## **Basics of Block Copolymer Directed Self-Assembly**

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For labmembers with high-resolution patterning needs, block copolymer directed selfassembly can be a low-cost, high-throughput complement to more traditional lithography techniques. Block copolymers consist of two or more chemically distinct polymers bound endto-end. When a block copolymer solution is spun onto a substrate, the film can be heated to induce self-assembly. In this process, the constituent polymers repel each other according to their Flory-Huggins interaction parameter ( $\chi$ ) to achieve their minimum free energy position. As the blocks segregate, like polymers are attracted to like polymers, leading to the formation of periodic domains. The shape of the self-assembled domains depends on the number of blocks in the block copolymer and on the relative proportion of those blocks. [1] This report will focus on diblock copolymers with two constituent polymers. Among the various domain shapes achievable, the ones most practical for lithography are lamellae and cylinders formed using 50:50 and 70:30 block copolymers, respectively.



*Figure 1:* Illustration of how domain shape varies for an A-B diblock copolymer as the fraction of Block A (f<sub>A</sub>) increases. The possible domain shapes include spheres, cylinders, gyroids, and lamellae. [1]

The size and spacing of the self-assembled lamellae or cylinders is fixed by the block copolymer's natural pitch (L<sub>0</sub>). For a block copolymer with a given L<sub>0</sub>, the domains will have a critical dimension (CD) of  $0.5 \times L_0$  and a pitch of L<sub>0</sub>. Since natural pitch is a function of the polymer length, the resolution of block copolymer lithography varies with the specific polymer being used: the shorter the block copolymer, the smaller the domains and the higher the resolution. However, the range of achievable resolution is limited on the upper and lower ends by the mechanics of the self-assembly process. If the block copolymer is too short, the constituent polymers will not repel each other sufficiently to achieve strong segregation, leading to disordered self-assembly. At the same time, a block copolymer that is too long will lack the agility to orient itself into the lowest free energy position and thus will self-assemble defectively. For the industry-standard block copolymer poly(styrene-*block*-methyl methacrylate) (PS-*b*-PMMA), the most commonly used polymer length has  $L_0 \approx 40$  nm. That said, the minimum CD for PS-b-PMMA domains is approximately 12 nm with  $L_0 = 24$  nm. An active area of research seeks to push the minimum resolution even lower using high- $\chi$  block copolymers that have enough repellent force between the blocks to segregate even at short lengths [2].

Although block copolymer films will self-assemble as-is, unguided self-assembly may yield domains with irregular spacing or that lay parallel to the substrate. For this reason, using chemical or topographical pre-patterns to guide the self-assembly process is recommended to achieve well-controlled results. Generally speaking, chemical guides are more helpful for large-area periodic patterns, while topographical templates are more helpful for small-area or aperiodic patterns. These guides can be fabricated using a complementary patterning technique, such as optical or e-beam lithography.



*Figure 2:* Scanning electron microscope images for chemo- and graphoepitaxy with cylinder- and lamellae-forming block copolymers. From the top-left clockwise, the images are from [4], [7], [6], and [3].

In chemoepitaxy, chemical prepatterns that attract one of the blocks and repel the other are used to anchor the selfassembled domains. This not only helps to orient the domains perpendicular to the substrate, but also enables more consistent domain spacing. Chemical guides should be of a size and shape similar to the targeted domain and can be made of HSQ or another material as suits the block copolymer. As a starting point, labmembers should position the chemical guides such that every four domains are anchored. [3, 4]

In graphoepitaxy, topographical wells are used to isolate single domains or clusters of domains. Relative to chemoepitaxy, graphoepitaxy enables more flexible placement of the block copolymer domains: the wells can be positioned as desired, and

the block copolymer domains will only form inside of the wells. Since the size and pitch of the domains is fixed by the polymer, increasing the well size also increases the number of domains inside the well. As well size increases, though, the placement accuracy of the domains within the wells degrades. For best placement accuracy, linear wells with no more than three domains are recommended. As a starting point for guiding well dimensions, labmembers should refer to [5], [6], and [7].

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