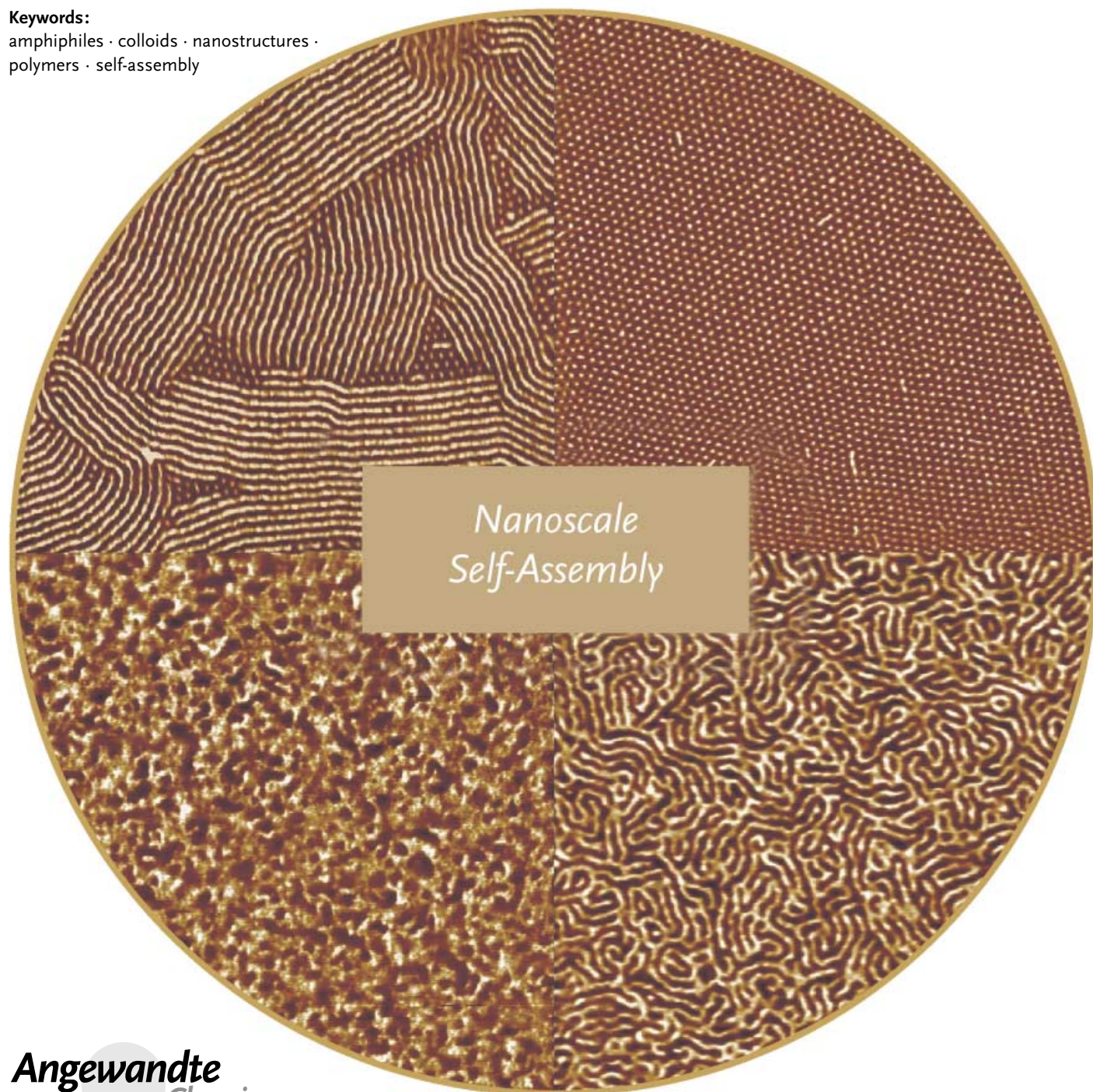


Soft Nanomaterials

Nanotechnology with Soft Materials*I. W. Hamley****Keywords:**amphiphiles · colloids · nanostructures ·
polymers · self-assembly

Nature exploits self-organization of soft materials in many ways, to produce cell membranes, biopolymer fibers and viruses, to name just three. Mankind is now able to design materials at the nanoscale, whether through atom-by-atom or molecule-by-molecule methods (top-down) or through self-organization (bottom-up). The latter method encompasses soft nanotechnology. Self-organization of soft materials can be exploited to create a panoply of nanostructures for diverse applications. The richness of structures results from the weak ordering because of noncovalent interactions. Thus, thermal energy is important as it enables transitions between phases with differing degrees of order. The power of self-organization may be harnessed most usefully in a number of nanotechnology applications, which include the preparation of nanoparticles, the templating of nanostructures, nanomotor design, the exploitation of biomineralization, and the development of functionalized delivery vectors.

1. Introduction

The last few decades have seen a huge growth in research on “soft materials”. The buzzword “nanotechnology” is now around us everywhere. Together these two terms herald the forthcoming era of “soft nanotechnology”. Just as the bronze and iron ages followed the stone age (when wood and other bio-derived materials were also vital) then surely the most recent materials age was one in which mankind learned to exploit the secrets of silicon and to design synthetic materials like polymers. A new era is upon us—many argue it is the bio-age, where the secrets of genetic codes and protein structures are unraveled, to bring in a new range of treatments, and possibly lifestyles. At the same time we are starting to be able to manipulate materials at the nanoscale. One way to do this is to move atoms or molecules around one by one. This procedure is required to make nonperiodic structures. However, an efficient route when a patterned nanostructure is needed, is to exploit self-assembly in soft matter. We are learning more every year about the huge number of nanostructures that can be formed through self-assembly and are beginning to learn how to exploit these to create materials with new mechanical, optical, or electronic properties as well as specific functionality. Devices can also be fabricated using an appropriate combination of self-organized elements, together with a suitable power source.

Soft nanotechnology encompasses the use of soft materials to pattern inorganic (“hard”) materials, a technique already used by nature to make bone, teeth, and shells. Inorganic nanoparticles can be created within self-assembled nanoreactors, such as micelles or vesicles, and then patterned into superstructures through an additional self-organization step. Or naturally occurring nanoparticles can be arranged using polymer or colloid self-assembly. The particles can be functionalized for nanotechnology applications, such as tagging or recognition. A recurring theme in this article is the templating of inorganic structures. Apart from making nanoparticles and hollow nanoparticles the templating of silica into regular arrays using crystals of colloidal sol particles is an

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important example. Similarly, lyotropic liquid-crystal phases formed by surfactants and block copolymers can

be used to template lamellar, hexagonal, and cubic (bicontinuous or micellar) structures in silica and other inorganic materials, which have attracted attention for application in catalysis as they are nanoporous materials, analogous to zeolites but with a nanometer (rather than Ångström) pore size.

A key challenge in nanotechnology is to design nanomotors and actuators. A number of strategies for this are described in Section 2.4. Some take inspiration from biological motors or muscle (powered by ATP synthesis) whilst others use concepts from physical chemistry, for example harnessing oscillating chemical reactions in polymer gels.

The self-organization of block copolymers is particularly interesting from the viewpoint of fabricating nanostructures where one block is, for example, a conductive or electroluminescent polymer. A number of rod-coil copolymers of this type have been synthesized, although not yet exploited in nanotechnology applications. All-polymer ferroelectric and waveguide materials are also possible using block copolymers. Self-organizing nanolaminates with unique barrier properties can also be envisaged. Nanotechnology applications involving thin films are particularly wide-ranging, and are discussed in Section 4.3; nanolithography and patterning of nanoparticles or holes (for membranes or filters) are among the possibilities.

In this review the principles of self-assembly underpinning nanoscale structure formation in soft materials are elucidated. Examples of the application of nanoscale self-assembly are provided. The topics selected reflect the preferences of the author. In such a broad subject there are inevitably omissions. Nanotube systems are not self-assembling systems in the

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sense intended here (see Section 2) and so are not discussed. In addition, nanotechnology applications of self-assembled monolayer structures are not considered. There is only a brief discussion of some aspects of bionanotechnology, since in the main the purpose of this review is to emphasize synthetic nanomaterials. Supramolecular chemistry is also not considered, although it is a powerful tool for the programmed self-organization of molecules,^[1] and has been proposed as a means to create nanomachines.^[2,3]

There have been few reviews of soft nanotechnology. Introductory textbooks on soft matter, primarily covering synthetic systems (colloids, polymers, surfactants and liquid crystals), have appeared recently.^[4,5] Niemeyer has reviewed DNA-based bionanotechnology.^[6] A brief review discussing some examples of molecular nanotechnology touches on some aspects of self-assembly for nanostructure fabrication.^[7] Brief accounts of selected applications of polymers in soft nanotechnology can also be found.^[8,9] A good review of colloidal routes to nanoparticle synthesis and ordering is available.^[10] There is little on the nanotechnology of self-assembling systems in the nanotechnology book by Timp,^[11] though the chapter by Deming et al.^[12] covers some aspects of the synthesis of proteins and peptides capable of forming tailored nanostructures. Similarly, the main thrust of the text edited by Edelstein and Cammarata^[13] is inorganic materials. One chapter does cover a limited subset of biological nanomaterials, in particular magnetic proteins,^[14] and the use of colloidal sols in sol-gel processing methodologies is encountered in chapter 7.^[15]

This review is organized as follows. In Section 2, the principles of self-assembly are outlined. In Section 3, self-assembly routes to the preparation of nanoparticles are considered, as well as applications in nanotechnology. Nano-objects are also briefly discussed. In Section 4, templating methods for the fabrication of inorganic nanostructures are summarized. Section 5 covers the nanotechnology applications of liquid-crystal phases, both lyotropic and thermotropic. Section 6 contains a summary and outlook.

2. Principles of Self-Assembly

The term “self-assembly” does not have a precise definition, and indeed has often been abused.^[16] It does not

refer to the formation of any assembly of atoms or molecules, rather the reversible and cooperative assembly of predefined components into an ordered superstructure. Two types of self-assembly have been identified by Whitesides.^[16] Static self-assembly involves systems at equilibrium that do not dissipate energy. The formation of a structure may require energy, but once formed it is stable. In dynamic self-assembly on the other hand the formation of structures or patterns occurs when the system dissipates energy. Examples are patterns formed by reaction and diffusion processes in oscillating chemical reactions. The focus of this section is on materials that form static self-assembled structures, although a brief summary of possible routes to the fabrication of nanomotors involving dynamic self-assembly is given.

Self-assembly in soft materials relies on the fact that the energy dissipated by fluctuations in the position and the orientation of the molecules or particles, which are the result of Brownian motion, is comparable to the thermal energy. Thermal energy has a dramatic influence on soft materials at the nanoscale as weak noncovalent bonds are broken and sometimes re-formed. This process enables the system to reach thermodynamic equilibrium, which is often a non-uniform state. Because of the relatively weak interactions between molecules, transitions between different structures can readily be driven by changes in conditions, for example, temperature or pH value. Such external triggers that induce phase transitions could lead to a host of responsive materials, or coupled with an appropriate source of energy to nanomechanical systems. There is a diversity of phase transitions between different structures in soft materials, examples of which are considered in subsequent sections.

2.1. Noncovalent interactions

For self-assembly to be possible in soft materials, it is evident that the forces between molecules must be much weaker than the covalent bonds between the atoms of a molecule. The weak intermolecular interactions responsible for molecular ordering in soft materials include hydrogen bonds, coordination bonds in ligands and complexes, ionic interactions, dipolar interactions, van der Waals forces, and hydrophobic interactions:

The hydrophobic effect arises when a nonpolar solute is inserted into water. The hydrophobic effect can be distinguished from hydrophobic interactions, which result from the association of two nonpolar moieties in water.^[17] The hydrophobic effect is conventionally ascribed to the ordering of water molecules around an unassociated hydrophobic molecule. This effect leads to a reduction in entropy. This entropy loss can be offset when the association of hydrophobic molecules into micelles occurs because this leads to an increase in entropy as the “structured water” structure is broken up. An enthalpy penalty for demixing of water and solute should also be outweighed by the entropy increase so that the Gibbs free-energy change for micellization is negative. The “structured-water” model is based on ordering of water molecules around the solute molecule. An alternative to the structured-water model proposes that the high



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free-energy cost of inserting a nonpolar solute into water is because it is difficult to find a suitable cavity between the small water molecules. However, Dill et al. have argued that the hydrophobic effect is more subtle, and depends on solute size and shape as well.^[17]

Hydrogen bonding is particularly important in biological systems, where many protein structures in water are held together by hydrogen bonds. Of course, the existence of life as we know it depends on hydrogen bonds, which stabilize H₂O in the liquid form. In proteins, intramolecular hydrogen bonds between N–H groups and C=O groups that are four residues apart underpin the formation of the α helix structure. On the other hand, hydrogen bonds between neighboring peptide chains lead to β sheet formation. Similarly, collagen fibers contain triple-helical proteins held together by hydrogen bonding. The folding pattern of proteins is also based on internal hydrogen bonding. The smaller the number of hydrogen bonds in the folded protein, the higher its free energy and the lower the stability. The reason that nature exploits hydrogen bonds in this way is because of the strength of this bond. Hydrogen bonds are weaker than covalent bonds (ca. 20 kJ mol⁻¹ for the former compared to ca. 500 kJ mol⁻¹ for the latter), so that superstructures can self-assemble without the need for chemical reactions to occur, but nevertheless the bonds are strong enough to hold the structures together once formed.

Molecular recognition between artificial receptors and their guests can be combined with self-organization to program the self-assembly of nanostructures.^[18] Many types of noncovalent interaction can be exploited in supramolecular chemistry, these include hydrogen bonding, donor–acceptor binding, and metal complexation. Diverse methods have been employed to create receptors for ionic and molecular guests. The use of cyclodextrins as hosts for the delivery of drugs or pesticides, for example. Details are outside the scope of this section, although further information is available elsewhere.^[1,19]

Stabilizing colloidal dispersions against aggregation (termed coagulation if irreversible, flocculation if reversible) is important in every-day applications, such as, food or personal-care products. Often the system is an oil-in-water dispersion that can be stabilized by adding interfacially active components, such as amphiphiles or proteins. These segregate to the oil–water interface and stabilize emulsions by reducing interfacial tension, the enhanced rigidity and elasticity of the membrane formed also help to prevent coalescence. Colloidal sols as found in paints and pastes also need to be stabilized to ensure a long shelf-life. This stabilization can be achieved in a number of ways. First, for charged colloidal particles in an electrolyte medium, the balance between the repulsive electrostatic and attractive van der Waals contributions to the total potential energy can be adjusted, so that a barrier to aggregation is created. A second method to prevent aggregation is steric stabilization. Long-chain molecules are attached to colloidal particles, and when the particles approach one another a repulsive force is created as the chains interpenetrate. The attached long-chain molecule may be chemisorbed (for example a long-chain fatty acid) or more commonly an adsorbed polymer. In contrast to charge

stabilization, steric stabilization works in nonaqueous media and over a wide range of particle concentrations. The choice and concentration of polymer is critical in steric stabilization, since at low concentration, polymer chains can attach themselves to two (or more) particles, which leads to so-called bridging flocculation. On the other hand, at higher polymer concentrations, if the polymer is nonadsorbing it can lead to depletion flocculation, the mechanism for which was first recognized by Asakura and Oosawa.^[20] The polymers cannot penetrate the particles, and are excluded from a depletion zone around them. When the particles are close together the depletion zones overlap, and the dispersal of polymers into the bulk solution is favored entropically. An osmotic pressure of solvent from the gaps between particles leads to an effective attraction between particles, and hence flocculation. When the colloidal particle concentration is such that they are on average further apart than a polymer coil radius, and the polymer concentration is high, depletion stabilization is possible.^[21] Forcing the particles together would require the “demixing” of polymer from bulk solution. This process increases the free energy so that the effective interaction between particles is repulsive.

2.2. Intermolecular Packing

At high concentration, the packing of block copolymer or low-molar-mass amphiphilic molecules in solution leads to the formation of lyotropic liquid-crystal phases, such as cubic-packed spherical micelles, hexagonal-packed cylindrical micelles, lamellae, or bicontinuous cubic phases. The phase formed depends on the curvature of the surfactant–water interface. In one approach to the understanding of lyotropic phase behavior, the free energy associated with curved interfaces is computed. The curvature is analyzed using differential geometry,^[22] neglecting details of molecular organization. In the second main model the interfacial curvature is described by a molecular packing parameter.^[23] These two approaches will be described in turn.^[4]

In the model for interfacial curvature of a continuous surfactant film, we use results from the differential geometry of surfaces. A surface can be described by two fundamental types of curvature at each point P on it: mean curvature and Gaussian curvature. Both can be defined in terms of the principal curvatures $c_1 = 1/R_1$ and $c_2 = 1/R_2$, where R_1 and R_2 are the radii of curvature. The mean curvature is $H = (c_1 + c_2)/2$ and the Gaussian curvature is defined as $K = c_1 c_2$.

Radii of curvature for a portion of a so-called saddle surface (a portion of a surfactant film in a bicontinuous cubic structure) are shown in Figure 1, although they can equally

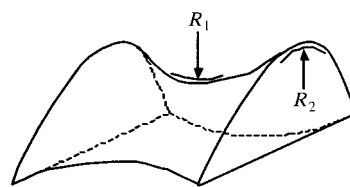


Figure 1. Principal radii of curvature of a saddle surface.

well be defined for other types of surface, such as convex or concave surfaces found in micellar phases. To define the signs of the radii of curvature, the normal direction to the surface at a given point P must be specified. The curvature is conventionally defined to be positive if the surface points outwards at point P. In Figure 1, c_1 is negative and c_2 is positive.

It should be noted that “end effects” in elongated micelles, a result of capping by surfactant molecules which lead to an ellipsoidal or spherocylindrical structure, are neglected. Such end effects will, however, change both mean and Gaussian curvatures, to an extent which depends on the relative surface area of the “cap” and “tubular” parts. The elastic free-energy density associated with the curvature of a surface contains, for small deformations, the sum of the contributions from mean and Gaussian curvature. The interfacial curvature model is thus useful because it defines the elastic moduli κ and $\bar{\kappa}$ for mean and Gaussian curvature, respectively. These parameters can be measured (by light scattering, for example) and characterize the flexibility of surfactant films. Uncharged surfactant films typically have elastic energies $F_{el} \leq k_B T$, that is, they are quite flexible ($k_B =$ Boltzmann's constant)

An alternative approach to the description of lyotropic mesophases in concentrated solution is based on the packing of molecules. The effective area of the headgroup, a , with respect to the length of the hydrophobic tail for a given molecular volume controls the interfacial curvature. The effective area of the headgroup (an effective molecular cross-sectional area) is governed by a balance between the hydrophobic force between surfactant tails which drives the association of molecules (and hence reduces a) and the tendency of the headgroups to maximize their contact with water (and thus increase a). The balance between these opposing forces leads to the optimal area per headgroup, a , for which the interaction energy is minimum.

Simple geometrical arguments can be used to define a packing parameter, the magnitude of which controls the preferred aggregate shape. For a spherical micelle, it can be shown^[4] that the following condition holds: $V/la \leq 1/3$, where V is the volume of a molecule and l is the length of an extended hydrophobic chain (which can easily be calculated). The term $N_s = V/la$ is called the surfactant packing parameter,^[24] or critical packing parameter. The surfactant packing parameter can be used to estimate the effective headgroup area a , or vice versa. The surfactant parameter is concentration dependent, and reflects changes primarily in a (but to a lesser extent in V) upon varying the amount of solvent.

Just as spherical micelles can be considered to be built from the packing of cones, which correspond to effective molecular volumes, other aggregate shapes can be considered to result from packing of truncated cones, or cylinders.

The surfactant packing model and the interfacial curvature description are related. A decrease in the surfactant packing parameter corresponds to an increase in mean curvature. The packing-parameter approach has also been used to account for the packing stabilities of more complex structures, such as the bicontinuous cubic phases. Here, the packing unit is a wedge, which is an approximation to an element of a surface with saddle-type curvature (Figure 1).

Then it is possible to allow for differences in Gaussian curvature between different structures, as well as mean curvature.

2.3. Biological Self-Assembly

Understanding the folding of proteins is one of the outstanding challenges of science, let alone biophysics and biochemistry. Although much progress has been made in modeling protein folding (for reviews see refs. [25–27]), there is no consensus on the best method. Most methods consider a protein folding energy landscape. The problem is that this is a rough surface, with many local minima, and it can often be hard to model the guiding forces that stabilize the native structure, and cause the free energy to adopt a “funnel” landscape. Many minimalist models are based on computer simulations of particles on a lattice, these are always based on coarse-grained approaches.^[26,28] Fully atomistic models seem some way off. Analytical methods have modeled the free-energy landscape based on random energy models, the most recent of which analyze the conformational transition in a random heteropolymer by using spin-glass methods.^[29–31] Mean-field methods based on replica techniques will also be developed further. Some structural insights into protein conformational dynamics have emerged from steered molecular-dynamics simulations in which Monte Carlo moves are used as well as molecular-dynamics trajectories.^[32]

DNA will be an important component of many structures and devices in nanobiotechnology. DNA computing is an application currently attracting considerable attention.^[33] In one approach^[34] single DNA strands are attached to a silicon chip. Computational operations can then be performed in which certain DNA strands couple to added DNA molecules. Multistep computational problems can also be solved.^[34] In these systems the DNA strands encode all possible values of the variables. Complementary DNA strands are then added, and attach themselves to any strand that represents a solution to one step of the computation. The remaining single strands are removed. This process is repeated sequentially for each step, and the DNA that is left is read out (via PCR amplification) to provide the solution (represented in binary form, a given binary number corresponding to an eight-nucleotide sequence).

The DNA-directed assembly of proteins, by using oligonucleotides capped with streptavidin, is another exciting realm of applications.^[35] The method can be used to fabricate laterally patterned arrays of many types of biotinylated macromolecules.^[35,36]

The charged nature of DNA has been exploited to bind metal ions, for example, silver, which aggregate into nanoparticles, these are then used as seeds for the further deposition of silver to produce nanowires.^[37] Positively charged C_{60} fullerene derivatives have also been condensed onto DNA.^[38] Similarly, CdS nanoparticles have been templated on the charged DNA backbone.^[39] Arrays of DNA-functionalized CdS nanoparticles have been assembled layer-by-layer on a gold electrode by using a set of two populations of DNA-capped CdS nanoparticles and a soluble DNA

analyte. The two oligonucleotides bound to CdS nanoparticles are complementary to the ends of the target DNA.^[40] The construction of nanoscale geometric objects^[41] and frameworks^[42] by using three- and four-arm synthetic DNA molecules has also been reported. The use of nanoparticle-tagged DNA solutions in gene-sequence detection is discussed in Section 3.2. Several reviews on the use of DNA in nanotechnology have appeared recently.^[35,43]

Vesicles formed by lipids (termed liposomes) are model systems for the cell membrane. The incorporation of channel-forming proteins (porins) into lipid bilayers has been studied for many years,^[44–48] and synthetic structural and functional mimics have been devised.^[49,50] It is straightforward to form vesicles from the lipid bilayers.^[4] Block copolymers form vesicles that can be polymerized,^[51] which is clearly advantageous in encapsulation applications. The incorporation of channel-forming proteins into planar polymerized triblock copolymer membranes has been reported.^[52,53] This result extends further the delivery/nanoreactor capabilities of the biomimetic structures. Recently, porous core-shell latexes with pH-dependent swelling properties have been developed.^[54,55] These are analogous to the pH-controlled pore opening of the protein shell of cowpea chlorotic mosaic virus.^[56] By appropriate surface functionalization, the recognition properties of bilayers can be enhanced, as required for many drug-delivery applications. A model recognition system is the biotin–streptavidin complex, for which the free energy of binding is comparable to that of a covalent bond.^[57,58]

2.4. Nanomotors

A key element of any nanomachine is a nanomotor. A variety of approaches to the manufacture of nanomotors is being followed. The crudest is to make miniature versions of motors from the macroscopic world, however, the ability to scale such structures downwards is limited by energy dissipation from friction.^[2,59] Alternative strategies include attempts to mimic motors in biological systems, and the simpler “motors” driven by chemical potential or concentration gradients, for example, in oscillating gels. Here, nanomotors based on soft matter are briefly discussed. Surveys of the vast literature on molecular nanomotors can be found elsewhere.^[60,61]

By considering biological motors as models for artificial motors we can define two classes. In the first, proteins, such as kinesin, dynein, and myosin behave as linear slides. Among rotary motors, well-studied systems include the ATP-synthesis complex, and bacterial flagellar motors. The proton gradient across the mitochondrion drives the synthesis of ATP by ATPase which is a multisubunit transmembrane protein with a complex structure consisting of a spindle to which six alternating (α , β -type) globular proteins are attached. The spindle attachment rotates in a sleeve formed by six copies of a binding protein. The rotation of the spindle drives binding changes of ADP such that the synthesis of ATP is catalyzed.^[62]

Flagella in eukaryotes (for example sperm-cell tails) and cilia move by the sliding of subfibers formed from microtubule arrays past one another.^[62] Linear sliding motions are

also responsible for the action of muscles. In all cases, the motion is driven by an ATPase that acts as a transducer, which converts the energy from ATP-to-ADP hydrolysis into mechanical energy.

Artificial motors exploit out-of-equilibrium chemical phenomena, for example, a concentration gradient, as in ATP synthesis. Using this knowledge, simpler systems than those operating in nature can be designed. A minimal system can be constructed based on osmotic pumping by using lipid vesicles in a solute concentration gradient.^[63] The lipid bilayers act as osmotic membranes, which allow the passage of water molecules but not of solute molecules. Thus, when placed in a high osmotic pressure environment, the vesicles shrink and in a uniform solution do not move. However, in a solute concentration gradient, a directional motion is imposed.^[63] Unidirectional motion can also be imparted to liquids confined in capillaries by a temperature gradient. A novel concept to drive fluid motion in microcapillaries uses optical trapping of colloid particles, which can be manipulated to create pumps and valves.^[64] Although the scale of the particles is on the order of micrometers, it would be exciting if this could be extended to the nanoscale using smaller particles and shorter-wavelength radiation. Other systems rely on the Marangoni effect.^[4] As a result of dynamic surface-tension fluctuations, surface-active molecules flow into higher surface-tension regions (or away from low surface-tension regions), to restore the original surface tension.^[65] This effect is the origin of the motion of camphor “boats” which move freely on the surface of water. The origin of this motion was explained over a century ago,^[66] but the system has been revisited recently as a simple analogue of artificial motors.^[67,68]

A particularly attractive artificial motor system relies on oscillating chemical reactions to drive volume changes in polymer gels. Yoshida et al. used the Belousov–Zhabotinsky (BZ) reaction to create an oscillating redox potential.^[69,70] This reaction was coupled to the most familiar polymer–gel system exhibiting a volume phase transition—poly(*N*-isopropylacrylamide) (PNIPAM) in water. The PNIPAM was modified by attachment through covalent bonds of ruthenium tris(2,2'-bipyridine) units which act as catalysts for the BZ reaction. Thus, the oscillations in the BZ reaction were translated into periodic swelling and deswelling of the gel as a result of changes in the charge on the ruthenium complex. Using the same concept, pH oscillations in a Landolt reaction have been used to drive volume changes in poly(methacrylic acid) gels in water.^[71]

3. Self-Assembly Methods to Prepare and to Pattern Nanoparticles

3.1. Nanoparticles from Micellar and Vesicular Polymerization Routes

The fabrication of nanoparticles of controlled size, shape, and functionality is a key challenge in nanotechnology.^[72–74] There are several established routes to nanoparticle preparation. Roughly spherical nanoparticles can be prepared by

very fine milling^[75]—this route is used, for example, to prepare iron oxide nanoparticles in ferrofluid dispersions^[76] or zinc oxide nanoparticles for use in sunscreens.^[73] So-called colloidal methods^[10,15,77] produce nanoparticles with much more uniform size and shape distribution than milling. Metal and metal oxide nanoparticles have been prepared using micellar “nanoreactors” where, for example, salts are selectively sequestered in the micellar core, and then reduced or oxidized.^[78–90] Such nanoparticles can be used in catalysis, separation media, biopolymer tagging, and light-emitting semiconductor (e.g. CdS) “quantum dots”. A good review of nanoparticles prepared within block copolymer micelles discusses several of these applications.^[91]

Recent work has shown that metal nanoparticles on surfaces can be patterned by using the self-organization of block copolymers. Two main routes have been exploited—nanoparticle formation within micelles in solution^[89,91,92] which may subsequently be deposited on a solid substrate,^[93] or direct patterning at the surface by using selective wetting. Examples of nanoparticle patterning at the surface of a diblock copolymer by the latter route are shown in Figure 2.^[94,95]

Nanocapsules, that is, shell particles with a hollow interior, can be prepared by a number of routes, which include the cross-linking of the shell of block-copolymer vesicles.^[51] The Möhwald group has recently developed an alternative approach using polyelectrolyte multilayers assembled around a colloidal core which is subsequently dissolved.^[96–98] Biological particles, such as apoferritin and cowpea chlorotic mosaic virus, with hollow fillable interiors are described in Sections 3.6 and 2.3, respectively.

3.2. Functionalized Nanoparticles

Functionalized nanoparticles will find numerous applications, for example, in catalysis and as biolabels. Gold nano-

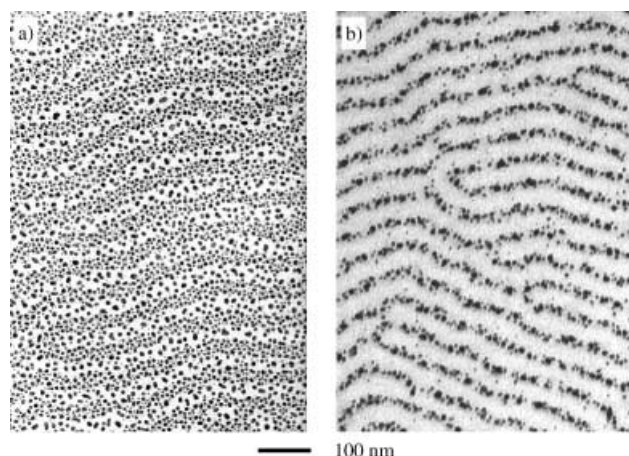


Figure 2. Examples of a) nanoparticle and b) nanowire arrays templated by a stripe pattern formed at the surface of a polystyrene-poly(methyl methacrylate) diblock copolymer by vapor deposition of gold. The gold selectively wets polystyrene domains.^[94,95] Reproduced with permission from W. A. Lopes and Nature.

particles functionalized with proteins have been used as markers for the detection of biological molecules for some time. They may also be used to deliver DNA in a so-called “gene-gun”. Further details on functionalized nanoparticles with applications in the biological sciences can be found in the review by Niemeyer.^[6]

Arrays of nanoparticles, can be prepared by “dip pen nanolithography”. For example, magnetic nanoparticles can be patterned into arrays, a process with potential applications in magnetic storage devices.^[99] In dip pen nanolithography,^[100] nanodroplets of an “ink” (e.g. 16-mercaptohexadecanoic acid) are chemisorbed with nm-scale resolution onto a substrate that is an atomic-force-microscope (AFM) tip (see Figure 3). Subsequently, “surfacted” (i.e. charged surfactant coated) Fe_3O_4 nanoparticles can be deposited from solution onto the charged ink patches on the surface in defined arrays of dots and stripes.^[99] Dip pen nanolithography can be extended from serial printing to parallel printing by using multiple pens (i.e. AFM tips).^[101] Clearly the method can be extended to pattern other materials that can be adsorbed onto the ink monolayers, for example proteins.^[102] Such protein arrays are expected to find applications in panel screening, for example, in immunoassays or proteomics.

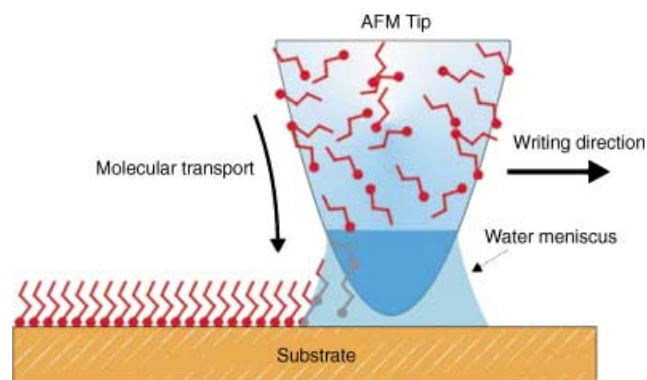


Figure 3. Schematic of dip pen nanolithography.^[100] Reprinted with permission from Science. Copyright ©1999 AAAS.

Functionalized nanoparticles are required for many biotechnological applications. A technique for detecting specific gene sequences that could be used in genetic screening has been developed,^[103,104] as illustrated in Figure 4. First, the sequence of bases in the target DNA is identified. Then two sets of gold particles are prepared—one has DNA attached that binds to one end of the target DNA, and the second set carries DNA that binds to the other end. The nanoparticles are dispersed in water. When the target DNA is added, it binds both types of nanoparticle together, linking them together to form an aggregate. The formation of this aggregate causes a shift in the light-scattering spectrum from the solution, that is, a color change in the solution that can easily be detected. Recently, this technique has been developed to allow the electrical detection of DNA.^[105] The principle is similar to that of the color-change-based detection system, except one end of the target DNA binds to a short “capture” oligonucleotide attached to the surface of a micro-

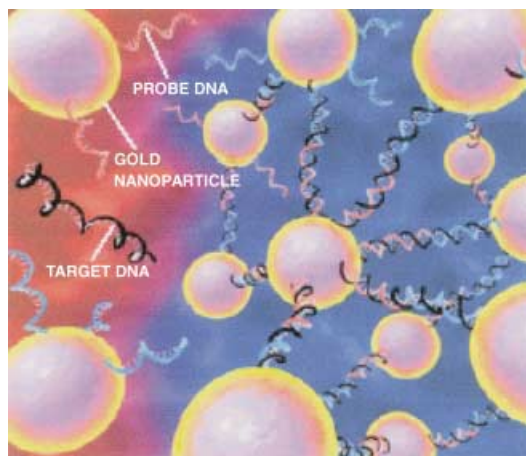


Figure 4. DNA-functionalized gold nanoparticle gene sequence detection system (Figure reproduced with permission from Scientific American, Sept 2001, p. 63).

electrode, and the other end binds to an oligonucleotide attached to gold nanoparticles. Binding of the target DNA causes gold nanoparticles to fill the gap between a pair of electrodes, an event that can be detected from capacitance or conductivity measurements. In practice, the sensitivity of the device was enhanced by silver deposition on the nanoparticles. Arrays of electrode pairs were assembled to form “DNA chip arrays” in which each pair contained a different oligonucleotide capture strand.

3.3. Colloidal Nanoparticle Crystals

There is an immense interest in photonic bandgap crystals because they can be used to confine photons, modulate or control stimulated light emission, or to construct lossless waveguides. A photonic bandgap crystal, also called a photonic crystal, is a structure with a periodic variation in its dielectric properties. The propagation of electromagnetic waves in such a crystal is analogous to that of electrons in semiconductors, in particular there are bandgaps that exclude the photon propagation modes in certain frequency intervals. In principle, 3D crystals could have a complete bandgap, that is, one for which photon propagation is prevented in all spatial directions, that is, throughout the Brillouin zone to adopt nomenclature from solid-state physics. The main focus on 3D structures has been the face-centered cubic (fcc) structure because the Brillouin zone of this lattice is most closely spherical, which might favor the formation of a complete photonic bandgap. However, for an fcc crystal formed by colloidal spheres (opal structure), it has been shown that, independent of the dielectric contrast, there is never a complete bandgap.^[106,107] The inverse structure (spheres of air in a continuous solid medium), however, is promising because calculations indicate the possibility of a complete 3D bandgap.^[107] By coating the air pores with nematic liquid crystal, a switchable photonic bandgap material can be formed.^[108] Here, the tunable localization of light or of waveguiding results from the electrooptic properties of the

liquid crystal, where an electric field can be used to orient molecules in a particular direction with respect to the lattice.

To create a 3D photonic bandgap, two conditions must be fulfilled. First, the colloidal particles must have low polydispersity, this favors formation of a cubic crystal. Second, the number of defects in the cubic crystal must be minimized. A number of strategies have been adopted to create macroscopic colloidal crystals. A common technique relies on sedimentation of particles under gravity. However, the resulting samples generally contain polycrystalline domains.^[109] Other approaches rely on surfaces to act as templates to induce order. For example, spin coating onto planar substrates can provide well-ordered monolayers.^[110] Flow-induced ordering has also been exploited.^[111] A method that relies on so-called convective self-assembly has been used to create ordered crystals upon rapid evaporation of solvent.^[112] A related technique is the controlled withdrawal of a substrate from a colloidal solution (similar to Langmuir–Blodgett film deposition), where lateral capillary forces at the meniscus induce crystallization of spheres. If the meniscus is slowly swept across the substrate, well-ordered crystal films can be deposited.^[113,114] Convective flow acts to prevent sedimentation and to continuously supply particles to the moving meniscus. Actually, the controlled evaporation process alone is sufficient to produce films of controlled thickness that are well ordered up to the centimeter size scale.^[109] Van Blaaderen et al. have employed an epitaxial mechanism, which uses a lithographically patterned polymer substrate to template crystal growth.^[115] Holes just large enough to hold one colloidal particle were created in a rectangular array. Controlled layer-by-layer growth on this template was then achieved by slow sedimentation of the silica spheres used. The formation of well-ordered crystal-monolayer “rafts” of charged colloid particles on the surface of oppositely charged surfactant vesicles has also been demonstrated.^[116]

As mentioned above, inverse opal structures offer the greatest potential for photonic crystals. The most promising materials for the matrix seem to be certain wide-bandgap semiconductors, such as CdS and CdSe, because they have a high refractive index and are optically transparent in the visible and near-IR region.^[117] The preparation of porous metallic (gold) nanostructures within the interstices of a latex colloidal crystal has been demonstrated. Here a solution of gold nanoparticles fills the pores between colloidal particles, and the latex is subsequently removed by calcination.^[118] A similar method has been used to fabricate inverse opal structures of titanium dioxide.^[119,120] The same idea has been applied to form a nanoporous polycrystalline silica (deposited by low-pressure chemical vapor deposition (CVD), see Figure 5.^[114] In a related approach, silica spheres are coated with gold (to reinforce the colloidal crystal) and then immersed in electroless deposition baths to deposit metal films within the porous template, the silica then being removed in a HF rinse.^[121] These types of approach have been extended to a “lost wax approach” to prepare high-quality arrays of hollow colloidal particles (or filled particles) of various ceramic and polymer materials.^[122] Here, a well-ordered silica colloidal crystal is taken and used as a template for polymerization in the interstices.^[123] If the pores are

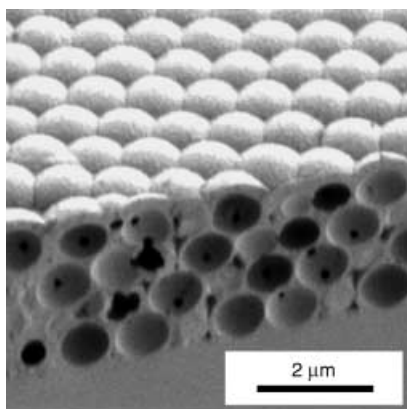


Figure 5. Cross-sectional scanning electron micrograph image of thin film inverse opal structure of polycrystalline silicon templated by 855 nm silica spheres.^[114] Reproduced with permission from D. J. Norris and Nature.

interconnected, the polymer forms a continuous porous matrix. By appropriate choice of polymer, either hollow or solid nanoparticles can be grown in it (the former grow from the polymer matrix inwards, the latter form within the voids).^[122] In this way it was possible to prepare colloidal crystals of solid or hollow TiO₂ particles, as well as conducting polymer nanoparticles. An extension of colloidal polymerization techniques can be used to prepare defined waveguides. Crossed laser beams were used to polymerize polymer precursors within particular pores. By scanning the laser beams, a waveguide with a chosen path and shape can be fabricated.^[124]

The use of microgel particles of PNIPAM to form colloidal crystal arrays that selectively diffract light has been reported.^[125] Poly(*N*-isopropylacrylamide) in aqueous solution has a volume phase transition at 32 °C, below which temperature gels are hydrated and swollen but above which the gel dehydrates and collapses. This transition has been used to vary the dimensions of PNIPAM microgel particles from 100 nm at 40 °C to 300 nm at 10 °C, a 27-fold volume change. This property can be exploited to prepare a switchable, selective diffraction array. Below the transition, the particles are swollen and only diffract light weakly, however, in the compact state the diffracted intensity increases dramatically because of the enhanced contrast between particles and medium (the Bragg diffraction wavelength is unaffected). Wavelength-tunable arrays were fabricated by polymerizing PNIPAM in the presence of 99-nm polystyrene spheres.^[125] The embedded polystyrene spheres follow the swelling or shrinking of the PNIPAM hydrogel so that the wavelength of the Bragg diffraction can be tuned across the visible range of the spectrum.

3.4. Self-Organizing Inorganic Nanoparticles

Within the last few years, there has been a surge of interest in composite materials consisting of a polymer filled with platelike particles, such as clay particles. Such fillers are

extremely effective in modifying the properties of polymers, and orders-of-magnitude improvements in transport, mechanical, and thermal properties have been reported. Examples of applications include low-permeability packaging for food and electronics, toughened automotive components, and heat and flame resistant materials.^[126,127] Polymer–clay nanocomposites have several unique features:^[128–134] First, they are lighter in weight than conventional filled polymers with the same mechanical performance. Second, their mechanical properties are potentially superior to fiber reinforced polymers because reinforcement from the inorganic layers occurs in two rather than one dimension. Third, they exhibit outstanding diffusional-barrier properties without requiring a multipolymer layered design, and thus can be recycled.

Clays are colloidal suspensions of platelike mineral particles, with a large aspect ratio. Typically the particles are formed from silicate layers combined with layers of octahedrally coordinate aluminum or magnesium atoms.^[21] The layer structure leads to a lamellar phase for the clay in water. The aim in applications is to retain this structure in the polymer–clay nanocomposite, possible structures for which are illustrated schematically in Figure 6. Exfoliation and phase separation should be avoided and there is an immense literature (especially patent literature) on how to achieve this by chemical treatment of the clay particles (in particular adsorption of organic molecules). The intercalated structure leads to enhanced barrier properties, which result from the tortuous path for gas diffusion around the clay platelets.

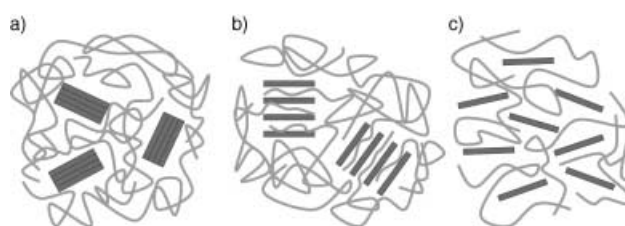


Figure 6. Possible structures for polymer–clay nanocomposites. a) Phase separated, b) intercalated, c) exfoliated. Reproduced with permission from ref. [130]. Copyright Springer Verlag, Heidelberg.

Liquid-crystal phases formed by mineral moieties have been known for almost as long as organic liquid crystals. Renewed interest in them has arisen because of the ability to combine the properties of liquid crystals, in particular anisotropy and fluidity, with the electronic and structural properties of minerals. They may also be cheaper to produce than conventional liquid crystals, which require organic synthesis. Rodlike mineral systems that form nematic phases have been well studied. Sheet-forming mineral compounds that form smectic (layered) structures in solution are also known.

The colloidal behavior of vanadium pentoxide (V₂O₅) has been investigated since the 1920s. Under appropriate conditions of pH, ribbonlike chains can be obtained by the condensation of V–OH bonds in a plane.^[135] A scanning electron micrograph of dried ribbons is shown in Figure 7. A

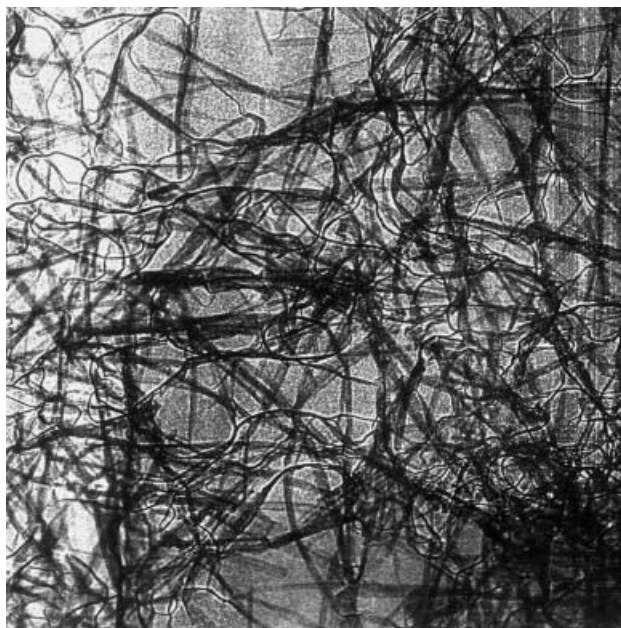


Figure 7. Scanning electron micrograph of a dried V_2O_5 suspension. Reproduced with permission from J. Livage.^[136]

nematic liquid crystal forms in aqueous suspensions if the particle volume fraction, ϕ , exceeds 0.7%. A sol–gel transition occurs at $\phi = 1.2\%$, which divides the nematic domain into a nematic sol and a nematic gel. For $\phi > 5\%$, a biaxial nematic gel phase is formed.^[135] Suspensions of V_2O_5 can be aligned in electric and magnetic fields, similar to the organic nematogens used in liquid-crystal displays.^[137] Laponite and bentonite montmorillonite clay particles also form nematic gels.

The formation of layered structures in intercalated clay suspensions has been discussed in the preceding section. It can be argued that these are not lamellar or smectic phases since long-range order is not preserved upon swelling, where exfoliation occurs.^[138] Colloidal smectic phases have been observed for β -FeOOH, which forms “Schiller layers” (from the German for iridescent). The rodlike β -FeOOH particles form layers at the bottom of the flask. The spacing between the layers is comparable to the wavelength of light, hence the iridescence.^[139] A swollen liquid-crystalline lamellar phase based on extended solidlike sheets (rather than rodlike particles) has been rationally prepared using a solid acid $H_3Sb_3P_2O_{14}$.^[138] In contrast, platelike $Ni(OH)_2$ nanoparticles (91 nm radius, 12 nm thick)^[140,141] and $Al(OH)_3$ nanodiscs (radius 200 nm, thickness 14 nm)^[142] self-assemble into columnar mesophases. A nematic phase has also been observed for the latter material. The formation of a smectic phase rather than a columnar phase is expected if the polydispersity in particle radius is large enough to prevent the efficient packing of columns.^[142,143] In fact, at very high volume fractions in the $Al(OH)_3$ suspensions, evidence was obtained for a smectic phase, which can accommodate the polydispersity in radius (although a low polydispersity of particle thickness is required).^[142]

3.5. Liquid-Crystal Nanodroplets

Figure 8 shows an array of block-copolymer micelles containing liquid crystals solubilized in the micellar core.^[144] The self-assembly of the block-copolymer micelles into a hexagonal close-packed arrangement is apparent. The long-range ordering of the structures could be improved as in other soft materials by the use of an alignment substrate or by annealing. The ability to pattern liquid-crystal nanodroplets at the nanoscale is not required for conventional display applications (which do not require a resolution beyond that of visible light) but may find applications in phased array optics. Phased array optics is a method to reconstruct a 3D image on a 2D surface.^[145] This can be done if the phase and amplitude of the light waves from the virtual image are controlled. An array of switchable light sources 200 nm apart is sufficient to reconstruct any desired light wave pattern.^[145] It has been proposed that liquid crystals can be used as switchable birefringent phase shifters. However, as yet the means to arrange the liquid crystal in nm-scale arrays has been lacking. Patterning of liquid crystals in micelles or microemulsions is a promising way to achieve this.

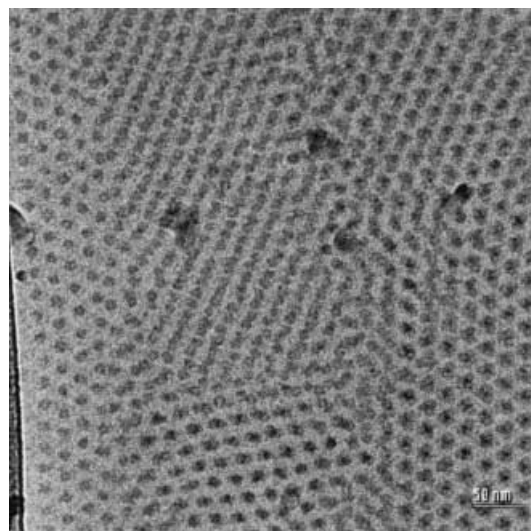


Figure 8. Transmission electron micrograph of a quench-cooled block-copolymer-micelle film of poly(styrene oxide)-*b*-poly(ethylene oxide) containing liquid crystal solubilized in the poly(styrene oxide) core.^[144]

3.6. Bionanoparticles

Viruses are natural nanoparticles, which have evolved into a variety of shapes. A number of nanotechnology applications of viruses are now considered. First, they may be used as responsive delivery agents. Recent work has focused on the use of modified cowpea chlorotic mottle virus nanoparticles as biocompatible responsive delivery agents. At $pH < 6.5$, the virus adopts a compact spherical structure, however, at $pH > 6.5$, the structure becomes porous allowing the pH-controlled release of encapsulated drug molecules, for example.^[146,147] In nonresponsive mode, viruses may be used as “trojan horses” for the delivery of genes in transfection applications. Gene

therapy is attracting immense attention as a means to treat diseases by modifying the expression of genetic material.^[148–150] Its premise is that disease can be prevented at the level of DNA molecules, thus compensating for the effects of abnormal genes. With an eleven-year history of clinical trials, and many more in progress, recent evidence that gene therapy may be efficacious in the treatment of medical conditions arising from the deficiency of single genes has attracted worldwide media attention.^[148]

Both viral and non-viral approaches have been used in clinical trials to treat illnesses, such as cystic fibrosis and several forms of cancer. Viruses have evolved efficient ways of targeting cells, delivering genetic material, and expressing it. However, inflammatory and immunology responses induced by viruses may limit their utility for repeated administration. Numerous systems have been studied for non-viral gene delivery, which include synthetic polymers, such as polylysine^[151–153] and poly(oxyethylene)-based block and graft copolymers,^[154,155] biologically derived liposomes,^[156] cationic lipids,^[152,157] and the cationic polyelectrolyte poly(ethyleneimine) (PEI). PEI has a very high cationic charge density, which makes it useful for binding anionic DNA within the physiological pH range^[158] and forcing the DNA to form condensates small enough to be effectively endocytosed, which is the primary mode of delivery of the PEI–DNA complex into the cell. Furthermore, it has been shown that PEI enhances transgene expression when DNA–polymer complexes are injected into the cytoplasm.^[159–161]

Magnetotactic bacteria exploit magnetic nanoparticles to navigate from regions of oxygen-rich water (toxic to them) to nutrient-rich sediment.^[14,162] The bacteria contain grains of magnetite aligned in chains, as shown in Figure 9. The chain of crystals (and hence the bacterium) aligns along a magnetic field, which contains vertical and horizontal components (except at the poles). In the Northern hemisphere, the bacteria move downwards by moving towards the north pole. In the Southern hemisphere, the bacteria are south-seeking. Nanotechnologists can take inspiration from nature's use of chains of magnetic particles as navigational aids.

The use of chemically modified versions of the iron-storage protein ferritin in high-density magnetic data storage devices is the focus of current commercialization efforts.^[163,164]

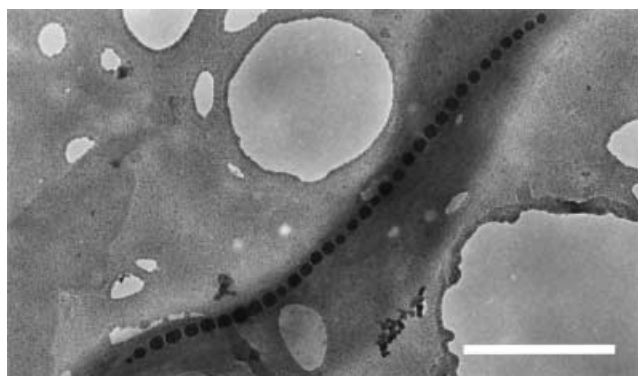


Figure 9. Chain of magnetite nanoparticles in a magnetotactic bacterium. Scalebar = 500 nm. Reproduced from ref. [162] with permission from S. Mann and Oxford University Press.

Ferritin is a nearly spherical protein with a 8-nm diameter core of ferrihydrite ($5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$).^[14,162] The core can be removed by reductive dissolution to produce the shell protein “apoferritin”. The core can then be “refilled” by incubation with metal salts, and subsequent oxidation. In this way, the core can be filled with magnetite (Fe_3O_4),^[165,167] which unlike the native ferrihydrite is ferrimagnetic at room temperature, thus the resulting ferritin is termed magnetoferritin.^[162]

3.7. Nanoobjects

Nanoparticles with shapes other than simple spheres, shells, or tubes have been prepared by soft-material-mediated methods. The photoinduced conversion of silver nanospheres into silver nanoprisms has been reported.^[168] Photoinduced fragmentation of silver nanoparticles is believed to produce the single-crystal prism-shaped particles (the faces of which correspond to planes of the crystal lattice). The growth habit of (nano)crystals can be controlled by using organic agents, such as surfactants (as well as through the degree of supersaturation or ionic strength), to produce polyhedra with faces controlled by the growth rate of certain planes in the crystal unit cell.^[162,169] Nanoparticles of CdSe with rod, arrow, teardrop, and tetrapod shapes may be fabricated^[170] by using surfactants to selectively control the growth of certain crystal faces. String and other superstructures of spherical nanoparticles may be prepared in the same way.^[171] Nature exploits soft materials to template the synthesis of hard nanostructures, this is discussed further in Section 4.2, which includes examples of the intricate structures made by certain organisms. Self-assembled nanostructures may also be used to template the formation of helical nanoparticles (using peptides in solution) or of string, necklace, or vesicular structures formed by block-copolymers in solution.^[172–174] The self-assembly of rod-coil block copolymers can, for example, be used to make mushroom-shaped nanoobjects that assemble into lamellar stacks which have polar ordering.^[175,176]

4. Templated Nanostructures

4.1. Mesoporous Silica

The self-assembly of surfactants can be exploited to template inorganic minerals, such as silica, alumina, and titania (titanium dioxide). The resulting structures resemble those of zeolites, except that the pore size is larger for the surfactant-templated materials than those in classical zeolite structures. In conventional zeolites, the pore size is typically up to 0.1 nm, whereas using amphiphile solutions it is possible to prepare an inorganic material with pores up to several tens of nanometers in diameter. Such materials are thus said to be mesoporous. They are of immense interest because of their potential applications as catalysts and molecular sieves. Just as the channels in conventional zeolites have the correct size for the catalytic conversion of methanol into petroleum, the pore size in surfactant-templated materials could catalyze reactions involving larger molecules. An excellent review of

the templating of mesoporous materials using lyotropic liquid crystals is available.^[177]

It was initially believed that the templating process simply consisted of the formation of an inorganic “cast” of a lyotropic liquid-crystal phase.^[177] In other words, pre-formed surfactant aggregates were envisaged to act as nucleation and growth sites for the inorganic material. However, it now appears that the inorganic material plays an important role, and that the structuring occurs through a cooperative organization of inorganic and organic material.^[177] Considering, for example, the templating of silica, a common method is to mix a tetraalkoxy silane and surfactant in an aqueous solution. Both ionic^[178–181] and nonionic^[182,183] surfactants have been used to template structures, as have amphiphilic block copolymers^[184,185] (these behave as giant surfactants, and enable larger pore sizes). The cooperative self-assembly process leads to a structure in which the silica forms a shell around amphiphilic aggregates, the latter being removed by calcination.

Figure 10 shows a hexagonal honeycomb pattern where the silica has been templated from the hexagonal-packed cylinder (H_1) phase. Layered or bicontinuous structures have been prepared in a similar manner, by templating lamellar (L_α) or bicontinuous phases, respectively. Similarly, highly monodisperse silica beads have been made by templating spherical micelles.

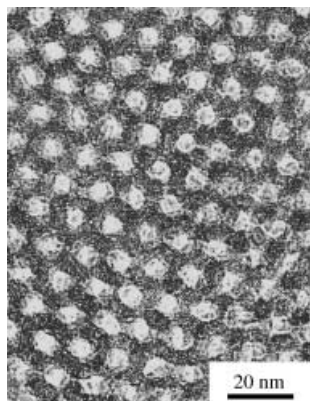


Figure 10. Hexagonal structure of calcined mesoporous silica, templated using an amphiphilic triblock copolymer.^[184] Reproduced with permission from G. D. Stucky and Science. Copyright ©1998 AAAS.

4.2. Biomineralization

Biomineralization involves the uptake and controlled deposition of inorganic moieties from the environment in biological systems. A recent textbook^[162] and several reviews^[169,186,187] cover the subject in greater depth (that the subject deserves), than can be done here. In this section, the focus is on nanoscale structures formed by biomineralization.

The main types of biominerals are the various forms of calcium carbonate (e.g. calcite and aragonite) and calcium

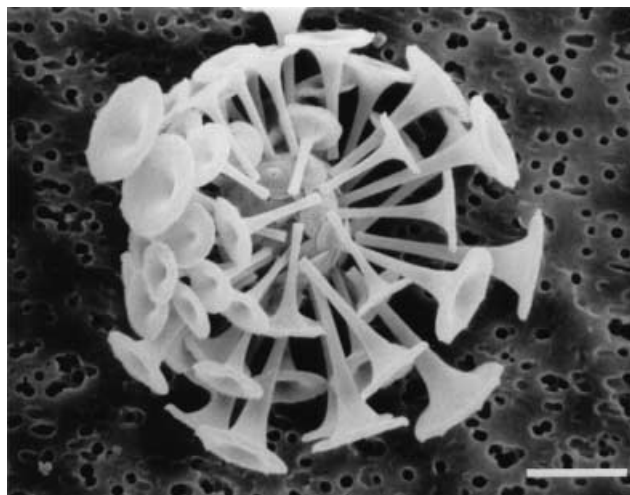


Figure 11. Example of a coccosphere.^[162] Scale bar = 3 μm . Reproduced from ref. [162] with permission from S. Mann and Oxford University Press.

phosphate. Calcium carbonate is the principal component of shells, which consist of an outer layer of large calcite crystals, and an inner region of layers of aragonite several-100 nm thick. Other marine organisms live within intricate exoskeletons formed by calcium carbonate. Examples include the so-called coccospheres (see Figure 11). Calcium phosphate is the building material for bone and teeth, in the form of hydroxyapatite, which can be represented as $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. Bone is formed by the organized mineralization of hydroxyapatite in a matrix of collagen fibrils and other proteins to form a porous structure. The mineral content controls the rigidity or elasticity of the bone. Tooth enamel also contains hydroxyapatite (more than in bone), and its ability to withstand abrasion results from a complex structure where ribbonlike crystals are interwoven into an inorganic fabric.^[162] A great deal of research activity is currently focussed on the construction of artificial bone for replacement joints, and as scaffolds for tissue engineering.^[188] However, the porous macrostructure of bone is outside the nanodomain, and so this fascinating subject is not considered further here.

Radiolarians and diatoms produce their beautiful microskeletons (Figure 12) from amorphous silica.^[162,187] Lamellar aluminophosphates can also be templated to create patterns that mimic diatom and radiolarian microskeletons.^[189,190] The nanoscale features of these microskeletons are formed by the self-assembly of minerals which is templated by biological structures. In particular, the lacelike structures are formed from vesicles, packed together at the cell wall. The vesicles are arranged in a thin foamlike film, and biomineralization occurs in the continuous matrix.

4.3. Nanostructures Templated by Block-Copolymer Self-Assembly

Masks made from block-copolymer films in which one component has selectively been removed have been used to pattern semiconductors.^[191–193] This is a novel technique for

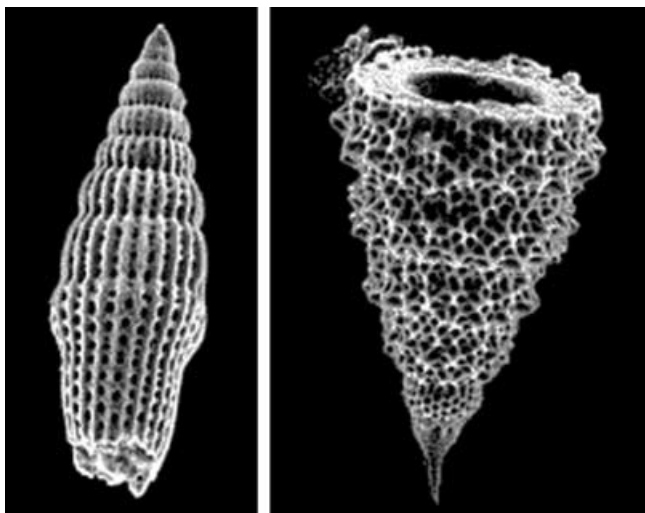


Figure 12. Examples of radiolarian microskeletons (reprinted with permission from <http://www.ucmp.berkeley.edu/protista/radiolaria/radmm.html>).

lithography at the nanoscale, which may be an attractive alternative to photolithography using hard (UV or X-ray) radiation. The feature density achieved is approximately 10^{11} holes cm^{-2} ,^[191] such a high capacity being of clear interest in regard to Moore's law for the density of components in integrated circuits. The block copolymer lithography method relies on the selective ozonation of polyisoprene or polybutadiene in block copolymers containing polystyrene as the other component. Ozone cleaves the double bonds in the unsaturated polymers, so that they can be etched away. This process leaves holes or stripes in a polystyrene matrix. This

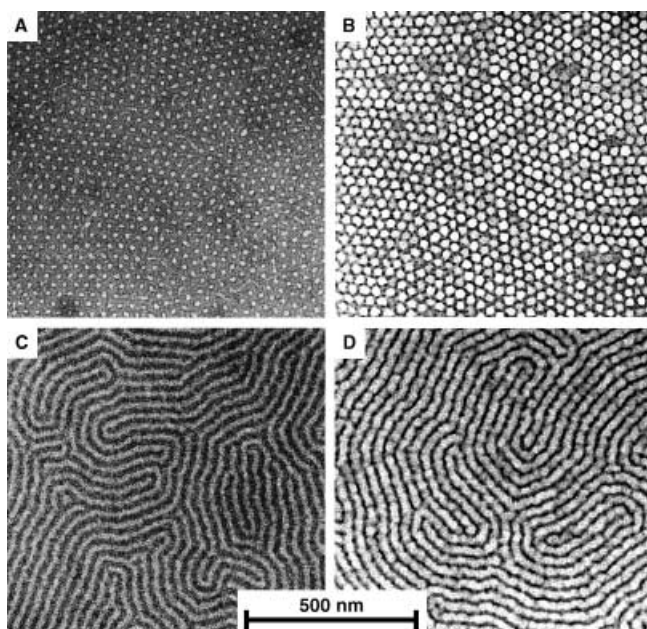


Figure 13. TEM micrographs of polystyrene-polybutadiene diblock copolymer film masks (a,c) and lithographically patterned silicon nitride (b,d).^[191] Reproduced with permission from C. Harrison and Science. Copyright ©1997 AAAS

pattern can be transferred from the block-copolymer mask into silicon by reactive ion etching (Figure 13).

Magnetic nanostructures have also been templated using block copolymer self-assembly. Several strategies have been pursued. One method is to prepare vertically oriented hexagonal-packed cylinders from an asymmetric copolymer and then remove the minority cylinder-forming component (Figure 14).^[194] Thurn-Albrecht et al. employed this method using polystyrene-poly(methyl methacrylate) (PS-PMMA) diblocks, the minority PMMA component being removed by short wavelength ultraviolet radiation (which also cross-links the PS domains ensuring that the glassy matrix is retained).^[194] The resulting nanopores were then filled with Co or Cu atoms by electrodeposition. The result is a magnetic nanowire array, with potential use as ultrahigh-density recording media.

An alternative lithographic method has also been demonstrated. Minority domains in a diblock film deposited on a metallic multilayer structure are selectively etched by reactive-ion etching (RIE) forming a mask (Figure 15).^[195] The diblock used was a polystyrene-polyferrocenyldimethylsiloxane (PS-PFS), in which the PS matrix can be selectively etched away in an O_2 plasma, leaving PFS spheres. An SEM image of the structure at this stage is shown in Figure 16. The mask pattern is transferred into silica (which improves pattern transfer) then into tungsten by RIE. The multilayer structure is necessary because magnetic materials, such as cobalt, nickel, and iron are not amenable to RIE. In the next step, the polymer and silica are removed. Finally, the pattern is transferred from the tungsten hard mask into the magnetic cobalt layer using ion-beam etching.

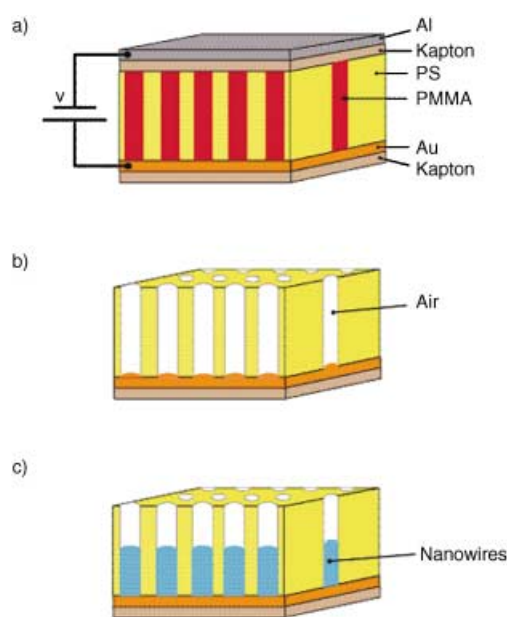


Figure 14. Schematic of high-density nanowire-array formation.^[194]

a) An asymmetric diblock copolymer is annealed above the glass transition temperature of the copolymer between two electrodes under an applied electric field. b) After removal of the minor component, a nanoporous film is formed. c) Nanowires formed by electrodeposition in the pores. Reproduced with permission from M. T. Tuominen and Science. Copyright ©2000 AAAS

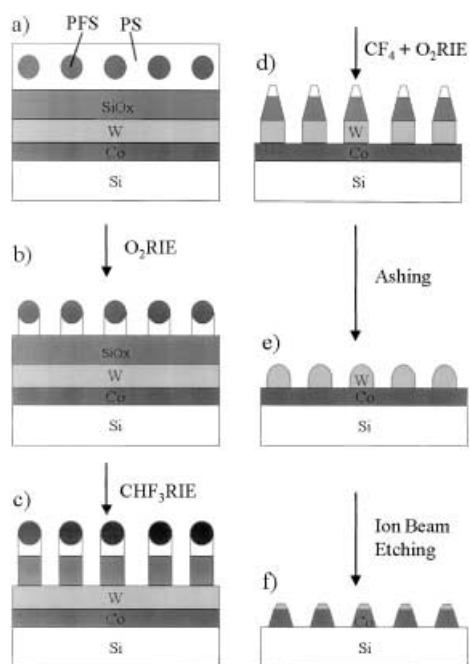


Figure 15. Fabrication of a magnetic cobalt dot array using block-copolymer nanolithography. a) The block-copolymer film is spin coated onto a multilayer. b) A mask is formed by selective etching of the PS domains by O_2 RIE, c), d) the silica and then tungsten layers are etched using different ion beams. e) The silica and polymer are removed by CHF_3 RIE. f) The cobalt dot array is formed using ion-beam etching. Reproduced with permission from ref. [195].

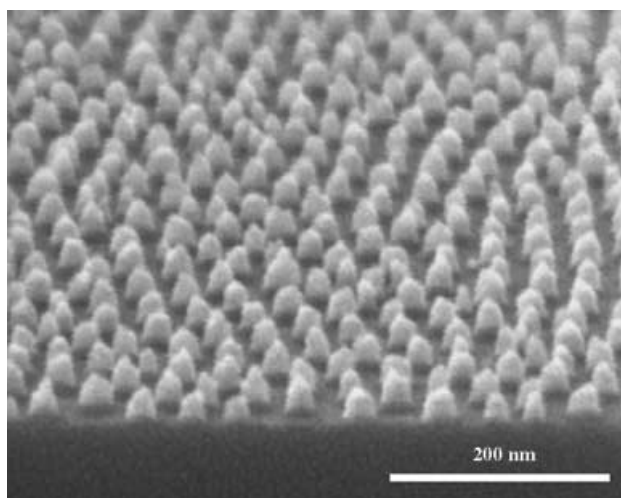


Figure 16. SEM image of PS-PFS mask, after the PS has been removed by O_2 RIE. Reproduced with permission from ref. [195]

The patterning of inorganic nanoparticles using block copolymer micelles adsorbed onto solid substrates is another exciting application of block-copolymer self-assembly, as discussed in Section 3.1.

5. Liquid-Crystal Mesophases

5.1. Micelles and Vesicles

Micelles and vesicles formed by surfactants and block copolymers are widely used in systems as diverse as personal-care products, agrochemicals, and pharmaceuticals to solubilize fragrances, pesticides/herbicides, or drugs. Usually the aim is to solubilize organic compounds in the core of micelles in aqueous media.

The primary nanotechnology applications of micelles and vesicles result from their use as templates to synthesize nanoparticles with a multitude of structures and functionalities. The use of core cross-linking reactions to form organic nanoparticles containing functionalized coatings (tailored through the choice of corona block) has also been reported.^[196–198] In particular, cross-linking of the nontoxic, biodegradable polylactide core of micelles with an end-functionalized poly(ethylene glycol) corona lead to sterically stabilized and biocompatible nanoparticles for drug-delivery applications.^[196,197] Another approach is to cross-link the shell and remove the core by, for example, ozonolysis.^[199] Similarly, cross-linking the shell of a vesicle leads to hollow nanoparticles that can be used to encapsulate compounds.^[51,53,200,201] Alternative methods to deliver drugs using molecular complexes, inclusion compounds, and micro-emulsions, are discussed elsewhere.^[202]

As mentioned in Section 3.1, micelles can also be used as media for the production of inorganic nanoparticles. The synthesis of metal nanoparticles in aqueous block-copolymer micelles has recently attracted a great deal of attention.^[78–91] Metal ions or complexes that are insoluble in water are sequestered in the micellar core. The block-copolymer micelles containing the metal compounds then act as nano-reactors where, upon reduction, the nucleation and growth of metal nanoparticles occurs. Applications of such metal nanoparticles are extensive, and include catalysis, electrooptical materials (quantum dots), and the patterning of semiconductors.^[90] Using block-copolymer micelles it is possible to control the size of the particles by changing the copolymer composition and molecular weight. This feature is very important for the synthesis of magnetic nanoparticles, to ensure that the nanoparticles are large enough to exceed the superparamagnetic limit but small enough to comprise a single domain (see Section 3.6).

5.2. Lamellar Phases

The lamellar phase (known as the smectic phase for low-molar-mass liquid crystals) is found in diverse systems, ranging from surfactants in solution to clays to block copolymers. The layered structures in clays and polymer-clay nanocomposites were discussed in Section 3.4. In this section the focus is on recent examples of high-tech applications for lamellar phases in block copolymers.

Noncentrosymmetric structures can have a macroscopic electric polarization, and hence piezo- and pyroelectricity as well as second-order nonlinear optical (NLO) activity. The

fabrication of noncentrosymmetric stacks of block-copolymer lamellae has been demonstrated in blends of ABC triblock and ac diblock copolymers (the letters refer to the different blocks in the polymers).^[203] The resulting structure is illustrated schematically in Figure 17. It is favored over others (macrophase separated, random lamellar, centrosymmetric lamellar stack) if the difference in the aA and cC contact energies is large enough.

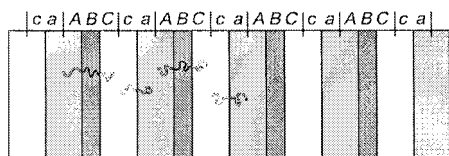


Figure 17. Schematic of a noncentrosymmetric lamellar structure observed in a blend of ABC triblock and ac diblock copolymers.^[203] Reproduced with permission from L. Leibler and Nature.

It has been proposed to exploit lamellar block-copolymer structures to self-assemble all-polymer solid-state batteries, by using a triblock copolymer where the three blocks correspond to the anode, electrolyte, and cathode.^[204] This approach has the advantage that possible leakage of a toxic liquid electrolyte is avoided, and furthermore the processing is straightforward (e.g. spin coating of thin films). Similar applications of lamellar block-copolymers in nanocapacitors^[91] and nanotransistors have also been envisaged.

Lamellar block-copolymer nanostructures can be used as selective 1D dielectric reflectors if the layer thickness is large enough (close to the wavelength of light) and the difference in refractive index between blocks is large enough. Polystyrene–polyisoprene diblocks swollen with the corresponding homopolymers was shown to have a limited angular range stop band at visible frequencies with potential applications in photonics,^[205,206] for example, in waveguiding.^[207,208]

Rod–coil diblocks can form a range of lamellar structures, as demonstrated by the work of Chen et al.^[209] on polystyrene–poly(hexylisocyanate) diblocks, which form wavelike lamellar, zigzag, and arrowhead morphologies. Distinct structures result because the rod block can tilt with respect to the layers, and the tilt can alternate between domains. The coupling of liquid-crystal ordering to that of block copolymers extends considerably the range of nanostructures available to the nanotechnologist.

Inspired by a similar concept, Ruokolainen et al. have shown that ordering as multiple lengthscales can be achieved using complexes of diblock copolymers and the amphiphilic, long-chain alcohol, pentadecylphenol (PDP).^[210,211] Hydrogen bonding of the alcohol to the –NH group in poly(4-vinylpyridine) (P4VP) produced a comblike block, whereas no hydrogen bonding occurred to the coil-like polystyrene block. The usual ordered structures were observed which result from microphase separation in the melt of the diblock, however, in addition, mesogenic ordering was observed within the P4VP–PDP phase as a result of formation of a lamellar structure below the liquid–crystal–isotropic phase transition for the

PDP. Since the lamellar–isotropic phase transition for the PDP/P4VP lamellae occurs below that for the PS–P4VP block copolymer, it is possible to switch off the lamellar ordering on one lengthscale independent of the other. It was shown that this transition was accompanied by a large change in the electrical conductivity (P4VP is a semiconducting side-chain conjugated polymer). The potential to create switchable nanoscale structures with ordering in two- and three-dimensions has implications for other applications, such as alignment layers in liquid-crystal displays, nanoscale sensors, and optical waveguides.

5.3. ABC Triblock Structures

The phase behavior of ABC triblock polymers is much richer than that of AB diblock polymers^[212–214] because in triblock polymers there are two independent compositional order parameters and three Flory–Huggins interaction parameters, the subtle interplay of which gives a varied morphospace. Examples of the intricate morphologies observed are shown in Figure 18 and Figure 19. A remarkable structure consisting of helices of a minority polybutadiene domain wrapped around polystyrene cylinders in a PMMA matrix has even been reported.^[215] These observations of complex phases formed by midblock segregation at the AC interface have been accounted for theoretically by Stadler et al.,^[216] the theory being in good agreement with experiments for several morphologies. However, it has to be emphasized that achieving thermodynamic equilibrium (e.g. through annealing) in ABC triblock copolymer melts is even more challenging than for diblock copolymers^[217] since they are usually more strongly segregated, so that great caution is required in assigning equilibrium phase behavior.

State-of-the-art self-consistent mean field (SCMF) theory calculations have been used to predict a number of intricate nanostructures at the surface of ABC triblock copolymers (Figure 20). It should be noted that the patterns in Figure 20 are simulated in a 2D system. As a result of confinement and surface-energy effects, such morphologies may not be realizable at the surface of a bulk sample,^[220,221] however, they could be accessed by sectioning of a glassy bulk sample. Potential exploitation of the surface structures formed by ABC triblock copolymers can be envisaged if domains are selectively doped with metal atoms or semiconductors (see Figure 2 for an example corresponding to the diblock copolymer case). Applications include nanowire arrays for addressing nanoscale electronic devices or three-color arrays for high-resolution displays.

5.4. Smectic and Nematic Materials

Conventional methods of fabricating liquid-crystal displays are not usually regarded as nanotechnology. Present-day displays are based on nematics sandwiched in thin films between electrode-coated glass substrates.

The fabrication of a liquid-crystal display on a single substrate, which could ultimately lead to flexible or paintable

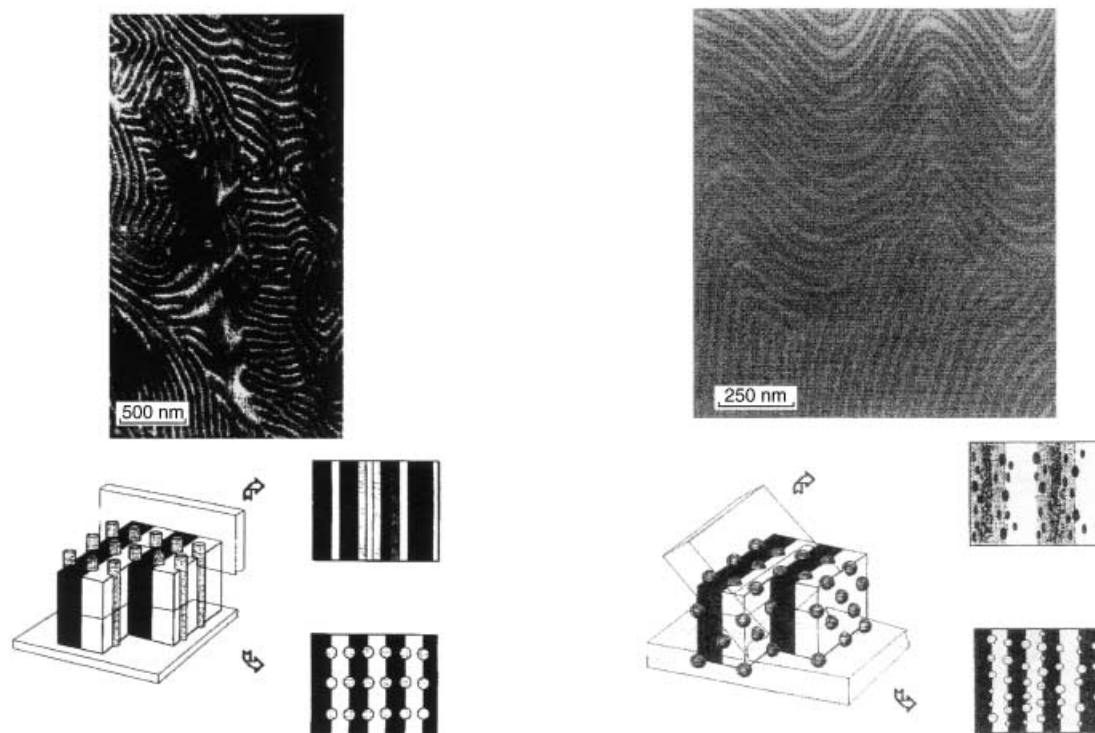


Figure 18. Examples of morphologies observed for polystyrene–polybutadiene–poly(methyl methacrylate) triblock copolymers with a minority midblock component.^[216] Left: cylinders at a lamellar interface, right: Spheres at a lamellar interface (“ball at the wall” morphology). The upper images are transmission electron micrographs. The lower figures are schematics. Reproduced with permission from ref. [216].

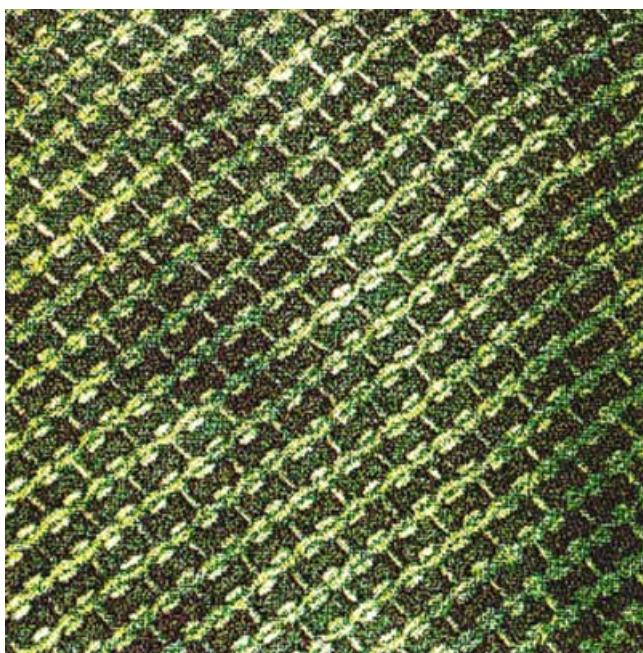


Figure 19. “Knitting pattern” morphology observed by TEM on a polystyrene–poly(ethylene-co-butylene)–poly(methyl methacrylate) triblock copolymer (stained with RuO_4). Reproduced with permission from ref. [218].

displays has recently been demonstrated based on an array of encapsulated liquid-crystal cells.^[222] Stratified polymer structures self-assemble through phase separation of a photopolymerizable prepolymer and a nematic liquid crystal.

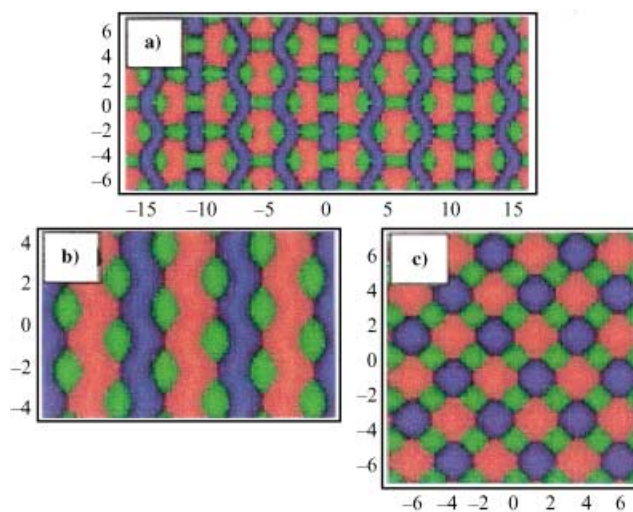


Figure 20. Examples of predicted morphologies for linear ABC triblock copolymers, from self-consistent mean field calculations. Reproduced with permission from ref. [219].

Horizontal stratification creates the walls of the cells and vertical stratification (using a different UV wavelength) produces lids. To date, the technique has been used to fabricate micron-size polymer cells, although extension to the nanoscale using harder radiation should be feasible.

Usually a nematic phase is cloudy because of light scattering from fluctuating micron-size domains with different orientations (creating refractive-index variations, since the refractive index of liquid-crystal phases is anisotropic).

The presence of nanometer-scale phase-separated structures in an inverse lyotropic structure of surfactant micelles in a liquid-crystal matrix has been shown to lead to a transparent nematic phase.^[223] In the “nanoemulsion” the droplets of surfactant disrupt the long-range orientational order of the nematic phase, which leads to optical isotropy and transparency, although the local nematic ordering is retained. Mixing spherical colloidal particles with liquid crystals likewise produces a phase-separated structure as colloidal particles are expelled from nematic droplets below the isotropic–nematic phase-transition temperature.^[224] The particles are expelled because the trapping of defects in the nematic phase by colloidal particles has too high an energy penalty. The colloid particles therefore separate into an interconnected network (the struts of which are several nanometers thick). The result is a waxy soft solid with a high storage modulus.

5.5. Discotic Liquid Crystals

Columnar phases formed by discotic liquid crystals, such as those based on triphenylene compounds, form 1D conductors, because of the overlap of π^* orbitals of the aromatic moieties which are surrounded by a hydrocarbon insulator coating.^[225,226] Each column thus acts as a nanowire, and applications in molecular electronics have resulted, in particular in gas sensors.^[227] They could also be used in molecular electronic devices, for example, in electroluminescent displays or in 3D integrated circuits.

6. Summary and Outlook

Self-assembly is responsible for nanostructure formation in colloidal, amphiphilic, polymeric, and biomolecular materials. In this review, the principles of self-assembly in synthetic and biological systems were considered. Then selected examples of self-assembly routes to the production of nanostructures and nanodevices were presented. A key theme is that self-assembly in soft materials (synthetic and biological) can be used to template nanostructures in inorganic matter, either in bulk or at a surface. The range of structures that can be fabricated in equilibrium depends (following the Gibbs phase rule) on the number of components in the system. In the case, for example, of ABC triblock copolymers this leads to a large number of possible nanostructures with different symmetries. An additional complexity in phase behavior results from the coupling of distinct types of order, for example, orientational order of liquid crystals with translationally ordered block-copolymer nanostructures.

Out-of-equilibrium processes can also be exploited, for example, in nanoscale motors or actuators. Out-of-equilibrium structures may also be useful, since they could be captured when templating a hard material. It has to be kept in mind that the rich structural diversity and access to out-of-equilibrium structures are both different aspects of the weak ordering resulting from noncovalent interactions that characterizes soft materials.

Many developments are underway to exploit self-assembling soft materials in nanotechnology. Considering nanostructures, the first commercial products are likely to be nanoparticles fabricated in micellar or vesicular nanoreactors, and mesoporous templated materials for catalysis and separation media. Uses of more intricate structures, such as those formed by ABC triblock copolymers are still some way off. Downstream applications of biomineralization (in prostheses, artificial bone and teeth) are less distant. The development of drug-delivery systems using functionalized nanoparticles is also the subject of intense research activity at present. Only a sample of the many different approaches being investigated has been covered here. The use of block-copolymer films in nanolithography and to pattern nanoparticles into regular arrays are the focus of much attention.

Arguably the most important nanodevice is the nanomotor, and self-assembly routes to the production of simple oscillating “motors” have already been developed. To fabricate directional motors with a renewable energy source, inspiration is being taken from nature, where ATP synthesis underpins distinct linear and rotary motors. Supramolecular chemistry has much to offer here, although this is outside the scope of this review. Other nanodevices will contain passive nanostructures which can be built by using self-assembly, examples include waveguides and optical filters. Nanowires and ferroelectric piezo- and pyroelectric structures can also be produced. Self-assembled nanocapacitors and nanotransistors can also be envisaged, although as yet there has been little research in this area. Using a combination of self-assembled nanostructure elements from the broad palette available, together with a suitable power source (e.g. a nanostructured-polymer solid-state battery) a customized nanodevice could readily be put together. The prime limitation is that certain nonperiodic structures require atomic or molecular manipulation, outside the realm of self-assembly.

The time is now ripe to harvest the benefits of research in the last few decades on soft materials, and to take advantage of self-assembly to prepare tailored nanostructures. The diversity of possible nanostructures and the techniques to make use of them constitute a rich smorgasboard. Only a taste has been provided here, hopefully enough to capture the flavor.

The AFM images of block-copolymer films for the collage on the frontispiece were obtained by Dr. T. Mykhaylyk, University of Leeds, UK.

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