PERSPECTIVES: MATERIALS SCIENCE

The ABCs of Self-Assembly

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The structure of biological macromolecules is typically determined by their sequence of different monomer units. In contrast, polymer chemists have long used large blocks of identical monomer units to tailor the microstructure of polymer materials. Recent work on such self-assembled block copolymers has led to materials exhibiting intricate three-dimensionally periodic structures (*1*–*3*). Such novel interconnected nanoscale patterns are providing opportunities in a variety of technological arenas from separation membranes to photonic crystals.

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The simplest block copolymer consists of two chemically dissimilar polymer chains, A and B, which form a single macromolecule. Such AB diblock copolymers can be thought of as giant amphiphiles whose components segregate into domains to avoid unfavorable contact with each other; complete phase separation is prevented by the covalent linkage between the components. The spatially periodic domain structure, whose domain size and spacing are typically on the 10- to 50-nanometer scale, must then minimize unfavorable interfaces and at the same time avoid overstretching the polymer blocks. Depending on the length of the A and B segments, spherical, cylindrical, or lamellar domains may form. Higher structural complexity is observed in three-component systems, and ABC triblock copolymers have proven a very fertile area for creating new microdomain patterns (*4*).

The three classical domain shapes in block copolymers—the sphere, the cylinder, and the flat layer—are also seen in surfactant systems. But in the late 1960s, Luzzati and Spegt found out that the structural complexity does not stop here. They discovered the first intricate interconnected triply periodic network domain structure in a strontium soap (*5*). At the time of its discovery, this complex domain structure was a complete surprise to the scientific community. In contrast, mathematicians had been familiar with triply periodic structures ever since Schwarz's studies on triply periodic minimal surfaces in the 1800s (*6*).

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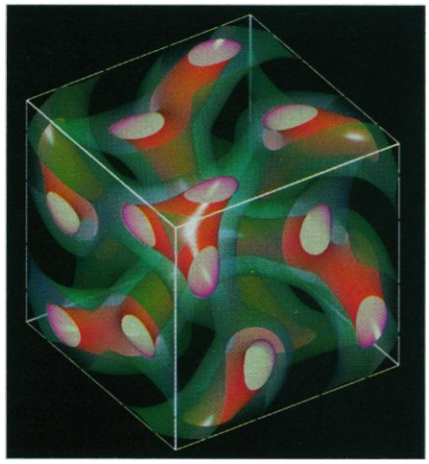
A minimal surface is one whose mean curvature is zero everywhere. Such surfaces are either flat or saddle shaped and have smaller areas than those of similar surfaces produced by small deformations of the minimal surface. If the area is to be minimized while keeping the volumes on the two sides of the surface fixed, the best surfaces are constant mean curvature (cmc) surfaces. Spherical and cylindrical domains are examples of cmc surfaces, whereas the flat layers in lamellar block copolymers and surfactants are an example of minimal surfaces (*7*).



Complex block polymer structures. Volume rendering over one unit cell of the pentacontinuous double-gyroid ABC triblock copolymer structure synthesized by (*1*, *2*).

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At about the same time as the strontium soap structure was discovered, Schoen, an applied mathematician and engineer, found many new saddle-shaped triply periodic minimal surfaces, including one with cubic symmetry, which he named the "gyroid" (*8*). In 1997, Grosse-Brauckmann proved the existence of a cmc family of gyroid structures and computed the surface area–volume fraction relations (*9*). The newly discovered ABC polymer structures (*1*–*3*) are closely related to members of this family and to the original Luzzati and Spegt structure.

In the cmc gyroid family, two independent networks are separated by a matrix. Therefore, an ABC gyroid structure can consist of separate A and C networks in a B matrix. Such a structure was found by researchers in Tokyo for a triblock copolymer with similar A and C volume fractions and similar interfacial tensions between the A and C blocks and the B block (*3*). Alternatively, an ABC gyroid structure can be made up of five separate three-dimensionally continuous regions, with two network regions consisting of an innermost A core concentrically surrounded by a B region in a matrix of the C block (see the figure). This is the structure that was recently found independently by groups in Bayreuth (*1*) and Minneapolis (*2*).

Determining the complex three-dimensional structure of these nanoscale domain patterns is challenging, necessitating a combination of real space investigation with transmission electron microscopy (TEM) and reciprocal space investigation with small-angle x-ray scattering. The dividing surfaces of the mathematicians are very important for constructing candidate model structures. In fact, the impressive resolution of the pentacontinuous and tricontinuous gyroid microdomain structures of the ABC polymers was critically dependent on TEM simulations based on construction of an appropriate dividing surface model (*1*–*3*).

Synthesizing polymers that can form topologically connected periodic patterns can result in useful materials. The Minnesota group envisions the core-shell double gyroid as a superefficient perm-selective membrane (*2*). Separation could occur by injection of a set of permeants into one of the rubbery regions, followed by selective transport through the surrounding glassy B domain and collection and extraction through the other rubbery domain. The materials may also be useful in optical applications. A periodic dielectric could be made using a gyroid dividing surface, and Martin-Moreno *et al.* (*10*) have predicted that, provided the ratio of the dielectric constants of the two partitioned regions is sufficiently large, a complete three-dimensional photonic band gap will occur. Self-assembled optical components based on block copolymers are now being realized (*11*), although no one has yet managed to create a gyroid structure with the required dielectric contrast and length scale. The huge ABC polymer parameter space available to synthetic chemists and the rich set of resultant self-assembled morphologies suggest that many more opportunities lie ahead.

References

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