

# IBM Research Report

## Self Assembly Kinetics of Cylindrical-Phase Diblock Copolymer Thin Films

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## **Self Assembly Kinetics of Cylindrical-Phase Diblock Copolymer Thin Films**

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### **ABSTRACT**

We have measured the time evolution of the self assembly process in perpendicular-oriented cylindrical-phase diblock copolymer thin films using statistical analysis of high resolution scanning electron microscope images. Within minutes of annealing above the polymer glass transition temperature, microphase separation between polymer blocks results in formation of uniform nanometer-scale domains whose relative position is initially largely uncorrelated. On further annealing, the cylindrical polymer domains organize into a two-dimensional hexagonal lattice whose characteristic grain size increases slowly with time ( $\sim t^{1/4}$ ).

The design and assembly of innovative functional materials can be accomplished using physical systems that self organize on a nanometer length scale. Self assembly processes are driven by forces that direct materials toward an equilibrium minimum-energy configuration exhibiting a degree of order.<sup>1</sup> Application of these types of materials in technology requires a minimization of processing time in order to accommodate manufacturing throughput requirements. Understanding the kinetics of material self assembly offers a window into their suitability for different types of applications.

Diblock copolymers are an appealing self-organizing material for technology applications, due to the rich variety of possible nanostructures,<sup>2</sup> their size tunability,<sup>3,4</sup> and their manufacturing process compatibility.<sup>5</sup> Assembly of diblock copolymers into ordered nanomaterials involves organization on two different length scales. Initially, polymer microphase separation results in formation of uniformly-sized nanometer-scale domains whose shape and size are determined by polymer block composition. Upon longer annealing, these polymer domains arrange themselves into structures exhibiting order over a longer length scale. While certain applications require only polymer domains of uniform size, others may involve registration between domains resulting in individual element addressability. Some beautiful recent experiments have begun to explore methods for improving the degree of long-range order in diblock copolymer films using pre-patterned surface topography.<sup>6,7</sup>

In this work we have quantified the degree of spatial correlation in perpendicularly-oriented cylindrical-phase diblock copolymer thin films as a function of polymer anneal time. Diblock copolymer thin films of the type we discuss here spontaneously assemble

into hexagonal arrangements, with larger scale structure characterized as a “polycrystalline” morphology consisting of grains with different crystal orientations. Previous studies of ordering kinetics in bulk (3D) diblock copolymers have involved indirect imaging techniques such as xray scattering<sup>8</sup> and depolarized light scattering.<sup>9</sup> More recently, detailed experiments have examined the time evolution of 2D cylindrical-phase diblock copolymer films oriented parallel to the substrate plane, resulting in a 2D striped pattern.<sup>10,11</sup> A combination of SEM and atomic force microscopy (AFM) have elucidated the mechanism of pattern coarsening in these films, whose correlation length increases slowly with polymer anneal time ( $\sim t^{1/4}$ ).

The diblock copolymers studied in this work are composed of polystyrene (PS) and poly(methyl methacrylate) (PMMA) of average molecular weight  $M_n=67\ 000\ g/mol$ , polydispersity index of 1.09, and PMMA weight fraction of 30 percent.<sup>12</sup> In the bulk, diblock copolymers of this molecular weight ratio spontaneously phase separate into a cylindrical phase.<sup>2</sup> This experiment examines the self assembly kinetics in a system where polymer cylinders orient perpendicular to the substrate.

We spin-cast the PS-PMMA diblock copolymer from a 1% wt. solution of toluene in order to form ~40 nm thick films on silicon substrates. The films were then annealed at 165 °C (well above  $T_g\sim 105\ ^\circ C$ ) in vacuum to facilitate microphase separation of the two polymer blocks and provide polymer mobility. Because of the molecular weight ratio of our diblock copolymer (70:30 PS:PMMA), the resulting polymer films consist of PMMA cylinders in a matrix of PS. In order to promote perpendicular PMMA cylinder orientation (relative to the substrate), we first treated the silicon surface with a random copolymer.<sup>13,14,15</sup> Prior to film analysis via scanning electron microscopy (SEM), we

removed the PMMA block from the annealed film by exposure to ultraviolet (UV) light ( $\sim 1.2 \text{ J/cm}^2$ , peak wavelengths 185 and 254 nm) and immersion in glacial acetic acid (20 min.). PMMA removal improved SEM contrast in order to better observe the film nanostructure.

We probed the intrinsic kinetics of polymer thin film self assembly by varying the anneal time for a fixed anneal temperature (165 °C). Initially, microphase separation of the PMMA and PS polymer blocks results in formation of nanometer-scale domains whose size and repeat distance are determined by polymer molecular weights. We have previously analyzed the time evolution of the uniformity of these individual polymer domains.<sup>3</sup> Evidence of the time scale for polymer microphase separation is apparent in Fig. 1(a), where uniformly sized PMMA cylinders (dark regions) are clearly visible after only 15 min of annealing, although the relative spatial orientation of the PMMA cylinders is largely uncorrelated. The standard deviation of the cylinder size distribution of a 15 min. annealed film is 20%, and is reduced a minimum of  $\sim 10\%$  after 6 hours [Fig. 1(c)].

While polymer microphase separation and PMMA cylinder formation occur within minutes at 165 °C, upon further annealing the PMMA cylinders self-organize on a longer length scale into an equilibrium two-dimensional (2D) hexagonal lattice. SEM images of polymer films annealed for four different times (15 min., 2 hr., 6 hr., and 24 hr.) show qualitatively improved spatial organization with increasing anneal time [Fig. 1(a-d)]. Films annealed for short times [Fig. 1(a)] show regularly shaped cylinders<sup>Error! Bookmark not defined.</sup> with largely random relative arrangements. After 15 min. only a small fraction of the film is composed of hexagonal domains. Upon increasing the anneal time, the

hexagonal cylinder domains grow in size [Figs 1(b)-(c)]. After 24 hours [Fig. 1(d)], the polymer film contains defect-free regions which are several hundred nanometers in size.

We quantify the degree of spatial crystallinity in the polymer film by tabulating a list of every inter-cylinder distance, calculated from cylinder center positions. This list is used to generate a histogram of cylinder separations for different polymer film anneal times. Maxima in the histograms therefore signify frequently-occurring cylinder separation distances. For example, in a film containing a random arrangement of cylinders, no inter-cylinder distance is more likely to occur than any other and thus the histogram would contain no characteristic peaks.

The cylinder separation spectrum of a perfect hexagonal array consists of a series of discrete peaks, which are depicted schematically in Fig. 2(c). Examples of distances which give rise to spectral peaks are shown in Fig. 2(b). Beginning from the cylinder position in the center of Fig. 2(b), the six nearest neighbors occur at a distance  $a$  away [ $a$  is the fundamental unit lattice vector [Fig. 2(a)]. Successive rings of neighbors occur at integral multiples of the underlying lattice vectors. Fig. 2(b) illustrates those spectral peaks corresponding to lattice vectors (1,0), (1,1), (2,0) and (2,1). Certain inter-cylinder distances occur with more frequency than others, resulting in variations in spectral line intensity. For example, inter-cylinder distances corresponding to (2,1) [shown in Fig. 2(b)] occur twice as often as either (1,0), (1,1), or (2,0).

The measured inter-cylinder separation spectrum for a PS:PMMA film annealed for 24 hours (Fig. 3) begins as a series of discrete peaks at small separation distances, transitions to a continuous curve containing well-defined local maxima for distances between 140 and 380 nm, and eventually broadens into a featureless constant background

above 400 nm [See Fig. 4(a)]. Spectral peaks correspond to frequently occurring inter-cylinder separations, and the fact that peaks at distances of 350 nm are still distinguishable from the continuous background indicates the film retains a degree of hexagonal ordering over this distance. Comparison between the measured spectrum and one calculated for an ideal hexagonal array (solid vertical lines in Fig. 3) facilitates assignment of peaks to specific multiples of the underlying hexagonal lattice vectors. Higher-order spectral lines become more densely spaced and merge to form broader peaks which are nevertheless distinguishable from the background. At larger distances, weaker-intensity peaks merge together to form a continuous background -- for example, lines at 140 nm, 166 nm, and 210 nm are obscured due to their proximity to more intense peaks. As shown in the figure, measured spectral peaks correlate well with calculated lines in both position and relative intensity out to distances beyond 350 nm, giving a straightforward way to assign a quantitative measure to the spatial extent of long-range order. We define the distance of the last discernable spectral peak as the film spatial correlation length,  $\mathbf{x}$ .

Figure 4 shows the inter-cylinder separation spectra for polymer films annealed for 5 different times, ranging from 15 min. to 24 hr. As clearly seen in the Figure (and illustrated in the SEM images of Fig. 1), the spatial correlation length ( $\mathbf{x}$ ) increases with anneal time, which is evidenced by the emergence of an increasing number of peaks at larger inter-cylinder distances. For example, the 15 min. annealed film [Fig. 1(a)] shows only 3 spectral lines out to a distance of  $\mathbf{x} \sim 130$  nm (uncertainty in  $\mathbf{x}$  is due to the width of the highest-order distinguishable peak). This third line is indexed to lattice vectors (2,1), implying that in this film the degree of perfect hexagonal ordering extends on

average over only 2 unit cells. The 1 hr. and 2 hr. films show 4 distinct spectral lines (out to  $\lambda \sim 150$  nm and  $\lambda \sim 160$  nm, respectively), while the 6 hr. film shows 7 distinct lines (out to  $\lambda \sim 260$  nm). As we have discussed above, the 24 hr. film remains both ordered out to  $\lambda \sim 380$  nm and also the sharpness of the spectral lines is improved. For example, the FWHM of the first spectral line (nearest neighbor distance) is reduced by 50% at 24 hours versus that at 15 min. Also, the two spectral lines at 67 nm and 82 nm are fully resolved after 24 hours, whereas for shorter anneal times the peaks overlap.

A plot of the film correlation length ( $\lambda$ ) versus anneal time [Figure 4(b)] reveals a power law relationship between the two quantities. The solid line in the Figure is the best fit to the data, and is of the form  $\lambda \propto t^{0.25 \pm 0.04}$ . The data suggest a scaling exponent of 1/4, which is smaller than that previously measured for bulk (3D) cylindrical phase diblock copolymers (grain volume  $V \propto \lambda^3 \propto t^{1.2}$ ). The  $t^{1/4}$  scaling exponent is similar to that seen in previous experiments in 2D cylindrical-phase diblock copolymer thin films oriented *parallel* to the substrate,<sup>10,11</sup> which is interesting given the different sample geometries and gives the hint that similar defect dynamics may apply.

The slow time evolution of long-range order in these polymer films limits their practicality for use in certain applications. For example, an application requiring hexagonal ordering over distances of 1  $\mu\text{m}$  would require a prohibitive polymer anneal time of  $4.4 \times 10^6$  sec ( $\sim 50$  days) at 165 °C. In this case the polymer anneal temperature can be used to speed up the kinetics of both microphase separation (formation of uniform size polymer domains) and longer-range ordering. Similar PS-PMMA films annealed at 180 °C (rather than 165 °C) show spatial correlation of  $\lambda \sim 260$  nm after only 1 hour of



annealing. If  $\lambda$  has the same  $t^{1/4}$  dependence at 180 °C as at 165 °C (as has been observed for 2D copolymer films oriented parallel to the substrate<sup>10,11</sup>), hexagonal domains of 1  $\mu\text{m}$  in diameter can be achieved after  $\sim 9$  days (still prohibitively long). Because the kinetics of diblock copolymer self assembly are exceedingly slow, several groups have begun exploring topographic means for improving the degree of long range order.<sup>6,7</sup>

We have used statistical analysis of high resolution SEM images to measure the time evolution of the spatial correlation length ( $\lambda$ ) in perpendicularly-oriented cylindrical-phase diblock copolymer thin films. Our analysis facilitates a straightforward determination of  $\lambda$  as the highest-order distinguishable peak in an intercylinder separation spectrum. This technique is general and can be used to study long range order in other self assembling systems such as nanocrystal films, spherical-phase diblock copolymer films, or anodic alumina templates. We find that in our films the spatial correlation evolves with a weak  $t^{1/4}$  time dependence, which is similar to that observed in such disparate systems as parallel-oriented cylindrical-phase diblock copolymer films and in electroconvection in nematic liquid crystals.<sup>16</sup>

**FIGURE CAPTIONS**

**FIGURE 1.** SEM images of self-assembled PS films annealed at 165 °C for different amounts of time. In order to improve image contrast, PMMA block has been removed from the film. (a) 15 min. anneal. (b) 2 hour anneal. (c) 6 hour anneal. (d) 24 hour anneal.

**FIGURE 2.** (a) Schematic representation of hexagonal unit cell, labeled with two unit vectors (0,1) and (1,0). Table of distances between points in a 2D hexagonal lattice. (b) Schematic 2D hexagonal lattice showing successive rings of intercylinder separation distances. (c) Histogram of intercylinder separation distances.

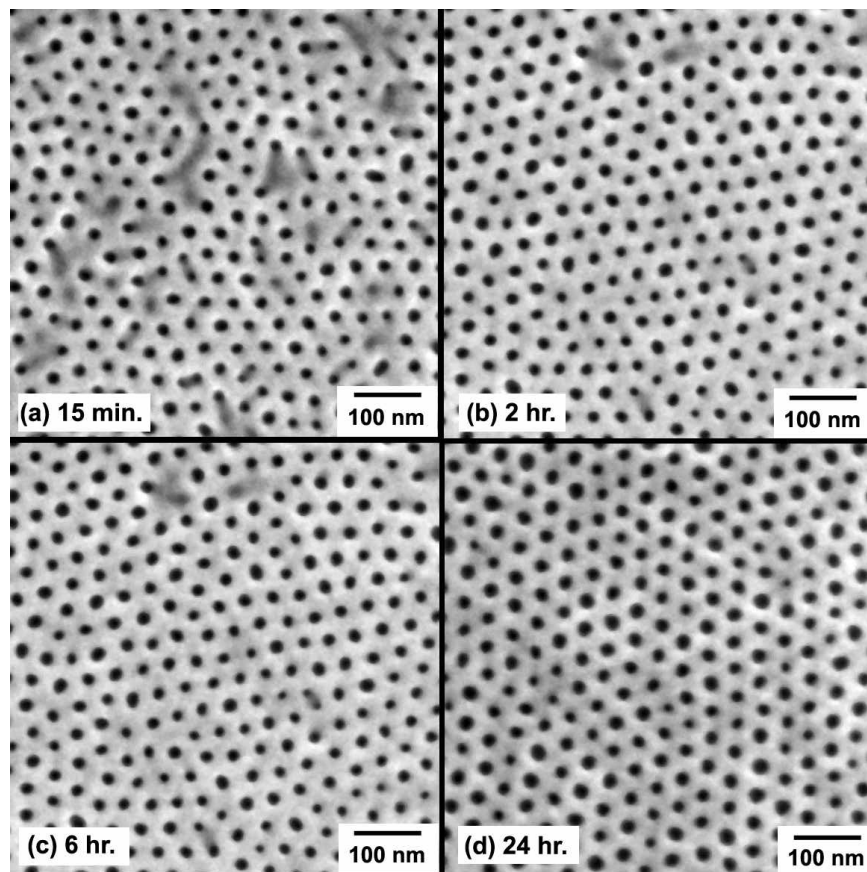
**FIGURE 3.** Intercylinder separation spectrum for diblock copolymer film annealed at 165 °C for 24 hours. Peaks in the spectrum match those of a perfect hexagonal array (black bars) out to distances of more than 350 nm.

**FIGURE 4.** (a) Intercylinder separation spectra for diblock copolymer films annealed at 165 °C for 15 min., 1 hr., 2 hr., 6 hr., and 24 hr. Spectra are offset by 100 counts for clarity. (b) Log-log plot of film coherence length versus anneal time for diblock copolymer film. The solid curve is the best fit power law ( $\propto t^{0.25 \pm 0.04}$ ).

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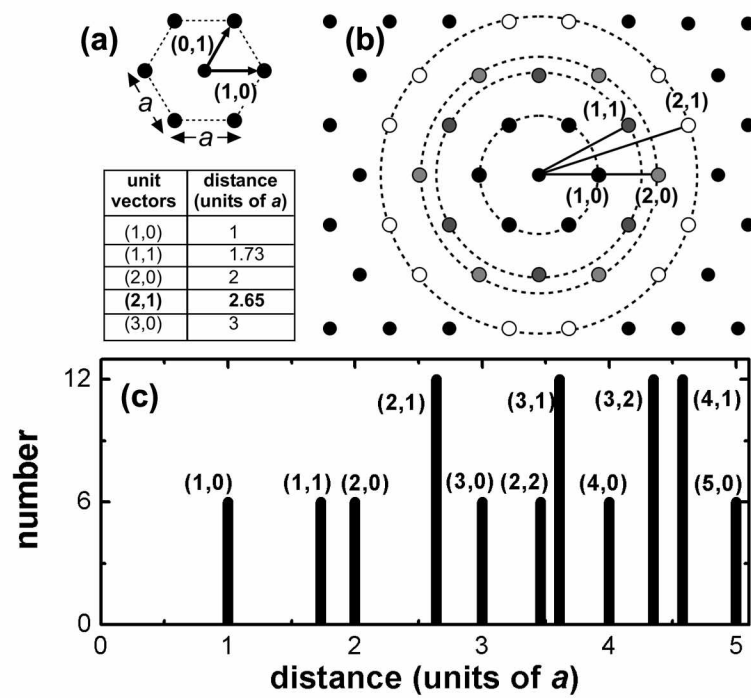
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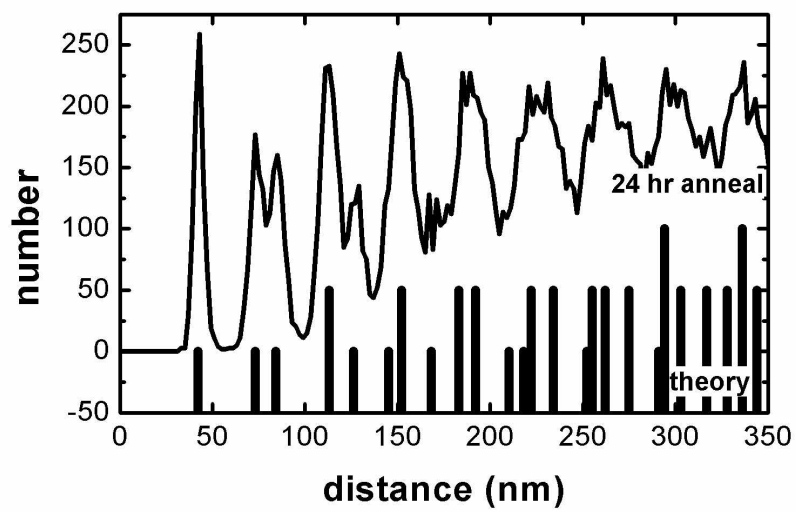
**FIGURE 1**

C. T. Black and K. W. Guarini, PRB



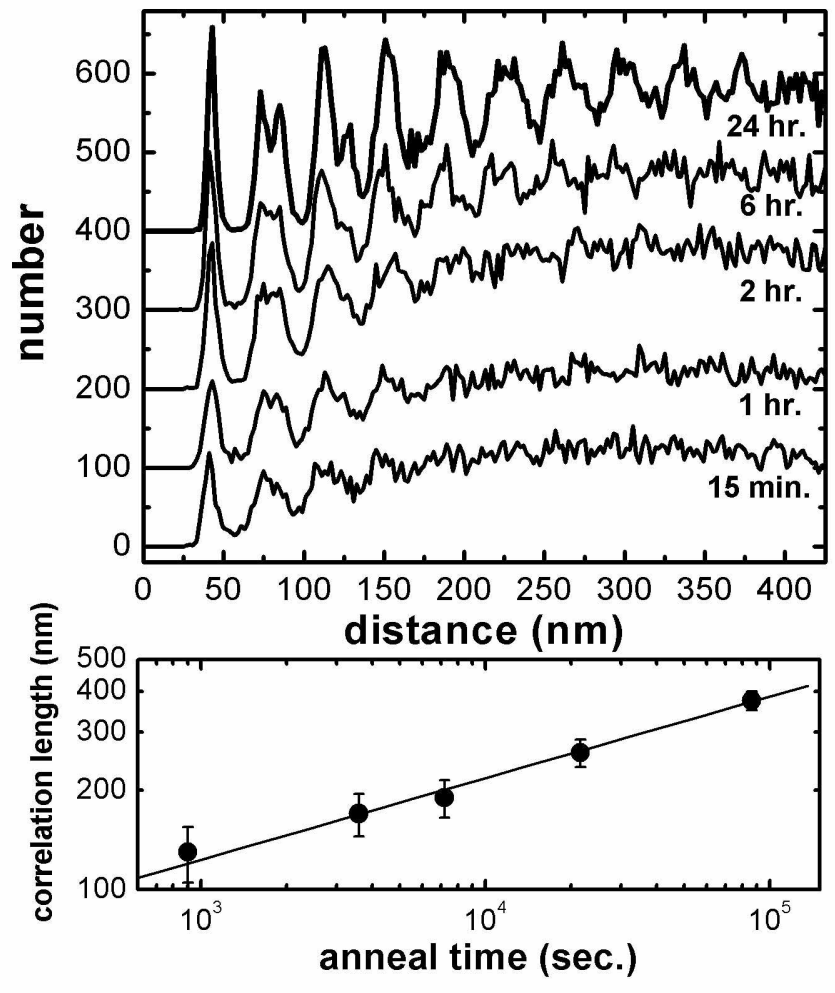
**FIGURE 2**

C. T. Black and K. W. Guarini (PRB)



**FIGURE 3**

C. T. Black and K. W. Guarini, PRB



**FIGURE 4**

Black and Guarini, PRB