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remarkably similar trajectories of F vs. t/d and ψ_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 experimental³⁸ and simulation³⁹ results for similar block copolymer thin film systems. For $1 < t/d < 3$, the local maxima in ψ_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-

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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 ψ_6 and t/d ; unlike PS-PHMA 21-77, which possessed a strong oscillation in both F and ψ_6 , PS-PHMA 30-86 showed almost no dependence of ψ_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 ψ_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 ψ_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.

Seeded Content – **Block Copolymer Membranes from Polystyrene-*b*-poly(solketal methacrylate) (PS-*b*-PSMA) and Amphiphilic Polystyrene-*b*-poly(glyceryl methacrylate) (PS-*b*-PGMA).** By Saleem, Sarah et al. *Polymers* (20734360). Jun2017, Vol. 9 Issue 6, p1-14. 17p.

Block copolymers are well known for the formation of many microphase separated morphologies depending on the architecture of the block copolymer(s) involved, molecular weight, composition and thermodynamic properties [1–3]. Anionic living polymerization provides a way to the creation of well-defined block copolymers by the sequential addition of monomers. It is mostly used to synthesize block copolymers with controlled compositional and structural parameters such as molecular weight, narrow molecular weight distribution, copolymer composition, branching, and other architectural parameters. However, polymers from monomers with “active” protons (i.e., OH, SH, or NH groups) cannot be directly synthesized through this technique, as these react immediately with the initiator anions or the growing chain end [4]. To overcome this difficulty, either controlled radical polymerization can be employed, or protective groups are introduced into the monomeric unit blocking the reactive site during the course of anionic polymerization and these protected groups can be easily and readily cleaved afterwards to get the required functional groups [5]. Functional block copolymers have received extensive scientific and technological attention due to their potential applications in electronics, drug delivery [6], nano reactors [7], and smart materials [8,9]. Loeb and Sourirajan introduced for the first time the fabrication of synthetic membranes with advanced functionality via the non-solvent induced phase separation (NIPS) or so-called “phase inversion” process [10]. Later, the combination of the self-assembly of block copolymers and non-solvent induced phase separation (SNIPS) process allowed the preparation of isoporous membranes with high porosity and sharp molecular weight cut-off. In 2007, the first isoporous block copolymer membrane was reported to be cast from polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) by utilizing the diblock copolymer self-assembly and non-solvent induced phase inversion process (SNIPS) [11]. Later on it was shown that different additives can support the membrane formation [12–14]. Additionally, post-modification of this type of membrane was done and led to superior properties, such as double stimuli-responsivity [15]. This concept was further extended to not only diblock copolymers, but also triblock terpolymers for the fabrication of integral asymmetric

membrane via self-assembly SNIPS [16,17]. Blending of block copolymers was shown to be a facile way to tune the pore size of isoporous membranes [18]. A detailed study of the influence of the solvent on the structure formation in block copolymer membranes showed that the selectivity of the solvent plays a large role and also controls the suitable block copolymer concentration in the casting solution [19]. The development of isoporous membranes with improved functionality derived by postmodification of the block copolymer functional groups after membrane preparation can be promising for applications like water purification or protein separation [20]. Ultra- and nano-filtration membranes are mainly contaminated by biological substances which are prone to deposit on the surface as well as inside the pores of membrane [21]. It has been investigated that membranes with more hydrophilic surface hinder the attachment or accumulation of the foulants on the surface [22]. Nowadays, highly selective and permeable membranes with efficient antifouling properties are in high demand for ultrafiltration applications.

The most-studied hydrophilic segments in the field of amphiphilic block copolymers are poly(ethylene oxide) [17], poly(methacrylic acid) [23], and poly(2-hydroxy ethyl methacrylate) [24]. Poly(glyceryl methacrylate) (PGMA) is a potential alternative for the less hydrophilic 2-hydroxyethyl methacrylate (HEMA) due to the presence of one extra hydroxyl group (–OH) per repeating unit of the polymer in products such as contact lenses, drug delivery, and hydrogels. Poly(isopropylidene glycerol methacrylate)—commonly known as poly(solketal methacrylate)—acts as a precursor polymer of PGMA which was reported for the first time in 1990. Mori et al. reported the sequential anionic polymerization of styrene and solketal methacrylate (polystyrene-*b*-poly(solketal methacrylate), PS-*b*-PSMA) followed by the deprotection of acetonide groups to obtain PS-*b*-PGMA [25]. Zhang et al. used a combination of living anionic polymerization of allyl methacrylate (PAMA) and afterwards functionalization of the allyl side groups with osmium tetroxide to achieve PGMA [26]. Recently, the first attempt to prepare a membrane from this diblock copolymer was reported by Hahn et al., who used PS-*b*-PSMA for air brush spraying on a PVDF support membrane [27].

In this manuscript, for the first time double hydrophobic PS-*b*-PSMA and amphiphilic diblock copolymers of PS-*b*-PGMA are employed to cast integral asymmetric membranes via SNIPS.

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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 *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.

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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 ψ_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 $2\ \mu\text{m} \times 2\ \mu\text{m}$ 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 (ψ_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 $150\ ^\circ\text{C}$. 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 studied, this polymer terraced (formed islands

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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.

5.8 References

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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

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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 (τ_{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, ψ_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, σ , 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:

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

where Ω is the angular velocity [rad/sec] of the rheometer plate and H_0 is the distance between the plate and the polymer film.⁷ The local viscosity of the PDMS layer, η , can be computed using the Carreau-Yasuda constitutive equation⁸:

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

where the fitting parameters η_0 (the zero shear viscosity), κ_1 , κ_2 , and κ_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:

$$\sigma(r) = \eta(r) \times \dot{\gamma}(r) \quad \text{Equation 6.3}$$