FABRICATING NANO-SCALE DEVICES: BLOCK COPOLYMERS AND THEIR APPLICATIONS

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In the earliest days of synthetic chemistry, scientists in the field attempted to control the ordering of atoms on a molecular scale in order to create useful compounds for various applications, such as synthetic medicines, dyes, and catalysts. Molecular-scale synthetic chemistry continues to thrive today, and has led to the discovery of synthesis schemes for millions of organic molecules, ranging from simple hydrocarbons such as methane to complex biological molecules such as Vitamin B12. However, as molecular-scale chemistry has flourished, new techniques in macromolecular chemistry, dealing with compounds of a thousand atoms or more, have emerged rapidly, enabling the control of atomic placement in macromolecules, which are found widely in commercial products and in biological systems.

One of the major focuses of macromolecular chemistry today is the production and processing of polymers, which are macromolecules made from repeating sub-units known as monomers. Molecules such as deoxyribonucleic acid and cellulose, polymers of ribose and glucose, respectively, play crucial roles in biological systems, highlighting their versatility and widespread use. In 1907, scientist Leo Baekeland completed the first successful synthesis of a polymer, Bakelite, which found use in an immense amount of commercial products such as brake pads and electrical insulation, and was coveted for its high resistance to heat and chemical corrosion. The creation of Bakelite ushered in the age of modern plastics, which resulted in the creation of many useful polymeric materials such as Nylon, Kevlar, and Teflon.

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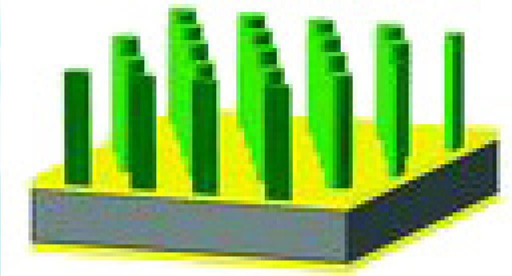
Today, while attempts to synthesize simple polymers continue, significant research effort is directed towards understanding the properties and applications of block copolymers. Unlike regular polymers, which are long chains of the same repeating monomer unit, block copolymers are assembled from "blocks" of different monomers, creating a large macromolecule with varying chemical composition at different points along the chain (Matsen and Bates, 1996). This added complexity in the case of block copolymers leads to a variety of interesting phenomena, all of which can be controlled and fine-tuned using synthetic chemical approaches, which enables the creation of a new class of functional materials.

Many of the interesting properties of block copolymers arise from the chemical interactions between different blocks of the polymer. In a traditional, molecular chemistry sense, unfavorable interactions between two molecules, such as water and oil, lead to repulsions and, if the forces are strong enough, phase separation. However, in a block copolymer, even though certain blocks may have unfavorable interactions with each other, they cannot simply separate like water and oil, because they are all part of the same macromolecule. Rather than driving phase separation processes such as those found in water-oil mixtures, the relative strengths of chemical interactions in block copolymers drive a process known as self-assembly, in which the blocks fold, twist, and re-organize into a more favorable three-dimensional structure that situates chemically similar blocks next to each other (Matsen and Bates, 1996).

Due to the complexity of self-assembly processes, they are best understood using a familiar analogy to highlight the atomic-scale driving forces that result in self-assembly. Each of the blocks in a block copolymer can be thought of as one person in a large gathering of ten thousand or more people. This gathering, however, has the odd caveat that every person must hold the hands of two random people, effectively linking everyone into one large chain. Due to the random selection of two adjacent people, it is completely possible, and in fact likely, that two people holding hands do not know each other at all. After some time, the large chain of people would re-organize into a folded structure due to the movement of people towards those that they know. Much like the reorganization of people in this gathering, blocks in block copolymer re-organize (either spontaneously or with sufficient thermal activation) in order to ensure that favorable chemical interactions are maximized. Some common three-dimensional structures found in many block copolymers include "striped" lamellae, packed cylinders, and gyroids (Matsen and Bates, 1996).

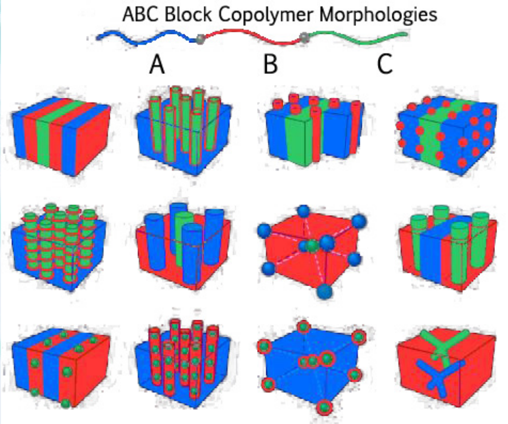
> *Much like protein folding in biological systems, the folding and self-assembly processes of block copolymers can be harnessed to create ordered structures on the scale of hundreds of nanometers, which can enable the creation of functional synthetic nanomaterials.*



A packed cylinder block copolymer morphology, used as a template for producing nanowires.

Much like protein folding in biological systems, the folding and self-assembly processes of block copolymers can be harnessed to create ordered structures on the scale of hundreds of nanometers, which can enable the creation of functional synthetic nanomaterials. Furthermore, due to modern characterization techniques such as X-Ray diffraction (XRD), and transmission electron microscopy (TEM), scientists can "see" in great detail the three-dimensional structures of macromolecules, enabling rational engineering of the self-assembly process to form useful materials with nano-scale ordering.

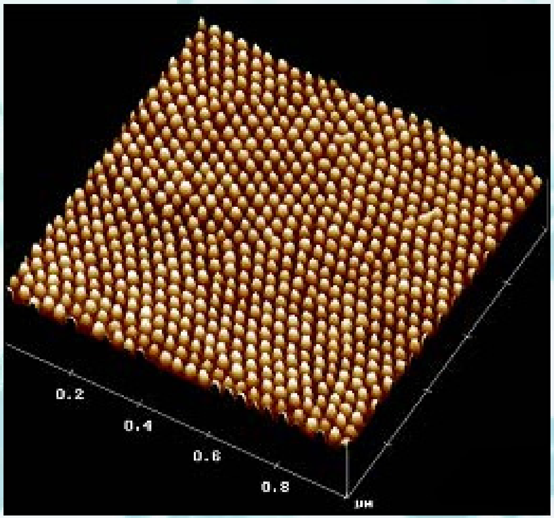
One major application of block copolymers is in the fabrication of nanowires, which are, micrometer-long wires with a length and thickness on a nanometer scale. These nanostructures are incredibly exciting due to their capability to link nano-scale devices much like regular wires link macro-scale electronic devices today. For example, quantum dot solar cells, which can harvest the solar spectrum to previously unattainable efficiencies (Nozik, 2002), need some method of transporting charge around the solar cell array. Of course, a regular metal wire would be far too large for such a purpose, so wires at the length scale of the quantum dots must be used (Zhang et al., 2012). As one may imagine, the placement of nanowires with such high precision at low length scales is nearly impossible, even with advanced techniques such as molecular beam epitaxy (Jung et al., 2010). Block copolymers, on the other hand, with blocks arranged in cylindrical morphologies, present the perfect template for growing nanowires, as they have near-perfect ordering on a length scale relevant for nanowire device applications.



Various self-assembled block copolymer morphologies.

Recently, a research group at MIT led by Prof. Caroline Ross succeeded in the nano-scale patterning of nanowire arrays using block copolymers. Using the block copolymer poly(styrene-block-dimethylsiloxane), which self-assembles (at a slightly elevated temperature) into a structure made of packed cylinders that are approximately fifteen nanometers wide. Using this macrostructure as template for nanowire deposition, the researchers etched away the polystyrene matrix, leaving behind cylindrical troughs where the polystyrene blocks once were. After etching, a thin layer of metal was deposited into these cylindrical troughs using sputter coating, a processing technique common in semiconductor fabrication. Once the templated metal was deposited, the rest of the polymer was etched away, leaving behind nanowires with a predictable size, shape and periodicity (Jung et al., 2010). Such a technique, achievable entirely due to block copolymer self-assembly, holds a high potential for device fabrication applications (Cheng et al., 2006), which require creating and placing nanowires of predictable size.

Another recent, exciting application of block copolymers has emerged in the fabrication of new quantum dot light-emitting diodes (LEDs), which can efficiently miniaturize the LED technology now used nearly ubiquitously in electronic displays. Traditional LEDs work by sandwiching a specifically designed semiconductor material between two different electrical contacts. By tuning the electronic properties of the semiconductor material, scientists have been able to engineer LEDs that emit light at different colors of the visible spectrum, which can then be combined into pixels on a visual display. Quantum dots, which are nano-scale semiconductor crystals, can not only miniaturize current LED technology, but also substantially reduce its power requirements, making them optimal choices for new LED displays (Sun et al. 2007).



Example of an array of GaAs quantum dots patterned using block copolymer self-assembly.

Until recently, however, quantum dot display technologies were hampered by their inability to be deposited as thin films resistant to oxidation from air exposure and other environmental degradation. Block copolymers, however, seem to present the perfect solution for such issues. Recently, a research group from Johannes Gutenberg University in Germany successfully created quantum dot thin films by grafting molecules of poly(para-methyl triphenylamine-block-cysteamine acrylamide), a block copolymer, onto the quantum dots. Due to the unique self-assembly properties of the block copolymer, each quantum dot assembled in a patterned manner, forming a thin film with excellent environmental stability and luminescent properties (Zorn et al. 2009). Furthermore, these devices were three times more efficient than previously created quantum dot LEDs, while also emitting light at a higher intensity (Zorn et al. 2009). These quantum dot thin film LEDs, while still in the early stages of development, show great promise for device applications due to the unique properties of block copolymers.

Synthetic chemistry has certainly come a long way since the creation of synthesis techniques to control molecular-scale ordering, and can now exert a high degree of control over atomic and structural ordering at a much larger length scale. Block copolymers, due to their self-assembly properties, present excellent opportunities for the creation of devices that operate at the nano-scale. Furthermore, since the chemistry of self-assembly can be well controlled, scientists can now bring synthetic chemistry techniques to bear on problems that operate at much larger length scales.

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