Liquid Crystals

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A New Twist on Chirality: Formation of Chiral Phases from Achiral Molecules in "Banana" Liquid Crystals through Elastic Deformations

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It was clear for more than one and a half centuries, since the days of Louis Pasteur,[1] that crystals which behave as mirror images of each other are made up of molecules which exhibit opposite handedness, or enantiomers, as they are now called. When such crystals are dissolved at equal concentrations in an isotropic solvent, the optical rotation of each of the resulting solutions is equal, but opposite in direction. Liquid crystals (formed, incidentally, from chiral molecules, namely, cholesteryl derivatives) were discovered only four decades after the groundbreaking insight provided by Pasteur in 1848.[2] Liquid-crystal phases that are composed of enantiomers exhibit equal scalar properties, such as melting point or birefringence, but their chiral properties, such as optical rotation, helical pitch, or spontaneous polarization, are opposite in sign. The effects of chirality are of huge importance in everything from biological functionality, the growth of plants and snails, the helical structure of DNA, and the design of drugs to the β decay of radioactive elements.[3] Chirality, or the lack of mirror symmetry, which is in fact a very tiny effect in comparison to other interactions, is at work in nearly every aspect of science, and thus life.

In the late 1990s, a new class of liquid crystals was discovered,[4] so-called bent-core mesogens or "banana" phases,[5–7] which exhibit polar and chiral properties,[8] such as antiferro- and ferroelectricity, although they are formed by achiral molecules. It was long believed that these properties can only be observed for tilted smectic phases composed of chiral molecules. Smectic phases are phases with a one-dimensional positional order in addition to the orientational order of elongated molecules. Banana phases also show smectic order; however, the spontaneous polarization needed for ferro- or antiferroelectricity results from steric effects, not a lack of molecular mirror symmetry. Like almost all other liquid-crystal phases, banana phases are birefringent, as can be demonstrated with a polarizing microscope, which shows their often aesthetically appealing textures.

Hough et al.[9] have now reported what is believed to be the first example of a chiral isotropic liquid formed from achiral molecules. Again, these molecules have a bent-core shape, and the respective phase does exhibit smectic layering with fluid order within smectic layers. Nevertheless, the coherence length of the smectic layering is only very short, a property attributed to the formation of saddle–splay deformations involving the elastic constant K_{24}. Saddle–splay director fields are not space-filling, and smectic layers are unstable against saddle–splay deformations, which are thus incompatible with long-range order. The reported phase only exhibits short-range orientational and positional order, just as a true liquid does exhibit some short-range correlations (generally over a few atoms or molecules). The phase is ordered locally, but disordered at length scales smaller than about 100 nm: a distance approximately equivalent to 20 times the molecular length. The degree of order of the phase was demonstrated by freeze–fracture transmission electron microscopy. The structure of the imaged phase was similar to that of the lyotropic sponge phase (Figure 1).

The phase structure is attributed to a chiral coupling of local tilt, polarization, and smectic-layer deformation. Macroscopically, on the order of approximately 100 μm, two types of conglomerate domains are formed. Each domain is homochiral, and both domains exhibit very strong rotatory powers of opposite sign (ca. $1°\,\mu m^{-1}$ for visible light). The area distribution of these two domains is equal, so that over very

Figure 1. Freeze–fracture TEM image of the dark conglomerate phase of a bent-core or banana mesogen, the structure of which is shown in the inset on the right. The inset on the left shows schematically the saddle–splay deformations that cause the formation of a structure similar to the sponge phase of lyotropic liquid crystals. (Reproduced with permission from Ref. [9].)

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large ("infinite") sample sizes, the chirality cancels out, as expected (a virgin, unpoled ferroelectric material has a similar type of structure). The isotropic character of this phase was indicated by the absence of birefringence; for this reason the phase is also called a dark conglomerate phase.

In a closely related report by the same research group in the same issue of *Science*,[10] Hough et al. describe another banana phase, commonly known as the B4 phase, which they refer to as the helical nanofilament (HNF) phase. The B4 phase also forms two homochiral domains from achiral molecules; however, in contrast to the liquid-crystal phase discussed above, this phase does exhibit birefringence, which indicates some kind of long-range order. As stated above, twist deformations are incompatible with smectic layering, that is, the formation of even a one-dimensional lattice. Instead, they may cause the formation of twist-grain-boundary (TGB) phases, which are the liquid-crystal analogue of the Abrikosov flux lattice phase of a type-II superconductor in an external magnetic field.[11,12] TGB phases appear as a consequence of the competition between chirality (helix formation) and thermodynamics (positional ordering into a lattice). The problem is solved by the introduction of arrays of screw dislocations; these defects mediate between blocks of planar smectic layers.

The structure of the B4 phase seems to be somewhat different. Strong rotatory power indicated a helical superstructure. X-ray investigations showed short-range smectic layering, but also a two-dimensional, hexatic order within the layers. All these features together are inconsistent with a TGB structure. Hough et al.[10] employed a battery of different imaging techniques to reveal the structure of the B4 phase: atomic force microscopy, freeze–fracture transmission electron microscopy, X-ray and electron diffraction, and depolarized transmission light microscopy. They found a local chiral structure which is formed by twisted smectic layers and which they call a nanoscale filament. These nanofilaments self-assemble into homochiral domains with a twist. Two domain types of equal distribution but opposite sign are formed. Three filament length scales were observed in the formation of the B4 phase: 1) the smectic-layer spacing of approximately 50 Å (related to the molecular length), 2) the width of the filaments of approximately 30 nm, and 3) the helical half-pitch of approximately 100 nm (Figure 2).

During the formation of the B4 phase, nanofilaments of either handedness nucleate and grow. A certain handedness of filament encourages further filaments of the same handedness to form in its vicinity, and thus two macroscopically chiral domain types with opposite handedness develop. Again, the size of these assembled domains is approximately 100 μm. One can perhaps think of this process as being similar to the stacking of left-handed and right-handed screws from the same batch. The left-handed ones will fit together, as will the right-handed ones. Left and right, on the other hand, will not mix easily.

Time and again, liquid crystals surprise with the formation of novel structures with new properties: The only known fluid ferroelectric materials are liquid crystals; twist-grain-boundary phases show strong analogies to solid-state physics; liquid-crystalline quasicrystals have been created; banana phases formed from achiral molecules exhibit chiral properties … It will be interesting to see what liquid-crystal research has to offer in the future, not only for the liquid-crystal specialist, but for sciencists in general.

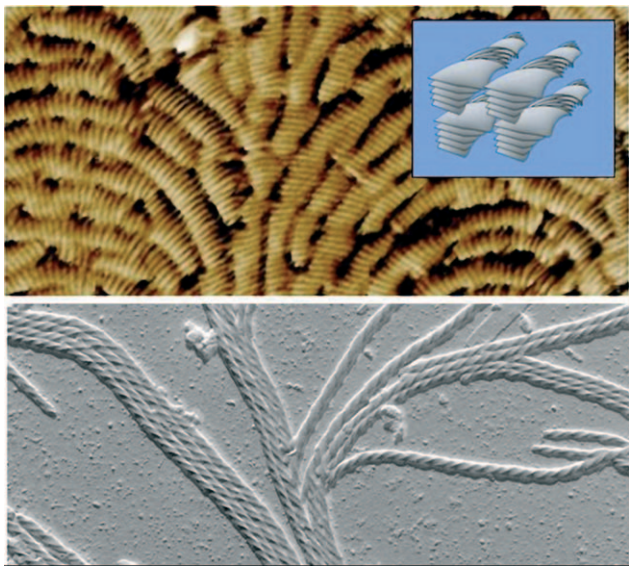

Figure 2. Top: AFM image of the nanofilaments of the B4 phase. The equidistant dark lines indicate the smectic layer thickness of approximately 5 nm; the filament thickness is approximately 30 nm. The inset illustrates schematically the helical arrangement of the smectic layers. Bottom: Freeze–fracture TEM image of singly and collectively growing nanofilaments. Filaments with the same handedness can pack and eventually form macroscopically homochiral domains. (Reproduced with permission from Ref. [10].)

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