Liquid Crystals and Carbon Materials

The macroscopic properties of carbon materials are determined by their structure at the nanometer length scale, and there is great potential to tailor their structure during the liquid-crystal phase of the synthesizing process.

Robert H. Hurt and Zhong-Ying Chen

Carbon atoms can be found in a variety of structures, including the tetrahedra of diamond, the stacked planes of graphite, and the celebrated fullerene spheres and nanotubes. The graphite family alone includes a rich variety of materials, ranging from pencil "lead" to interstellar dust to chimney soot, and from metallurgical coke to activated charcoal for water filtration to lightweight composites for aerospace components—such as the nose cone of the space shuttle, for which carbon composites were chosen because of their high strength at elevated temperatures.

The modern carbon materials industry imports raw organic matter from diverse sources—including synthetic polymers, coal, wood, and petroleum—and transforms it by heating, sometimes in combination with partial oxidation or mechanical stretching, into various commercial products, such as fibers, activated charcoal, and electrodes. Each of these end products is composed primarily of solid elemental carbon but also contains small amounts of hydrogen, oxygen, inorganic matter, and other impurities. The rich variety in the properties and function of carbon materials arises in part because the materials are not single graphite crystals but rather collections of graphene layers—finite-sized planar units with the basic two-dimensional structure of graphite—stacked in different three-dimensional configurations (see figure 1).

The graphite lattice is highly anisotropic in its bonding characteristics and, consequently, in its properties. Strength, elastic modulus, electrical conductivity, and thermal conductivity are much higher within the covalently bonded planes than across them. For example, single-crystal graphite is about 30 times stiffer within the covalently bonded planes than between them. The opposite trend is observed for the coefficient of thermal expansion, which is about 30×10^{-6} K^{-1} across the planes, but less than 10^{-6} K^{-1} within the planes.

As a result of the anisotropy in the graphite lattice, the arrangement of the graphite snippets in real carbon materials—the carbon nanostructure—strongly influences the bulk properties of practical materials and their directional dependencies. For example, the stiffness (modulus) of carbon fibers may be 30 GPa if the graphene layers are oriented randomly, but can reach 800 GPa if the layers have a high degree of alignment along the fiber axis (as in figure 1b). Nanostructure also determines the space-filling properties of the solid phase and thus the ultrafine pore structure that governs the access of small probe molecules to internal surface sites (see figure 1c). This access is central to the high adsorptivity of activated carbons, which have total internal surface areas of as much as 1500 m^2/g. (By comparison, a collection of large, spatially separated graphitic sheets exposed on both sides to adsorbing molecules has a surface area of about 2600 m^2/g, an estimate of the theoretical maximum achievable inner surface.)

A key to designing carbon materials, therefore, is the ability to tailor their nanostructures. Disordered nanostructures are desirable when high internal porosity is desired, such as for the adsorption of organic impurities from water, and ordered nanostructures are preferred when high stiffness, strength, or conductivity along a specified direction are desired, such as for carbon fibers used in aerospace applications and for graphite electrodes used in steelmaking. To understand how to tailor carbon nanostructure, we must turn our attention to the formation process, termed carbonization, in which the spatial arrangement of graphene layers is first established.

In many carbon materials, a crude sheetlike structure is first established by a transition to a liquid-crystal phase in the early stages of carbonization, when the decomposing organic precursor is in a fluid state. Liquid crystals (LCs) are fluid phases formed by rodlike or disklike (discotic) molecules that possess orientational order but lack at least one degree of positional order (see box 1 on page 41). The LC in carbon systems is referred to as carbonaceous mesophase, a discotic fluid that nucleates from the isotropic liquid upon heating. Prior to the discovery of fullerenes, the most celebrated advance in carbon science was the discovery in 1965 of carbonaceous mesophase, the only known naturally occurring discotic LC.[1,2] (See box 2 on page 42.)

Despite its early discovery, carbonaceous mesophase is not as well understood as many other LC systems, such as those used in optical displays. Its complex composition and chemical instability have discouraged systematic investigation of its key fundamental properties. Because of its importance in carbon materials, however, there is a great incentive to overcome these challenges and to begin to develop a deeper understanding of carbonaceous mesophase as an LC and an important precursor to carbons.

From organic matter to carbon

Carbons are synthesized by heating organic matter in the absence of oxygen. When wood, coal, polymers, or pitch—a mixture of high-molecular-weight organic compounds generated by the distillation of coal tar or petroleum—is carbonized, many of the original chemical bonds are ruptured, and most of the noncarbon atoms are released as gaseous products. The new bonds that are formed preferentially arrange the carbon atoms in aromatic ring structures with delocalized electrons. These new compounds belong to the class of polycyclic aromatic hydrocarbons (PAHs), which have high thermal stability and are often

Robert Hurt *is a professor of engineering at Brown University in Providence, Rhode Island (Robert_Hurt@brown.edu).* **Zhong-Ying Chen** *is a senior scientist at Science Applications International Corp in McLean, Virginia (zhong-ying.chen@saic.com).*

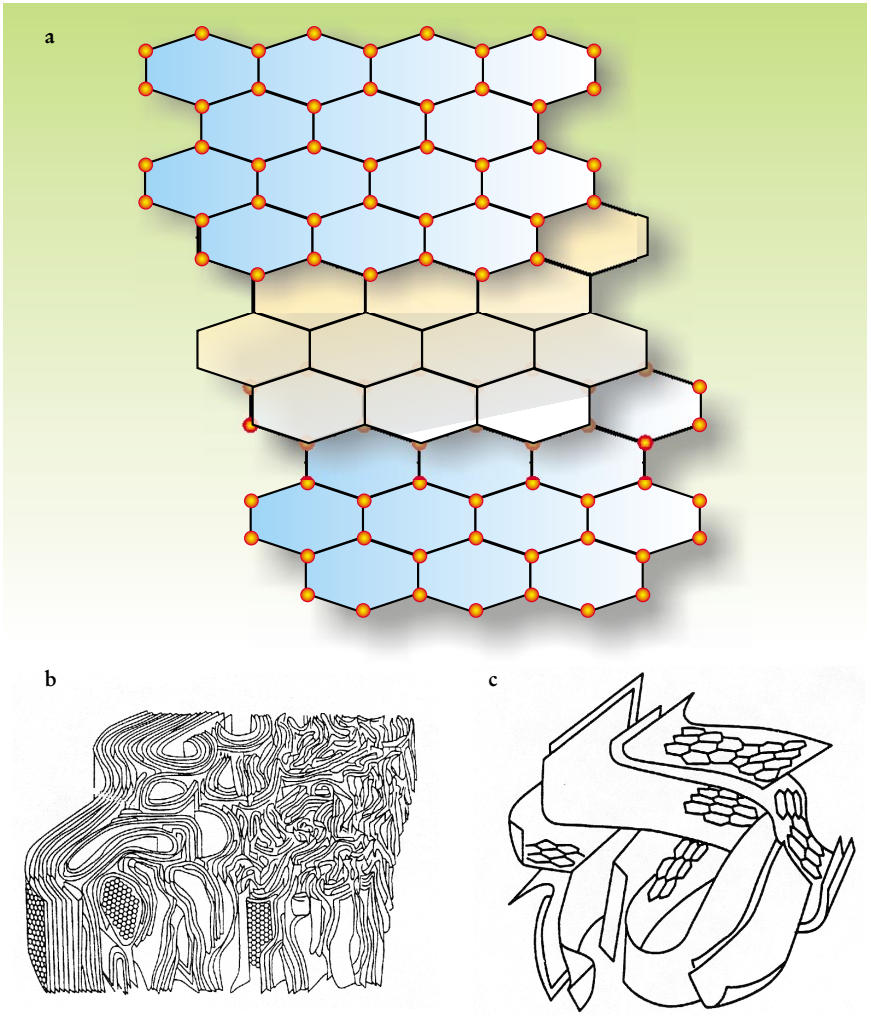


FIGURE 1. GRAPHITIC LAYERS form the basis of many carbon materials. **(a)** Exploded view of the perfect graphite crystal lattice, which consists of planar sheets of covalently bonded carbon atoms in a hexagonal array. The sheets form parallel stacks separated by about 3.35 angstroms. The bonding characteristics and material properties of graphite are highly anisotropic. The arrangement of graphitic layers in carbon materials determines their properties. **(b)** Axial alignment yields high axial stiffness and strength in carbon fibers. (Adapted from ref. 14.) **(c)** Disordered arrangements are desirable for high surface area in activated carbon. (Adapted from ref. 15.)

planar and disklike at high molecular weight, with a honeycomb shape as sketched in figure 1c. The many competing reaction pathways in the early stages of carbonization produce a complex "chemical soup" consisting of hundreds or thousands of distinct components—even when a single compound is used as the organic raw material.

The formation of planar PAHs in this chemical soup establishes the basic two-dimensional kernel of the graphitic layer structure early in the carbonization process. Many organic materials soften upon heating, imparting high mobility to these disklike molecules and allowing an LC phase to form and orientational order to be established. Further heating brings about chemical coalescence of the discotic clusters, leading to increases in molecular weight and a loss of mobility. Eventually, the molten system undergoes a glass transition to form a solid carbon material that retains the essential nanostructure at the time of solidification. In some sense, then, these freshly formed carbon materials can be regarded as frozen LC phases. Even after severe heat treatment at temperatures above 3000 °C, carbon materials retain some memory of their nanostructure in the liquid phase. Thus, liquid-phase ordering is fundamental to controlling the nanostructure and properties of carbon materials.

The formation route through carbonaceous mesophase is the most effective way to establish long-range order in a carbon material. The mesophase LC structure is preserved in the glassy solid, and further heat

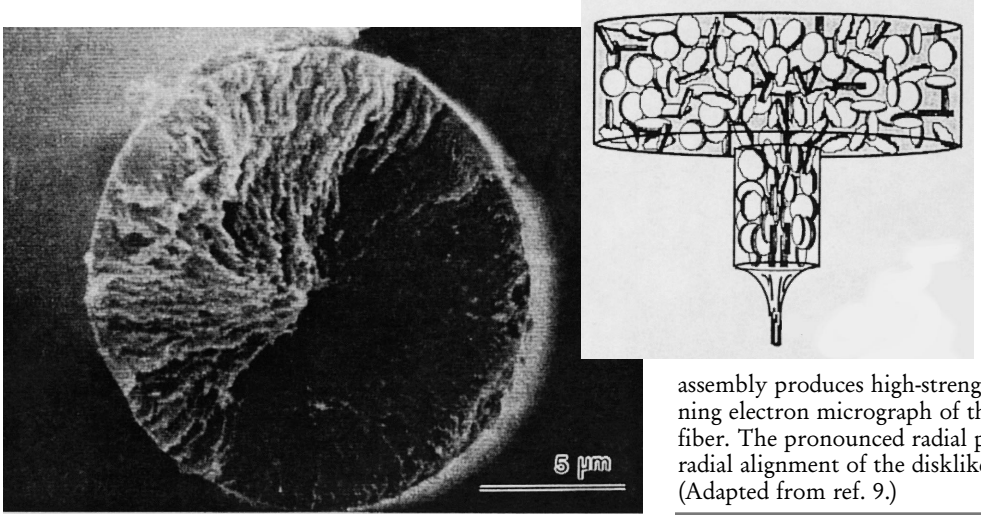


FIGURE 2. FLOW-INDUCED alignment of carbonaceous mesophase can tailor the axial nanostructure in carbon fibers. The sketch depicts the alignment of disklike organic compounds in mesophase at various stages of the fiber-spinning process. The random arrangement in the bulk fluid is transformed into the cylindrical radial alignment by flow through the narrowed passage of the spinneret. Such directed assembly produces high-strength fibers. The image is a scanning electron micrograph of the transverse texture of the final fiber. The pronounced radial pattern reflects the underlying radial alignment of the disklike molecular building blocks. (Adapted from ref. 9.)

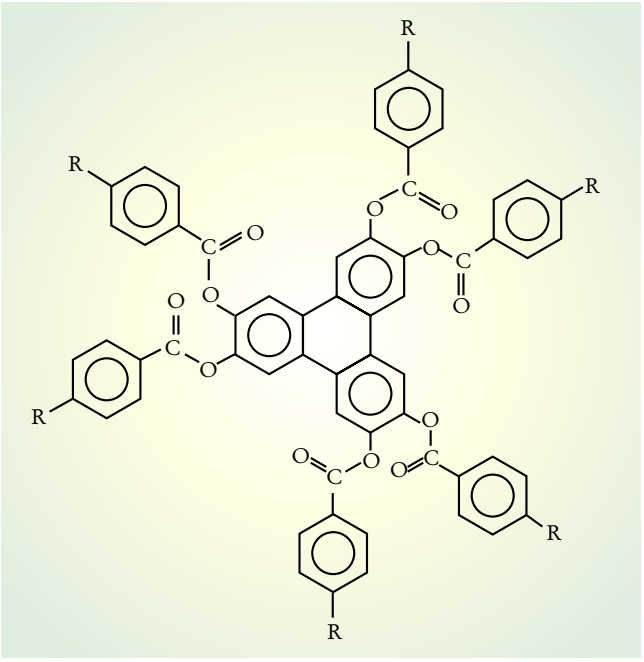


FIGURE 3. THIS FAMILY OF ORGANIC COMPOUNDS, hexa-N-alkyl- or alkoxybenzoates of triphenylene, constitute the first pure disk-shaped compounds found to form nematic liquid-crystal phases.[12] Such phases only form for a certain class of side chains, denoted "R."

treatment in the solid state can heal the local defects and produce a graphite of high crystalline perfection over long length scales. In some cases, however, the glass transition can compete with the LC transition, and if the glass transition occurs first, the material will solidify with only short-range order. Further thermal processing will not produce quality graphite—wholesale structural rearrangement of disordered carbon solids to produce long-range crystalline order is rarely observed. In the synthesis of graphitic materials requiring long-range crystalline order, therefore, the game is won or lost early, in the fluid phase of carbonization, when the nanostructure is first established—and therein lies the critical importance of carbonaceous mesophase.

The mesophase transition

Many aspects of carbonaceous mesophase can be understood through analogy with conventional LCs, whose phase transitions have been treated with mean-field approaches[3] and Monte Carlo and molecular dynamics simulations.[4] The classic theory of Lars Onsager, developed in 1947, describes LC formation based on hard-core repulsive interactions. Here the order–disorder transition in three-dimensional rod assemblies is governed by two parameters: the rods' aspect ratio and number density. Two analogous parameters are thought to be key to carbon systems: the disklike molecules' aspect ratio, which is influenced by their size and planarity; and the number density of the large disks—that is, their concentration in solution amid lower-molecular-weight material.

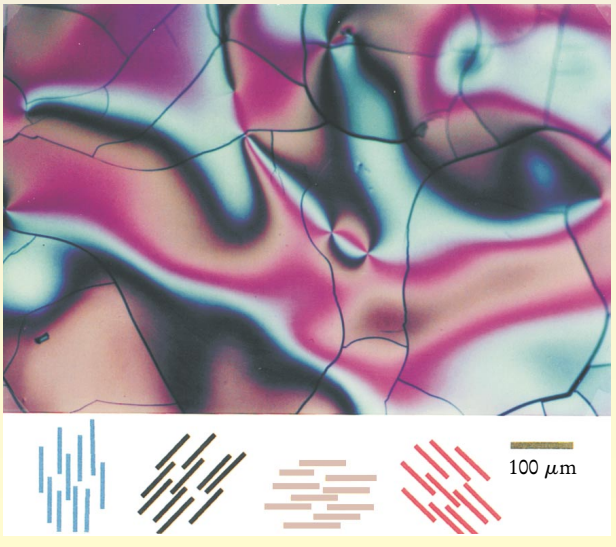
Temperature does not appear in the Onsager model, but it is known to be important in many LC systems, including carbonaceous mesophase. In general, LC phases are classified as either thermotropic (those that form as temperature decreases) or lyotropic (those that form as the concentration of elongated molecules in solution increases). Carbonaceous mesophase has a dual thermotropic and lyotropic nature. Its thermotropic nature was demonstrated in Irwin Lewis's hot stage experiments on naphthalene-derived pitches,[5] in which a reversible isotropic–LC transition was observed between the temperatures of 350 and 475 °C. A lyotropic nature is also apparent: LC formation is promoted by removing low-molecular-weight material by vaporization, polymerization, or solvent extraction, thereby concentrating species with high molecular weights.[6]

Box 1. Discotic Liquid Crystals

Liquid crystals (LCs) are ordered fluids composed of elongated molecules that are either rodlike or disklike. Rodlike LCs, discovered over 100 years ago, account for most of the known LC systems and all the present device applications. The much less common disklike LCs, or "discotics," were first synthesized[12] only in 1977. Although commercial applications of discotics have yet to be developed, some recent studies have proposed their use as arrays of molecular wires in xerographic and laser printing applications.[13]

Discotic LCs can exist in several different phases. The simplest LC phase is the nematic, in which the molecules are preferentially aligned along a common vector—that is, they have orientational order—but there is no long-range positional order. The term "nematic" comes from the Greek word for "thread," and it describes the threadlike patterns seen when these LC systems are viewed with polarized light under a microscope. Such optical texture arises from disclinations—defects or transition zones between orientationally ordered domains. Nematic texture can be seen in the accompanying photograph of a sample of mesophase pitch that has been heated to 300 °C and then cooled rapidly. The cracks are shrinkage fissures that formed during cooling. The various colors arise from different orientations of the graphitic layers, as sketched below the photo.

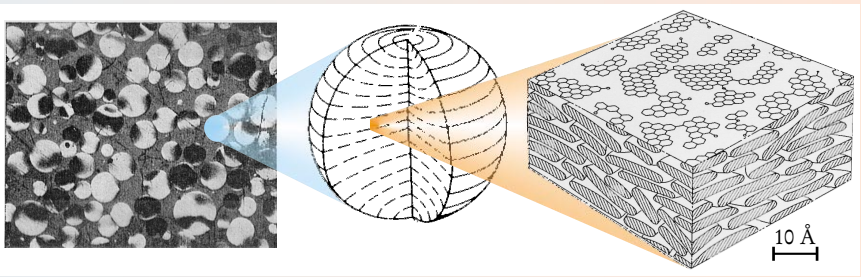
Another discotic phase—and the most common in synthesized systems—is the columnar phase. In contrast to nematic phases, columnar phases possess at least one degree of long-range positional order—the column stacking—in addition to orientational order. Orientational order in LC systems can be induced by increasing the concentration of the elongated molecules by solvent removal, which forces their alignment to achieve high packing density; by decreasing temperature, thereby reducing the thermal energy for orientational randomization; or by applying electric or magnetic fields.



Box 2. History of Carbonaceous Mesophase

The liquid-crystal (LC) nature of carbonizing systems was first reported by Geoff Taylor and J. D. Brooks, based on their findings at the Wongawilli coal seam in New South Wales, Australia.[1,2] A portion of the seam had been carbonized by a geothermal gradient, leaving a spatially resolved fossil record of the individual stages of the carbonization process. Examining a series of samples of increasing degree of thermal metamorphosis, Taylor first observed signs of fluidity, followed by the appearance of optically anisotropic spheres imbedded in an isotropic matrix. Later experiments with model organic compounds led Brooks and Taylor to conclude that the spheres were LC intermediate phases. The optical anisotropy was a direct expression of anisotropy in the carbonaceous nanostructure.

The structure of the spheres found by Taylor and Brooks is illustrated in the accompanying figure. On the left is an optical image of a polished sample showing spheres with diameters on the order of 50 μm. The mobile aromatic molecules that constitute the spheres self-organize into a so-called equatorial, or bipolar, structure (middle), forming layers that curve near the sphere's surface to maintain the energetically preferred perpendicular alignment at the phase boundary there. At higher magnification (right), one can see the basic layered nematic molecular structure in the interior of the spheres. (Figure adapted from refs. 2 and 6.)



Brooks and Taylor's 1965 *Nature* paper[2] began the systematic study of carbonaceous mesophase, the only known naturally occurring discotic liquid crystal. Although carbonaceous mesophase was discovered in 1965, the synthesis of the first discotic pure compound exhibiting LC behavior did not occur until 1977, with the first pure nematic discotics[12] following in 1979.

The most basic mean-field theory of LCs, the Maier–Saupe theory, uses a model potential that gives the energy of interaction between an elongated molecule and its surroundings as a function of the molecule's orientation.[3] The orientational potential takes on only finite values, and so the equilibrium states (those with the minimum free energy) are temperature dependent. The Maier–Saupe theory and its extensions are thus capable of describing thermotropic transitions.

To account for the partial lyotropic nature of carbonizing systems, mixture effects must also be considered. Geoffrey Luckhurst and his coworkers at the University of Southampton (in England) have developed an extension of the Maier–Saupe theory for mixtures of LC components with different phase-transition temperatures.[7] The carbonization process invariably involves such mixtures: The disklike molecules differ in size and planarity, and thus in their propensity to form LC phases. The Luckhurst group has further extended the theory to include the effects of spherical solvent molecules, which reduce the anisotropic interaction between the nonspherical molecules and lower the temperature of the transition between the isotropic and LC phases. A sufficiently large solvent concentration leads to significant regions of coexistence between the LC and isotropic phases.

These modern developments in LC theory are just beginning to have an impact on carbon science and technology. Kunio Arai and his colleagues at Tohoku University (in Japan) have applied the theories of Luckhurst and his coworkers to pitch, in an attempt to obtain the first quantitative description of the LC phase transitions therein.[8] Using statistical mixture theory, they succeeded in predicting the correct trends in an experimental phase diagram. Further application of theories targeted originally at conventional LC systems should greatly improve our understanding of carbonization.

Manipulating alignment

As in other LCs, molecular orientations in carbon systems can be modified by flows, surfaces, and external fields. For example, figure 2 shows the alignment of disklike molecules in the narrow nozzle used to "spin" carbon fibers. Dan Edie at Clemson University has shown that the Leslie–Erickson continuum theory, originally developed for dynamic processes in nematic rodlike LCs, correctly predicts the transverse alignment of the disks and the radial texture seen in the carbonized fiber's cross section.[9] Most other problems involving the flow of this complex anisotropic fluid have not been treated quantitatively, despite the fact that, in practice, carbonaceous mesophase is almost always in motion. Even simple confined pools of pitch, when heated to their softening point, exhibit molecular orientations that are largely dictated by flow, which is driven in turn by convection currents and by the growth and migration of vapor bubbles.

The discotic organic molecules formed in carbonization are expected to anchor with specific orientations at phase boundaries. These phase boundaries include air interfaces—such as the outer surface of a body or the interior surface of a bubble cavity—or the surfaces of foreign solids added as second components in composite materials. An example is the nanostructure found in the binder component of carbon–carbon composite materials. In these materials, carbon fibers are woven into a desired shape and then impregnated with pitch, which fills the spaces between them. Subsequent carbonization yields a dense structural material. The discotic molecules in the pitch align along the fiber surfaces as a result of surface energy minimization or flow—forced flow of the pitch along the fibers tends to align the domains. The carbonized pitch thus forms an "interphase," in which alignment and bulk properties have been influenced by the presence of the fibers. The fundamental rules governing surface anchoring, such as preferred angles and energies, are essential for the systematic understanding and modeling of carbon material synthesis, but they have yet to be properly established. The disklike polycyclic aromatic compounds in carbonizing melts have also been observed to align in magnetic fields,[6] and this phenomenon is also not yet widely exploited in practical applications.

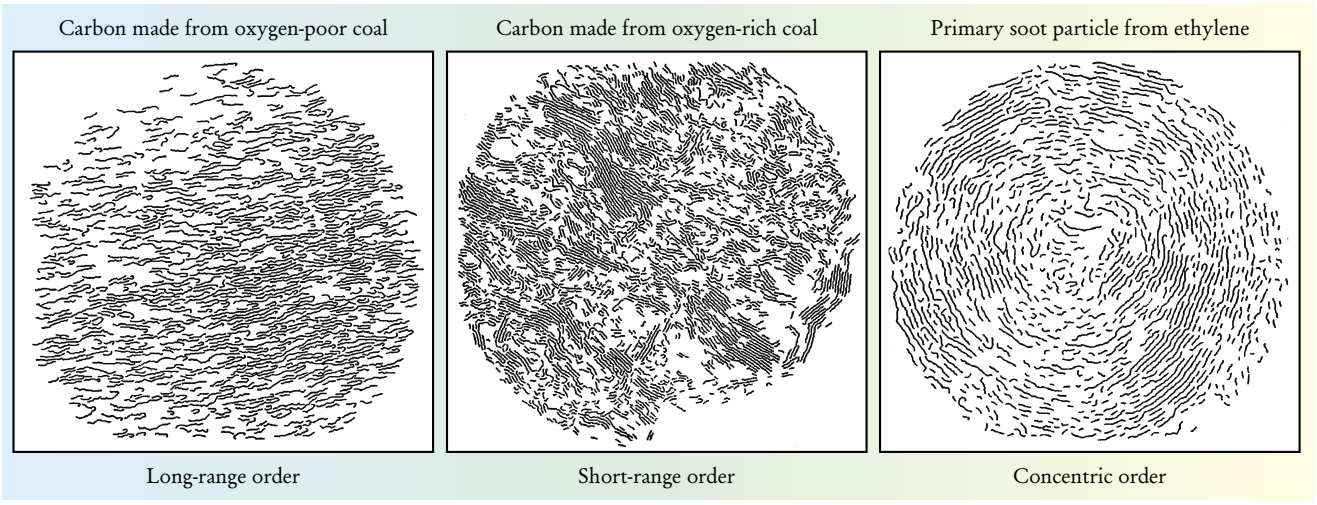


FIGURE 4. NANOSTRUCTURES IN REAL CARBON MATERIALS. These digitally enhanced high-resolution transmission electron microscopy fringe images show the arrangement of graphitic layers in carbon materials obtained by rapid flame heating of different organic starting materials. The spacing between the layers is about 3.4 Å, similar to the interlayer spacing in graphite, 3.35 Å. (Adapted from ref. 16.)

Although carbonaceous mesophase shares many features with conventional LC systems, there are some notable differences:

▷ The carbonaceous LC phase has to date only been observed in mixtures, not for any pure compound representative of the pitch constituents.

▷ In practice, carbonaceous mesophase typically forms upon *heating*, in contrast to most LC systems, which form ordered configurations upon cooling.

▷ LC transitions in carbon systems can have a strong kinetic signature: The competition between the growth of disklike molecules, which increases their aspect ratio, and their alignment, which depends on their mobility, leads to carbon materials with various degrees of order.

▷ Carbonaceous LCs are opaque, a practical difference that precludes many optical device applications involving transmitted light.

Several of these points of contrast raise interesting physical issues. We begin with the issue of mixture behavior.

The pitch paradox

Although discotic LC behavior is common in carbonization, it is rare elsewhere in nature. Even today, known discotic LCs—other than carbonaceous mesophase—are restricted to a few homologous series of organic compounds, in which each compound contains a planar aromatic core and multiple side chains consisting of single carbon–carbon bonds attached to its periphery. Unlike carbonaceous mesophase, these synthesized discotic compounds tend to form columnar phases instead of nematic. Furthermore, the discotic phase is typically observed only when the length of the side chains falls within a certain range. For example, in one class of chemical compounds—hexa-N-alkoxybenzoates of triphenylene (figure 3)—the nematic phase occurs only in the presence of side chains of the formula $R = C_nH_{2n+1}O$, with n from 8 to 11.

This dependence on side-chain length, note Pierre-Gilles de Gennes and Jacques Prost, suggests that the stability of columnar phases requires some kind of amphiphilic interaction similar to what is found in surfactants: The aromatic cores are preferentially attracted to other cores, and the side chains are attracted to other side chains.[3] The cores and chains thus tend to segregate, producing a columnar structure. In this formation, the chains also provide lubrication between the columns, and that promotes liquidlike behavior.

Most molecules in pitch, however, do not possess such long side chains—typically, they have either no side chains or a few chains containing one to three carbon atoms. Within this family of polycyclic aromatic hydrocarbons that constitute pitches, discotic LC behavior has *never* been observed—an intriguing paradox.

A likely resolution to the pitch paradox lies in the phase behavior of mixtures.[10] De Gennes and Prost discuss the possibility of observing LC behavior in binary mixtures, in which one or both pure components do not themselves form LC phases.[3] The free energy of mixing lowers the melting points of the pure solid phases, just as salt lowers the melting point of ice. In certain cases, the reduced melting point can reveal underlying LC regions in the phase diagram. If we generalize this idea to a complex chemical soup containing hundreds or thousands of distinct components, the melting points of crystalline solid phases are severely depressed, and large regions of the phase diagram contain liquid phases, making carbonaceous mesophase a common occurrence.

The role of temperature

The formation of carbonaceous mesophase upon heating has led some researchers to question the fundamental nature of the phase transition. In traditional thermotropic LCs, the transition occurs upon cooling. There is strong evidence, however, that the LC transition in carbonization has the same fundamental nature as other LC phase transitions, and that the unusual temperature behavior is due to the collateral effects of heating on chemical growth and vaporization.

Heating induces chemical reactions, which produce a form of two-dimensional polymerization that increases the mean size and aspect ratio of the disklike molecules and thus increases their tendency to form LCs. In addition, heating causes vaporization of the mixture's smaller molecules, which have weak LC-forming tendencies; thus there is an increase in the concentration and mutual interaction of the larger molecules. In practice, these two effects combine to overcome the thermotropic effect, which

by itself favors disorder on heating. Carbonaceous mesophase therefore appears as the temperature is raised. Only when chemical growth and vaporization are suppressed, such as in Lewis's experiments on pitches of high chemical stability,[5] does carbonaceous mesophase appear on cooling, thereby revealing the true thermotropic nature of the phase transition.

Kinetics of orientational ordering

An additional effect of temperature is its role in overcoming energy barriers to molecular motion. For some organic precursors and under some carbonization conditions, the rotational mobility of the molecules is insufficient for the system to achieve the equilibrium ordered state over long length scales, and the orientational order is correlated only over short length scales on the order of tens of nanometers. This correlation length is small enough to cause such systems to be classified as isotropic—as determined by optical microscopy, the traditional characterization tool in carbon science.

The isotropic carbon structure can be the result of a kinetically limited, or frustrated, ordering process.[11] Recent simulations using a two-dimensional toy model illustrate the effects of simultaneous growth, rotation, and translation of rigid lines. The main input parameter is a dimensionless ratio of the orientational mobility to the chemical growth or polymerization rate. At high mobility-to-growth ratios, mutual avoidance causes the lines to align during the later stages of growth. Then a transition to a glass phase occurs, producing an immobile phase having orientational order on a length scale comparable to the size of the simulation. At lower ratios, the alignment is hindered and the final state has short-range order only, similar to the distinct crystallites with random orientation seen in isotropic carbon materials. For zero mobility or infinite growth rate, the model simulations produce a random structure.

Potential applications of this frustrated-growth model include nonequilibrium cooling of isotropic liquid phases, and the synthesis of carbon materials. In its simplest form, the model distinguishes two important classes of carbon materials. One consists of isotropic carbons formed through all-solid-state routes in which molecular mobility is severely limited. Such carbons include those made from geologically young, oxygen-rich coal; wood; cellulose; and oxygen-rich polymers such as some polyurethanes. The other class consists of anisotropic carbons formed from precursors that pass through a mobile, liquid-phase intermediate, such as geologically older, oxygen-poor coal, pure aromatic hydrocarbons, some polymers, and petroleum and coal tar pitches. (See figure 4.) Additional carbon materials such as high-rank fossil fuels can be described by incorporating partially ordered initial states. The US Department of Energy's National Energy Technology Laboratory is pursuing these frustrated-growth ideas to achieve a deeper understanding of carbons derived from coal.

The role of oxygen in inhibiting the mesophase transition is due to its divalency. Oxygen (as well as sulfur) forms two bonds per atom, which can lead to cross-linking between planar aromatic clusters. The resulting compound structures are kinked or branched and are locally disruptive to LC formation. There are other inhibitors, too. For instance, the five-membered rings that promote curvature in fullerenes are also thought to form in condensed phases during carbonization, where they reduce the planarity of the graphene layers and suppress LC formation. In synthesized LCs, these "enemy" structures can be avoided by selection and purification of the starting materials—an option that is not possible in the carbonization of natural substances. The carbonization process thereby offers a unique opportunity to study the physics of LC disruption by branched or nonplanar molecules.

Because of the differences between carbonaceous mesophase and other, traditional LCs, some researchers in carbon science have described carbonaceous mesophase as something analogous to an LC rather than as a true member of the LC family. However, there is an emerging consensus that carbonaceous mesophase is indeed a true LC, but one in which many classical LC behaviors are masked or perturbed by superposition of other phenomena, such as high-melting solid crystalline phases, kinetic limitations on phase transitions, and chemical growth processes.

There is great potential to apply the modern tools of LC research to improve our understanding of carbonization. The effects of fields, flows, surfaces, and confined spaces are all fertile research topics, as is the determination of the fundamental elastic constants and surface anchoring properties, which are needed for quantitative modeling. In addition, the special complexities of carbonaceous mesophase provide new opportunities for physicists, such as the description of phase transitions in the presence of chemical growth and limited mobility. More systematic study of the physics of mobile discotic graphene layers and their ensembles will eventually make it possible to tailor the structures of practical carbon materials to society's significant technological and economic advantage.

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