrangement, and sheared films of incommensurate thickness showed poorly-ordered, highly-defective patterns. However, for diblocks with higher weight fractions of PS, these effects were increasingly mitigated, such that the polymers with highest PS content showed essentially the same film structure by AFM regardless of film thickness. PS-PHMAs of increased molecular weight similarly showed a reduced dependence on film thickness; however, these films also possessed predominantly dot patterns, even in the vicinity of a monolayer. For shear-aligned films, the composition series showed that alignment quality after shear is highly correlated with the fractional coverage by in-plane cylinders prior to shearing: i.e., films which showed in-plane cylinders pre-shear, showed better alignment post-shear. Increasing molecular weight showed no clear effects on alignment quality post-shear, despite the persistence of dots in the films prior to alignment. Alignment quality in diblock films is limited by two factors: the presence of isolated dislocations in the microdomain lattice and undulations in the cylinder trajectories. In PS-PHMA diblock thin films forming PS cylinders, the dislocation density increases with PS content, while the undulation magnitude decreases with PS content, such that the highest quality of alignment is obtained for polymers whose compositions lie in the middle of the cylinder-forming region.
Chapter 5: Cylinder Orientation and Shear-Alignment in Thin Films of PS-PHMA Diblock Copolymers

5.8 References


Chapter 5: Cylinder Orientation and Shear-Alignment in Thin Films of PS-PHMA Diblock Copolymers


Chapter 6

Progression of Alignment in Thin Films of Cylinder-Forming Block Copolymers upon Shearing

6.1 Introduction

While shear alignment has successfully produced well-ordered films, there is still much to be discovered regarding the factors which influence the ease and ultimate quality of alignment in shear-aligned films. Previous work has shown that the magnitude of the applied stress, the time and temperature of shear, and the polymer film thickness, specifically its proximity to the preferred monolayer thickness, can all drastically influence the alignment quality. In addition, the mechanism by which alignment occurs is still an open topic. To model shear alignment in sphere-formers, Wu et al. proposed that any polymer grains which are misaligned relative to the direction of the applied shear experience an effective reduction in their order-disorder transition temperature; with sufficient stress, the most misaligned grains will selectively melt and reorder in the shear direction. They described this phenomenon with a “melting-recrystallization model”, and showed that this model reproduces the dependence of alignment quality on applied stress.
shear stress reasonably well for sphere-formers.\(^1\)\(^,\)\(^3\) Later, Pelletier et al. modified this model for cylinder-formers and also found good agreement with experimental data.\(^2\) Marencic et al. then systematically probed the effects of applied stress and misorientation angle and found the stress required for alignment increased monotonically as the difference between the microdomains’ orientation and the shear direction decreased.\(^4\)

The chief aim of the present work is to systematically examine the influence of key material, film, and process parameters on the alignment behavior (alignment quality vs. stress and time) of cylinder-forming block copolymers. The parameters studied are the volume fraction of the cylinder-forming block, overall molecular weight, film thickness (number of cylinder layers), and wetting condition at the substrate. To examine these, we utilize the same series of cylinder-forming polystyrene-poly(\(n\)-hexyl methacrylate) (PS-PHMA) block copolymers described in the previous chapter, and shear them using a rotational rheometer apparatus (see Figure 2.6b). The film alignment quality is assessed via atomic force microscopy (AFM) and compared to the melting-recrystallization model, which provides a convenient method to systematically and quantitatively interpret the data, and creates a degree of predictive capability.

### 6.2 Rheometer Shearing and Applied Stress Calculation

Solutions of PS-PHMA in toluene (~ 1-5 wt. %) were prepared and spin-cast onto silicon wafers, producing thin films of uniform thickness, \(t\) (\(±\) 1 nm). The wafers were liberally rinsed with toluene prior to use. After deposition, the films were thermally annealed under vacuum at 150 °C (above the glass transition temperature, \(T_g\), for both blocks) for 2 hours. Film thicknesses, prior to and after annealing, were measured via
ellipsometry and consistently agreed within ± 0.5 nm, indicating that insignificant residual solvent was present in the as-spun films. The PS-PHMA films were shear-aligned using the rheometer shearing method at 150 °C for a prescribed time ($\tau_{\text{shear}}$, between 5 and 120 minutes) over fixed stress range (see Figure 6.1a for a schematic of the process). After removing the poly(dimethylsiloxane) (PDMS) oil used during shearing, the alignment quality is accessed via AFM and subsequent computation of the orientational order parameter, $\psi_2$. In general as the applied stress increases, the quality of alignment improves (as shown by the representative images in Figure 6.1c-f).

The applied shear stress, $\sigma$, at a given position on the film was determined as a function of the radial distance from the center of the sheared area, $r$ (the determination of $r$ for each image is discussed in Chapter 3.2.6) by first computing the shear rate, $\dot{\gamma}$, via:

$$\dot{\gamma}(r) = r \Omega / H_0$$  \hspace{1cm} \text{Equation 6.1}$$

where $\Omega$ is the angular velocity [rad/sec] of the rheometer plate and $H_0$ is the distance between the plate and the polymer film. The local viscosity of the PDMS layer, $\eta$, can be computed using the Carreau-Yasuda constitutive equation:

$$\eta(r) = \eta_0 [1 + (\kappa_1 \dot{\gamma}(r))^{\kappa_2}]^{\kappa_3}$$  \hspace{1cm} \text{Equation 6.2}$$

where the fitting parameters $\eta_0$ (the zero shear viscosity), $\kappa_1$, $\kappa_2$, and $\kappa_3$ were determined by measuring the PDMS oil viscosity as a function of shear rate (from 0.02 – 2 s$^{-1}$, the range over which shear-alignment was conducted) using a cone-and-plate tool and fitting to Equation 6.2 (see Figure 6.2). The local shear stress is then computed by:

$$\sigma(r) = \eta(r) \times \dot{\gamma}(r)$$  \hspace{1cm} \text{Equation 6.3}$$
Chapter 6: Progression of Alignment in Thin Films of Cylinder-Forming Block Copolymers upon Shearing

Figure 6.1 (a) Schematic of the experimental setup for imparting a gradient of shear stress to a polymer film using a parallel plate rheometer. (b) Top-down view of the applied stress gradient. (c-f) Representative AFM phase images from a monolayer of PS-PHMA 21-77, sheared at 150 °C for 30 min, showing the progressive increase in alignment quality as the applied stress is increased: (c) 0 Pa ($\psi_2 = 0.09$, computed over the entire 2 μm × 2 μm area of the full image), (d) 800 Pa ($\psi_2 = 0.51$), (e) 1200 Pa ($\psi_2 = 0.82$), (f) 2000 Pa ($\psi_2 = 0.98$). Scale bar = 500 nm.
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Figure 6.2 Viscosity of DMS-T72 PDMS oil at 150 °C as a function of shear rate, measured experimentally using a cone-and-plate rheometer tool (open symbols) and fit to the Carreau-Yasuda model\(^7\)-\(^8\) (solid line, equation shown in figure) where \(\eta_0\) = the viscosity at zero shear rate (measured to be 4940 Pa·s), and \(\kappa_1\), \(\kappa_2\), and \(\kappa_3\) are fit parameters. The best fit to the Carreau-Yasuda model occurs when \(\kappa_1 = 1.710\) s, \(\kappa_2 = 1.140\), and \(\kappa_3 = 0.7804\).
6.3 Influence of Polymer Composition

Monolayers of PS-PHMA 21-77 (t = 28 nm), 30-86 (t = 39 nm), 34-77 (t = 39 nm), and 48-88 (t = 47 nm) were sheared using stresses ranging from 0 – 6000 Pa. These four polymers systematically vary in their weight fraction of PS, $w_{PS}$, but have nearly constant overall number-average molecular weight, $M_n$ (~ 115 ± 20 kg/mol). Examination of the sheared samples by AFM revealed the dependence of alignment quality on applied shear stress as displayed in Figure 6.3. At the lowest stresses, before any significant alignment occurs, $\psi_2$ scatters about an average of zero; the sizable magnitude of the scatter reflects the fact that the average grain size is not greatly smaller than the AFM image size. Above a threshold stress, which monotonically increases with $w_{PS}$, the cylinders begin to align, leading to an increase in $\psi_2$ until it reaches a plateau value. For the two lowest-$w_{PS}$ polymers, PS-PHMA 21-77 and 30-86, the transition from nonaligned to well-aligned occurs over a narrow range of applied stresses (~ 1000 Pa), while the two higher-$w_{PS}$ polymers, PS-PHMA 34-77 and 48-88, display much broader transition ranges (>4000 Pa) and appear not to have reached their terminal alignment quality at the maximum stress applied. The upper limit of applied stress accessible in this particular setup was limited by the tendency of the oil to escape the gap over time, the result of outward normal forces exerted by the oil due to its viscoelasticity. For shear times of ~ 0.5-2 hr, 6 kPa is the largest maximum stress which can be imparted before any leaking becomes detectable.
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Figure 6.3 Alignment quality, measured by $\psi_2$, as a function of applied shear stress for (a) PS-PHMA 21-77, (b) 30-86, (c) 34-77, and (d) 48-88, all after 30 min of shearing at 150 °C. Symbols correspond to experimental values determined from AFM phase images of the sheared films, while the black lines show the least-squares fits of the melting-recrystallization model to the experiments. The best-fit model parameter values for each polymer are displayed in the corresponding graphs, with ± 1 standard deviation of the fit.
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To quantitatively compare the four block copolymers and to gain further insight into the origin of the differences in alignment behavior as a function of composition, these data were compared to the melting-recrystallization model, first described for cylinder-formers by Pelletier et al. The model states that cylinders which are sheared at an angle to their axis experience an effective reduction in their order-disorder transition temperature, $T_{ODT}$, the strength of which depends on the magnitude of the applied stress and the degree of misalignment to the shear direction, as shown in Equation 6.4:

$$T_{ODT}^* = T_{ODT}[1 - \frac{\sigma}{\sigma_c} \sin^2(\alpha(\theta - \theta_0))]$$

Equation 6.4

where $T_{ODT}^*$ is the effective $T_{ODT}$, $\sigma$ is the applied shear stress, $\theta - \theta_0$ is the misorientation of a grain with respect to the shear direction, and $\sigma_c$ is a parameter termed the critical stress. Equation 6.4 is derived from a Landau model with an added anisotropic diffusion term which represents the energy induced by shearing. Using phenomenological and symmetry arguments proposed by Angelescu et al., this diffusion term is set as proportional to the shear rate squared; this is the origin of the exponent of 2 on the stress and sine terms in Equation 6.4 (note that in the model derivation for sphere-formers the stress has an exponent of unity).

When $T_{ODT}^*$ is less than the shearing temperature, $T$, the misoriented grains “melt” and then recrystallize in the direction of applied shear. The rates of melting and recrystallization, which are assumed equal, are given by:

$$\frac{\partial A_\xi}{\partial \tau} = \Gamma \frac{T_{ODT}^* - T}{T_{ODT}}$$

Equation 6.5
where $A_g$ is the area of a grain and $\Gamma$ is a rate constant which describes how quickly the limiting alignment is reached. The predicted degree of alignment can then be computed by:

$$
\psi_{2a} = D \frac{\int_0^{\pi/2} A_g(\theta - \theta_0) \cos(2\alpha(\theta - \theta_0)) d(\theta - \theta_0)}{\int_0^{\pi/2} A_g(\theta - \theta_0) d(\theta - \theta_0)}$

Equation 6.6

where $D$ is a Debye-Waller-like term which reflects the terminal quality of order at high stresses. In the context of this study, the primary utility of the melting-recrystallization model is that the critical stress, $\sigma_c$, and alignment rate constant, $\Gamma$, can be extracted via a best fit of the model to each data set, providing a convenient, quantitative comparison across experiments.

The melting-recrystallization model was fit to the four data sets (shown as solid lines in Figure 6.3) by comparing the model prediction of $\psi$ vs. stress to the data and minimizing the sum of the residuals by iteratively varying the critical stress ($\sigma_c$) and alignment rate constant ($\Gamma$) starting from initial guesses. Since the polymers all appear to approach $\psi_2 = 1$ at high stress, we set $D = 1$. In addition, because none of the polymers studied possesses a thermally accessible $T_{ODT}$ (the materials degrade before their $T_{ODT}$ can be reached) we estimated the $T_{ODT}$ for each diblock using the available literature (see Section 6.6 for details); because the Flory-Huggins interaction parameter for PS-PHMA is known to be very weakly dependent on temperature,\textsuperscript{11-12} all the estimated $T_{ODT}$ values are quite high ($>400$ °C), in the regime where the model prediction is insensitive to the value of $T_{ODT}$ ($T_{ODT} \gg T$). The best-fit parameters for the four polymers as functions of $w_{PS}$ are shown in Figure 6.4. In general the $\psi_2$ vs. applied stress behavior is well matched
Figure 6.4 Values of the critical stress, $\sigma_c$ (red diamonds), and alignment rate constant, $\Gamma$ (blue circles), from the melting-recrystallization model fits in Figure 6.3, plotted against the weight fraction of minority block in the copolymer. Filled symbols indicate neat block copolymers, while the open symbols show the results from a copolymer blend. Error bars indicate $\pm 1$ standard deviation of the model fit.
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by the model, though the data for PS-PHMA 30-86 (Figure 6.3b) show a steeper transition from nonaligned to aligned than the model captures.

Given the complexity of the governing equations, estimates of the uncertainty of the fits are difficult to determine analytically, so instead the statistics of the best-fit parameters can be approximated using a resampling method known as “bootstrapping.”

Bootstrapping is a technique for estimating properties of a population when only a sampling of the total population (in this case the experimentally measured $\psi$ vs. stress data) is available. To execute the technique, a series of resampled data sets ($m_i$) of identical size ($\bar{\xi}$) to the original set are populated by randomly choosing data points from the original data set ($m_0$) with replacement $\bar{\xi}$ times. These resampled data sets are then fit to the melting-recrystallization model, in the exact manner as $m_0$, and $\sigma_{c,i}$ and $\Gamma_i$ are computed. The number of bootstrap data sets is chosen to be sufficiently large such that the average and standard deviation of $\sigma_{c,i}$ and $\Gamma_i$ converge to a stable value. Figure 6.5 shows the bootstrap sampling algorithm applied to the data for a monolayer of PS-PHMA 21-77 (the original data and best fit are shown Figure 6.3a). After approximately 500 bootstrap iterations, the best-fit parameter statistics do not change significantly, indicating that the sampling algorithm has converged. The final “best-fit” parameter values for this experimental data set are then taken as the average best-fit values for all of the bootstrap iterations, and the uncertainty ($\pm$) is quoted as one standard deviation. For consistency and rigor, we chose to use 1000 bootstrap iterations to generate the statistics for all experimental data sets.
Figure 6.5 Average (a) and standard deviation (b) of critical stress values, $\sigma_c$, obtained from a best fit to the melting-recrystallization model vs. number of bootstrap iterations. The values above were generated by fitting the experimental data for a monolayer of PS-PHMA 21-77 (shown in Figure 6.3a). After approximately 500 iterations, the scatter in the average value is less than 10% of the standard deviation, indicating that the bootstrap analysis has converged to a solution.
Also shown in Figure 6.4 are the best-fit $\sigma_c$ and $I^*$ for a monolayer ($t = 35$ nm) of a 50:50 blend (by weight) of PS-PHMA 30-86 ($w_{PS} = 0.26$) and 34-77 ($w_{PS} = 0.30$), which has $w_{PS} = 0.28$. This blend was made to probe the transition between the polymers with relatively “fast” kinetics ($w_{PS} \leq 0.26$) and those with “slow” kinetics ($w_{PS} \geq 0.30$) at $M_n \approx 110$ kg/mol; the 50:50 blend, by weight, of PS-PHMA 30-86 and 34-77 was produced by co-dissolving the polymers in toluene prior to film casting. To determine the thickness at which a monolayer of cylinders would form for this precise blend, we employed the procedure outlined in Chapter 5 to optimize the film thickness for shear alignment of the neat block copolymers. The blended solutions were flowcoated\(^1\) to produce films with a thickness gradient (spanning $\sim 10 - 70$ nm) and were then thermally annealed for $\sim 24$ hours at 150 °C to allow the film’s nanostructure to develop and to remove any residual solvent. The samples were imaged, via AFM, at various positions along the film and their morphology examined as a function of film thickness. Like the constituent block copolymers, the blended film morphology displayed either hexagonally packed dots, meandering parallel line patterns, or mixtures of dots and lines. The fractional coverage of lines in an image, $F$, was computed\(^1\) and plotted vs. film thickness (see open symbols in Figure 6.6a). The thickness gradient film was then shear-aligned, transverse to the thickness gradient, using 10 kPa of stress via the pad-shearing technique\(^6\) and the alignment quality ($\psi_2$) computed and plotted as a function of film thickness (closed symbols in Figure 6.6a). The optimal monolayer thickness ($t_{mono}$) is identified as the thickness near one interlayer spacing, $d$, which shows a local maximum in $F$ and $\psi_2$. For hexagonally-packed cylinders, the interlayer spacing can be estimated as $d = p_{AFM} \sqrt{3} / 2$ where $p_{AFM}$ is the cylinder periodicity as measured by AFM. It is interesting to note that,
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Figure 6.6 Data for a 50:50 mixture (by weight) of PS-PHMA 30-86 and PS-PHMA 34-77, yielding a blend with \( w_{PS} = 0.28 \). (a) Fractional coverage of in-plane cylinders \( (F, \text{open squares}) \) and alignment quality \( (\psi_2, \text{filled squares}) \) vs. film thickness. (b) Alignment quality vs. stress for a 35 nm film (green triangles) and the corresponding best fit of the melting-recrystallization model (black line).

In this particular blend, \( d \) was found to be \( 37.7 \pm 0.5 \) nm which is actually smaller than the values for the neat 30-86 and 34-77 polymers, which possess \( d = 38.9 \pm 0.7 \) nm and \( 39.0 \pm 0.4 \) nm respectively. This blend does not show a sharp maximum in \( F \) or \( \psi_2 \); however it does show a steady plateau from \( \sim 28 - 35 \) nm. Therefore for \( t_{mono} \) we choose the thickness within this window which is closest to \( d \) (35 nm). A film of the blend was spin-coated at this thickness and sheared, via the parallel-plate rheometer method, over a range of stress from \( \sim 0-6000 \) Pa. Alignment quality \( (\psi_2) \) was measured as a function of stress and the data were fit to the melting-recrystallization model, yielding best-fit alignment parameters of \( \sigma_c = 1620 \pm 260 \) Pa and \( \log_{10}(\Gamma [s^{-1}]) = -3.48 \pm 0.39 \). The experimental data and model fit are shown in Figure 6.6b.
As $w_{PS}$ increases, $\sigma_c$ increases nearly linearly, while over the same range, $\Gamma$ decreases by more than an order of magnitude. The model thus indicates that any apparent qualitative difference between the polymers with sharp and gradual alignment transitions may be understood through their substantial, but smoothly varying, differences in alignment rates. To explore this idea further, additional experiments were done with the “fastest” (21-77) and “slowest” (48-88) polymers in this set, in which identical monolayer films were sheared under the same conditions but for shear durations varying over the practical range. The minimum shear time is dictated by the maximum cooling speed of the Peltier plate (~ 100 °C/min); a minimum shear time of 5 minutes was chosen, to reduce the influence of the ~ 0.5 min cool (under shear) from 150 °C to the PS $T_g$. Conversely, the maximum shear time is limited by the oil leakage from the gap described earlier, ~ 2 hours for the stresses of interest. Using the best-fit $\sigma_c$ and $\Gamma$ previously measured for each polymer, we compute the $\psi_2$ vs. $\sigma$ behavior expected for various shear times and compare with the analogous experiments (Figure 6.7). The model prediction for the “fast” polymer shows that $\Gamma$ is sufficiently large that even 5 min of shear produces the limiting quality of alignment at each stress; this prediction is well corroborated by the experiments. In the case of the “slow” polymer, the model shows a substantial time dependence over the range investigated that is in remarkable agreement with the data (within the experimental scatter). These results provide compelling evidence that the melting-recrystallization model accurately captures the kinetics of the shear alignment process.
Figure 6.7 Alignment vs. stress for (a) PS-PHMA 21-77 and (b) 48-88 for varying shear times. The symbols display the experimental results from AFM, while the lines show the predictions of the melting-recrystallization model for each polymer: (a) PS-PHMA 21-77: $\sigma_c = 860 \text{ Pa}, \log_{10}(\Gamma [\text{s}^{-1}]) = -1.73$; (b) PS-PHMA 48-88: $\sigma_c = 2250 \text{ Pa}, \log_{10}(\Gamma [\text{s}^{-1}]) = -3.83$. 

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6.4 Molecular Weight Scaling

The above results illustrate that for nearly constant overall molecular weight, $\sigma_c$ increases and $\Gamma$ decreases monotonically with increasing $w_{PS}$ across the cylinder-forming region. The following presents a complementary study in which composition was kept (nearly) constant ($w_{PS} = 0.23 \pm 0.02$), but molecular weight was varied by a factor of ~3.5. Monolayers of PS-PHMA 31-108 ($t = 40$ nm), 60-191 ($t = 59$ nm), and 87-256 ($t = 86$ nm) were sheared. At low stresses, before any substantial alignment occurs, the PS-PHMA 60-191 and 87-256 films displayed mixed patterns of both in-plane cylinders and hexagonally packed dots; these dots are likely cylinders which have reoriented perpendicular to the substrate (as discussed in Chapter 5). To accurately capture any alignment of these dots, we employ $\psi_6$ here in place of $\psi_2$, even in instances in which the polymer shows no dots (PS-PHMA 21-77 and 31-108). The experimental results and best fits to the melting-recrystallization model are displayed in Figure 6.8. PS-PHMA 87-256 showed no discernable alignment over the range of stresses employed and thus could not be meaningfully fit to the model. For these films, a terminal value of $\psi_6 = 0.93$ is observed in the data of Figure 6.8, thus setting the value of $D$ (Equation 6.6) for these experiments.
Figure 6.8 Alignment quality, measured by $\psi_6$, vs. applied shear stress for (a) PS-PHMA 21-77 sheared for 30 minutes (same sheared film for which data were presented in Figure 6.3a, but here using $\psi_6$, rather than $\psi_2$, to quantify the orientation), (b) 31-108 sheared for 30 minutes, and (c) 60-191 sheared for 2 hours. The symbols show the experimental results, while lines show the best fits to the melting-recrystallization model.
The dependence of $\sigma_c$ and $\Gamma$ on molecular weight is shown in Figure 6.9. The critical stress scales linearly with $M_n$, while $\Gamma$ shows a much stronger dependence, roughly scaling as $M_n^{-4.3 \pm 0.9}$. Previously, $\Gamma$ was postulated to be proportional to the block copolymer’s self-diffusion coefficient. Recall that from reptation theory, the self-diffusion coefficient $D_S \propto M^{-2}$ for entangled homopolymers, but the observed scaling for $\Gamma$ with $M_n$ in our block copolymer films is stronger. Indeed, Lodge and Dalvi, and later Yokoyama and Kramer, argued that self-diffusion should scale much more strongly with molecular weight for microphase-separated block copolymers because of a thermal activation barrier which must be overcome for chains to “hop” between microdomains.

While a quantitative molecular interpretation of $\Gamma$ remains elusive, the relationships displayed in Figure 6.9 are still useful to predict which PS-PHMA diblocks will or will not align given a set of shearing conditions. As an example, one can predict the quality of alignment expected for PS-PHMA 87-256 (the polymer which showed no alignment upon shearing) at the shear conditions employed ($\sigma_{max} = 6000$ Pa, $t_{shear} = 120$ min). Extrapolating to the appropriate molecular weight, the scaling relationships predict that PS-PHMA 87-256 should possess $\sigma_c = 3890$ Pa and $\Gamma = 2.5 \times 10^{-5}$ s$^{-1}$. Using these parameters, a model prediction was generated (see Figure 6.10), which showed that indeed no detectable alignment should occur. This fully corroborates our null observation and suggests that a shearing time of $\sim$10 hours at 6 kPa (well above what we can achieve experimentally) would be needed to unambiguously observe alignment in this system.
Figure 6.9 Best-fit parameter values from Figure 6.8 plotted vs. molecular weight: (a) $\sigma_c$ vs. $M_n$, (b) $\log_{10}(\Gamma)$ vs. $\log_{10}(M_n)$. Lines indicate the best fits to the data; error bars indicate ± 1 standard deviation in the melting-recrystallization model fits.
Figure 6.10 Alignment ($\psi_6$) vs. applied shear stress for PS-PHMA 87-256; open symbols indicate experimental data after 120 min of shearing, while solid line shows melting-recrystallization model prediction using $\sigma_c = 3890$ Pa, $\Gamma = 2.51 \times 10^{-5}$ s$^{-1}$, and $D = 0.93$.

6.5 Film Thickness, Wetting Condition, and Film-Substrate Interactions

In addition to molecular parameters such as $w_{PS}$ and $M_n$, details concerning the film itself, specifically its thickness, wetting condition (whether the majority or minority block wets the substrate), and film-substrate interactions can potentially influence the microdomains’ response to shear. Previous work has shown that small deviations in film thickness away from the monolayer thickness can lead to substantial reductions in the quality of alignment observed upon shearing. This effect was also observed in the
present study; when sheared, PS-PHMA films with an incommensurate thickness require
greater stresses from the rheometer before alignment occurs, and the terminal alignment
quality is poor as compared to the monolayer case, as discussed extensively in Chapter 5.
At commensurate thicknesses (integer multiples of the monolayer thickness), the
alignment behavior is qualitatively similar to the monolayer case. As a complement to the
results in Chapter 5, the following experiments illustrate how the ease of alignment is
influenced by film thickness/number of cylinder layers.

Films of PS-PHMA 21-77 corresponding to 2 ($t = 57$ nm), 3 ($t = 85$ nm), 4 ($t =
115$ nm), 5 ($t = 143$ nm), and 10 layers ($t = 285$ nm) of cylinders were sheared at $T = 150$
°C, $t = 30$ min, $\sigma \approx 0 - 3000$ Pa and compared with the results for the corresponding
monolayer film. Selected results are displayed in Figure 6.11a. In all cases the same
qualitative behavior is observed, with no alignment at the lowest stresses and a sharp
transition to a well-aligned state at moderate stresses. Fitting the melting-recrystallization
model to these data reveals the dependence of the alignment parameters on the number of
cylinder layers (see Figure 6.11b). The critical stress first decreases, by approximately
3×, perhaps reflecting a cooperativity between layers (with a hexagonal packing of
cylinders), and then appears to plateau at about 4-5 layers. By contrast, the alignment rate
constant shows no discernable dependence within the scatter, consistent with the idea that
$\Gamma$ reflects an intrinsic material property (such as diffusivity) and would thus be unaffected
by film thickness.
Figure 6.11 (a) Alignment ($\psi_2$) vs. applied stress for PS-PHMA 21-77 films with thicknesses corresponding to 1 (red squares), 3 (green triangles), and 5 (purple hexagons) cylinder layers. Curves show the respective best fits to the melting-recrystallization model. (b) Best-fit parameter values vs. number of cylinder layers: $\sigma_c$ (red diamonds) and $\Gamma$ (blue circles). Error bars indicate ± 1 standard deviation in the model fits.
The substrate wetting condition of the film and the “penetrability” of the substrate were also examined for their effects on the alignment response. To prepare the different substrates, suitable polymers, synthesized as follows, were grafted onto Si wafers. Styrene (S), \(n\)-hexyl methacrylate (HMA), and 2-hydroxyethyl methacrylate (HEMA) were purchased from Aldrich, passed through an inhibitor removal column, degassed under vacuum, and stored in a glove box freezer at -20 °C. Statistical copolymers of poly(styrene-\(r\)-2-hydroxyethyl methacrylate) (P(S-\(r\)-HEMA)) and poly(\(n\)-hexyl methacrylate-\(r\)-2-hydroxyethyl methacrylate) (P(HMA-\(r\)-HEMA)) were then synthesized via classical free radical polymerization in bulk using azobisisobutyronitrile (AIBN, purchased from Sigma-Aldrich) as initiator. The initiator and monomers were added into test tubes in an inert atmosphere (MBraun UNILab glovebox with N\(_2\) atmosphere, O\(_2\) and H\(_2\)O concentrations <0.1 ppm) and sealed with a septum. The tubes were removed from the glovebox and placed in a 70 °C water bath for a fixed time (until the desired conversion, \(\sim\)20\%, was reached). The polymerizations were terminated by precipitation into methanol. Polymer compositions of 1 mole % HEMA were targeted by calculating the expected molar composition based on previously measured reactivity ratios\textsuperscript{22}: \(r\textsubscript{S/HEMA} = 0.27\), \(r\textsubscript{HEMA/S} = 0.48\), \(r\textsubscript{HMA/HEMA} = 0.841\), \(r\textsubscript{HEMA/HMA} = 0.982\). The reactivity ratios for HMA-HEMA were not available, so we approximated them using the known reactivity ratios between HEMA and \(n\)-butyl methacrylate (BMA).\textsuperscript{23} The presence of HEMA in the copolymer was confirmed by \(^1\)H NMR spectroscopy using a 50/50 v/v mixture of CDCl\(_3\) and deuterated dimethylsulfoxide (DMSO); the mixed solvent is needed because the HEMA hydroxyl resonance\textsuperscript{22} cannot be resolved in pure CDCl\(_3\), but the polymers are insoluble in pure DMSO.\textsuperscript{24} The molecular weight and dispersity of each copolymer was
measured using size-exclusion chromatography (weight-average molecular weight, $M_w$, from light scattering, dispersity, $D$, from differential refractometry, see Chapter 3.1.2). Because the HEMA fraction in each copolymer is modest, we ignored its contribution to $dn/dc$ when determining the copolymer molecular weights. Table 6.1 lists the copolymers used in this study.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$ [kg/mol]</th>
<th>$D$</th>
<th>$t_{\text{graft}}$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(S-r-HEMA)-56</td>
<td>55.9</td>
<td>1.84</td>
<td>9</td>
</tr>
<tr>
<td>P(HMA-r-HEMA)-64</td>
<td>63.7</td>
<td>2.12</td>
<td>9</td>
</tr>
</tbody>
</table>

Films of random copolymers, ~ 50 nm thick, were spin-cast onto clean, as-received Si wafers with a native oxide surface. The films were thermally annealed, under vacuum, at 150 °C for 12 hours to allow the HEMA to covalently bond with the silicon oxide substrate. After annealing, the films were thoroughly rinsed with toluene to remove any ungrafted polymer, dried under nitrogen, and the grafted layer thickness, $t_{\text{graft}}$, measured via ellipsometry. To identify the monolayer thickness of PS-PHMA 21-77 on these modified substrates, thickness gradient films of the block copolymer were deposited, via flowcoating, onto the grafted substrates and thermally annealed for 2 hours at 150 °C. The thin film morphology was then examined, via AFM, as a function of film thickness and compared to that for films deposited on unmodified Si wafers (no graft). When the substrate possesses a grafted P(HMA-r-HEMA) layer, one expects a film morphology (or more specifically an $F$ vs. film thickness behavior) similar to the reference case (PS-PHMA on an unmodified Si substrate), as in both instances the PHMA matrix block will preferentially wet the substrate (see Figure 6.12a, b); however,
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Figure 6.12 Schematics of cylinder-forming PS-PHMA films on various substrates, with the PS blocks in red and the PHMA blocks in blue: (a) on Si substrate (gray) bearing the native oxide, (b) on a substrate grafted with PHMA chains (bright blue), (c) on a substrate grafted with PS chains (bright red), where the brush-like wetting layer of block copolymer is indicated by the dashed chains.

when a P(S-\text{r}-HEMA) layer is grafted to the substrate, instead the minority PS component of the block copolymer will preferentially wet the surface, producing a “wetting layer” of block copolymer chains, above which the normal cylinder morphology should form. The wetting layer most likely consists of either a half-lamella (as shown in Figure 6.12c) or a hemi-cylinder layer\textsuperscript{25} with a thickness of $\sim d/2$. As such, the $F$ vs. thickness data should possess the same qualitative shape as the previous two cases; however, the features should all be shifted to higher thicknesses by $d/2$. Figure 6.13 shows the $F$ vs. $t$ data for the three cases. As predicted, the unmodified “no graft” substrate and PHMA-grafted
Figure 6.13 Fractional coverage of in-plane cylinders vs. normalized film thickness for PS-PHMA 21-77 on bare Si wafer with native oxide (purple), on a layer of grafted P(S-r-HEMA)-56 (red), and a layer of grafted P(HMA-r-HEMA)-64 (blue). For ease of comparison, the P(S-r-HEMA)-56 data have been shifted to the left along the x-axis by \( t/d = 1/2 \).

substrate data are nearly indistinguishable, while the PS-grafted case showed the same behavior but shifted to a higher thickness by \( d/2 \). These results confirm the PS-PHMA thin film structures drawn in Figure 6.12, with PHMA typically wetting both interfaces, except in the special case of induced preferential wetting of the substrate by PS, in which case a wetting layer forms at the substrate. Additionally, in the PS-graft case, at very low
film thicknesses \((t/d < 1/2)\), terracing (island and hole formation) was observed in the block copolymer overlayer, which is noteworthy because on the bare Si substrate, this polymer is never observed to terrace.

Monolayer films of PS-PHMA 21-77 were deposited on PHMA-preferential and PS-preferential substrates. The PHMA-grafted substrate yields the same wetting conditions for PS-PHMA as on the bare Si wafer, for which alignment data were already shown in Figure 6.3a: the PHMA matrix wets both substrate and air interfaces (Figure 6.12a). However, on the PHMA-grafted substrate (Figure 6.12b), the PHMA blocks of the copolymer matrix could penetrate the substrate (the grafted layer) to some extent, while the bare Si wafer presents an impenetrable substrate. By contrast, the substrate wetting condition differs for the PS-grafted substrate (Figure 6.12c); in this case, an additional brush-like wetting layer of block copolymer forms at the substrate.26 The cylindrical microdomains, and the chains that form them, “ride upon” this brush-like layer and thus do not contact the substrate.27 The monolayer films were sheared at 150 °C for 30 minutes over a stress range of 0-5000 Pa; recall from Figure 6.3a that PS-PHMA 21-77 has “fast” alignment kinetics and thus should be well-aligned under these shear conditions. As shown in Figure 6.14, no significant difference in alignment versus stress behavior was observed among the three cases. Given the “fast” alignment of this polymer, it is perhaps unsurprising that no differences in alignment kinetics are observed; it would take a substantial change in \( \Gamma \), half an order of magnitude or more, for this effect to be unambiguously detectable. However, the lack of change in \( \sigma_c \), which can be measured in “fast” polymers with much more sensitivity, between the bare Si and PHMA-grafted substrates indicates that any penetration of the grafted layer by the block
copolymer chains does not affect the stress required for microdomain alignment. Moreover, “decoupling” the chains which form the microdomains from the substrate, by creating the wetting layer in between via the PS-grafted substrate, does not affect the stress required for alignment. These results suggest that one can broadly change the surface energy (and therefore the substrate-wetting block), as well as the “penetrability” of the substrate surface, without compromising the alignment behavior of the overlying block copolymer layer.

![Graph](image)

**Figure 6.14** Alignment ($\psi_2$) vs. applied stress for monolayers of PS-PHMA 21-77 on bare Si wafer with native oxide (purple), on a layer of grafted P(S-$r$-HEMA)-56 (red), and on a layer of grafted P(HMA-$r$-HEMA)-64 (blue).
6.6 Estimation of $T_{ODT}$ for Melting-Recrystallization Model Fits

The $T_{ODT}$ of the block copolymer is an important material parameter used in the melting-recrystallization model (see Equations 6.4 and 6.5). Figure 6.15 shows both experimental data and model predictions of alignment quality vs. applied stress for PS-PHMA 21-77 and 60-191 (the “fastest” and “slowest” polymers studied, respectively), where the model calculations use fixed values for the critical stress ($\sigma_c$) and alignment rate constant ($\Gamma$) but vary $T_{ODT}$. When $T_{ODT}$ is relatively small (<1000 K, vs. shearing temperature $T = 423$ K), changes in the value of $T_{ODT}$ have a noticeable effect on the model prediction. However, as $T_{ODT}$ becomes larger this effect is reduced, and the model calculations approach an asymptotic limit as $T_{ODT} \to \infty$, where the stress corresponding to the “knee” in the calculated curve ($\sigma_{\text{threshold}}$ where $\psi_2 = 0^+$) approaches $\sigma_c$ from below. In a complementary analysis, presented in Figure 6.16, we show how the best-fit values of $\sigma_c$ and $\Gamma$ to the experimental data for these two polymers change when $T_{ODT}$ is varied logarithmically. As $T_{ODT}$ increases, the best-fit values of $\sigma_c$ and $\Gamma$ decrease, but when $T_{ODT}$ becomes large (>10$^3$ K, vs. shearing temperature $T = 423$ K), the impact on the fit parameters becomes statistically insignificant as $\sigma_c$ and $\Gamma$ asymptote to terminal values. This behavior is expected when considering the limit of Equations 6.4-6.6 as $T_{ODT} \to \infty$. In this limit, the expression $(\sigma/\sigma_c)^2 \sin^2(\alpha(\theta - \theta_0))$ approaches unity, and $\sigma_{\text{threshold}}$ approaches $\sigma_c$. Therefore, as long as $T_{ODT}$ is sufficiently large, the exact value of $T_{ODT}$ employed for calculation does not significantly impact the model fits.
Figure 6.15 Plots showing alignment quality vs. applied stress for PS-PHMA (a) 21-77 and (b) 60-191 using fixed values for the critical stress ($\sigma_c$) and alignment rate constant ($\Gamma$). Curves illustrate the model predictions for various values of $T_{ODT}$, while the open symbols indicate experimental data (reproduced from Figure 6.3a for 21-77 and Figure 6.8c for 60-191).
Figure 6.16 Plots showing best-fit values of the critical stress (a) and alignment rate constant (b) as functions of $T_{ODT}$ for PS-PHMA 21-77 (black squares) and 60-191 (red circles). Error bars indicate ± one standard deviation of the model fit.

Unfortunately, none of the polymers used in the present study showed a thermally accessible $T_{ODT}$ (as assessed by small-angle X-ray scattering, SAXS) so we must estimate values using previously published studies of PS-PHMA phase behavior. One study by Ruzette et al.\textsuperscript{11} measured the temperature dependence of the Flory-Huggins interaction parameter ($\chi$) between PS and PHMA using a symmetric diblock of molecular weight, $M_n$.
Chapter 6: Progression of Alignment in Thin Films of Cylinder-Forming Block Copolymers upon Shearing

$\chi = 0.035 + 3.93 \text{ [K}/T$. In the above expression, $\chi$ has a minimum value of 0.035, which sets the maximum $M_n$ for which PS-PHMA can have a finite $T_{ODT}$. Their data suggest that for all but one of our polymers $T_{ODT}$ is infinite (PS-PHMA 21-77 is predicted to have a finite, but very large, $T_{ODT} \approx 6000 \text{ K})$. In a more recent study Ahn et al.\textsuperscript{12} examined the phase behavior of PS-PHMA using blends of two slightly longer polymers ($M_n \approx 36-40 \text{ kg/mol}$) and found that $T_{ODT}$ varies linearly for the blends within this range. While the two studies both indicate that $\chi$ is relatively insensitive to temperature (so only a narrow range of molecular weights will yield a measurable $T_{ODT}$) they disagree on how strongly $T_{ODT}$ should scale with molecular weight (i.e., $T_{ODT}^{-1} \sim M_n^{-1}$ vs. $T_{ODT} \sim M_n$). These two studies thus provide a means of bracketing the $T_{ODT}$ of our systems. In both cases one must extrapolate far beyond the measured data (and far beyond the polymers’ decomposition temperatures) to yield estimates for our polymers, so the range of plausible $T_{ODT}$ values is quite large.

Table 6.2 lists the $T_{ODT}$ estimates for our polymers. The PS volume fraction ($f_{PS}$) was calculated using the polymer weight fraction (measured by $^1$H-NMR) and the homopolymer densities at $T = 150 \text{ °C}$ (PS density = 0.998 g/cm$^3$, PHMA density = 0.921 g/cm$^3$).\textsuperscript{28-29} The values for $\chi N$ at $T_{ODT}$ were estimated from a phase diagram\textsuperscript{30} (generated using self-consistent field theory) for a conformationally asymmetric diblock ($a_A/a_B = 1.5$, where $a$ is the statistical segment length),\textsuperscript{31} corresponding roughly to PS-PHMA ($a_{PS}/a_{PHMA} \approx 1.33$).\textsuperscript{32-34} The lower bound $T_{ODT}$ was obtained by rescaling Ahn et al.'s\textsuperscript{12} $T_{ODT}$ vs. $N$ data (for a symmetric diblock) in terms of $T_{ODT}$ vs. $M_n$. To account for compositional ($f_{PS}$) differences among our polymers, we computed $M_{n,\text{effective}}$ by
Chapter 6: Progression of Alignment in Thin Films of Cylinder-Forming Block Copolymers upon Shearing

Table 6.2 $T_{ODT}$ for PS-PHMAs

<table>
<thead>
<tr>
<th>PS-PHMA</th>
<th>$M_n$ [kg/mol]</th>
<th>$f_{PS}$</th>
<th>$(\chi N)_{ODT, PS-PHMA}$</th>
<th>$T_{ODT}$ Lower Bound [K]</th>
<th>$T_{ODT}$ Upper Bound [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>21-77</td>
<td>97.8</td>
<td>0.197</td>
<td>22.3</td>
<td>680</td>
<td>6000</td>
</tr>
<tr>
<td>30-86</td>
<td>116.1</td>
<td>0.245</td>
<td>17.9</td>
<td>1270</td>
<td>$10^6$</td>
</tr>
<tr>
<td>34-77</td>
<td>110.5</td>
<td>0.283</td>
<td>15.3</td>
<td>1480</td>
<td>$10^6$</td>
</tr>
<tr>
<td>48-88</td>
<td>135.6</td>
<td>0.332</td>
<td>13.3</td>
<td>2320</td>
<td>$10^6$</td>
</tr>
<tr>
<td>31-108</td>
<td>130.7</td>
<td>0.207</td>
<td>21.2</td>
<td>1180</td>
<td>$10^6$</td>
</tr>
<tr>
<td>60-191</td>
<td>251.2</td>
<td>0.226</td>
<td>19.2</td>
<td>3130</td>
<td>$10^6$</td>
</tr>
<tr>
<td>87-256</td>
<td>343.7</td>
<td>0.235</td>
<td>18.4</td>
<td>4720</td>
<td>$10^6$</td>
</tr>
<tr>
<td>13-30</td>
<td>42.9</td>
<td>0.283</td>
<td>15.2</td>
<td>220</td>
<td>210</td>
</tr>
<tr>
<td>13-47</td>
<td>59.8</td>
<td>0.203</td>
<td>21.6</td>
<td>230</td>
<td>180</td>
</tr>
</tbody>
</table>

* $T_{ODT}$ upper bound is infinite; this limit is approximated using an arbitrary large value (see justification above)

Multiplying $M_n$ by the ratio of $(\chi N)_{ODT, ref}$ to $(\chi N)_{ODT, PS-PHMA}$, where the reference $(\chi N)_{ODT}$ is that for a symmetric diblock (using the same phase diagram mentioned above). The upper bound $T_{ODT}$ is estimated using the relationship for $\chi$ measured by Ruzette et al. and solving for the temperature at which $(\chi N) = (\chi N)_{ODT, PS-PHMA}$. In the cases where the upper bound $T_{ODT}$ is predicted to be infinite (all PS-PHMA diblocks but 21-77) we assign it a large, arbitrary value of $10^6$ K (as discussed above and shown in Figure 6.15, at this value of $T_{ODT}$, the fits are essentially independent of $T_{ODT}$).

In addition to the polymers used in the shear alignment study, two additional PS-PHMA diblocks, 13-30 and 13-47 (listed at the bottom of Table 6.2), were synthesized using identical methods. Both of these polymers were found by SAXS to be disordered in the melt. Examination of these polymers by AFM shows some microphase separation, but no long-range order, indicating that the features are compositional fluctuations which have vitrified (see Figure 6.17 for a representative image). This observation was
supported by our unsuccessful attempts to shear align these materials; upon shearing, no alignment is seen and the short, disordered domains evident in Figure 6.17 persist. Estimates of the $T_{ODT}$ values of these materials (using the methods described above) are consistent with our observations and indicate that at room temperature (and especially at the shearing temperature) both materials should be disordered.

Using the estimated upper and lower bounds for $T_{ODT}$ listed in Table 6.2, we compute the corresponding $\sigma_c$ and $\Gamma$ values for our polymers. Figure 6.18 shows the impact that choice of $T_{ODT}$ has on the scaling of $\sigma_c$ and $\Gamma$ with composition and molecular weight. In general, the differences between the upper and lower bound parameter values are within the uncertainty ($\pm 2$ standard deviations) of the model fit, indicating that for both estimates $T_{ODT}$ is sufficiently large such that the precise choice of its value does not significantly impact the results. The only polymer which does not fall into this category is

Figure 6.17 AFM phase micrograph of PS-PHMA 13-30. Scale bar indicates 250 nm.
Figure 6.18 Plots showing the spread in model parameter values generated with the lower (solid triangles) and upper (open diamonds) bound estimates for $T_{ODT}$ (values listed in Table 6.2): (a) critical stress and (b) logarithm of the alignment rate constant vs. weight fraction of PS, (c) critical stress vs. $M_n$, and (d) alignment rate constant vs. $M_n$ on a log-log scale. Error bars indicate ± one standard deviation in the model fit.
PS-PHMA 21-77, whose spread in $\sigma_c$ (though not in $\Gamma$) is greater than the fit uncertainty ($\sim 4 \times$ the standard deviation of the fit). This correspondingly leads to differences in the slopes of the scaling relations presented in Figure 6.9 (see Table 6.3), although these differences are still modest: within either one ($\Gamma$) or two ($\sigma_c$) standard deviations of the linear-fit uncertainty.

Therefore, from the above analysis we are confident that despite the uncertainty in assigning $T_{ODT}$ values to these polymers, for which $T_{ODT}$ cannot be measured directly, the ultimate significance of this assignment for the parameters extracted from the model fits is modest, due to the very large values of $T_{ODT}$. In situations where this is not the case (i.e., polymers whose $T_{ODT}$ values are in reasonable proximity to the shearing temperature, $T_{ODT}/T < 2$), a better estimate (or preferably a direct measurement) of $T_{ODT}$ would be needed to accurately determine $\sigma_c$ and $\Gamma$. For the purposes of the present work, we chose to employ the upper bound $T_{ODT}$ values listed in Table 6.2 to generate the fits shown in this chapter.

**Table 6.3** $\sigma_c$ and $\Gamma$ Scalings with $M_n$

<table>
<thead>
<tr>
<th>$T_{ODT}$ limit</th>
<th>Slope of $\sigma_c$ vs. $M_n$ [Pa*mol/kg]</th>
<th>Slope of $\log_{10}(\Gamma)$ vs. $\log_{10}(M_n)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>lower limit</td>
<td>$8.1 \pm 1.8$</td>
<td>$-4.8 \pm 0.8$</td>
</tr>
<tr>
<td>upper limit</td>
<td>$11.3 \pm 1.5$</td>
<td>$-4.3 \pm 0.9$</td>
</tr>
</tbody>
</table>

* ± indicates 1 standard deviation in the best fit
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6.7 Viscosity of PS-PHMA Thin Films

Throughout this work, the magnitude of shear stress imparted at the surface of the polymer film has acted as the control variable upon which alignment quality depends. This choice was made primarily out of convenience; the imparted stress is easy to control and precisely vary. However, it is possible that stress is not the only (or even most important) aspect of the applied shear which dictates alignment. Instead, factors such as the strain or strain rate may be the controlling variable. Unfortunately, these are not generally practical to measure or apply to the film in a controlled way. To probe these variables, a series of experiments which attempt to directly measure the strain rate and viscosity of a PS-PHMA thin film were performed and compared to simulations performed by Nikoubashman. For this we employed the pad shearing approach discussed previously and used predominantly in Chapter 5. Polymer films were sheared via the pad shearing technique at $T = 185 \, ^\circ C$. After some time (typically between 1 min and several hours) the shear stress was removed and the translation of the pad ($\sim 1-10$ mm) measured using an optical microscope (which is attached to the ellipsometer) with a stage capable of $\pm 10 \, \mu m$ lateral movement. The apparent shear rate was then computed using the distance of translation, the film thickness, and the time of applied shear.

To validate this approach, the shear viscosity of thin films of three PS homopolymers with $M_w = 17.5, 23.8,$ and $47.5 \, kg/mol$ was measured (by dividing the applied stress by the apparent shear rate). The film thickness was $t = 100 \, nm$ (thick enough that the film results could reasonably be compared to bulk measurements of PS viscosity), and the applied shear was well below the onset of shear-thinning in all cases. Zero-shear viscosities of $\eta_0 = 105, 242,$ and $3443 \, Pa \cdot s$ (each $\sim \pm 15\%$) were measured;
these are in very good agreement with the corresponding literature values of $\eta_0 = 105, 313, \text{ and } 3725 \text{ Pa}\cdot\text{s}$.\(^{39}\) Thus, we can conclude that the applied pad shearing method can be employed for measuring the (apparent) shear viscosity of thin polymer melts.

The shear rate of a monolayer ($t = 28 \text{ nm}$) of PS-PHMA 21-77 was then measured using a variety of applied shear stresses (see Figure 6.19) and compared with simulations by Nikoubashman \textit{et al.}\(^{36}\) The curves represent the best fits of the data to:

$$\sigma = \eta_{\text{apparent}} \dot{\gamma}^\kappa$$

\textbf{Equation 6.7}

where $\eta_{\text{apparent}}$ is the apparent shear viscosity, and $\kappa$ is a dimensionless index which characterizes the degree of shear thinning in the fluid. The experiments and simulations are in reasonable quantitative agreement ($\eta_{\text{apparent}} = 210 \text{ Pa}\cdot\text{s}^\kappa$ for the experiments, $\eta_{\text{apparent}} = 500 \text{ Pa}\cdot\text{s}^\kappa$ for the simulations) and both display similar shear thinning behavior ($\kappa = 0.9$). The nearly Newtonian response may seem surprising, but in fact a similar nearly Newtonian behavior has previously been reported for cylinder-forming triblock copolymer films in bulk measured via capillary rheometry,\(^{40-41}\) over a comparable range of shear rates. The sources for the discrepancy between the experiments and simulations are uncertain, but are discussed by Nikoubashman.\(^{36}\) One obvious concern is the unknown degree of slip between the PS-PHMA film and the PDMS pad. Slip would lead to larger displacement of the pad, effectively lowering the measured apparent viscosity; if slip were the primary culprit, the true film viscosity would be larger, making the experiments more consistent with the simulations.

It is conceivable that the apparent viscosities for films which are aligned, nonaligned, or anti-aligned may be different. Unfortunately, we could not probe this effect using the present technique as the films align in the direction of shear almost
Figure 6.19 Plot of shear stress vs. shear rate for a monolayer of PS-PHMA 21-77. The experimental results (black x) are compared to simulations\(^{36}\) (red crosses). Error bars indicate ± 1 standard deviation in the measured shear rate.

immediately (we must use high temperatures and large stresses to observe measurable displacements, which in turn dramatically increases the rate of alignment). Therefore, during the majority of the experiment, we measure the viscosity of aligned cylinders, regardless of the film’s initial condition, so the contribution of any misalignment during the beginning of the experiment becomes negligible. We confirmed this by comparing the apparent viscosity of films which were pre-aligned in the shear direction, pre-aligned orthogonal to the shear direction, and nonaligned, and found that they all exhibited the same apparent viscosity.
The viscosity of a PS-PHMA 21-77 monolayer was compared to that for a bilayer and 5-layer film. All of the films displayed the same measured viscosity within the measurement uncertainty. This is consistent with the findings reported in Chapter 6.5, which showed that the alignment rate constant (which is likely related to the apparent viscosity) is independent of number of cylinder layers.

6.8 Conclusions

In cylinder-forming PS-PHMA thin films, the cylinders retain their initial polygrain structure at low applied shear stresses, but with increased stress the cylinders transition from a nonaligned to a highly aligned state. The stress at which this transition occurs, as well as its breadth, is strongly dependent on the material properties of the block copolymer studied. All of the experiments were compared to a melting-recrystallization model through which two alignment parameters, a critical stress and an alignment rate constant, are extracted to provide a quantitative means of comparing across experiments. The critical stress needed to induce alignment increases linearly with PS weight fraction and overall block copolymer molecular weight; conversely, the rate of alignment dramatically decreases, with an especially strong dependence on molecular weight ($\Gamma \propto M_n^{-4.3 \pm 0.9}$). To confirm that the dramatic differences in the breadth of the nonaligned-to-aligned transition between different polymers were due to their substantial differences in $\Gamma$, select films were sheared identically, but for varying shear durations; the time dependence of the shear response was well reproduced by the model. Combining the model equations with the measured scaling rules for the model parameters thus provides an avenue for predicting alignment response for a given material under a specified set of
shear conditions. In addition to the material properties discussed above, the effect of film properties (film thickness/number of cylinder layers, substrate wetting condition) were also assessed. The critical stress needed to induce alignment decreases with an increasing number of cylinder layers and reaches a plateau value at ~ 5 layers thick. Interestingly, the alignment rate constant, which is highly sensitive to block copolymer composition and molecular weight, shows no measurable dependence on film thickness. In addition, neither the block copolymer wetting condition, nor the penetrability of the substrate surface, was found to have a measurable impact on either $\sigma_c$ or $\Gamma$. Moving forward, it would be interesting to see how the scaling trends observed here could suggest modification to the shearing process to permit very rapid shear-alignment of thin films of properly-designed polymers. In addition, similar studies using other common block copolymer morphologies which are of interest to the nanolithography community (notably sphere- and lamellae-forming systems) might provide additional insight into the mechanisms underpinning shear alignment in block copolymer thin films.
6.9 References


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Chapter 7: Coatings with Thermally Switchable Surface Energy Produced from PEO-PDMS Block Copolymer Films

Chapter 7

Coatings with Thermally Switchable Surface Energy Produced from PEO-PDMS Block Copolymer Films

7.1 Introduction

Materials and coatings with tunable and/or switchable properties are of broad interest, with potential applications including drug delivery, biosensors, and “smart” textiles. Typically, these materials alter their physical conformations or properties in response to changes in external stimuli or the local environment (e.g., temperature, pH, or mechanical deformation), which act as the property “switch”. Polymers are excellent candidates for such switchable materials as simple changes in the chain length (molecular weight), composition, or architecture can lead to dramatic differences in their responses to specific stimuli. Introducing chemical heterogeneity into the polymer chains provides a powerful design tool by which functional coatings, with tunable surface properties (e.g., wettability, adhesion), can be realized. Recently, great effort has been undertaken to synthesize polymeric coatings whose wetting behavior (i.e., hydrophilic vs. hydrophobic) can be manipulated. Much of this work utilizes heterogeneous polymer brush layers which have been chemically grafted to an underlying substrate. Motornov et al. grafted
mixtures of two liquid polymers, one hydrophilic and one hydrophobic, onto substrates to produce textured, hybrid brush layers whose wetting behavior switched between hydrophobic and hydrophilic states when exposed to air and water, respectively.\(^4\) They attributed this responsive behavior to local rearrangements of the grafted polymers, enabled by the brush’s liquid-like state, such that the chains which produce the lowest interfacial energy present themselves at the coating’s surface. Block copolymers have been employed to produce similar surfaces.\(^7\)\(^-\)\(^11\) Mori \textit{et al.}\(^8\) and later Senshu \textit{et al.}\(^9\) demonstrated that as-cast films (or films thermally annealed in air) of various amphiphilic block copolymers were hydrophobic, but that upon exposure to water, the hydrophobicity quickly decayed as the hydrophilic chains emerged. Upon re-annealing in air (above the glass transition temperatures, \(T_g\), of all the blocks), the coating reverted to its hydrophobic state, although the transitions were not completely reversible, and the hydrophilic-to-hydrophobic transition was slow.

In the above approaches, the environment (air \textit{vs.} water) acts as the stimulus, with the surface rearranging accordingly. However, it is often advantageous for the property “switch” which controls surface composition to be orthogonal to changes in the use environment (\textit{i.e.,} to set the material’s wetting behavior independently of the environment in which it is used). An example of this approach was demonstrated by Zhang \textit{et al.}, who synthesized linear ABC triblock copolymers, where the homopolymers of the three distinct constituent blocks cover a modest range of wettabilities (water contact angles, CA, ranging from 75° - 93°). They showed that the measured CA of the film’s surface could be switched over a limited range, between 89° and 96°, simply by quenching from
different annealing temperatures, where different blocks presented themselves at the surface.\textsuperscript{11}

In the present work, we demonstrate an alternate approach for producing polymer coatings with thermally switchable surface energies, using amphiphilic block copolymers with a modest order-disorder transition temperature, $T_{ODT}$, which acts as the property switch. Above $T_{ODT}$, a block copolymer film exists as a disordered, homogeneous melt, but upon cooling to ambient temperature, the $T_{ODT}$ is crossed, causing the polymer melt to self-assemble into periodic nanostructures.\textsuperscript{12} The block which wets the polymer-air interface can be controlled by manipulating the humidity of the film’s environment while annealing (above $T_{ODT}$) and during the subsequent cooling step (\textit{i.e.}, when cooled in dry air the hydrophobic block presents itself at the surface, when cooled in humid air the hydrophilic block wets). Ideally, crossing the $T_{ODT}$ should “lock in” the film’s morphology, and therefore wetting behavior. The coating can be repeatedly reprocessed simply by reheating and cooling through the film’s $T_{ODT}$, thus erasing its previously “set” wetting behavior (see Figure 7.1 for a schematic of the proposed switching process). This approach should enable fast and reversible switching. It could even be employed to achieve patterned, local control of the wetting behavior via a resistive heating array incorporated into the substrate,\textsuperscript{13} which would make these coatings of interest for electronically reconfigurable printing plates compatible with digital-direct and digital-offset lithography.\textsuperscript{14}

We explore a route towards such coatings based on block copolymers of poly(ethylene oxide) (PEO) and poly(dimethylsiloxane) (PDMS). PEO and PDMS serve as model hydrophilic and hydrophobic polymers, respectively, that are widely available.
Figure 7.1 Schematic illustrating the concept of thermally switchable coatings enabled by block copolymer self-assembly. (a) At sufficiently high temperatures, the block copolymer coating is in a disordered, homogeneous state (purple). (b) Upon cooling below $T_{ODT}$ in ambient air, the block copolymer microphase-separates, yielding alternating lamellae with the hydrophobic block (red) wetting the air interface. (c) This pattern can be erased upon reheating above $T_{ODT}$ and then (d) reset with the hydrophilic block (blue) exposed at the surface upon cooling below $T_{ODT}$ in humid air.
and whose properties have been extensively studied. Recently, PEO-PDMS block copolymers have been examined as vehicles for hydrophobic drug delivery and have been incorporated into comb-like brushes (similar to those described above) to create coatings with adaptive adhesive properties. In addition, the bulk and solution phase behavior of PEO-PDMS block copolymers has been previously investigated. Due to the strong chemical incompatibility between the blocks, these materials will microphase-separate even at very low molecular weights. Therefore PEO-PDMS block copolymers are strong candidate materials for the present application: accessible $T_{ODT}$ (<100 °C) at low molecular weight (and therefore low melt viscosity, enabling fast “switching” kinetics), and the desired hydrophilic/hydrophobic character.

7.2 PEO-PDMS Synthesis

Low molecular weight PEO-PDMS block copolymers were synthesized via Pt-catalyzed hydrosilation coupling of end-functionalized oligomers. All of the polymers used in this study were monofunctional, thus their coupling yielded diblocks. $\alpha,\omega$-allyl,methyl-ended PEO oligomers were generously provided by Clariant. The two PEO oligomers used in this study (AM1100 and AM450, hereafter denoted PEO$_{1.2}$ and PEO$_{0.5}$; the subscripts indicate the block molecular weights in kg/mol) were measured to have number-average molecular weights, $M_n$, of 1170 and 460 g/mol, and dispersities, $D$, of 1.09 and 1.25, respectively. Monohydride-ended PDMS was purchased from Gelest (MCR-H11, hereafter PDMS$_{1.3}$) with measured $M_n = 1320$ g/mol and $D = 1.19$. $M_n$ was determined by end group analysis, via $^1$H-NMR spectroscopy in CDCl$_3$ (see Figures 7.2 and 7.3). $D$ was measured using size-exclusion chromatography (SEC). PEO and the
Figure 7.2 $^1$H-NMR spectrum of PEO$_{1.2}$ in CDCl$_3$ with different proton types labeled.

Molecular weight calculated as follows: 

$$\frac{\text{Peak}_1 + \text{Peak}_2}{\text{Peak}_3 + \text{Peak}_4 + \text{Peak}_5} = \frac{3}{5 + 4N}$$

solving gives $N = 25.0$. The number-average molecular weight ($M_n$) is calculated by adding the mass of the end groups to $m$ times the repeat unit molecular weight; this yields $M_n = 1170$ g/mol.
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Figure 7.3 $^1$H-NMR spectrum of PDMS$_{1.3}$ in CDCl$_3$ with different proton types labeled.

Molecular weight calculated as follows: 
\[
\frac{\text{Peak}1}{\text{Peak}5 + \text{Peak}6 + \text{Peak}7} = \frac{1}{12 + 6N};
\]

solving gives $N = 15.3$. $M_n$ is calculated by adding the mass of the end groups to $m$ times the repeat unit molecular weight; this yields $M_n = 1320$ g/mol.
diblock copolymer were run in tetrahydrofuran (THF), while PDMS was run in toluene. The separate systems were needed due to the very small refractive index increments for PEO in toluene, and PDMS in THF (see Figure 7.4 for chromatograms of PEO$_{1.2}$ and PDMS$_{1.3}$).

The hydrosilation coupling reaction was catalyzed using a homogeneous organoplatinum Karstedt’s catalyst purchased from United Chemical Technologies (PC072, 2 wt. % platinum-divinyltetramethyl disiloxane complex in xylene). To synthesize the diblocks, PEO and PDMS were dissolved in toluene (ACS grade, purchased from EMD) at ~ 20 wt. % solids; the PEO was added at ~ 30% stoichiometric excess to ensure that all of the hydride end groups reacted to completion. The catalyst was added at a 1:5,000 molar ratio of Pt-complex to silane (Si-H) groups. The reaction proceeded overnight at room temperature and its completion was confirmed via $^1$H-NMR (when the Si-H peak, ~ 4.5-4.7 ppm, became undetectable). The excess unreacted PEO was removed via repeated washing (3-5 times) of the reaction mixture with water; the PEO homopolymer is preferentially extracted into the dense aqueous phase, while the diblock creates a water-toluene emulsion. Once the unreacted PEO becomes undetectable (by SEC, see Figure 7.4), the purified block copolymer is collected by removing the solvents from the emulsion (first under flowing N$_2$, then under vacuum). Two block copolymers, PEO$_{1.2}$-PDMS$_{1.3}$ (a waxy solid at room temperature) and PEO$_{0.5}$-PDMS$_{1.3}$ (liquid at room temperature), synthesized by this method were used in this study (chromatographs of PEO$_{1.2}$-PDMS$_{1.3}$ and its constituent oligomers are shown in Figure 7.4).
Figure 7.4 Size-exclusion chromatographs (plotting differential refractive index vs. polystyrene-equivalent molecular weight) showing the molecular weight distributions for the precursor oligomers PEO\textsubscript{1.2} (blue), PDMS\textsubscript{1.3} (red), and the final, fractionated, PEO\textsubscript{1.2}-PDMS\textsubscript{1.3} diblock copolymer (purple).
7.3 Bulk PEO-PDMS Characterization by SAXS

The bulk phase behavior of the two PEO-PDMS block copolymers was assessed via one-dimensional small-angle X-ray scattering (SAXS). At room temperature, PEO<sub>0.5</sub>-PDMS<sub>1.3</sub> showed no peak in the SAXS pattern, indicating that it forms a disordered melt. However, PEO<sub>1.2</sub>-PDMS<sub>1.3</sub> displayed two peaks at room temperature: a broad peak centered around \( q' \approx 0.5 \text{ nm}^{-1} \) and a relatively narrow peak at \( q^* = 0.82 \text{ nm}^{-1} \) (see Figure 7.5a). Upon heating to 50 °C, the peak at \( q' \) completely vanishes, indicating that this peak corresponds to scattering from semicrystalline material (differential scanning calorimetry shows that the melting temperature, \( T_m \), for the precursor PEO<sub>1.2</sub> oligomer is \( \sim 35 \) °C). Upon heating to 64 °C, the \( q^* \) peak broadens and drops in intensity (see Figure 7.5b, c), indicating \( T_{ODT} = 64 \pm 2 \) °C. Below \( T_{ODT} \), PEO<sub>1.2</sub>-PDMS<sub>1.3</sub> is microphase-separated with a characteristic domain spacing \( d = 7.7 \text{ nm} \) (where \( d = 2\pi/q^* \)); given the near-symmetric composition of the copolymer (volume fraction \( f_{PEO} = 0.43 \) at 70 °C, based on homopolymer densities\(^{25} \), PEO density = 1.093 g/cm\(^3\), PDMS density = 0.922 g/cm\(^3\)), the microdomains are likely alternating lamellae, although no higher-order peaks were observed in the SAXS pattern. The value of \( T_{ODT} \) can also be continuously tuned by blending small amounts of PEO<sub>0.5</sub>-PDMS<sub>1.3</sub> into PEO<sub>1.2</sub>-PDMS<sub>1.3</sub> (see Figure 7.5d); the blends were produced simply by co-dissolving the polymers and casting from toluene. Since \( f_{PEO} < 0.5 \) in PEO<sub>1.2</sub>-PDMS<sub>1.3</sub>, and is even smaller in PEO<sub>0.5</sub>-PDMS<sub>1.3</sub> (\( f_{PEO} = 0.23 \)), small additions of PEO<sub>0.5</sub>-PDMS<sub>1.3</sub> depress \( T_{ODT} \) significantly.
Figure 7.5 Plots showing the phase behavior of PEO$_{1.2}$-PDMS$_{1.3}$ as probed via small-angle x-ray scattering (SAXS). (a) Held at room temperature (~19 °C, solid curve) overnight (allowing for PEO crystallization) and 50 °C (above $T_m$) for 15 minutes. The patterns indicate that at room temperature there is a coexistence of both smaller-period ($q^* = 0.82$ nm$^{-1}$, microphase-separated melt) and larger-period ($q' \approx 0.5$ nm$^{-1}$, semicrystalline solid) microdomain structures. (b) SAXS patterns as a function of temperature (above $T_m$) reveal a transition from an ordered structure (with a domain spacing of 7.7 nm) to a disordered melt. (c) $T_{ODT}$ is determined as the temperature at which there is a sharp decrease in peak intensity (open squares) and a corresponding increase in the peak width at half the maximum intensity (blue circles); $T_{ODT} = 64 \pm 2$ °C. (d) $T_{ODT}$ can be tuned via blending with a modest fraction of PEO$_{0.5}$-PDMS$_{1.3}$. 
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7.4 Film Preparation and Switchable Wettability

Films of PEO$_{1.2}$-PDMS$_{1.3}$ were prepared both by drop-casting concentrated solutions of the polymer (~20 wt. % in toluene) and by simple melting at 100 °C onto Si wafers (with native oxide, liberally rinsed with toluene prior to use). Both methods yielded relatively thick films (~40-80 μm, assessed by cross-sectional optical microscopy); such thick samples prevent the polymer from dewetting and eliminate any influence of the substrate on the film’s surface morphology. To control the wetting behavior of these films, the samples were placed on a hot plate and heated to 80 °C (well above the polymer’s $T_{ODT}$) and held for 15 minutes. To prepare a hydrophobic surface, the film was cooled in ambient air to room temperature (~19 °C) at ~10 °C/min; annealing and cooling the film under vacuum also produces hydrophobicity. For a hydrophilic coating, the film is similarly annealed at 80 °C for 15 min and cooled to room temperature, but in a humidified atmosphere. The saturated water vapor environment is produced by placing a small reservoir of liquid water onto the hot plate adjacent to the film and covering both with an inverted crystallization dish (effectively a “bell jar” style solvent vapor anneal$^{26}$, see Figure 7.6).

After cooling to room temperature, the films are allowed to rest, in ambient air, for 10 minutes and then their static water contact angle (CA) values are measured. Films of the precursor PEO$_{1.2}$ and PDMS$_{1.3}$ oligomers had CA values of 35 ± 6° and 98 ± 2°, respectively (± indicates one standard deviation in the values measured for 3 or more separately prepared samples), comparable to literature values.$^{27-28}$ PEO$_{1.2}$-PDMS$_{1.3}$ films prepared in ambient air possessed a CA = 91 ± 2° (see Figure 7.7a), while films prepared in humidified air displayed CA = 36 ± 5° (Figure 7.7b). This result is consistent with our
Figure 7.6 Schematic of annealing setup to produce (left) hydrophobic films by annealing in ambient air and (right) hydrophilic films by annealing in humidified air.

The proposed scheme in Figure 7.1, where PDMS domains form at the surface upon cooling through $T_{ODT}$ in ambient air, while PEO domains cover the surface when cooling through $T_{ODT}$ in humidified air, even after removal from the humid environment. To test the reversibility of the film surface energy upon cycling, a hydrophilically prepared film was reannealed under ambient conditions and its CA measured to be $90 \pm 2^\circ$ (see Figure 7.7c, $\pm$ indicates one standard deviation in the values measured on 3 or more spots along the same sample); this shows that the initial hydrophilicity of the coating has been completely erased and that the wetting behavior can be easily reset. This switching behavior was demonstrated over multiple cycles (see Figure 7.7d); the film showed no signs of degradation or loss of hydrophobic/philic properties over the range investigated.
Despite this demonstration that the wetting behavior of these materials can be easily set and reversibly switched, the wetting behaviors observed were only transiently stable at room temperature. When exposed to water, the CA values of the hydrophobically-prepared films decayed from $\approx 90^\circ$ to $\approx 40 - 60^\circ$ over the course of
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minutes (see Figure 7.8), due to rearrangement of the polymer chains at the surface induced by the sessile water droplet. This rapid rearrangement to a hydrophilic state is consistent with previously examined amphiphilic block copolymer films.\(^8\)\(^9\) Mori et al. observed that as-cast films of low-\(T_g\) block copolymers showed an immediate (within a few seconds) reduction in their CA when exposed to water; annealing the films created somewhat more stable coatings, but even these lost their hydrophobicity within minutes.\(^8\) The rearrangement times of our materials seem consistent with the latter preparation, whose increased stability (compared to the as-cast films) can be attributed to the greater degree of ordering (and therefore enrichment of hydrophobic blocks at the surface). In addition, similar to the findings of Mori et al.,\(^8\) we observe that the converse rearrangement, from hydrophilic back to a hydrophobic state (by simply allowing the film to rest for a prolonged time in ambient air) is much slower; after ~1 day, the CA for \(\text{PEO}_{1.2}-\text{PDMS}_{1.3}\) increases by only ~5-10°.

Interestingly, the rate and terminal value of the CA decay were dependent on the films’ thermal history. Films which were “freshly prepared”, as described above, lost their hydrophobicity more quickly, and after ~5 min displayed CA values consistent with the hydrophilically-prepared films. Films which were allowed to sit overnight at room temperature, or which were more deeply cooled (placed in a -10 °C freezer for 15 min), did not show as rapid a CA reduction, nor did the CA decay to as low a value. The primary difference between these film preparations is the degree of crystallinity present in the PEO block. Freshly prepared films possess undetectable crystallinity (as determined below); however, given sufficient time, or subambient cooling, the PEO blocks crystallize. These crystals likely act as physical crosslinks which retard the chain
Figure 7.8 Plot showing water contact angle (CA) as a function of time for a hydrophobic film cooled to and held at room temperature (red circles), and one cooled to -10 °C for 15 min and reheated to room temperature (orange squares). Also shown for reference is a hydrophilic film (blue triangle) which shows no change in CA over time. (a-f) Representative images showing the evolution of CA with time for both hydrophobic film preparations; corresponding time points are indicated on main figure.
rearrangements; however, they cannot eliminate them completely, given PEO’s solubility in water.

7.5 Crystallinity in PEO-PDMS Films

The presence of PEO crystals in films of PEO$_{1.2}$-PDMS$_{1.3}$ was confirmed via one-dimensional wide-angle X-ray scattering (WAXS, see Figure 7.9). The samples were prepared by melting thick films (~ 0.5 mm) at 80 °C onto silica substrates (Fisher precleaned microscope slides), cooling to room temperature (~ 10 °C/min), and annealing at a fixed temperature and time. After ten minutes of annealing at 19 °C, no crystallinity (only amorphous scattering) is observed. After 1 hour at 19 °C, two peaks, one at 19.1° and the other at 23.2° in $2\theta$, become visible, indicating the growth of crystals in the film. These peaks continue to grow with time and saturate in intensity after 1.5 days at room temperature. Annealing at -10 °C produces similar results, but with accelerated kinetics (the peaks reach their maximum intensity after 1 hour). To confirm that the crystallinity is due to PEO, a thick film of the PEO$_{1.2}$ oligomer was measured after annealing at room temperature for 2 days (pattern shown in the inset in Figure 7.9). The peak positions perfectly match those of the block copolymer and are consistent with those previously reported for PEO.$^{29}$
Figure 7.9 1D-WAXS patterns (scattered intensity vs. scattering angle $2\theta$) of PEO$_{1.2}$-PDMS$_{1.3}$ which has been “freshly prepared” (10 min, green curve), or fully crystallized (1.5 days at room temperature, red curve). The inset shows the pattern for the PEO$_{1.2}$ oligomer. The common features indicate that the crystallinity is from the PEO block.
To gain further insight into the crystallization kinetics of PEO$_{1.2}$-PDMS$_{1.3}$, isothermal crystallization experiments were performed via differential scanning calorimetry (DSC, see Figure 7.10). A freshly prepared sample held at room temperature possesses no detectable PEO crystallinity during the first 10 minutes, but subsequently crystallizes, saturating to ~ 15% overall crystallinity after 2 hours. A film cooled to -10 °C, however, immediately crystallizes (<1 min) to a level comparable to the film held at room temperature for 2 hours or more. Thus, chain rearrangement at room temperature can be slowed during the initial “setting” process by cooling from above $T_{ODT}$ to -10 °C to induce crystallization, followed by reheating to room temperature. The same experiment (isothermally annealing at 19 °C for long times) was performed on the PEO$_{1.2}$ homopolymer which was measured to have a maximum enthalpy of fusion, $\Delta H_{fus} = 99.6$ J/g; the $\Delta H_{fus}$ for 100% crystalline PEO$^{30}$ is 197 J/g, thus the PEO$_{1.2}$ homopolymer has a degree of crystallinity of ~ 51%. When annealed for long times, the PEO$_{1.2}$-PDMS$_{1.3}$ block copolymer possesses a degree of crystallinity of ~15% (or 30% of the PEO block), much less than observed for the PEO homopolymer.
Figure 7.10 Differential scanning calorimetry thermograms (on heating) for PEO₁₂-PDMS₁₃ which has been isothermally crystallized at (a) 19 °C and (b) -10 °C for various durations. The increasing degree of crystallinity in the block copolymer upon annealing is reflected by the area of the melting endotherm.
7.6 Conclusions

We have shown that coatings with thermally switchable wetting properties (hydrophobic vs. hydrophilic) can be achieved using low molecular weight PEO-PDMS block copolymers, readily synthesized via coupling of commercially available end-functionalized oligomers. Heating above the polymer’s $T_{ODT}$ erases the material’s nanostructure, and subsequent cooling in the presence of dry or wet air creates a hydrophobic or hydrophilic surface, respectively. Static contact angle measurements demonstrated the efficacy and complete reversibility of the method. The primary limitation of this material is the residual chain mobility present at ambient conditions, which allows the domains to reorganize within minutes when exposed to water, causing the initial hydrophobic character to decay; these rearrangements can be retarded, but not eliminated, by crystallization of the PEO block. While this study has demonstrated proof of concept, practical application of such materials would be better enabled if the wetting behavior could be more effectively “locked in.” One approach would be to employ at least one glass-forming block, with $T_{room} < T_g < T_{ODT}$; upon cooling, the block copolymer will first order and then vitrify, more effectively preserving the film structure, although even this may not completely eliminate rearrangement. A good candidate material for the hydrophobic block might be a high-$T_g$ polysiloxane (e.g., poly(diphenylsiloxane), $T_g = 40 \, ^\circ C$), whose similar chemistry to PDMS would make it compatible with the synthetic approach employed here.
7.7 References


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Chapter 8

Conclusions and Future Work

8.1 Dissertation Summary

To meet the relentless demands for continued miniaturization of feature sizes for device fabrication and materials design, a multitude of techniques are being developed. Block copolymers, due to their ability to self-assemble at the relevant nanoscale feature sizes, are particularly attractive as candidate templates for nanolithographic processes. As such, the development of techniques which can order and manipulate the microdomains within block copolymer thin films is an area of intense and diverse study. The goals of this dissertation were to explore approaches to better control block copolymer thin film morphology, with the ultimate goal of increasing the efficacy of these materials for use in nanolithography or specialty coatings.

Chapter 4 discussed a comprehensive analysis of the flowcoating technique used to generate polymer thin films which possess a thickness gradient. Numerous films were produced using a variety of polymer solutions and coating settings, and the film thicknesses were compared to a known fluid mechanics model. We found that the film thickness, \( t \), is governed by Landau-Levich flow (\( t \sim Ca^{2/3} \), where \( Ca \) is the capillary number) and is proportional to a characteristic length scale (the rear meniscus height). The measured film thicknesses were in excellent quantitative agreement with those predicted by the model over a wide range of operating conditions. However, deviations from the model were observed as the evaporation-driven coating regime was approached.
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\((Ca < 10^{-4})\). This study culminated in a design equation which can be used to create polymer films with programmed thickness profiles (e.g., precise step changes, linear gradients). Collectively, these results provide both greater understanding of the principles which govern flowcoating and greater control of the polymer films which can be created with the device. This will enable more widespread use of this technique, especially for studies which can leverage the high-throughput potential offered by thickness-gradient films.

In Chapter 5, we examined the dependence of microdomain orientation (both in-vs. out-of-plane orientation for nonaligned films, and quality of in-plane alignment for sheared films) on film thickness (through application of the flowcoating technique discussed in Chapter 4) using a series of cylinder-forming polystyrene-poly(n-hexyl methacrylate) (PS-PHMA) block copolymers. These polymers are useful for pattern transfer, but their thin film morphologies have proven difficult to control due to the ambiguity in the films’ preferred monolayer thicknesses. To probe these thickness effects, as well as the effects of block copolymer composition and molecular weight, a series of PS-PHMAs were anionically-synthesized, gradient thickness films were produced, and their thin film morphology accessed via atomic force microscopy (AFM). In general, nonsheared films of these polymers at incommensurate thicknesses did not terrace, but the PS-PHMA with the lowest polystyrene weight fraction \((w_{PS})\) did display pseudo-terracing (height variations corresponding to ~ \(\frac{1}{2}\) a cylinder layer spacing). All of the polymers displayed a pre-shear morphological dependence that was sensitive to film thickness such that in the vicinity of a monolayer, or integer-multiple thereof, the cylinders oriented in-plane, while at incommensurate thicknesses the cylinders oriented
out-of-plane. This effect became increasingly mitigated (i.e., the morphology became independent of film thickness) as $w_{ps}$ or number-average molecular weight ($M_n$) increased, which stabilized either the in- or out-of-plane orientation, respectively. Upon application of shear (using sufficiently large stress to induce alignment across the entire sheared area) via the pad shearing method, the thicknesses which displayed the highest fractional coverage of in-plane cylinders pre-shear showed the highest quality of alignment post-shear, as measured by an orientational order parameter. In well-aligned films, orientational order was limited by two factors: the presence of isolated dislocations in the microdomain lattice and undulations in the cylinders’ trajectories. Dislocation density increased with greater PS content, while the magnitude of the cylinders’ undulations decreased with increased PS. Therefore, the highest quality of alignment was achieved with polymers whose compositions lie in the middle of the cylinder-forming region.

In Chapter 6, we studied the factors which influence the progression of shear alignment using the same series of cylinder-forming PS-PHMA s studied in Chapter 5 as a model system. Using the rheometer shearing method, which applies a positionally-varying stress gradient (which allows for rapid evaluation of the dependence of alignment quality on applied stress), the influence of certain material ($M_n$, $w_{ps}$), film (number of microdomain layers, substrate conditions), and process (stress, time) parameters on alignment quality were studied. At low stresses, the cylinders retained their initial polygrain structure, but as the stress increased, the cylinders transitioned from their nonaligned to a highly aligned state. The stress needed to induce this transition and the breadth of the transition increased as $w_{ps}$ and $M_n$ increased. To quantitatively compare
across experiments, all data were fit to a melting-recrystallization model which allowed for computation of a critical stress ($\sigma_c$) and alignment rate constant ($\Gamma$). The critical stress for alignment increased linearly with $w_{PS}$ and $M_n$, while the rate constant dramatically decreased. The scaling of $\Gamma$ with $M_n$ was stronger than previously postulated (regular diffusive scaling, $\Gamma \propto M_n^{-2}$), though this may be consistent with the stronger dependence of diffusion on molecular weight predicted for microphase-separated block copolymers.

Time-dependent studies were performed and showed that the seemingly qualitative differences between polymers with sharp vs. gradual nonaligned-to-aligned transitions can be well understood through their substantial, but smoothly varying, differences in $\Gamma$; this time dependence was remarkably well reproduced by the simple phenomenological model. Combining the measured scaling relationships ($\sigma_c$ or $\Gamma$ vs. $w_{PS}$ or $M_n$) with the model equations provides a design rule by which the alignment response of the polymer can be predicted for a given set of shear conditions. The influence of film parameters (film thickness/number of cylinder layers, substrate conditions) on the progression of alignment was also studied. As the number of cylinder layers increased, $\sigma_c$ decreased modestly, while $\Gamma$ remained unchanged (noteworthy, given the exceptionally strong dependence of $\Gamma$ on the material parameters studied). The substrate conditions, namely the preference of PS vs. PHMA to wet the substrate and the difference in penetrability between a “soft” polymer-grafted substrate and a “hard” Si substrate, had no measurable influence on alignment response over the range of conditions investigated. In Chapter 6, simple shear viscosity measurements of PS-PHMA thin films were also performed and compared to simulations.
Chapter 7 presented a study by which film morphology can be manipulated not through changes in film thickness or the application of shear, but by controlling the environmental conditions upon annealing. The goal was to produce coatings with thermally switchable wetting properties (hydrophobic vs. hydrophilic) using low molecular weight amphiphilic poly(ethylene oxide)-poly(dimethylsiloxane) (PEO-PDMS) block copolymers. These materials were synthesized via Pt-catalyzed coupling of commercially available end-functionalized oligomers. Small-angle X-ray scattering experiments on the bulk PEO-PDMS revealed a microphase-separated, presumably lamellar morphology at room temperature and an order-disorder transition temperature, $T_{ODT} = 64 \pm 2 ^\circ C$. Thick films of the PEO-PDMS were produced by melting or drop-casting, and their wetting properties, assessed via their static water contact angle, were measured as a function of thermal history. Heating above the film’s $T_{ODT}$ erased the polymer’s nanostructure, and subsequent cooling in the presence of dry or wet air created a hydrophobic or hydrophilic surface, respectively. This process was completely reversible; the material’s wetting behavior could be reset simply by reheating above the $T_{ODT}$ and re-cooling in the appropriate environment. The primary limitation of this material was its chain mobility at ambient temperature, which allowed the domains to reorganize within minutes when exposed to water, causing the initial hydrophobic character to decay. Increasing the crystallinity of the PEO block, through longer “resting” times or sub-ambient cooling, mitigated this effect, but could not eliminate it entirely, thus limiting this material’s practical application. However, this study did successfully demonstrate proof of concept, and with some modifications (discussed in Chapter 8.2.3)
these materials could provide a viable route towards production of thermally switchable coatings useful for printing applications.

Collectively, these results represent substantial progress in our efforts to better understand the physics of block copolymer films (especially their response to shear) and to better control their thin film morphology. The latter should prove especially important for efforts to employ these materials for production of next-generation nanodevices and polymeric coatings. Of course, despite this progress, there is still much yet to be done. The following is a discussion of some possible future directions for this research.

8.2 Recommendations for Future Work

8.2.1 Universality of Shear Alignment Scaling Trends

The scaling trends observed in Chapter 6 provide a powerful potential route towards the design of materials and processes which might enable either very rapid or highly effective (high order parameter, low lattice defect density) shear alignment of block copolymer thin films. However, while the trends for the present series of PS-PHMA are convincing, it is unclear to what extent these observations are universal; i.e., will the same trends hold for other block copolymer systems? It would be interesting to examine a variety of materials using the same approach employed here: shear a sample via the rheometer method, measure the alignment, fit the melting-recrystallization model to the data, and quantify how $\sigma_c$ and $\Gamma$ vary with $M_n$ and any other relevant parameters. The first systems of study could be PS-cylinder-forming polymers of other rubbery-matrix-block chemistries, e.g., polystyrene-poly(ethylene-alt-propylene) (PS-PEP) or polystyrene-poly(2-ethylhexyl methacrylate) (PS-PEHMA). These polymers would be
convenient for study as they can all be readily imaged by AFM and can be synthesized using techniques similar to those employed in this thesis (PS-PEHMA can be synthesized identically to PS-PHMA$^1$, while the synthesis of PS-PEP$^2$ is well established). The shear alignment behavior of series of these polymers, varying in $M_n$ or $w_{ps}$, can then be compared to the PS-PHMAs. One difference across these systems is their varying degrees of chain entanglement and viscoelasticity, which may prove an interesting area of study (see Chapter 8.2.2). In addition to studying other cylinder-formers, this approach should be applied to other morphologies of interest to the nanolithographic community, namely spheres and standing (out-of-plane) lamellae. The shear alignment behavior of both spheres$^{3-5}$ and lamellae$^6$ have previously been studied; however, the influence of the above-mentioned material parameters on alignment was not comprehensively investigated. In particular, it would be interesting to see, given the appropriate optimization, if better alignment can be achieved in lamellae-forming systems; in previous work, very large stresses were needed to induce orientation, and the degree of order was comparatively poor.$^6$ Perhaps a properly-designed (e.g., sufficiently low molecular weight) lamellar block copolymer would align much more readily. Finally, it would be interesting to compare the alignment response of symmetric triblocks with their diblock analogues. Triblock copolymers with glassy endblocks and rubbery midblocks are useful in many industrial applications because of their resilient mechanical properties (e.g., as thermoplastic elastomers). This increased mechanical strength could have advantages in nanofabrication and other thin film applications so it could prove valuable to assess how conducive these materials are to shear alignment. In particular, do the same features which make these materials good elastomers (physical crosslinking due to the
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glassy endblocks) hinder or enhance their response to shear? Upon completion of the above studies, the universality of the scaling trends presented here will be much better understood. This will then enable more effective and properly targeted application of the shear alignment technique for device and nanomaterial production.

8.2.2 Viscoelastic Contrast

Studies on the shear alignment of bulk block copolymers introduced the idea that viscoelastic contrast, or differences in the viscoelastic properties, namely the glass transition temperature, $T_g$, and the entanglement molecular weight, $M_e$ (which is the average chain mass between entanglement points), between the two blocks may prove important for determining the direction and mechanism of microdomain alignment.\textsuperscript{7-8} In addition, it has been postulated that the persistent undulations in the trajectories of shear-aligned cylinders may be related to the degree of entanglement ($N_e = M_n/M_e$) or the rubbery plateau modulus ($G^\prime$)\textsuperscript{9-10} of the matrix block. Unfortunately, the studies presented in this thesis did not allow for any clear investigation of these effects: all of the polymers used to study shear alignment were of the same chemistry (thus had similar viscoelastic contrast), and all blocks were only modestly entangled (the polymers in the composition series all had 1 – 2 entanglements per block, while the blocks of the largest polymer in the molecular weight series possessed only $\sim$ 5-6 entanglements). A systematic study which employs a series of cylinder-forming block copolymers whose block combinations vary greatly in their viscous and elastic properties would provide important information as to the significance of this contrast. In all cases, the materials would be shear-aligned, via the rheometer method, and their alignment compared to the
melting-recrystallization model. In addition, a defect density analysis similar to that shown in Figure 5.15 may prove informative for assessing the effect on terminal alignment quality.

Table 8.1 lists the block chemistries (and their relevant properties) that could prove useful for these studies. To begin, several groups of polymers can be synthesized that each have varying degrees of viscoelastic contrast: PS-P2VP, PS-PDMS, and PVCH-PEP. In each case several polymers can be synthesized such that the overall molecular weight and the chemistry of the minority block can be varied. For example, complementary sets of PS-P2VP polymers, one set forming PS cylinders and the other set P2VP cylinders, can be studied. By simply inverting the minority block chemistry as described, the influence of a large number of block and block-pair specific parameters (e.g., segmental friction, the Flory interaction parameter) can be minimized. PS-P2VP block copolymers represent the scenario with minimal viscoelastic contrast; PS and P2VP have nearly identical $T_g$, $M_c$ (though the majority block will have 2 – 3 times the number of entanglements, depending on copolymer’s composition), and $G^0$. Conversely, PVCH-PEP block copolymers provide a high degree of viscoelastic contrast with large differences in $T_g$, $M_c$, and $G^0$. PS-PDMS block copolymers provide an intermediate scenario, with comparable entanglement lengths and rubbery moduli, but vastly different $T_g$.

One difficulty of conducting the above experiments is imaging via AFM. Since AFM relies on mechanical contrast between the blocks, the PS-P2VP polymers will likely prove difficult to image. One potential solution is exposing the film to a selective solvent, which will swell one of the blocks (e.g., tetrahydrofuran preferentially swells
Table 8.1 List of polymers which may be useful for studying viscoelastic contrast

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_e$ [$\text{kg/mol}$]</th>
<th>$T_g$ [$^\circ\text{C}$]</th>
<th>$G_0$ [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene (PS)</td>
<td>18$^9$</td>
<td>100$^{11}$</td>
<td>0.20$^9$</td>
</tr>
<tr>
<td>Poly(vinyl cyclohexane) (PVCH)</td>
<td>39$^{10}$</td>
<td>140$^{12}$</td>
<td>0.06$^{10}$</td>
</tr>
<tr>
<td>Poly(2-vinylpyridine) (P2VP)</td>
<td>17$^{13}$</td>
<td>104$^{11}$</td>
<td>0.13$^{14}$</td>
</tr>
<tr>
<td>Poly(ethylene-alt-propylene) (PEP)</td>
<td>2.0$^9$</td>
<td>$-62^{15}$</td>
<td>1.15$^9$</td>
</tr>
<tr>
<td>Poly(methyl methacrylate) (PMMA)</td>
<td>16$^9$</td>
<td>135$^{16}$</td>
<td>0.62$^9$</td>
</tr>
<tr>
<td>Poly($n$-butyl methacrylate) (PBMA)</td>
<td>30$^9$</td>
<td>$20^{11}$#</td>
<td>0.22$^9$</td>
</tr>
<tr>
<td>Poly($n$-hexyl methacrylate) (PHMA)</td>
<td>46$^9$</td>
<td>8$^*$</td>
<td>0.087$^9$</td>
</tr>
<tr>
<td>Poly($n$-octyl methacrylate) (POMA)</td>
<td>57$^9$</td>
<td>$-20^{11}$#</td>
<td>0.033$^9$</td>
</tr>
<tr>
<td>Poly(dimethylsiloxane) (PDMS)</td>
<td>12$^9$</td>
<td>$-127^{11}$</td>
<td>0.24$^9$</td>
</tr>
</tbody>
</table>

#measured on free-radically synthesized polymer which would have different tacticity (and therefore different $T_g$, by as much as 10-20 $^\circ\text{C}$ for poly(alkylmethacrylate)s) than the anionically-polymerized polymers intended for use here
*measured via dynamic mechanical thermal analysis on polymer which was anionically synthesized in-house

P2VP over PS$^{17}$, inducing height variations (visible by AFM) corresponding to the microdomain patterns. However, this method does run the risk of interfering with the shear-aligned morphology, making it difficult (or impossible) to definitively assess the response of these systems to shear. PDMS-PS (majority PS) and PEP-PVCH (majority PVCH) diblocks may pose a similar imaging problem, as the rubbery cylinders lie beneath the surface, and AFM may not be able to “see” these cylinders through a glassy matrix. In this case, selective swelling via solvent may be utilized, or the film could be lightly etched, thus revealing the microdomain pattern.$^{18}$ Alternatively, transmission electron microscopy (TEM) may be employed either by floating the films onto water (by
casting the films onto a poly(4-styrenesulfonic acid) release layer, see Chapter 3.2.2) and collecting it with a TEM grid (see Chapter 5.5) or by casting the film onto a substrate with SiNₓ windows (these are supported substrates coated with ~ 50-100 nm of SiNₓ, this provides “transparency” to the electron beam).¹⁹ Many of the systems of interest (e.g., PS-PDMS or PS-poly(alkyl methacrylate)s) should have sufficient intrinsic contrast for TEM imaging, or the materials may be differentially stained with a heavy metal (e.g., through RuO₄) to further enhance contrast.

To isolate the influence of entanglement contrast more thoroughly, several additional scenarios could be explored: neither block entangled, both blocks entangled, only the cylinders entangled, and only the matrix entangled. The proposed experiments to explore these four cases are summarized in Table 8.2. Some of these scenarios will have similar imaging issues as those discussed above. However, this list provides a comprehensive set of experiments which enable the investigation of the significance of entanglements in both the minority and majority domains. The case in which the cylinders are unentangled, but the matrix is entangled, provides a greater degree of synthetic flexibility as several block combinations satisfy this scenario. This allows for the independent tuning of the entanglement ratio, or the relative degree of entanglement of the matrix compared to the dispersed domains, over a substantial range (~ 5 – 60).

Aside from the imaging issues discussed above, the chief technical challenge of this work will be synthesizing the large number of polymers required. Fortunately, our lab has experience with all of these chemistries, so synthesizing all of these polymers, while intensive, should prove tractable. This study will be especially interesting if the scaling trends of σₑ or Γ vs. molecular weight show a transition between the unentangled and
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well-entangled states similar to that seen in many bulk polymer properties (e.g., below $M_e$ polymer melt viscosity is proportional to $M$, but above $M_e$, viscosity scales much more strongly, as $M^{3.4}$).\textsuperscript{20}

Table 8.2 Experiments to probe importance of entanglement contrast in shear alignment

<table>
<thead>
<tr>
<th>Case</th>
<th>Minority Block</th>
<th>Majority Block</th>
<th>$w_{\text{minor}}$</th>
<th>$A$-Block $M_n$ [kg/mol]</th>
<th>$N_e$</th>
<th>Ratio (Major/Minor)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Minor</td>
<td>Major</td>
</tr>
<tr>
<td>both lightly or unentangled</td>
<td>PS</td>
<td>POMA</td>
<td>0.25</td>
<td>10-30</td>
<td>0.56</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20-60</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>30-90</td>
<td>1.7</td>
<td>1.6</td>
</tr>
<tr>
<td>both entangled</td>
<td>PMMA</td>
<td>PBMA</td>
<td>0.25</td>
<td>50-150</td>
<td>3.1</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100-300</td>
<td>6.3</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>150-450</td>
<td>9.4</td>
<td>15</td>
</tr>
<tr>
<td>cylinders entangled</td>
<td>PEP</td>
<td>PVCH</td>
<td>0.25</td>
<td>5-15</td>
<td>2.5</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10-30</td>
<td>5</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20-60</td>
<td>10</td>
<td>1.5</td>
</tr>
<tr>
<td>matrix entangled</td>
<td>PS</td>
<td>PDMS</td>
<td>0.25</td>
<td>10-30</td>
<td>0.55</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20-60</td>
<td>1.1</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>30-90</td>
<td>1.7</td>
<td>7.5</td>
</tr>
<tr>
<td>PS</td>
<td>PEP</td>
<td>0.25</td>
<td>5-15</td>
<td>0.28</td>
<td>7.5</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10-30</td>
<td>0.55</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20-60</td>
<td>1.1</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>PVCH</td>
<td>PEP</td>
<td>0.25</td>
<td>10-30</td>
<td>0.26</td>
<td>15</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20-60</td>
<td>0.51</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>30-90</td>
<td>0.77</td>
<td>45</td>
<td></td>
</tr>
</tbody>
</table>

*It is possible that not all of the polymers displayed in this table will be microphase-separated. If that proves to be the case, the range of molecular weights investigated will need to be adjusted accordingly.*
8.2.3 Next Generation of Thermally Switchable Coatings

In Chapter 7, it was demonstrated that amphiphilic block copolymers with a thermally accessible \( T_{\text{ODT}} \) could be utilized as coatings with thermally switchable wetting properties. Unfortunately, the first generation materials used in this study could not “lock in” their hydrophobic character; when exposed to water, the hydrophobicity was lost as the polymer chains rearranged to yield a hydrophilic surface. As such, to make this approach robust enough for industrial application, the surface morphology of the coating must be more firmly fixed into place. One method to achieve this would be the utilization of one or more glass-forming blocks, with \( T_{\text{room}} < T_g < T_{\text{ODT}} \). Upon vitrification, the film morphology should be more stably fixed in place and less responsive to environmental changes. The simplest approach to incorporate a glassy block into these materials would be to replace PDMS as the hydrophobic block and instead employ a higher-\( T_g \) polysiloxane (see Table 8.3). This approach would be synthetically compatible with the Pt-catalyzed coupling reaction employed here to produce the PEO-PDMS block copolymers. Alternatively (or in addition), the hydrophilic block could be replaced with a higher-\( T_g \) component such as poly(vinyl alcohol) or poly(2-hydroxyethyl methacrylate) (PHEMA); however, it is unclear to what extent this would prevent structural rearrangement as these blocks would be plasticized upon exposure to water, thereby reducing their \( T_g \). In addition the synthetic route to produce these block copolymers would be less straightforward. HEMA can be anionically polymerized (via a protected-monomer route\(^21\)), so the production of well-defined PHEMA-poly(siloxane) block copolymers may prove tractable, and could provide a greater degree of control over composition and molecular weight than the present approach. Replacing PEO with the
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Table 8.3 List of candidate blocks for production of thermally switchable surfaces

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_g$ [°C]</th>
<th>Water CA [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(dimethylsiloxane)</td>
<td>-123$^{22}$</td>
<td>107$^{23}$</td>
</tr>
<tr>
<td>poly(diphenylsiloxane)</td>
<td>40$^{24}$</td>
<td>-$^*$</td>
</tr>
<tr>
<td>poly(di-p-tolylsiloxane)</td>
<td>50$^{24}$</td>
<td>-$^*$</td>
</tr>
<tr>
<td>poly(ethylene oxide)</td>
<td>-66$^{11}$</td>
<td>48$^{25}$</td>
</tr>
<tr>
<td>poly(vinyl alcohol)</td>
<td>85$^{11}$</td>
<td>51$^{23}$</td>
</tr>
<tr>
<td>poly(2-hydroxyethyl methacrylate)</td>
<td>57$^{11}$</td>
<td>45$^{21}$</td>
</tr>
</tbody>
</table>

*measurement unavailable

above candidates would also eliminate the crystallinity in these films; though crystallinity retarded the chain rearrangement upon exposure to water, avoiding this effect would simplify the system.

The principal caveat to the above proposal (changing block chemistry to raise $T_g$) is that replacing the current block chemistries could have large implications for the system’s $\chi$. In Chapter 7, the justification for employing materials with exceptionally large $\chi$ was presented; if $\chi$ were to become lower, then larger molecular weights would be needed to achieve microphase separation. This could potentially slow the material’s switching kinetics dramatically. At this point it is unclear where this balance might prove optimal, but exploring this question would be a productive area of study and could greatly enhance the attractiveness of these materials for thermally switchable coatings.
8.3 References


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Appendix A

List of Publications


