# Stability of Order in Solvent-Annealed Block Copolymer Thin Films

## Sanjun Niu and Ravi F. Saraf\*

Department of Chemical Engineering, Virginia Tech, Blacksburg, Virginia 24061

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ABSTRACT: One way to produce high order in a block copolymer thin film is by solution casting a thin film and slowly evaporating the solvent in a sealed vessel. Such a solvent-annealing process is a versatile method to produce a highly ordered thin film of a block copolymer. However, the ordered structure of the film degrades over time when stored under ambient conditions. Remarkably, this aging process occurs in mesoscale thin films of polystyrene–polyisoprene triblock copolymer where the monolayer of vitrified 15 nm diameter polystyrene cylinders sink in a 20 nm thick film at 22 °C. The transformation is studied by atomic force microscopy (AFM). We describe the phenomena, characterize the aging process, and propose a semiquantitative model to explain the observations. The residual solvent effects are important but not the primary driving force for the aging process. The study may lead to effective avenue to improve order and make the morphology robust and possibly the solvent-annealing process more effective.

#### **1. Introduction**

Self-assembly<sup>1</sup> is a powerful principle to fabricate organized structures and devices in the mesoscale, bridging the gap between molecular and macroscopic scales.<sup>2</sup> Monolayers of block copolymers<sup>3</sup> are attractive template materials that self-assemble to create broad range of nanostructures because they can be tailored to spontaneously from variety of periodic features, such as spheres, cylinders, etc., with characteristic length on the order of 10<sup>1</sup> nm.<sup>4</sup> The discrete features are chemically dissimilar from the matrix and may be selectively etched away to form templates by a variety of wet and dry processing methods.<sup>5-8</sup> Furthermore, these nanoscale discrete features may be manipulated by electric field,<sup>9</sup> mechanical strain,<sup>10</sup> chemically tailoring the film/ substrate interface,<sup>11</sup> or rapid solvent evaporation<sup>12</sup> to create anisotropic ordered structures. Several interesting functional structures and devices have been demonstrated using block copolymers, such as, InGaAs/ GaAs quantum dots for laser emission,<sup>13</sup> a array on nanowires,14 nanoscale-patterned barium titanate,15 and a nanoarray of photoluminescent nanoparticles.<sup>16</sup>

A challenge of using these materials, as mask to stencil patterns for commercial applications is to produce a stable, long-range order of the nanoscale discrete features. In principle, the self-assembly process leads to defect-free organization, because the structure is close to thermodynamic equilibrium.<sup>1,17</sup> Thus, an understanding of the dynamics of self-assembly leading to the final optimum (equilibrium) state are important in tailoring the process to achieve a long-range, defect-free, ordered structure. Recently, kinetic studies during thermal annealing are shown to improve order in block copolymer monolayer films primarily by quadrapolar annihilation of two pairs of (oppositely oriented) disclinations, since they produce fewer dislocations than a dipolar annihilation process.<sup>18</sup> The topotaxy method in combination with thermal annealing has demonstrated great promise in producing long-range order.<sup>19</sup> The solvent-influenced ordering, referred to as "solventannealing" subsequently in this paper, is another approach to produce a long-range ordered film<sup>20,12</sup> in

amorphous and crystalline block copolymers. In this procedure, the order is produced by solvent casting the block copolymer film in a sealed vessel to reduce the evaporation rate. The high residence time of the solvent in the film produces adequate mobility to influence longrange order in the film without any thermal treatment.

In our previous report, we describe a dynamical feature in highly ordered block copolymer films made by solvent-annealing, where the monolayer of  $\sim 15$  nm diameter cylinders gradually sink into a  $\sim$ 20 nm thick film over a period of several days when stored under ambient conditions.<sup>21</sup> In this report, we discuss the mechanism of this aging phenomena. From our study, it appears that such a transformation in the morphology cannot be explained by simply considering the differential shrinking of the matrix vs cylinders due to the gradual evaporation of the residual solvent that may be trapped in the film during the solvent-annealing process. Another mechanism is proposed where the sinking phenomenon is a consequence of lowering of the total surface free energy by planarizing the air/film interface (i.e., surface). The observed spontaneous planarization of the undulations caused by the cylinders seems to occur by thickening of the air/film interface. Thus, the central (proposed) idea is that the thickness of the interfacial layer is thinner than a melt-processed film because the solvent-rich environment lowers the air/film interfacial tension. This lower interfacial thickness influences better order and at the same time makes the film more sensitive to aging during storage in ambient air. Understanding of this nonequilibrium nature of solvent-annealed film may eventually lead to better maneuverability of the process to influence higher order.. We also note that long-term stability (i.e., shelf life) of the ordered structures will be critical if block copolymers were to be considered as stencil materials to fabricate nanostructures on solid substrates.

#### 2. Experimental Section

A polystyrene–polyisoprene–polystyrene (PS/PI/PS) triblock copolymer of molecular weight 100 000 Da and polydispersity index 1.09 is spun cast at 3000 rpm on a silicon wafer with native oxide from a 1% (by weight) solution in toluene. The polymers were specially synthesized samples by Dexco Corp., with <1% PI homopolymer content. The molecular

<sup>\*</sup> Corresponding author. E-mail: rsaraf@vt.edu.



**Figure 1.** Typical  $2 \times 2 \mu$ m phase images of sample A obtained by AFM at the aging times indicated on each image. The inset of each image shows the corresponding fast Fourier transform (FFT). The lighter regions are PS cylinders. The sample is the same; however, the area imaged varies in each set.

weight of PI is 64 000 Da and each of the terminal PS blocks is 18 000 Da. The wafer is treated in 30/70  $H_2O_2/H_2SO_4$ Piranha solutions to form a silanol-terminated substrate. The film is immediately placed in an enclosed chamber for solvent annealing, a process developed and described elsewhere.<sup>20</sup> For our process, the volume of the solvent-annealing chamber is 4 cm<sup>3</sup> with 7  $\mu$ L of reservoir solvent at the initiation of the process. The chamber is maintained at 25 °C. The chamber is a stack of two 2.5 in. glass plates spaced with an "O" ring and a dead weight on the top plate. As the reservoir solvent evaporates in the closed chamber the drying of the film is impeded. We note that the saturated vapor pressure at 25 °C for toluene is ~5 KPa, which requires only ~0.95  $\mu$ L (i.e., ~7 times smaller than reservoir solvent) if the chamber was airtight. In our setup, the dead weight, *W*, is not adequate to achieve airtight seal, thus evaporation of solvent from the film is ensured. The extent of seal is varied by applying different W on the top glass plate. To maintain reproducibility, the glass plates and the "O" ring are thoroughly cleaned in ethanol prior to assembly. (No vacuum grease is applied.) Three type



**Figure 2.** Schematic of the block copolymer monolayer with cylinders along the *z* axis and aligned parallel in the *x*-axis direction. Since PS has higher surface energy the air/film interface is PI. The period and amplitude of undulations due to the cylinders are  $\lambda$  and *h*. The "surface-layer" of thickness,  $\xi$ , is defined at the air/film interface with dotted line nominally tangent to the cylinder. This permeable PI membrane is conformal to part of PS cylinders.

of samples are made by regulating  $\mathit{W}\xspace$  and time in the chamber (i.e., solvent-annealing time),  $\mathit{t}_{sa}$ 

sample A:  $t_{sa} = 1.5$  h; W = 220 g sample B:  $t_{sa} = 1.5$  h; W is twice that of sample A sample C:  $t_{sa} = 8$  h; W is twice that of sample A

All of the samples are then aged in a covered bell jar under



ambient air at  $\sim$ 22 °C. The jar is covered with Al foil to avoid UV radiation. The topography and surface structure of the film is studied as a function of aging time, *t*. Where *t* = 0 is defined as the time at the completion of the solvent-annealing process.

The topography and structure is measured by a Nanoscope III Atomic Force microscope (AFM) made by Digital Instruments.

### 3. Results and Discussion

**3.1. Post-Solvent Annealing Transformation: The Phenomena.** In this section we describe the observation of the aging phenomena after the solvent-annealing process.

Parts a–f of Figure 1 compare the surface structure of sample A as it ages over time. The AFM images are at different spots since several spots are analyzed for a given aging time. As reported earlier,<sup>21</sup> as aging progresses, the cylinders appear to sink into the film leading to spontaneous planarization. At longer aging time discontinuities in the cylinders begin to appear that further degrade the order in the film. The corresponding fast Fourier transform (FFT) indicated in the inset is consistent with the visual trend of degradation of order. As *t* progresses, the sharpness of the first order peak remains nominally invariant; however, a "halo" around the center begins to appear. The "halo" analogous to "amorphous scattering" in glasses and liquids is increased disorder in the structure. (The amorphous halo



**Figure 3.** Similar to Figure 1, showing typical  $2 \times 2 \mu m$  phase images of sample B.

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**Figure 4.** Similar to Figure 1, showing typical  $2 \times 2 \mu m$  phase images of sample C.

is quantified later in Figure 13.) The number of pair of spots on the FFT pattern corresponds to the number of "grains" in the image. For example, for 0 h sample, there is one grain corresponding to one pair of spot. The arcing of the spot in the polar direction is due to orientation distribution of the domains. Since the AFM image on a sample is chosen at random, the number of spot and the "arcing" has no systematic bearing on the aging behavior.

Figure 2 shows the schematic view of measured morphology. The topographic parameters measured by

AFM are the height of the cylinders above the surface, h and the periodicity of the ordered structure,  $\lambda$ . Since the PI surface energy is slightly lower than that for PS, i.e.,  $\sim$ 31 vs  $\sim$ 35 dyn/cm<sup>2</sup>,<sup>22</sup> the surface will be enriched with a thin layer of PI shown as the surface layer of thickness,  $\xi$ . The existence of such a surface layer is well documented in the literature. For the present sample, the thickness of the films measured by X-ray reflectivity is about 20 nm. The diameter of the cylinders (measured by transmission electron microscopy) is  $\sim$ 15 nm and the inter cylinder spacing  $\lambda \sim$  36 nm.



**Figure 5.** Changes in surface topography,  $1/h^2$ , compared as a function of aging time, *t*, for samples A, B, and C. The inset is a magnified view of the first 100 h of the aging behavior to indicate the complexities in sample B. The *h*(0) for samples A, B, and C are 2.44  $\pm$  0.413, 3.242  $\pm$  0.0988, and 3.976  $\pm$  0.132 nm, respectively.

At constant pressure, temperature, annealing chamber geometry, and solvent reservoir volume, the aging behavior is sensitive to W and  $t_{sa}$ . As will be discussed later (see Figure 9) that sample A is equilibrated after  $t_{sa} = 90$  min, thus a longer  $t_{sa}$  has little effect on the aging behavior for the seal condition, W = 220 g. We thus refer to sample A, as being under the optimum *condition.* However for W = 440 g (i.e., samples B and C),  $t_{sa} = 90$  min is not sufficient to achieve equilibration, making these conditions sensitive to  $t_{sa}$ . Figures 3 and 4 compare the aging behavior of samples B and C. The comparison indicates significant differences: Both samples are highly ordered at t = 0. however sample B ages significantly faster than sample C. For example, the FFT pattern and AFM images indicate that sample B is disordered for aging beyond 152 h, while significant order is visible in sample C beyond 300 h. A strong FFT peak is visible for sample C aged  $\leq$  369 h. Interestingly, the FFT for sample B at t = 0 has a lower order reflection due to high density of disclination defects, probably in process of being annihilated as observed in thermal annealing process.18

The change in h vs t behavior shown in Figure 5 indicates significant differences between the aging characteristics of the three samples. The *h* is averaged over >380 undulations of PS cylinders measured over several spots on the sample. The error bars around  $1/h^2$ are asymmetric because the error is defined as the standard deviation with respect to average h. The asymmetry in the error bars may be explained as follows: The variation measured is  $(h + \Delta h)$  and  $(h - \Delta h)$  $\Delta h$ ). If one plots  $1/h^2$ , then the upper and lower error bars are  $(1/(h - \Delta h)^2) - (1/h^2)$  and  $(1/h^2) - (1/(h + \Delta h)^2)$ , respectively. On simplification, the upper and lower error with respect to average  $(1/\langle h \rangle)^2$  are  $\{2h\Delta h - \Delta h^2\}/$  $\{h^2(h-\Delta h)^2\}$  and  $\{2h\Delta h+\Delta h^2\}/\{h^2(h+\Delta h)^2\}$ , respectively. Thus, the upper bar is higher than the lower and the bars are symmetric when  $2dh/h \ll 1$ . The rationale for plotting  $1/h^2$  rather than h will become apparent later with respect to the model (see eq 4). All the samples tend to spontaneously planarize, i.e.,  $1/h^2 \rightarrow$  $\infty$ . Apart from the differences in the details of the aging behavior, there are two effects common to the observed





**Figure 6.** Comparison of typical  $2 \times 2 \mu m$  phase-images of sample A, (a) after solvent annealing (t = 0) and (b) (the same sample) after drying in 0.01 Torr vacuum at 50 °C for 2 h.

behavior for all the three samples: (i) There is an initialaging period where *h* is relatively a smooth function of *t*. (ii) Subsequently the *h* decreases with abrupt "jumps" over time. Consistent with Figures 1, 3, and 4, in the *optimum condition* sample A, the cylinders sink by *h* decreasing monotonically.<sup>21</sup> The jumps in sample A are significantly smaller than sample B and C with larger *W*. In sample C there are two large abrupt jumps around 35 and 200 h. sample B has one abrupt jump around 100 h. Sample A has two smaller jumps amounting to a single jump of sample B. However the first jump around ~75 h is not significant and is within the early stage period (as shown later in Figure 7).



**Figure 7.** "Early-stage" aging behavior of samples A, B, and C. The data statistics is the same as in Figure 5. The straight line fit has  $R^{2}$  of 0.957, 0.989, and 0.624, respectively. The values of h(0) calculated from the intercept of the fitted line compares well with the measured value.

As shown in the inset of Figure 5, the behavior of sample B is complex—the *h* first decreases similar to other samples, but then it *increases* followed by similar behavior as other samples. As seen in the inset of Figure 5, in sample C, the cylinders sink monotonically with a very small initial aging period prior to the abrupt jump. This is manifested in the large disorder in AFM and FFT of sample C at  $t \sim 65$  h. (Figure 4b) compared to higher corresponding order in samples A and B (Figures 1b and 3b) for similar aging time.

Thus, as *W* increases, the abrupt jumps in *h* become larger. However, if the  $t_{sa}$  is small to evaporate enough residual solvent (i.e., sample B), the initial aging period is complex with *h* increasing during the aging in the initial period.

In the subsequent discussion, we offer a simple explanation for the observed initial period (section 3.3) and abrupt jumps (section 3.4) and the effect of W and  $t_{sa}$ . The understanding will hopefully lead to avenues to improve the ordering process and the stability of the morphology. The stability of order is critical if solvent-annealed block copolymers were to be considered as mask to fabricate nanostructures for commercial applications.

**3.2. Residual Solvent Effects.** The simplest explanation for the observed aging behavior is the presence of residual solvent in the film that evaporates gradually over time causing the spontaneous planarization. In this section, we consider the possible effects of residual solvent. Since the residual solvent in these thin films is not measurable by thermogravimetric analysis, the inferences are drawn indirectly.

Two possibilities that may occur due to residual solvent in the film during the aging process are as follows: (a) The film may have differential shrinkage between the matrix and the cylinders in such a way that the latter are pulled into the matrix causing planarization (i.e., *h* decreasing over time). (b) The order in the film may alter as the residual solvent evaporates during aging. Both possibilities are considered below.

(a) The differential shrinkage can occur due to differences in solubility of toluene in PS and PI. Toluene has higher solubility in PI than PS.<sup>23</sup> In an extreme case, all of the residual solvent is trapped in the PI. Furthermore, in this extreme case scenario, e.g., the

entire solvent trapped in PI is just below the PS cylinders. From X-ray reflectivity the films are  $\sim 20$  nm thick and the diameter of the cylinders from TEM are  $\sim$ 15 nm. Thus, to accomplish a displacement of the center-of-mass of the cylinders by <2 nm (see Figure 5) PI should have at least  $^{2}/_{5}$  or  $\sim 40\%$  solvent.<sup>24</sup> Such a large amount of solvent retention is unlikely since the over all thickness of the film observed by X-ray reflectivity remains relatively constant. The insignificance of the residual solvent effect is also confirmed experimentally by placing the film in a vacuum to drive off the solvent. Sample A is subjected to 0.01 Torrs vacuum at 50 °C for 2 h. Figure 6 compares the sample before and after the vacuum treatment. The average *h* in Figure 6a and 6b is  $2.5 \pm 0.6$  and  $1.3 \pm 0.2$  nm, respectively. Although a one-to-one correspondence with samples aged under ambient conditions is not possible since the sample is subjected to elevated temperature and vacuum, as a guide, the structure in Figure 6b corresponds to h at  $t \sim 70$  h in Figures 5 and 7. If the aging was solely due to residual solvent, the structure after the vacuum treatment would be highly planarized, similar to Figure 1, part d or part e. Thus, the effect of residual solvent on the observed aging for sample A is insignificant. We also note in passing that the sample after vacuum treatment at 50 °C continues to age with conspicuous cylindrical topography until  $t \sim 350$  h.

(b) The signature of residual solvent during the aging process *is present* when the *W* is large and *t*<sub>sa</sub> is not long enough for the film to equilibrate. Sample B is an example of such a situation. In this film W(B) = 2 W(A)and  $t_{sa}(B) = t_{sa}(A)$ . The film is expected to have significantly larger amounts of residual solvent than sample A. The behavior is complex with two simultaneous processes-the differential shrinkage as described above and the ordering process as the residual solvent evaporates. The complexity is observed in Figure 5: (a) *h* decreases from t = 0 to 33 h, perhaps the solvent removal is uniform, and the sinking phenomena is primarily due to reasons similar as sample A; (b) h*increases* from t = 33 to 51, perhaps due to further ordering caused by solvent evaporation; (c) h decreases subsequently until the film planarizes, and perhaps the solvent effects are no longer significant making the behavior similar to sample A.

In sample C, where W(C) = W(B) but  $t_{sa}(C) > t_{sa}(B)$ , the complex behavior observed in sample B is not observed. Thus, it is likely that in sample C  $t_{sa}$  of 8 h is sufficient to evaporate a significant amount of residual solvent so as not to have any measurable signature in the sinking curve (Figure 5).

**3.3. Mechanism of Transformation Process: Initial-Stage Aging Model.** An alternative explanation for the observed planarization phenomena is considering the interfacial energy of the film. As the environment of the film changes from a solvent-rich air (chamber) to solvent-free air (ambient), the film/air interfacial energy will increase. The corresponding change in surface tension will be,  $\Delta \sigma = s_{ambient} - s_{chamber} > 0$ . The system will reduce the surface energy by planarizing the surface to decrease the interfacial area. The planarization can occur by increasing the surface layer thickness,  $\xi$  in Figure 2 to reduce the undulations due to the cylinders. Thus, the driving force for diffusion of PI chains to the surface from the continuous matrix in the bulk will be the reduction of air/film interfacial area.



**Figure 8.** Typical  $0.5 \times 0.5 \mu$ m phase images at t = 0 h of (a) sample A, (b) sample B, and (c) sample C. The inset of each image shows the corresponding FFT. The lighter regions are PS cylinders.

The planarization process will be balanced by the internal structure of the film, such as topological constraints on chain due to the ordered morphology and stiffness of the surface layer. In the solvent-annealing process, the driving force is small enough to ceases the process well before the planarization. As the film is



**Figure 9.** Initial height of various samples processed at W = 220 g, similar to sample A. however the solvent-annealing time is varied from  $t_{\rm sa} = 1.5$  to 9 h. The statistics is identical to the Figure 5. Note that since the ordinate is  $h_0$  rather than  $1/h_0^2$ , the error bars are symmetrical. The slope of the line  $-0.01027 \pm 0.05219$  is essentially zero, indicating that  $h_0$  is constant for  $t_{\rm sa} > 1.5$  h at seal condition W = 220 g. The average  $h_0$  from the intercept is  $2.42993 \pm 0.26359$  nm.

bought in ambient condition (i.e., during aging) the driving force for the chains to diffuse toward the surface becomes larger to commence the planarization process toward completion. Qualitatively, it is therefore expected that as the vapor pressure in the chamber increases (i.e., larger *W*), the film will be rougher, i.e., larger *h*. The subsequent aging will be faster. Both the observations are consistent with Figure 5 and the discussion in section 3.1. Furthermore, since the smaller the  $\xi$  the larger topographic feature, *h*, as *W* increases  $\xi$  decreases.

The driving force for diffusion of PI chains to the air/ film interface is estimated by calculating the change in surface energy as PI chains diffuse into the surfacelayer. We assume no change in the "bulk" free-energy since average chemical composition of surface layer and matrix PI is the same. The change in (Helmholtz) free energy,  $\delta F$ , due to change in surface area,  $\delta A$ , is  $\delta F =$  $(\Delta \sigma) \delta A = (\Delta \sigma) b \delta s$ , where *b* is the (arbitrary) depth in the *z* direction (see Figure 2) and *s* is the contour length of the surface in the *x* direction per period,  $\lambda$ . Since the contour function has the form,  $g(x) = h \cdot f(2\pi x/\lambda)$  where *f*(.) is a periodic function corresponding to the structure of the block copolymer, the contour length per period is  $s = \lambda g(h/\lambda)$ . Thus,

$$\delta F = \sigma b g' \delta h \tag{1}$$

The change,  $\delta h$  occurs due to diffusion of PI of amount  $\delta m$  to the surface layer that increases thickness,  $\xi$ . If conservation of volume is assumed (i.e., no excess volume of mixing), then,  $\delta m = \rho b[\delta(\xi s)]$ , where  $\rho$  is the density of PI. By eq 1, the chemical potential of the surface layer driving the PI diffusion process is

$$\Delta \mu = \frac{\delta F}{\delta m} = \frac{\Delta \sigma}{\rho \xi} \left[ 1 + \frac{g}{g'} \frac{\lambda}{\xi} \frac{1}{H} \right]^{-1}$$
(2)

where  $h = h(\xi)$  is the constitutive equation that describes stiffness of the surface layer.

Equation 2 is the driving force for the PI chains to diffuse toward the film/air interface. Qualitatively, eq 2 indicates that the driving force (i) is proportional to

the interfacial surface energy,  $\Delta \sigma$ , (ii) decreases as  $\xi$  increases and eventually vanishes as  $\xi \rightarrow \infty$ , (iii) depends on the geometry of the contour, i.e.,  $\lambda$ , and (iv) depends on the elasticity of the surface layer, i.e.,  $h = h(\xi)$ . The description of the driving force seems reasonable based on the above four dependences. Since the torsion on the cylinders, as PI chains diffuse to the surface, is not considered, the above equation is valid only for the initial time before generation of any significant (torsional) stress.

Two simplifying assumptions are made: (A) As  $\xi$ increases, *h* should decrease such that  $h \rightarrow 0$  as  $\xi \rightarrow \infty$ and *h* is at a maximum at  $\xi = 0$ . A reasonable (constitutive) function may be,  $h(\xi) = (R^2/\kappa) \exp(-\xi/\kappa)$ , where the front factor, *R* is nominally the radius of the cylinder and  $\kappa$  is like a "persistence length" of the surface layer that will depend on both stiffness and the interfacial tension which is constant as the film ages. As the surface film becomes stiffer,  $\kappa$  will increase. Assuming,  $\xi < \kappa$  (a reasonable assumption for the studied geometry), the above form of  $h(\xi)$  is reasonable: *h* will decrease as  $\kappa$  or/and  $\xi$  increases. (B) For simplicity, to obtain an analytic expression, the surface contour is modeled as a triangular function. This does not mimic the actual profile, but will lead to a closedform expression that should explain the essential (scaling) features of the aging phenomena. Thus,  $s = \lambda g(h/$  $\lambda = \lambda \{1 + (2h/\lambda)^2\}$ . Since  $\lambda \gg h$  for the structure studied,  $(s/\lambda)$  may be viewed as a truncated power series of  $\sum_{n}$  $(2h/\lambda)^{2n}$  where n = 0, 1, 2, ..., with terms up to second order. Substituting  $g(h/\lambda)$  and  $h(\xi)$  in eq 2,  $\Delta \mu$  becomes

$$\Delta \mu = -\frac{8\Delta\sigma}{\rho\kappa}\frac{h^2}{\lambda^2} \tag{3}$$

Equation 3 is qualitatively reasonable: (i) During the slow drying process, i.e., large *W*, the air contains large solvent vapors leading to smaller  $\sigma_{\text{chamber}}$ . Thus, the driving force for planarization *during solvent annealing* will be smaller for larger *W*. The surface undulation will be dictated more by the ordering process. The system will equilibrate at a larger *h* at the end of the solventannealing process. This is consistent with larger (equilibrium) h(0) observed for sample C compared to sample A in Figure 5 (and Figure 7). (ii) As the film is exposed to solvent free-air during the aging process the  $\sigma$  will abruptly change by  $\Delta \sigma$  (>0). The larger the change in  $\Delta \sigma$ , the bigger will be the driving force,  $\Delta \mu$ , for aging. Since  $\sigma_{\text{chamber}}$  for sample A is larger than that for samples B and C due to smaller *W*, smaller rate of aging is expected in the former. Figure 5 is consistent with this expectation, where the aging process increases as Wincreases. (iii) As the surface film's bending modulus increases (i.e., stiffer polymer),  $\kappa$  increases. Equation 3 indicates that the driving force to smoothen the film will decrease (this is one of the internal structural parameter indicated earlier in this section that will ultimately determine the equilibrium h. Thus, in stiffer block copolymers, for example, PS and poly(methyl methacrylate) (PMMA), the aging should be significantly less, compared to present system studied. Furthermore, in the PS/PMMA system  $h_0$  should be more conspicuous (provided that the change in other parameters, such as  $\sigma$  and  $\lambda$ , are nominally constant). This is consistent with the literature, where topography of PS-PMMA films is easier to probe by AFM,<sup>18</sup> while poltstyrene-polybutadiene or PS-PI-based systems are more difficult to study by surface probe techniques.<sup>25</sup>

The diffusion flux (and hence the rate of aging) can be estimated by linerizing the gradient: The diffusion flux of PI toward the surface is  $L \operatorname{grad}(\Delta \mu)$ , where L is Onssager's mobility.<sup>26</sup> By assuming a linear profile, the flux of PI toward the surface,  $j = L[\Delta \mu/\xi] = (w\lambda\rho)^{-1}\delta m/$  $\delta t$ . Since,  $\delta m = \rho w[\delta(\xi s)]$ , the flux equation can be solved (using the exponential constitutive function,  $h(\xi)$ , and triangular contour,  $g(h/\lambda)$ ) to yield

$$\frac{1}{h^2} = \frac{1}{h_0^2} + \frac{32L(\Delta\sigma)}{\rho\lambda^2\kappa^3}t$$
 (4)

where  $h_0$  is *h* at t = 0. According to eq 4, the rate of aging depends on vapor pressure in the chamber (i.e., *W* that affects  $\Delta \sigma$ ), the properties of the polymer constituting the interfacial layer (i.e.,  $\kappa$ ,  $\rho$ , and L), and the block copolymer architecture (i.e.,  $\lambda$ ). Equation 4 suggests, that at early-stage aging (i.e.,  $t \leq 70$  h for sample A), when the effects of deformation on the PS cylinders due to diffusion are small,  $(1/h^2)$  vs t should be linear. Figure 7 shows good agreement between the experimental data and t vs h dependence predicted by eq 4 for sample A. The agreement in samples B for a smaller length of time before the *h* begins to increase may be fortuitous because it is a combination of three effects—surface layer thickening that will decrease h, differential shrinkage that may reduce the *h*, and compositional changes on solvent evaporation that may increase the *h* by improving order. The poor agreement in sample C indicates that there is virtually no initial period and the sample begins to age at a fast rate immediately after the solvent-annealing process. As indicated above (section 3.3, second paragraph),  $\xi$ decreases as W increases, thus in sample C, the  $\xi$  may be significantly thin to breakup at low aging time. This is consistent with small early-stage aging and a large abrupt sinking. The same holds for sample B, which also exhibits big jumps in the aging characteristics shown in Figure 5; however, the residual solvent prolongs the initial period and delays the abrupt aging (i.e., a jump in the aging curve).

On the basis of the driving force explanation in eq 3, as *W* increases  $\xi$  decreases, and the topography will be more developed with larger *h*. Thus,  $h_0$  should increase as *W* increases. This is consistent with the measured topography in Figure 7 at t = 0, where  $h_0$  for sample C is the highest, followed by sample B and then sample A. Figure 8 compares the AFM and corresponding FFT of samples A, B, and C immediately after the solvent annealing, i.e., at t = 0. An equal size and smaller area is chosen with a single "grain" to avoid broadening effects due to grain size. Samples A and C have a strong three orders of peaks due to inter cylinder packing, while sample B shows a faint third order. The slightly poor order in sample B is attributed to residual solvent. One should note that although sample C has thinner  $\xi$ than sample A (see Figure 7) the intercylinder order is comparable.

The insignificance of residual solvent in sample A may be demonstrated as follows. If the solvent-annealing process for a given *W* is equilibrated, then  $h_0$  should be independent of  $t_{sa}$  beyond that point. Figure 9 shows the average  $h_0$  for samples annealed for different times at W = W(A) = 220 g. The  $h_0$  remains nominally constant for  $t_{sa}$  90 min. Thus, 90 min annealing for sample A is adequate to obtain an equilibrium structure. This is also the rationale for labeling sample A as



**Figure 10.** Typical  $0.5 \times 0.5 \mu$ m phase images of sample A obtained by AFM at the aging time indicated on each image. The inset of each image shows the corresponding fast Fourier transform (FFT). The lighter regions are PS cylinders. The sample is the same for the various images shown.

"optimum". However we note that this condition is not unique and will depend on the reservoir solvent, *W*, initial film thickness, substrate chemistry, temperature, and pressure.

**3.4. Order Disruption: Late-Stage Aging.** Next we consider the late-stage morphology where the cylinders appear to break. As discussed above, during aging the surface layer thickness,  $\xi$  increases with time by diffusion of PI toward the surface. Although the PI chains

is topologically constrained by the two PS chains imbedded in the same or a different (vitrified) PS cylinder, it is not surprising to expect such a transport (of PI) toward the surface. The high activation diffusion process can occur in these samples because the PS chains in the cylinders are not significantly entangled. The entanglement-molecular-weight for PS is  $\sim 18\ 000\ (27)$ that is comparable to the PS block in the polymer for study. However, as the process of PI diffusion continues,



**Figure 11.** Similar to Figure 10, showing typical  $0.5 \times 0.5 \,\mu$ m phase images of sample B obtained by AFM.

the strain energy stored in the cylinder due to PI diffusion process will become significant. The stored energy will eventually be released by breaking the cylinders. This fracturing process of the cylinder seems consistent with the steps in the aging curve shown in Figures 1, 3, and 4.

Parts a-f of Figure 10 show single-grain AFM images and corresponding FFT of sample A as the film ages from the initial-aging period to late stages where abrupt steps in aging are observed. In the initial stage, i.e., Figure 8a and Figure 10a, the cylinders are continuous. The corresponding FFT show multiple orders for intercylinder packing. However, with time the number of orders reduce indicating increase in disorder. The jump from t = 70 to 82 h (see Figure 5) is consistent with the appearance of discontinuity in the cylinders seen in Figures 10a compared to Figure 10b. As time progresses, the higher order peaks vanish (i.e., t = 106 h). Eventually, at  $t \ge 118$  h, the peak due to inter cylinder order disappears, and the AFM images show high instances of discontinuities in the cylinders. The cylinders continue to fracture leading to a nominally planarized surface. At 314 h, the FFT is slightly anisotropic, indicating that there is some structure reminiscent from the striated order due to the cylinders.

Parts a-d of Figure 11 show the single-grain AFM images and corresponding FFT for sample B. The two orders of peak in the FFT are present and gradually reduce in t = 0 (Figure 8b) to the 74 h (Figure 11b) range

corresponding to the initial period where *h* exhibits complex behavior with no abrupt jumps (see Figure 5). After the first jump at t = 152 h in Figure 5, the order vanishes as seen in the image and corresponding FFT (Figure 11c). The change after the jump in sample B is more abrupt than sample A where the inter cylinder peak is present after the second jump at t = 166 h (Figure 10e). At t = 273 h in Figure 11d the structure in sample B is more isotropic than sample A, indicating that the aging and planarization in the latter is faster than in the former. The faster degradation in sample B compared to sample A is consistent with the earlier inference of smaller  $\xi$  in the former.

Parts a-e of Figure 12 show the single-grain AFM images and corresponding FFT for sample C. Although the jump in sample C at t = 65 h is as large as sample B after t = 152 h, the structure in the former is significantly more ordered, exhibiting a clear first-order peak due to inter cylinder order for much longer time (see Figure 12b). The order gradually degrades in the plateau region (see Figure 5) from t = 43 to 175 h. In comparison to t = 152 h for sample B (Figure 11c), the cylinders are better formed at t = 150 h for sample C (Figure 12c). After the second jump (in Figure 5) at t =223, the structure degrades further; however, complete planarization does not occur up to t = 369 h. Comparing sample C (Figure 12b) with sample A (Figure 10c) seems to indicate that the initial order is disrupted quicker for films annealed under higher solvent vapor pressure.



Figure 12. Similar to Figure 10, showing typical 0.5  $\times$  0.5  $\mu$ m phase images of sample C obtained by AFM.

The inference is again attributed to thinner  $\xi$  in sample C than sample A.

One way to compare the disorder due to fracturing of the cylinders is by examining the FFT along the direction of the cylinders. Since the disorder leads to a "halo" at the center of the FFT, total integrated value along the cylinder direction will be an index of cylinder fracturing. Since the scan is perpendicular to the intercylinder order peaks, the total area under the halo will not have significant background error due to FFT signal from the inter-cylinder order. Figure 13 compares the area of the halo as a function of aging time for the three samples. As expected, in sample B the stability is the lowest. The disorder process is most abrupt. Samples A and C reach nominally similar levels of disorder. However the overall fracturing process in sample C (despite the large jumps in Figure 5) is slightly slower than in sample A. This is also apparent from Figure 5, where at late stages, the slope is lowest for sample C followed by sample A and worst for sample B. Since in



**Figure 13.** Total area under the central amorphous halo shown in Figures 10-12 as a function of aging time. To avoid any contribution from the structural signature of the cylinder packing (see insets of Figures 10-12), the slice is perpendicular to the axis of the cylinders. Furthermore, to avoid the FFT of the edges (for example in Figure 12b) images were analyzed with cylinders not parallel to the edges.

all cases the morphology is eventually disrupted, it may be best to store solvent-annealed films under a solventrich air environment to ensure stable structures over a long time.

**3.5.** Avenue for Improved Order by Solvent Annealing. The central idea of improved high order in the solvent-annealing process is to diminish the interfacial constraint on the amplitude of the undulations that occur due to the ordered morphology of the film. A detrimental effect of this reduced interfacial tension during solvent annealing is the smaller  $\xi$  that leads to higher susceptibility to aging. Thus, two criteria need to be addressed to achieve well ordered thin film by solvent annealing—high t = 0 order and low rate of aging.

It is apparent from the above study that larger W(i.e., better seal) with long  $t_{sa}$  will lead to higher order. However, higher W will require longer  $t_{sa}$  to avoid residual solvent effects. The practical length of  $t_{sa}$  will therefore determine the upper limit of W. It may be desirable to use a solvent with high saturation vapor pressure to allow for a significant evaporation rate at high W. Increasing the temperature (without affecting the evaporation significantly) and/or lowering the pressure may have a similar effect. The process may also be performed in stages, where initially one has a low saturated vapor pressure condition. Such a two-stage process may lead to lower overall  $t_{sa}$ .

The challenge of improving stability is more difficult. The central goal is to reduce the driving force for increasing  $\xi$ . Lets assume the morphology (i.e., h) and the solvent process (i.e.,  $\Delta \sigma$ ) is fixed. From eq 4, the aging kinetics is a sensitive function of  $\lambda^{-2}$  and  $\kappa^{-3}$ . Thus, by increasing  $\lambda$  and/or  $\kappa$ , the aging can be diminished to achieve a more stable film. To increase  $\lambda$ , block copolymer with larger molecular weights would be desirable. Larger  $\kappa$  can be achieved by changing the chemistry of the polymer. For example, in block copolymer composed of PS and PMMA, both moieties are vitrified and significantly stiff at room temperature compared to PI or polybutadiene. Thus, a solvent-annealing PS/PMMA block copolymer system under

large W and appropriately long  $t_{sa}$  to avoid residual solvent effects would be an optimal system to produce high order with low (or no) aging kinetics.

The distortions in the late-stage process caused by cylinder fracturing may be reduced by lowering the molecular weight of the discrete structure polymer below its entanglement molecular weight.

Adding a low molecular weight homopolymer of the low surface energy component (i.e., PI for this study) will reduce the strain on the cylinder. During aging of such a system, the  $\xi$  can thicken by diffusion of the low molecular weight homopolymer. However the composition will have to be optimized to ensure excess amount of homopolymer to allow for surface layer thickening during aging without constraining the cylinders but low enough to minimize alterations in the desired ordered morphology.

#### 4. Summary

Following is a summary of inferences derived from our study on solvent-annealed PS–PI–PS triblock copolymer thin film:

1. In a solvent-annealed film, a high order is achieved; however, the order degrades over time (i.e., aging), if the film is stored under ambient conditions. In this study, we propose that the improved high order in solvent-annealing process occurs by diminishing the interfacial constraint on the amplitude of the undulations that occur due to the ordered morphology of the film

2. During the aging process, the film spontaneously tends to planarize where the cylinders gradually appear to sink into the film. The proposed mechanism is thickening of the surface layer, i.e.,  $\xi$  increase with time during aging.

3. The aging process has two regimes the initial stage aging, where h decreases gradually followed by latestage where there are conspicuous jumps in h. The first stage seems to be thickening of the surface layer by simple diffusion process. In the second stage, the diffusion process begins to deform the ordered structure due to covalent connectivity between the matrix and latter structure (i.e., cylinders for the present study). The sudden drop in h occurs as the cylinders fracture due to the deformation.

4. The driving force for the aging is interfacial forces, although residual solvent may play a role in the early time interval of the process if the annealing time is not adequate.

5. Residual solvent has a detrimental effect on the overall order and increases the rate of aging.

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