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# Coupling between mean curvature and textures in block copolymer thin films deposited on curved substrates<sup> $\dagger$ </sup>

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Received Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXX 20XX First published on the web Xth XXXXXXXX 200X DOI: 10.1039/b000000x

We study the dynamics of coarsening in a cylinder-forming polystyrene-block-poly(ethylene-alt-propylene) block copolymer thin film deposited on a topographically patterned substrate. Thermal annealing leads to highly ordered arrays of polystyrene cylinders embedded in the poly(ethylene-alt-propylene) matrix, lying in-plane and oriented perpendicular to the trenches of the substrate. We show that this configuration corresponds to an equilibrium state. The coupling between the block copolymer morphology and the mean curvature of the substrate is dictated by the out-of-plane deformations of the block copolymer structure. Thus, with appropriate control over the substrate features, it should be possible to obtain novel structures with controlled orientation.

#### 1 Introduction

During the last decade, block copolymers have attracted considerable attention due to their ability to self-assemble into highly regular structures on the scale of tens of nanometers <sup>1,2</sup>. In these systems, while the periodicity is primarily controlled by the molecular weights of the individual blocks, the symmetry is determined by a complex interplay between entropic and enthalpic free energy contributions<sup>3</sup>.

When a block copolymer is confined on the nanoscale, the equilibrium morphologies observed in the bulk can be profoundly modified. For example, novel structures and symmetries have been found to arise under confinement into nanofibers or nanodroplets with a characteristic size comparable to the period of the copolymer domains<sup>4–9</sup>.

Upon confinement into thin films, the block copolymer morphology is strongly affected by the confining surfaces and the affinity of each block for the interfaces <sup>10</sup>. Although a myriad of morphologies can be obtained upon confinement in thin films (depending upon film thickness, surface energy, temperature and block copolymer structure), two of the most useful structures consist of arrays of self-assembled domains with hexagonal or smectic symmetries <sup>5,10</sup>. Block copolymer thin

films with these two symmetries have been employed to obtain, via nanopattering, structures for a wide variety of applications, including nanowire polarizer grids, high-density arrays of metal nanodots, and magnetic media<sup>10–16</sup>. The standard technique employed to obtain self-assembled block copolymer thin films is spin coating from a dilute polymer solution in a volatile solvent. During this process, as the solvent evaporates, the order-disorder temperature of the thin film increases above room temperature and the blocks separate on the nanoscale. This separation process leads to the appearance of a distorted structure that unavoidably contains defects.

Given that most applications require well ordered structures, one of the main drawbacks of this approach is the lack of long range order due to the presence of topological defects like domain walls, disclinations, and dislocations<sup>10</sup>. While these defects can be removed by thermal treatment above the glass transition temperatures of the blocks, it has been found that this process is prohibitively slow for most technological purposes<sup>17–21</sup>.

In order to obtain well-ordered patterns, a variety of techniques, including shear flow, electric field, or a sweeping temperature gradient, have been employed to remove the topological defects which disturb the long-range order. One of the most successful methods to control long-range order and orientation involves pre-treating the substrate to create either topographic structures or chemical patterns<sup>22–28</sup>. This approach, while limited in its area of coverage, has proven to be very effective to obtain well- ordered domains in smectic and hexagonal systems.

Topographically patterned substrates with different square wave grating patterns have been employed to obtain perfectly aligned defect-free monolayers of cylinder-forming block

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copolymers<sup>22,26</sup>. In these systems, the substrate consists of a periodic array of trenches separated by flat mesas of different widths. Due to the strong lateral confinement effect generated by the trenches, it was observed that the equilibrium configuration consists of cylinders aligned with the trench walls. However, different experiments also show the existence of a long-lived metastable configuration where the cylinders become oriented perpendicularly to the trench walls. Although this unexpected configuration was argued to emerge from capillary flow of the block copolymer from the trenches to the mesas<sup>25</sup>, at present it is not clear what the dominant mechanism behind the appearance of this anomalous orientation is.

In this work we study the dynamics of ordering of a monolayer of a cylinder-forming polystyrene-block-poly(ethylenealt-propylene), PS-PEP, diblock copolymer deposited onto a gently curved substrate. The kinetics of ordering are also studied through a phase field model that adequately captures the main features of the ordering kinetics and viscoelastic interactions in the system. Here we show that the process of coarsening in this system is strongly affected by the anisotropic elasticity of the block copolymer phase that leads to the appearance of well ordered patterns under curvature.

#### 2 Experimental

Published on 16 August 2013. Downloaded by University of Aberdeen on 16/08/2013 14:50:32.

The cylinder-forming block copolymer used in this work is a polystyrene-block-poly(ethylene-alt-propylene) diblock (PS-PEP 4/13) synthesized through sequential living anionic polymerization of styrene and isoprene followed by selective saturation of the isoprene block (see ref.<sup>29</sup> for more details). The number-average block molecular weights for the block copolymer are 4 kg/mol for PS and 13 kg/mol for PEP. The bulk morphology of the block copolymer consists of hexagonally packed PS cylinders embedded in the PEP matrix. For this system the glass transition temperature for the PS block is about 330K, while the order- disorder temperature is  $T_{ODT} = 417$ K (the glass transition temperature of the PEP block is well below room temperature). In thin films the cylinders adopt a configuration parallel to the substrate because of large surface energy differences between the blocks. The repeat spacing for the block copolymer is 19 nm (as measured on thin films by atomic force microscopy (AFM)).

The substrate employed here consisted of a solventannealed photoresist array of trench patterns deposited onto a silicon nitride wafer. Square-wave grating patterns of photoresist were fabricated using a lithography system. Shipley UV-6 deep UV photoresist was spin coated onto a silicon wafer bearing a 0.5  $\mu$ m SiN layer, to a thickness of 0.5  $\mu$ m. The patterns were exposed with an ASML 5500/350 stepper (wavelength 248 nm). The pitch was fixed at 2.2  $\mu$ m. Mesa heights and widths were 0.5  $\mu$ m and 1.0  $\mu$ m, respectively. The substrates with the square-wave photoresist patterns were then solventannealed under methoxy-2-propanol vapors at room temperature for about 10 min. During solvent annealing, the photoresist flows, producing the smooth curved surface shown in Fig. 1. After solvent annealing the pitch remains at 2.2  $\mu$ m while the height of the crests decreases to 100 nm. Figures 1b and 1c show SEM and AFM images, respectively, of the substrates employed here. After solvent annealing, the substrate was washed with toluene, dried under flowing nitrogen and annealed at T=373K for 2 hrs.

The block copolymer thin film was prepared via spin coating from a 1 wt. % solution in toluene, a good solvent for both blocks. By manipulating the spin speed, the thickness of the film can be controlled. Though a direct measurement of the film thickness on the corrugated substrate was not possible by ellipsometry, the spin speed chosen (3500 rpm) produced a monolayer of cylinders, plus the associated brush-like substrate wetting layer<sup>15</sup>, when the same polymer was spun onto a flat silicon wafer bearing a native oxide layer (~ 30 nm thick film of PS-PEP 4/13). Order was induced through annealing at T=373K, above the glass transition of the PS block and below the *T*<sub>ODT</sub> of the block copolymer.

SEM images of the topography of the substrates were obtained with a Philips FEI XL30 FEG-SEM. The thin films were imaged using a Veeco Dimension 3000 AFM in tapping mode. The spring constant of the tip (uncoated Si) was  $\sim 40$ N/m and its resonant frequency was 300 kHz.

#### **3** Results and Discussion

The physics behind the process of self-organization in twodimensional striped phases has been intensively studied in the last three decades. Striped phases develop in ferrimagnetic films with dipolar interactions, block copolymers, Langmuir monolayers, Rayleigh-Bénard convection cells and liquid crystals, among others<sup>30</sup>. In these systems it has been found that order is dictated by competing interactions and the phase separation mechanism around the critical point is roughly universal and independent of the specific Hamiltonian driving the order. However, although there has been recent progress in understanding equilibrium phenomena in these systems, still little is known about the kinetic pathways leading to equilibrium.

Nematic liquid crystals are anisotropic fluids characterized by a local orientation specified by a director field. In these systems, defects involve distortions in the director field that are typically referred as dislocations and disclinations. While dislocations break the translational order and introduce only marginal distortions in the director orientation, disclinations produce highly energetic elastic distortions that destroy the orientational order. Note that irrespective of the mechanism leading to the ordered state, spinodal decomposition or nucleation and growth, the formation of topological defects is completely unavoidable. Therefore, in general the population of defects is out of equilibrium and different mechanisms may participate in the pathways towards the ground state.

Since the energy of interaction between defects not only depends on the topological charge but also on the elastic constants, the mechanisms of annihilation behind the coarsening usually involve complex arrays of defects. For example, in planar systems with smectic symmetry the orientational correlation length of the domains grows according to a power law. In this case, the orientational correlation length is controlled by the density of disclinations and the dominant mechanism of ordering involves the annihilation of multipoles of disclinations (mainly tripoles and quadrupoles). In addition, given that the process of disclination annihilation is mediated by the diffusion of dislocations, the densities of disclinations and dislocations and the orientational order parameter follow a similar dependence on time.

According to the Frank model for nematic systems there are four energies to consider: layer compressibility, splay, bend, and twist. However, upon confinement in flat two-dimensional systems, twist is not allowed. Previously it has been found that assembled monolayers of cylindrical block copolymer microdomains have the symmetry of a two-dimensional smectic, which consists of liquidlike order along one axis and a mass density wave along an orthogonal axis. This symmetry emerges as consequence of the strong energetic penalty for layer compressibility imposed by the radius of gyration of the block copolymer molecules. Thus, in two-dimensional systems the features of the block copolymer texture are dictated almost exclusively by molecular splay.

If a texture is allowed to escape from flat space, the liquid crystalline order can become coupled to the geometry in which the system exists 31-34. Theoretically, a strictly twodimensional liquid crystalline phase has been studied on different topologies with non-Euclidean geometry. In this case, defects must usually be included in the ground state in order to satisfy topological requirements. For example, laying a nematic onto a sphere implies the presence of at least two positive disclinations  $^{9,31,35,36}$ . This topological requirement is given by the Gauss-Bonnet theorem which relates the integral of the Gaussian (intrinsic) curvature to the total disclination charge. In these systems it has been found that the charge and distribution of defects on the sphere depends on the ratio between the splay and bend constants. Defect configurations including hedgehog, spirals, and quasibaseball have been identified<sup>31,33</sup> and recently observed by self-consistent calculations of lamella-forming block copolymers<sup>37</sup>. In addition, in non-Euclidean space the ground state may involve an equilibrium population of defects even when there are no topological requirements for defects, such as on Gaussian bumps<sup>32</sup> or curved sinusoidal substrates<sup>38</sup>.

In experimental systems, even in very thin films, the role

For example, in the scheme shown in Figure 2 the substrate is topologically equivalent to a plane and thus, there is no topological requirement to include defects in the ground state. In addition, in a strictly two-dimensional system the energy is independent of the specific orientation of the texture. However, due to the finite film thickness, the texture can couple with the mean curvature of the substrate, breaking the azimuthal symmetry. Note in this scheme that parallel and perpendicular orientations may involve different out-of-plane bending constants and then the energy becomes dependent on the orientation of the texture with regard to the substrate. In the configuration shown on the left, where the cylinders are perpendicularly aligned with regard to the substrate undulations, the mean curvature does not affect the lattice constant of the texture. However in the parallel configuration, although the average lattice constant is undisturbed, there are regions simultaneously under compressional and dilational strain fields. Thus we can expect this configuration to have a higher energy.

Figure 3 shows Cahn-Hillard dynamic results of the coarsening process of a monolayer of cylinders lying on a cylindrical curved surface with varying mean curvature that confirm this hypothesis. The Gaussian curvature for this substrate is zero and thus it is topologically equivalent to the sinusoidal substrate shown in Fig. 2 and to flat space; there is no need for defects in the ground state. At early times we can observe that the system is relatively disordered, although it shows a very strong length scale selectivity, imposed by the competing short- and long-range interactions. As time proceeds, we found that the system orders through the annihilation of dislocations and disclinations and that the texture becomes perpendicularly oriented with regard to the long axis of the cylindrical substrate. A similar coupling between texture and geometry was observed on a cylinder with constant mean curvature (see right panel of Fig. 3).

As we show below, the experimental results are also in agreement with the hypothesis that the anisotropic bending energy of the quasi-two-dimensional smectic phase can lead to a coupling with the mean curvature of the substrate.

In the experimental system, the as-spun block copolymer thin film shows morphologies that are indistinguishable from those observed on unpatterned substrates. At this stage the self-assembly process leads to patterns with a very shortSoft Matter Accepted Manuscript

of the third spatial dimension cannot be neglected and there is natural coupling with any sort of out-of-flatness distortions. Thus, in addition to the coupling with the non-Euclidean geometry mentioned above, the texture can also become coupled to the mean curvature. The effect of extrinsic (mean) curvature in the equilibrium configuration of columnar phases was studied by Santangelo et al.<sup>32</sup>. In that case, it was found that the curvature of the substrate may act as an effective ordering field if the elastic energy associated with extrinsic curvature is taken into account<sup>33</sup>.

ranged order where there is a poor connectivity between the PS cylinders. After annealing above the glass transition temperature of the PS block, the highly disordered structure starts to order by increasing the connectivity between near-neighbor cylinders via the annihilation of dislocations and disclinations. During this stage the microdomains show the characteristic fingerprint-like patterns observed in flat block copolymer thin films, while there is a strong tendency to dewet at the regions of the substrate with the highest curvature (crests). It was found that the thin film dewets at the very early stage of relaxation, and annealing for only 5 min at T=443K is enough to clearly identify holes in the thin film (Figure 4). These holes rapidly propagate along the crests, producing stripe-shaped holes that involve about 7% of the total area of the system. Due to the high curvature of the crests (smallest radius of curvature  $\sim 75$  nm), the thin film dewets from the substrate in these regions, producing a boundary layer that acts as a lateral confining wall. During further thermal annealing the dewetted area remains stable. In the rim around the interface of the dewetted area we observed that the orientation of the PS cylinders along the boundary is predominantly random, although in some regions we observe a small tendency for parallel alignment.

As the annealing time increases, we observe a progressive increase in the degree of order while the density of defects is monotonically reduced. Figure 5 shows the pattern configuration at an intermediate coarsening time, where it is possible to identify well-ordered regions, disturbed by dislocations and arrays of disclinations. Note that ordered domains are located preferentially in the flatter regions of the substrate while the density of defects increases in the neighborhood of the dewetted area.

In flat systems, it was found that during the process of coarsening the densities of both dislocations and disclinations are reduced by annihilation events<sup>18</sup>. It was also found that disclinations can act as sources or sinks for dislocations and that dislocations can facilitate the motion of disclinations (the diffusion of disclinations proceeds via iterative steps which involve dislocations). In order to satisfy topological constraints, the coarsening process maintains equal contents of positive and negative disclinations while the orientational correlation length  $\xi_6$ , a measure of the average domain size, grows in time according to a sub-diffusive power law ( $\xi_6 \sim t^{1/4}$ )<sup>18</sup>.

Here we observe that the order in the flatter regions of the substrate evolves by a similar process. That is, order increases mainly through the annihilation of arrays (multipoles) of disclinations. Figure 6 shows a quadrupole of disclinations that annihilates upon further annealing, leaving a more ordered pattern.

In our experimental system there are two factors that break the azimuthal symmetry: the rim around the dewetted area and the coupling between the texture and the mean curvature. The boundary layers produce a lateral confinement field. The confinement exerted by two opposite rims may destabilize the parallel configuration if the confinement length scale is not commensurate with the average distance between cylinders. However during most of the coarsening process this effect is strongly screened out by the large content of orientational defects.

Note that the elastic energy excess can be easily dissipated in the neighborhood of the dewetted area because the system can release the splay energy stored in the defects via the straightening of PS cylindrical domains. This mechanism of energy dissipation can be assisted by the highly mobile dislocations that can be produced or annihilated at the boundary layer<sup>39,40</sup>.

Figure 6 also shows the thin film configuration in the neighborhood of the dewetted zone. At this stage most defects in the system have been removed and the major orientational distortions in the pattern are produced by the presence of disclinations. Note that as negative disclinations involve both bending and splay deformations, their distortional fields are strongly screened out by other defects. A similar behavior has also been observed during coarsening of cylinder-forming block copolymers with smectic symmetry deposited on flat substrates<sup>18</sup>.

Figure 7 shows an AFM image of the block copolymer texture observed after thermal annealing at T=373K for 2 hrs. This image is characteristic of the configuration and degree of alignment observed in several independent experiments. The perpendicular orientation of the cylinders with regard to the crests is noteworthy and evidences a strong coupling between the block copolymer morphology and the substrate's topography. The only imperfections in the pattern are caused by the existence of isolated dislocations and disclinations. Further annealing of the sample removes the remaining defects, resulting in a perfectly aligned pattern, with the cylindrical domains aligned perpendicularly to the crests.

We note that here the distance between the confining walls is relatively large as compared with the inter-cylinder distance, and it can be expected that with stronger confining conditions the parallel alignment would become preferential. Thus, an appropriate combination of confinement and curvature, as competing interactions, would allow control over the orientation of the cylinders with regard to the pattern features.

#### 4 Conclusions

In conclusion, in curved space, block copolymer thin films manifest the anisotropy of the out-of-plane bending constant by coupling the mean curvature of the substrate to the smectic texture. In regions with high curvature, the thin film can become unstable, dewetting from the substrate. Published on 16 August 2013. Downloaded by University of Aberdeen on 16/08/2013 14:50:32.

Finally, here we show that through the engineering of the substrate curvature and confinement conditions it is possible to control the pattern features and also to obtain novel structures unreachable in flat space.

#### 5 Acknowledgements

We gratefully acknowledge financial support from Universidad Nacional del Sur, the National Research Council of Argentina (CONICET), ANPCyT (Argentina) and the National Science Foundation: (DMR-1105417) and the MRSEC Program through the Princeton Center for Complex Materials (DMR-0819860).

#### 6 Supplementary Material. Cahn-Hilliard Dynamics

The free energy of a wide variety of systems with strong wavelength selectivity, like Langmuir films, block copolymers, magnetic garnets, and ferrofluids, can be phenomenologically described as a Ginzburg-Landau expansion in powers of the order parameter and its gradient fields <sup>30,41</sup>.

One of the simplest models to describe the dynamics of microphase separation in systems with competing interactions is to consider the Ohta-Kawasaki free-energy functional together with Langevin dynamics for a conserved order parameter<sup>42–45</sup>:

$$\frac{\partial \psi}{\partial t} = M \nabla^2 (\frac{\delta F}{\delta \psi}) + \zeta(\mathbf{r}, t). \tag{1}$$

Here the order parameter  $\psi$  is defined in terms of the local densities of each block in the block copolymer

$$\psi(\mathbf{r},t) = \frac{\rho_A(\mathbf{r},t) - \rho_B(\mathbf{r},t)}{2\rho_0}$$
(2)

where  $\rho_A(\mathbf{r},t)$  and  $\rho_B(\mathbf{r},t)$  are the local segment densities of the blocks *A* and *B*, respectively, *M* is a phenomenological mobility coefficient, and  $\zeta$  is a random noise term, with zero average and a second moment given by the mobility coefficient and the noise strength  $\eta_0$  through the fluctuation-dissipation relationship<sup>46</sup>:

$$<\zeta(\mathbf{r},t)\zeta(\mathbf{r}',t')>=2M\eta_0\delta(\mathbf{r}-\mathbf{r}')\delta(t-t')$$
(3)

The free energy functional  $F(\psi)$ , splits as:

$$F(\psi) = F_s(\psi) + F_l(\psi) \tag{4}$$

where each term models short- and long-range interactions.

The long-range free energy contribution arises from the chain connectivity of the two blocks and can be expressed as 42.

$$F_{l}(\boldsymbol{\psi}) = \frac{\beta}{2} \int d\mathbf{r}' d\mathbf{r} G(\mathbf{r} - \mathbf{r}') \boldsymbol{\psi}(\mathbf{r}) \boldsymbol{\psi}(\mathbf{r}')$$
(5)

where  $G(\mathbf{r})$  is a solution of  $\nabla^2 G(\mathbf{r}) = -\delta(\mathbf{r})$ . The shortrange term has the typical Landau form,

$$F_{s}(\boldsymbol{\psi}) = \int d\mathbf{r} [H(\boldsymbol{\psi}) + \frac{D}{2} |\nabla \boldsymbol{\psi}|^{2}]$$
(6)

where  $H(\psi)$  stands for the mixing free energy of a homogeneous blend of the disconnected A and B homopolymers, and  $\frac{D}{2}|\nabla\psi|^2$  represents the free energy cost for spatial composition inhomogeneity. The positive constant *D* scales<sup>42,45</sup> with the Kuhn statistical segment length *b* as  $D \sim b^2$ .

Here  $H(\psi)$  takes the form:

$$H(\psi) = \frac{1}{2} \left[ -\tau + A(1-2f)^2 \right] \psi^2 + \frac{1}{3}\lambda(1-2f)\psi^3 + \frac{1}{4}\sigma\psi^4$$
(7)

The parameters A,  $\lambda$ ,  $\beta$  and  $\sigma$  are related to the vertex functions derived by Leibler<sup>47</sup>. The constant f is the block copolymer asymmetry<sup>42</sup> and the parameter  $\tau$  depends linearly on the Flory-Huggins parameter  $\chi$  and provides a measurement of the depth of quench. In this free-energy model, which belongs to the Brazovskii class<sup>48</sup>, the disordered phase becomes unstable to periodic modulations just as the block copolymer melt traverses the spinodal line. By mapping the Leibler free energy functional<sup>47</sup> onto the Brazovskii free energy expression, Fredrickson and Helfand<sup>49</sup> and Podneks and Hamley<sup>50</sup> were able to extract fluctuation corrections for block copolymers. It was found that the Brazovskii fluctuations modify the phase behavior in the neighborhood of the critical point and that the order-disorder transition moves towards higher temperatures.

In this work the block copolymer composition was fixed at f = 0.4, and the phenomenological parameters were fixed at A = 1.5,  $\sigma = 0.38$ ,  $\lambda = 0.23$ , D = 0.3, and  $\beta = 0.03^{51,52}$ . The mean-field equilibrium structure for these parameters is a hexagonal array of cylindrical domains characterized by a dominant wave number  $k_0$  ( $k_0^4 = \frac{\beta}{D}$ ). Here equation (1) was numerically solved on a confining cylindrical ring with either circular (constant mean curvature) or pseudo-elliptical (varying mean curvature) cross-section. We employed periodic boundary conditions along the z-axis of the cylinder.

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**Fig. 1** Substrates employed in this work. a) Scheme showing the solvent annealing approach employed to obtain smoothly varying topographies. b) Scanning electron micrograph (SEM) image of the substrate. c) AFM height image, 2.4  $\mu$ m x 2.4  $\mu$ m, showing the profile of the substrate.



**Fig. 3** Coarsening process of a cylindrical phase deposited on a cylinder with a quasi-elliptical cross-section. At early times (panel a), the system is relatively disordered but presents a strong length scale selectivity. At longer times (panel b), the system orders, driven by the interaction and annihilation of defects. Note the preferential orientation of the cylinders on the substrate. A similar configuration was obtained on a cylinder with a circular (constant mean curvature) cross-section (panel c).



**Fig. 2** Schematic representation of two possible configurations for the block copolymer thin film. If driven exclusively by mean curvature, the ground state of the film should consist of PS cylinders perpendicularly oriented with regard to the substrate trenches (left). In a configuration where the cylinders are aligned parallel to the trenches (right), there is a free energy penalty due to the anisotropic bending constant of the ordered structure.



**Fig. 4** 3D AFM phase-height image of the block copolymer thin film after annealing at T=373K for 5 min (phase image size: 2.4  $\mu$ m x 2.4  $\mu$ m; height scale: 100 nm from crest to valley). In the regions with the highest curvature, a dewetting area rapidly propagates along the crests of the substrate.



**Fig. 5** 3D AFM phase-height image of the block copolymer thin film after annealing at T=373K for 60 min. Note the presence of  $\pm 1/2$  disclinations (circles) and a dislocation (rectangle) that disturb both orientational and translational order (phase image size: 1.8  $\mu$ m x 2.4  $\mu$ m; height scale: 100 nm from crest to valley).



**Fig. 6** AFM phase images of the block copolymer thin film after annealing at T=373K showing the structure of defects in the flatter regions (left panel) and in the neighborhood of the dewetted area (right panel). In the flat regions, the coarsening proceeds by the annihilation of multipoles of disclinations. Here the circles mark the positions of the  $\pm 1/2$  disclinations forming a quadrupole (black diamond). Right panel: To the right of the dewetted area, note the presence of three +1/2 disclinations. In the portion of the image to the left of the dewetted area, the defects have been completely removed. Scale bars=200nm



**Fig.** 7 AFM phase image of the block copolymer thin film after annealing at T=373K for 1.5 hr (2.4  $\mu$ m x 2.4  $\mu$ m). The presence of a +1/2 disclination and a dislocation have been emphasized with a circle and a rectangle, respectively. These defects can be removed by further thermal annealing.

View Article Online DOI: 10.1039/C3SM51904J



Equilibrium configuration of a cylinder-forming block copolymer thin film deposited on a curved substrate.