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Spontaneous Planarization of Nanoscale Phase Separated Thin Film

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Structure of complex fluid at mesoscales is influenced by interfacial effects. We describe the dynamic response in such films to sudden change in interfacial tension. In a self-assembled block copolymer film, the monolayer of 15 nm diam cylindrical discrete phases close to the surface commence to sink at an average rate of 0.16 nm/day in response to the interfacial tension change. Surprisingly, this spontaneous planarization occurs, even though the cylinders are covalently stitched to the matrix. A simple model explains the observed behavior. The observation may lead to approaches to tailor the structure of mesoscale thin films of complex fluids for long-range order that are desirable for nanoscale device fabrication.

Self-assembling properties of complex fluids, such as, proteins,¹ DNA,² colloidal suspensions,³ surfactants,⁴ block copolymers,⁵ and liquid crystals,⁶ are attractive due to their potential application as template materials for hybrid organic/inorganic nanostructure and device fabrication. In the mesoscale regime where film thickness is comparable to the characteristic size of the building-block, i.e., the diameter of the colloid particle, or the size of the discrete phase of the block copolymer, or the radius of gyration of the protein molecule, etc., the interfacial properties have a profound effect on the structure of the complex fluid. Wetability is shown to influence the equilibrium phase segregation⁷ and impart topography defined by the size and shape of the discrete phase.⁸ In block copolymers, altering the fluid/substrate interfacial tension, the discrete phase can be oriented parallel or perpendicular to the plane of the film.⁹ In mesoscale polymer films, the surface enhanced mobility causes depression of the glass transition temperature¹⁰ and significant increase in crystalline order.¹¹ Furthermore, the self-assembled structures of liquid crystals,¹² multiphase complex fluids,¹³ and colloids¹⁴ can be preferentially oriented by a patterned substrate. It is thus reasonable to expect that the self-assembled

structure of complex fluids at mesoscale film thickness will respond to dynamical changes in interfacial property that may occur due to, say environmental factors, external fields, or subsequent deposition of foreign matter. The understanding of such dynamical effects may lead to avenues to tailor self-assembly processes for applications such as, nanostructure fabrication. In this letter, we report, the dynamic response to sudden change in interfacial tension in a 57 nm thick block copolymer film composed of a monolayer of 15 nm diam phase separate cylindrical phase. Surprisingly, the cylinders commence to sink due to the change in air/film environment, even though the phases are stitched together with a covalent bond and the cylindrical phases are vitrified. The spontaneous planarization process initiated due to such a change in surface tension contrasts with numerous atomic force microscopy (AFM) studies on similar mesoscale systems where topography conforming to the underlining block copolymer structure is obtained.¹⁵ The observed dynamic behavior indicates that significant flow can occur in mesoscale thin films due to surface forces.

Figures 1(a) and 1(b) shows a height and phase image of a solvent cast polystyrene–polyisoprene–polystyrene (SIS) triblock copolymer obtained by an AFM. The molecular weights of each polystyrene (S) and polyisoprene (PI) block are 18 000 and 64 000 g/mole, respectively, with polydispersity of 1.09. Thin film is prepared by spin coating a 1% toluene solution of SIS on the Si substrate. The film is then dried for 150 min in a nominally sealed vessel under toluene vapors well below saturated vapor pressure.¹⁶ The thickness of the film after solvent annealing, measured by x-ray reflectivity is 57 nm. The thickness remains constant over 1 month, indicating insignificant residual solvent. The image in Fig. 1a reveals long-range

order of polystyrene cylinders. The apparent height of the cylinders immediately after solvent annealing i.e., at aging time, t_0 is 2.44 \pm 0.10 nm and the intercylinder distance is 29 nm.

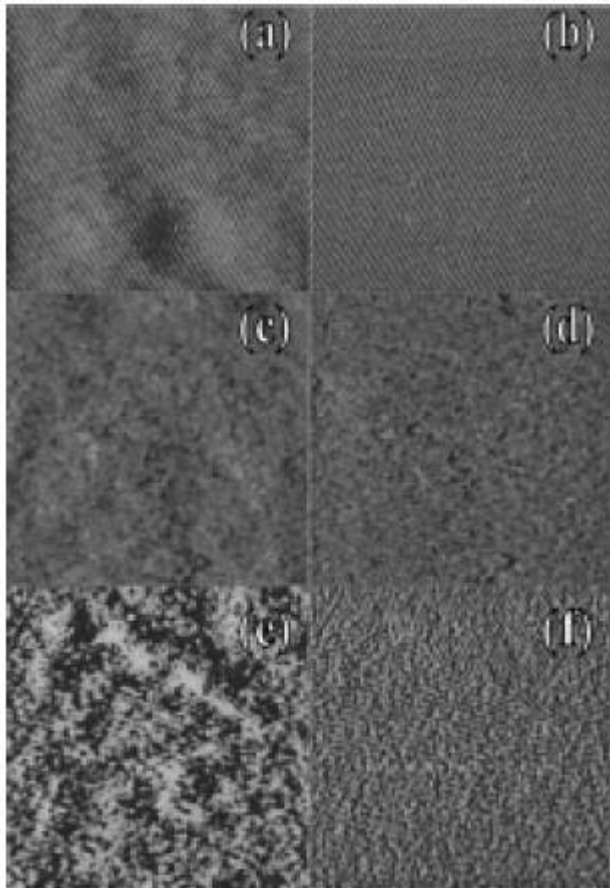


FIGURE. 1. AFM images of the surface topography i.e., height image left side and surface hardness i.e., phase image right side of SIS sample after the solvent annealing process. The lighter regions at higher elevation/ hardness are PS cylinders. The sample is the same, and the area imaged varies in each set. Each image is 2 by 2 μm .

Subsequently, the film is allowed to age at 25 $^{\circ}\text{C}$ under ambient air. The morphology is monitored by AFM. The height images in Figs. 1a and 1c indicates that after 314 h of aging, the

cylinders disappear in the height image. However, in the phase image in Fig. 1d they are still observable. Thus, the cylinders have sunk but the softer PI layer is not thick enough to obscure the local changes in surface hardness due to underlying PS cylinders. After 1 month of aging, the surface appears fully planarized with no apparent structure

in height and phase image. However, after reactive ion etching of a 314 h aged sample, the ‘‘fingerprint’’ pattern reappears in both height and phase images Figs. 1e and 1f indicating that the cylinders are imbedded in the sample. The average amplitude of the undulation due to the cylinders h defined in Fig. 3a at a given aging time t is obtained by measuring the topography over 380 cylinders from six images with eight cross sections per image. Figure

2a shows $1/h^2$ versus t behavior. The error bar is the standard deviation over the 380 points. The rationale for plotting $1/h^2$ rather than h is to make a comparison with the theory discussed subsequently in Eq. 1 more apparent. Two features emerge: i The sinking is over 2 nm in 300 h or an average sinking rate of 0.16 nm/day. ii The reduction of h i.e., increase in $1/h^2$ in Fig. 1a is gradual before 70 h followed by an abrupt increase at $t=70$ and 106 h.

The planarization phenomena can be explained as an interfacial behavior.¹⁷ In the solvent-annealing chamber the film is in contact with a air/toluene mixture that has higher surface tension than air. As the film is brought out of the chamber to toluene-free air, the film/air interfacial tension abruptly increases i.e., step function. The Helmholtz free energy of the film will reduce by decreasing the surface area, i.e., ‘‘dampening’’ the surface undulation caused by the cylinders. The undulations can be dampened by increasing the thickness of the surface layer by diffusing more PI from the ‘‘bulk’’ to the surface. Although the PI chains are topologically constrained by the two PS chain ends imbedded in the cylinder, it is not surprising to expect such a high activation energy process. A rationale for such a diffusion process to occur is the fact that the PS chains in the cylinders are not significantly entangled.¹⁸ However, as the process continues to evolve, the deformation energy stored in the cylinder due to

this PI diffusion process will become significant. The stored energy is eventually released by breaking the cylinders. This fracturing process of the cylinder seems to manifest as steps in the aging curve shown in Fig. 2a: up until $t=70$ h, defined as the “early aging-period” in the aging curve, the cylinders are continuous as seen in Figs. 2b and 2c. The stripes become discontinuous in Fig. 2d, indicating that the cylinder commence to break for $t=70$ h. The number of breaks in the cylinders further increase at $t=118$ h as seen in Fig. 2e compared to $t=82$ h. This is consistent with the second abrupt change in sinking kinetics seen in Fig. 2a. The cylinders continue to break, gradually leading to morphology similar to Figs. 1d or 1f.

are asymmetric more clearly visualized in Fig. 3b because the error is defined as the deviation with respect to average h . b–e are 500 by 500 nm phase images at the aging times indicated. The lighter stripes are PS cylinders. In the initial stages of the planarization process (i.e., for $t \leq 70$ h) where the deformation effect may be ignored, the chemical potential driving the PI diffusion can be calculated by a simple model that assumes a PI surface layer that covers the “bulk” PI matrix and the PS cylinders. The existence of such a surface layer well known in the literature is because PI has a lower surface energy than PS, therefore the film minimizes the total free energy by forming such a layer at the film/air interface. Figure 3(a) shows a schematic diagram of the structure and the surface layer of thickness ξ . As the PI chains move toward the surface, ξ will increase. Since the surface layer undulations “damp” with larger ξ , $\Delta h/\Delta t < 0$.

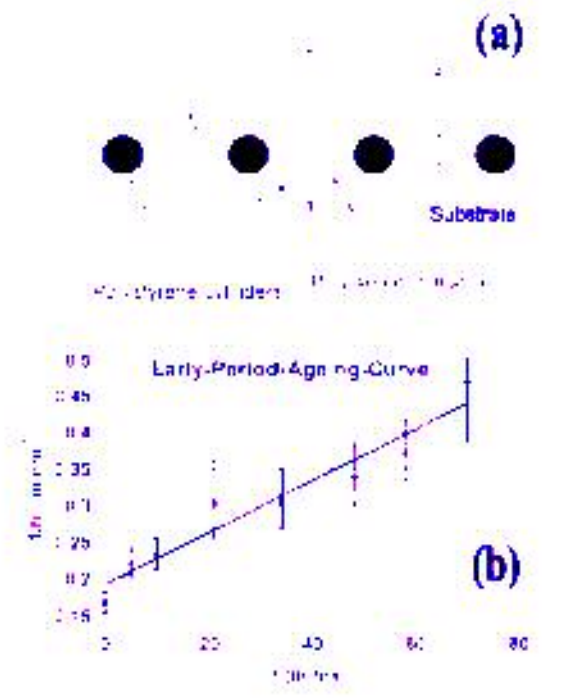
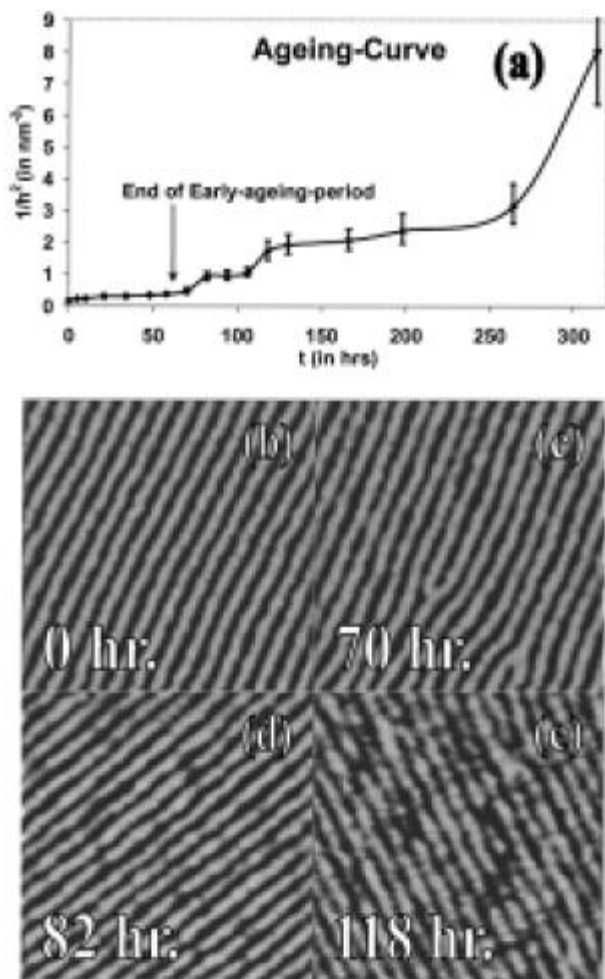


FIG. 2. a The aging curve plotted as t vs $1/h^2$ shows three steps at 70–82 h, 106–118 h, and 264–314 h. The h is averaged over 380 undulations over PS cylinders. The error bars around $1/h^2$

FIG. 3. (a) A schematic of the block copolymer monolayer with cylinders along the z axis and aligned parallel in the x axis direction. The period and amplitude of undulations due to the cylinders are λ and h . By AFM, 29 nm and $h=2.44 \text{ nm}$ ($t=0$) to 0.35 nm ($t=314 \text{ h}$). The permeable PI surface layer of thickness δ is defined at the air/film interface with the dottedline nominally tangent and conformal to the cylinder. (b) The aging behavior replotted from Fig. 2b to indicate the t vs $1/h^2$ linear behavior in air ($0 - 70 \text{ h}$ period, predicted by Eq. (2).

Change in free energy. $\delta F = \sigma \delta A = \sigma w \delta s$, where δA is change in surface area, σ is the (change in) air/PI surface tension, w is unit depth (in the z direction), and s the contour length per period λ of the surface (in x direction). Thus, the chemical potential difference between the surface layer and matrix PI, $\Delta\mu = \delta F / \delta m$, where the mass diffusion $\delta m = \rho w [\delta(\xi s)]$. To obtain the scaling relationship, we assume: (i) a constitutive equation, $h(\xi) = (R^2/\kappa) \exp(-\xi/\kappa)$.

Where R is nominally the radius of the cylinder and κ is like a ‘‘persistence length’’ of the surface layer that will depend on its stiffness¹⁹ and (ii) a triangular function to model the surface

contour leading to $s(h) = \lambda [1 + (\pi h/\lambda)^2]^{-1/2}$. The chemical potential then becomes $\Delta\mu = -(\sigma w / \rho \kappa) (h^2/\lambda^2)$.

By assuming a linear profile for $\Delta\mu$, the diffusion flux²⁰ of PI toward the surface becomes $j = D [\Delta\mu / \xi] = (w \lambda \rho)^{-1} \delta s w / \sigma \lambda$, is proportional to Onsager’s mobility. Using the $h(\xi)$ and $s(h)$ functions, and integrating, the flux equation yields

$$\frac{1}{h^2} = \frac{1}{h_0^2} + \frac{32 D w}{\sigma \lambda^2 \kappa^2} t, \quad (2)$$

where $h_0 = h(t=0)$. Figure 3(b) shows a good agreement between the experimental data and t versus $1/h^2$ dependence predicted by Eq. (2) for early stage aging (i.e., $t < 70 \text{ h}$).

The significant flow in film due to change in surface tension where PS cylinders are vitrified indicates the dominance of the constraints imposed by interfaces. Such interfacial constraints caused by surface layer geometry and (chain) topology will

perturb the long-range order in the thin film monolayer structure. In thermal annealing, the mobility to annihilate defects is increased,²¹ leading to better order, but the constraint to maintain an equilibrium surface layer is unchanged. This partially explains the observation of significantly longer-range order in solvent-annealed film compared to films made by thermal annealing.²² Thus processes that will diminish the interfacial constraints will improve longrange order. R.F.S. would like to thank Carilion Biomedical Institute, VA, Optical Science and Engineering Center, Virginia Tech, and IBM’s T. J. Watson Research Center, NY for financial support.

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