Persistence Pays Off

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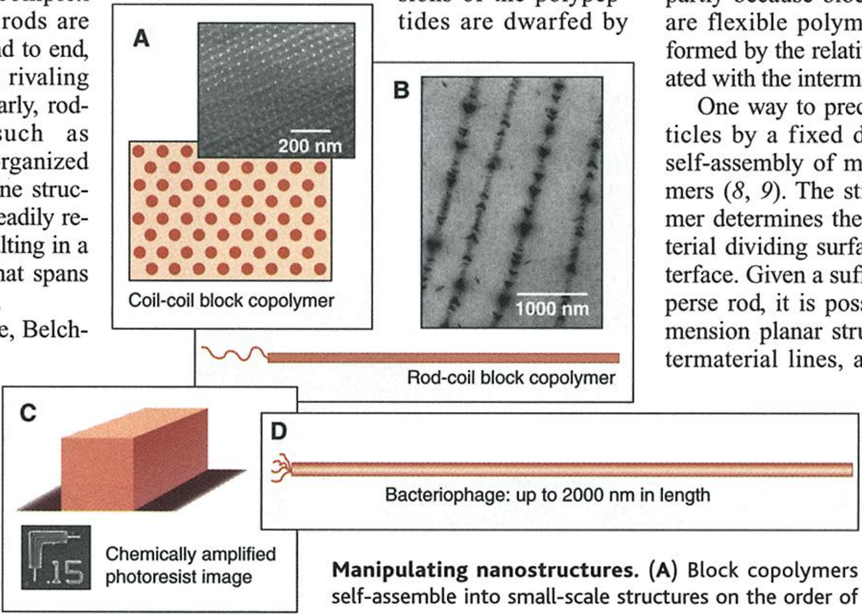
Supermolecular structures can potentially act as scaffolds for the organization of inorganic nanoparticles. This approach has applications in optical, electronic, and magnetic materials. For example, precise spacing of magnetic domains might allow extremely high-density memory storage. How can these nanostructures be formed? Rod-shaped molecules in low–molar mass liquid crystals can form complex mesophases in which the rods are lined up side by side and end to end, producing an organization rivaling that of solid crystals. Similarly, rodlike macromolecules such as polypeptides can also be organized into ordered liquid crystalline structures, and the organization readily retained in the solid state, resulting in a single layer of molecules that spans micrometers (see the figure).

On page 892 of this issue, Belcher and co-workers (*1*) use biomolecular engineering to construct an ordered nanocomposite from semiflexible, shape-persistent bacteriophages and ZnS nanoparticles. By combining bacteriophages engineered with ZnS-specific binding groups at one end with nanoparticles of ZnS, they produced liquid crystalline suspensions that could be easily cast into highly organized solids with the ZnS constrained to widely spaced, uniform layers.

Liquid crystallinity in suspensions of viruses has been recognized for some time. Using similar bacteriophages, Marvin and coworkers formed liquid crystal phases in solution by suspending sufficiently high concentrations of viral rods in appropriate solvents (*2*). Such mixtures are birefringent and can be aligned in magnetic or electric fields. The bacteriophage has a diameter of about 6 nm, making it much larger than most rodlike macromolecules. In addition, whereas a typical axial (length to width) ratio of low–molar mass liquid crystals is 6:1, in bacteriophages it is on the order of 150:1 with controllable lengths as long as 2000 nm. Like the recently reported rodlike, poly(benzyl glutamate) polymers produced by bacterial-growth methods (*3*), the length of the viral structures can be varied over several orders of magnitude while maintaining monodispersity. However, the dimensions of the polypeptides are dwarfed by those of the viral assemblies. The viral rods can be organized into assemblies with lines less than 50 nm wide, periodically spaced by the length of the rods. This scale is smaller than can be accessed by advanced optical or electron beam lithography (*4*).



Manipulating nanostructures. (A) Block copolymers self-assemble into small-scale structures on the order of 5 to 200 nm. Structures and sizes depend on molecular weight and volume ratio. The hexagonal array formed by self-assembly of a coil-coil polymer is shown (looking down the cylinders). The inset is an electron micrograph of a thin film of block copolymer. **(B)** By stiffening one of the block segments, larger scale structures can be formed. The competition between rigid and flexible segments leads to novel microstructures with up to micrometer dimensions. **(C)** Chemically amplified resists have enabled the microelectronics revolution. Exposure to ultraviolet light enables submicrometer pattern formation. The scheme shows a figure representing a resist line 150 nm in width, and the inset is a micrograph of a photoresist test pattern in which each line is 150 nm wide. **(D)** The bacteriophage dwarfs these objects and can form extended structures by organization through the liquid crystal state.

The only other methods that can be used to form nanostructures with dimensions less than 50 nm are patterning techniques that use scanning probe methods or self-assembly of other natural or synthetic macromolecules. For example, dip-pen lithography is a patterning technique that permits the formation of arbitrary lines and shapes at this dimension, but it would take a great deal of time to span the dimensions covered by the viral assemblies (*5*). Self-assembly of block copolymers allows the formation of regular arrays of hexagonally arranged disks on the order of 20 to 50 nm. The resulting thin-film patterns have been examined as templates for the creation of quantum dots (*6*) and electrode arrays (*7*). However, there are many unresolved challenges to using self-assembly of polymers for nanostructure organization, including the difficulty of creating defect-free structures over long distances. To date, narrow-width lines that would allow precise placement of functional particles have not been formed with this block copolymer patterning method. This is partly because block copolymers typically are flexible polymers, and the pattern is formed by the relatively weak forces associated with the intermaterial dividing surface.

One way to precisely separate nanoparticles by a fixed distance is through the self-assembly of more rigid, rodlike polymers (*8*, *9*). The stiffness of the rod polymer determines the nature of any intermaterial dividing surface and favors a flat interface. Given a sufficiently long, monodisperse rod, it is possible to create large-dimension planar structures with narrow intermaterial lines, as in the bacteriophage assemblies, but with more precise registration in the solid state. In block copolymers, the location of the functional component is determined by the nature of the covalent linkage between the block segments. The structure that is formed is a result of the competition between packing geometry, the relative rigidity of the different components, and the volume ratios of the phases. However, it remains difficult to incorporate functional inorganic materials into block copolymer arrays without complex postassembly processing.

Bacteriophages offer another way to form large-dimension patterned assemblies by merging biomolecular science with materials science. Key to this process is the engineering of the phage to specifically bind functional components, as has been done for a variety of inorganic materials (*10*). Because the phage are strongly bound to

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the inorganic components, the phage are participants rather than bystanders in the assembly process. Relatively small (~20 nm in diameter) particles are easily organized into the layered structure formed by the viral rods, leading to well-populated lines only a few tens of nanometers across spaced by the length of the bacteriophages. Incorporation of various appropriate molecular components could allow this self-assembly process to generate a variety of optical, electronic, or magnetic devices.

References

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PERSPECTIVES: PHYSICS

Superconducting Qubits—a Major Roadblock Dissolved?

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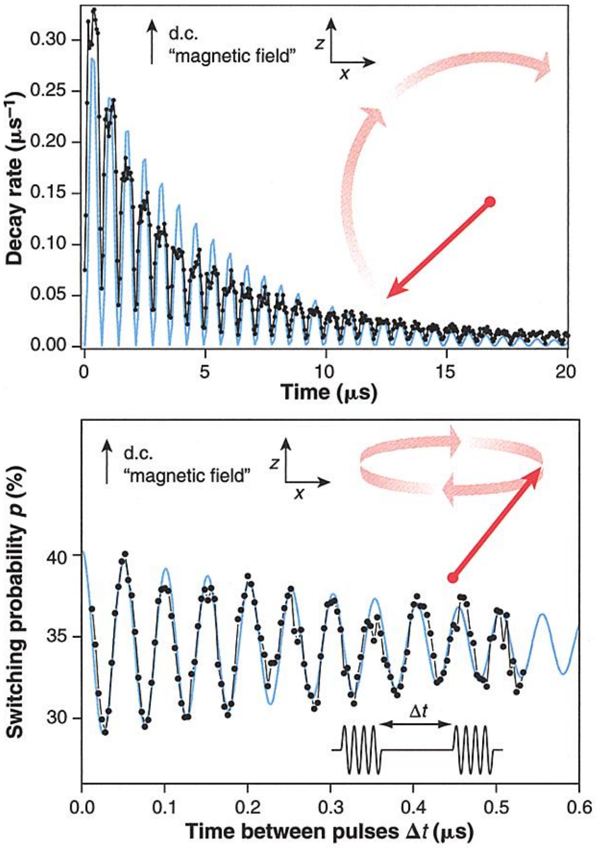
In the race to implement a real quantum computer, systems based on macroscopic electrical circuits incorporating Josephson junctions have until now been something of a dark horse. Such systems may be scalable up to the minimum number of qubits that would make a real-life quantum computer useful. In addition each qubit can be individually addressed by conventional techniques of electrical engineering. However, by the phenomenon of decoherence (*1*), any irreversible interaction of a quantum-mechanical system with its environment destroys the phase relations between the different branches of its wave function. These phase relations are at the very heart of proposals for quantum computing (*2*) and decoherence has been thought to be a serious drawback. Two papers in this issue [Yu *et al.* on page 889 (*3*) and Vion *et al.* on page 886 (*4*)] have now shown that this view may be too pessimistic.

A qubit—the basic element in a quantum computer—can be formed by any physical system whose motion is effectively restricted to a two-dimensional Hilbert space (that is, whose state is restricted to being an arbitrary superposition of two "basis" states). It is often convenient to represent such a system as a "particle" of spin $^1/_2$, subject to a fictitious "magnetic field" whose direction we conventionally take to define the z axis; however, in some cases the most easily observable quantity turns out to be the x component of the "spin," S_x. In any case, what is of most interest in the context of quantum computing is the extent to which the phase relation between the "spin-up" and "spin-down" components of the wave function is preserved, and this turns out to be equivalent to the extent to which the direction of the xy-plane component of the spin vector remains well-defined. The effect of decoherence in randomizing the relative phase, and thus this direction, is usually quantified by the inverse of the "phase relaxation time" T_φ (T_2 in the conventional NMR language), or equivalently by the quantity Q_φ, which is half the product of T_φ and the (angular) Larmor precession frequency (that is, Q_φ is approximately the number of revolutions for which the direction of the xy component of spin remains well-defined). It is generally believed that successful quantum computation requires, as a minimum, that Q_φ should be at least of the order of 10^4. Information on Q_φ can be obtained from Rabi-oscillation experiments, in which the system is driven by an rf field with frequency close to the Larmor frequency and the expectation value of the z component of spin is monitored (sufficiently noninvasively) as a function of time, and more directly from "Ramsey-fringe" (free-precession) experiments that effectively measure the expectation value of the x component as a function of the time for which the precession has lasted. In addition to T_φ, it is sometimes useful to define the "longitudinal" or "energy" relaxation time T_1; in practice T_1 is almost always longer than T_φ. Proposals to use Josephson systems as qubits have up to now mostly concentrated (*5*) on two specific implementations, the "Cooper-pair box" ("charge qubit") and the "rf SQUID ring" ("flux qubit"). In the first case, a small superconducting grain is connected to a superconducting reservoir by a Josephson junction. The eigenstates of S_x correspond to states with N and $N + 1$ Cooper pairs (electronic "quasi-molecules") on the grain. (Other possible states have much higher energies and can be ignored). At a suitable bias voltage on the grain relative to the reservoir, these states are degenerate in the absence of Josephson tunneling, but such tunneling splits them. Using the "spin" analogy, this provides a magnetic field in the z direction. In this system the most serious source of decoherence is believed to be fluctuations in the biasing voltage ("charge noise"); despite this, Nakamura *et al.* (*6*) were able to perform free-precession experiments



Probing coherence in macroscopic systems. In a Rabi-oscillation experiment **(top)** the z component of "spin" displays the expected damped sinusoidal behavior. In a Ramsey-fringe experiment **(bottom)** the x component as probed at a frequency Ω_P shows damped sinusoidal oscillations at the beat frequency $\Omega_P - \Omega_L$ (Ω_L = Larmor frequency).

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