

Nanolithography with Block Copolymers

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The development of nanotechnology depends on the abilities to manipulate materials and structures at the nanoscale, i.e. less than 100 nanometer or 100 billionths of a meter. Nanofabrication with self-assembly of molecules is being developed as one of the promising alternatives for conventional lithographic methods such as photolithography and electron beam lithography^{1,2}. Block copolymers are given much attention for this approach due to their ability to form micro domains at the nanoscale as well as the tunability of the size and shape of these microdomains.

Block copolymers are composed of long sequences of two or more chemically distinct polymer blocks. These blocks can be connected in different ways as shown in figure 1.

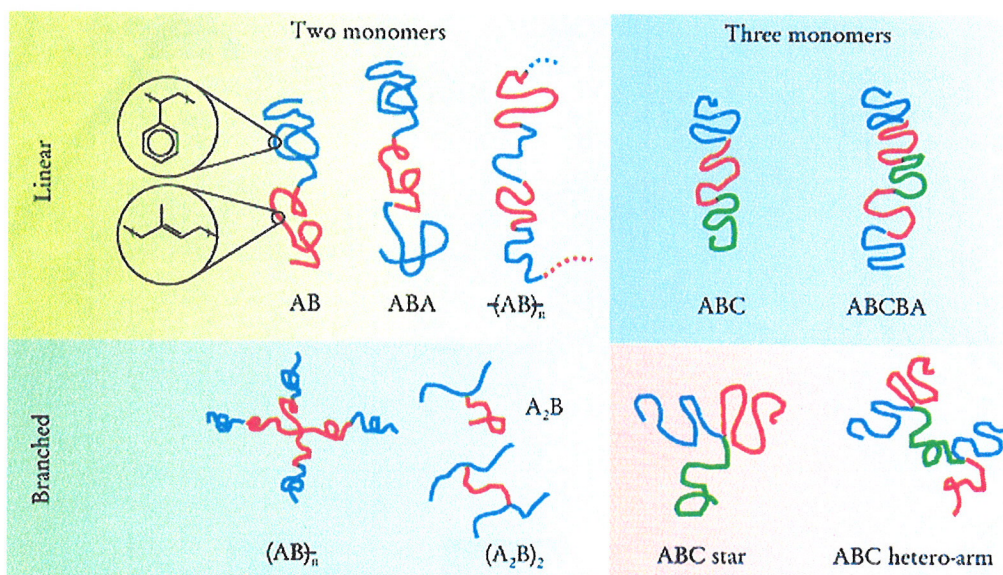


Figure 1: Structures of block copolymers.³

The general method for preparing block copolymers is sequential addition or coupling with truly living or controlled polymerized chains.⁴ Living ionic polymerization together with other methods such as controlled radical polymerization or living synthesis for polyolefins⁵ have widened up the monomer range, giving various tools for synthesizing and designing block copolymers.

Because of the incompatibility between the component blocks, they tend to segregate into different phases. However, the thermodynamic forces driving separation are counterbalanced by the entropic forces from covalent linkages between the blocks. This results in no macrophase separation, but microphase separation in the order of nanoscale. Therefore, diblock copolymers can self assemble into different morphologies: spheres, cylinders, lamellae or gyroid, depending

on the degree of polymerization (N), the composition (f) and Flory-Huggins interaction parameter (χ) between component blocks.^{3,6}

The self assembly of block copolymers into microphases with different chemical and physical properties has been utilized in nanolithography for patterning dense periodic arrays of structures such as nanowires, quantum dots, magnetic storage media, flash memory devices, photonic crystals and silicon capacitors.⁷⁻⁹ In this patterning process, a thin film of a block copolymer spontaneously self assemble into microphase separated nanoscale domains. The domains are chemically treated such as one domain with double bonds being degraded with ozone or stained with osmium in order to change the etching rates and acting as a mask during etching for creating patterns onto the substrate.

The greatest challenge for this patterning approach is how to control the order of microdomains of block copolymers in large scale. The microphase separation in block copolymers forms well-ordered structures just in a nanoscale regime. On a larger scale, there are a lot of dislocations, disclinations and other defects that limit the use of block copolymers in patterning large area. Much effort has been done in order to get control of the order of the microdomains in block copolymers, using external field such as shear¹⁰, and electrical field¹¹, or epitaxy onto crystalline substrates¹² or chemically patterned substrates¹³, or confinement onto topographically patterned substrates (graphoepitaxy)¹, or using directional crystallization of solvents¹.

References

1. Park, C.; Yoon, J.; Thomas, E. L. Enabling Nanotechnology with Self Assembled Block Copolymer Patterns. *Polymer* **2003**, *44*, 6725-6760.
2. Gates, B. D.; Xu, Q.; Stewart, M.; Ryan, D.; Wilson, C. G.; Whitesides, G. M. New Approaches to Nanofabrication: Molding, Printing, and Other Techniques. *Chem. Rev.* **2005**, *105*, 1171-1196.
3. Bates, F. S.; Fredrickson, G. H. Block Copolymers - Designer Soft Materials. *Phys. Today*. *February* **1999**, 32-38.
4. Hillmyer, M. Block Copolymer Synthesis. *Cur. Opi. Solid State Mater. Sci.* **1999**, *4*, 559-564.
5. Hadjichristidis, N.; Pispas, S.; Floudas, G. A. *Block Copolymers: Synthetic Strategies, Physical Properties, and Applications*. **2003**, John Willey & Sons, New Jersey, 1-172.
6. Segalman, R. A. Patterning with Block Copolymer Thin Films. *Mater. Sci. Eng.* **2005**, *R 48*, 191-226.
7. Park, M.; Harrison, C.; Chaikin, P. M.; Register, R.A.; Adamson, D. H. Block Copolymer Lithography: Periodic Arrays of $\sim 10^{11}$ Holes in 1 Square Centimeter. *Science*, **1997**, *276*, 1401-1404.

8. Cheng, J. Y.; Ross, C. A.; Chan, V. Z.-H.; Thomas, E. L.; Lammertink, R. G. H.; Julius Vancso G. Formational of a Colbalt Magnetic Dot Array via Block Copolymer Lithography. *Adv. Mater.* **2001**, *13*, 1174-1178.
9. Stoykovich, M. P.; Muller M.; Kim, S. O.; Solak, H. H.; Edwards, E. W.; de Pablo, J. J.; Nealey, P. F. Directed Assembly of Block Copolymer Blends into Nonregular Device-Oriented Structures. *Science*, **2005**, *308*, 1442-1446.
10. Angelescu, D. E.; Waller, J. H.; Register, R. A.; Chaikin, P. M. Shear-Induced Alignment in Thin Films of Spherical Nanodomains. *Adv. Mater.* **2005**, *17*, 1878-1881.
11. Thurn-Albrecht, T.; Schotter, J.; Kastle, G. A.; Emley, N.; Shibauchi, T.; Krusin-Elbaum, L.; Guarini, K.; Black, C. T.; Tuominen, M. T.; Russell, T. P. Ultrahigh-Density Nanowire Arrays Grown in Self-Assembled Diblock Copolymer Templates. *Science*, **2000**, *290*, 2126-2129.
12. De Rosa, C.; Park, C.; Lotz, B.; Wittmann, J.; Fetters, L. J.; Thomas, E. L. Control of Molecular and Microdomain Orientation in a Semicrystalline Block Copolymer Thin Film by Epitaxy. *Macromol.* **2000**, *33*, 4871-4876.
13. Kim, S. O.; Solak, H. H.; Stoykovich, M. P.; Ferrier, N. J.; de Pablo, J. J.; Nealey, P. F. Epitaxial. *Nature*, **2003**, *424*, 411-414.